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PM 2.5 CONCENTRATION VALUES IN URBAN ATMOSPHERE OF CLUJ-NAPOCA

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ABSTRACT. Fine particles concentration was monitored in Cluj-Napoca through a series of 12-24 hours measurements, using a direct-reading instrument, the DustTrak aerosol monitor, model 8520. In order to highlight areas with different types of exposure (both those that show a high risk for health, and those with a low risk), the measurements were carried out in several neighborhoods with a different air quality (Zorilor, Andrei Mureșanu, Gruia, Mănăștur and Grigorescu). The results showed that the variability in time and space of the fine particles (PM_{2.5}) concentrations depend on many factors. Among these factors, based on correlations, the most significant are both the wind direction and speed, and the proximity to the highways. In most cases, the averages we obtained exceeded the limit set on 25μg/m³ according to World Health Organization and European legislation. Therefore the exposure to concentrations above the permissible value ranged from 40-100%.

Key words: PM_{2.5}, urban air quality, exposure, health risk

INTRODUCTION

The World Health Organization (WHO) describes air pollution as “a major risk for health” and influences two million premature deaths recorded every year around the world. Concerning its impact towards both health and the environment (acid rains, fog and dry depositions, impact on radiative balance of the Earth and subsequently on climatic change), the atmosphere pollution with suspended particles matter represents one of the current problems at global scale (Penner et al., 2001; Halthore et al., 2009; Gunturu, 2010). This is present both in developed countries, as well as in overcrowded urban areas from the less developed regions (Chaloulakou et al., 2003; Dunn et al., 2004; Cao et al., 2005; Kulkarni, 2006; Chunram et al., 2007; Kakooei and Kakooei, 2007).

Airborne particulate matter (PM) is a complex mixture of solid and liquid particles with organic or inorganic origin that are suspended in air, whose effective diameter is bigger than that of a molecule, but smaller than 100 μm (Lazaroiu 2006). These come both from natural and anthropogenic processes, the main sources being the mineral dust (Al₂O₃, Fe, Ti, Sr, CaCO₃, Mg, Mn, K), the emissions that comes from generating energy (Na, Cl, Mg), transports (organic and elemental carbon) and marine aerosols (only in the case of PM₁₀- Na, Cl, Mg).

Unlike other pollutants, these represent aggregates of hundreds of individual compounds, of varied shapes and dimensions and with different chemical and thermodynamic properties (Olson and Boison, 2005). Concerning the processes of transport and dynamic, they came to the conclusion that among the properties of aerosols, the size of the particle, the concentration and the chemical composition influence the most of their behavior in the atmosphere as well as on the respiratory tract (Moldoveanu, 2005). So, the smaller the dimensions of the particles are, the bigger their impact over the human health (Burnett and Goldberg, 2003; O'Conner et al., 2008).

After analyzing the studies in the field, WHO signed that compared to any other pollutant, this one affects a greater number of people. Taking into account the gravity of the affections on the respiratory tract (Kleinman, 2000; Kulkarni, 2006; O'Connor et al., 2008; Nastos et al., 2010) and on the cardiovascular device Petters et al., 2001; Simkhovich et al., 2008), according to the dimension of the inhalable particles (PM_{10} , $PM_{2.5}$, PM_1), regulations that limit the emissions of suspended particles matter were imposed on a global scale.

Beginning with 1971, when the US Environmental Protection Agency (US-EPA) developed the first legislative regulations for aerosols, the established limits suffered countless modifications in time, depending on the results obtained after the measurements (www.who.int; www.epa.gov; www.ec.europa.eu). Some specific regulations, established by the experts from WHO during the meeting at Bonn in 2005, embodied more drastic standards for particulate matter (the medium value of $PM_{2.5}$ in the course of one year must not be over $10\mu\text{g}/\text{m}^3$ and $25\mu\text{g}/\text{m}^3$ along 24 hours). In 2006, US-EPA included PM on the list of major pollutants, along with CO, Pb, NO_2 , SO_2 and O_3 . According to the international quality standards of the air, the average level over three consecutive years must not be over $15\mu\text{g}/\text{m}^3$ and the 24 hour mean is $35\mu\text{g}/\text{m}^3$. In European Union (EU), the Directive 2008/50/CE includes the latest modifications regarding the fine particles. This was transposed in national legislation through the law 104/2011, the mean value of $PM_{2.5}$ in one year being established at $25\mu\text{g}/\text{m}^3$. Concerning the concentration level in 24 hours, in 2004, during the Clear Air for Europe program, it was proposed a limit of $35\mu\text{g}/\text{m}^3$ but this was not approved by the legislation.

In Cluj-Napoca, an important problem that creates discomfort for the inhabitants is the high amount of dust. The main identified sources of PM_{10} and $PM_{2.5}$ were high traffic, activities in constructions and industry. Because of the variation of the concentration in time and space depending on certain factors (Penner et al., 2001; Rodriguez et al., 2004; Amodio et al., 2010), the monitoring made by the Environmental Protection Agency in town has a reduced relevance in the field, especially when it comes to the level of fine particles that has been measured recently and only in one location.

The lack of data concerning the concentration of $PM_{2.5}$ in the urban atmosphere and the knowledge of its effect over health from specialized sources were at the base of this study. It must be noted here that we tried to take into consideration the meteorological parameters that could influence the concentration values of fine particles and we also tried to localize the main sources of pollution.

MATERIALS AND METHODS

The sampling points and the monitoring period

In the present case, the evaluation of the concentration of PM_{2.5} from the urban atmosphere of Cluj-Napoca was made through a series of 12-24 hour measurements made over two periods of monitoring: April – June and September 2011. The distance between the measurements was established in order to obtain relevant results in the given meteorological context and at the same time to respect the legislative regulations concerning the monitoring of particulate matter.

The success of the measurements was conditioned by the lack of precipitations (their presence leads to the purification of the atmospheric air, and the results concerning the concentration levels of material particles is irrelevant), in this case the making and respecting of a certain monitoring schedule being impossible.

Because the values we obtained could vary depending on the proximity of the main sources of pollution or the meteorological parameters (Dunn et al., 2004; Kulkarni, 2006; Chunram et al., 2007; O'Connor et al., 2008; Satsangi et al., 2011), the checking points were selected randomly. The main condition was to cover zones with a high degree of exposure to PM_{2.5} as well as zones that had a low threat to health, thus being picked 6 points situated in the districts of Zorilor, Mănăştur, Andrei Mureşanu and Gruia (see **Fig.1**): P1- 1A Sputnik Street, Zorilor district; P2- 19 Pajiştei, Zorilor district; P3- 20 Eugen Ionesco, Zorilor district; P4- 9 Predeal, Andrei Mureşanu district; P5- 16 Ilie Măcelarul, Mănăştur district; P6- 60A Emil Racoviţă, Gruia district.

Following the comparison of results obtained in different days and seasons, we also tried to highlight, if possible, the risk factors, in each point where we made two or three sets of measurements during the two monitoring periods.

The sampling equipment

The evaluation of the concentration of PM_{2.5} from the urban atmosphere in Cluj-Napoca was made with an aerosol monitor 8520 frequently used in such studies (Cao et al., 2005; Diapouli et al., 2008). It allows the concentrations measurements of PM₁₀, PM_{2.5} and PM₁, both of the inside air and that of the ambient air, by means of four operating modes (Survey mode that allows the real time measurement of concentrations and LOG 1, 2 and 3 used for statistical determinations – medium, minimum or high registered value). In this situation, for obtaining data regarding PM_{2.5} the method LOG 2 was used, the logging interval being 1 minute.

It must be specified that in all cases, the measurements were made in the yards of the houses, as much far away as possible from the house so they won't be influenced by the inside air, and the device in its protection box was placed on the level of the airways (between 1 and 2 meters).

As far as the correlations with different meteorological parameters (temperature, humidity, direction and speed of the wind, atmospheric pressure, precipitations), the data regarding the weather were obtained from the Paragliding Association (ASPAR), placed near the international airport in Cluj-Napoca.



Fig.1. Representation of the sampling points in Cluj-Napoca.

RESULTS AND DISCUSSIONS

Sampling point no.1- 1A Sputnik Street, Zorilor district

The importance of traffic influence over concentration of particulate matter revealed by numerous studies (Pope and Dockery, 2006; Diapouli et al., 2008; Satsangi et al., 2011); these studies also highlighted the impact over health in relation with the distance between houses and the main road (Hoffmann et al., 2007). In order to be able to follow its contribution, the first measurement of 24hr was made in the proximity of two important traffic arteries (Calea Turzii represents the main access road from Bucharest).

The medium value obtained during the first day ($36\mu\text{g}/\text{m}^3$), was higher than $25\mu\text{g}/\text{m}^3$ which is the maximum value suggested by WHO for protection of health and also than the values fixed by US-EPA and EU. Data obtained revealed that in 14 hours – the equivalent for 60% of a day, the inhabitants of this area were exposed to a level $\text{PM}_{2.5}$ higher in average with $10\mu\text{g}/\text{m}^3$ than the threshold level. Regarding to the results of first day measurements, these may indicate an increased health risk especially in the morning and in the evening (see Fig. 2).

PM 2.5 CONCENTRATION VALUES IN URBAN ATMOSPHERE OF CLUJ-NAPOCA

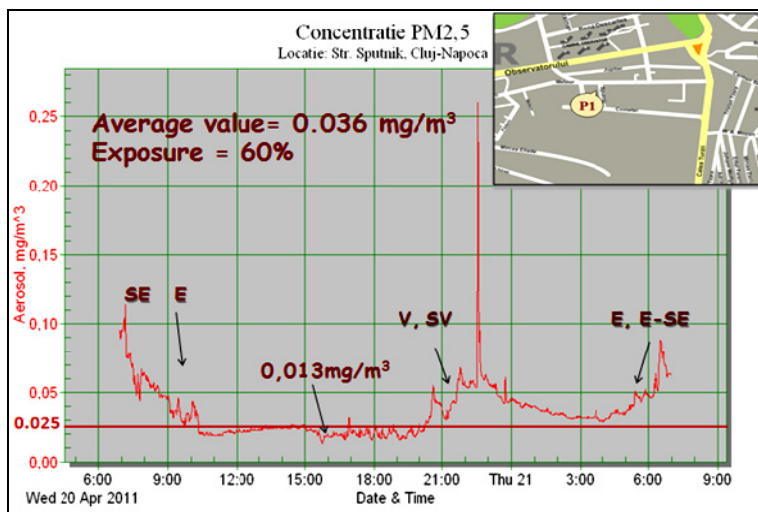


Fig. 2. Variation of PM_{2.5} concentration level during the first day of measurements in sampling point no.1.

A cause of the exceed of the threshold level may be the congestion of morning traffic on Calea Turzii Street and Observatorului Street, which are 5 minutes away from the sampling point. But still it doesn't explain the lower values in the afternoon (see Fig. 2).

Because the concentration level of PM generally depends on the atmosphere conditions and meteorological parameters (Penner et al., 2001; Amodio et al., 2010; Satsangi et al., 2011), data obtained was correlated with air temperature, relative humidity, wind direction and speed (see Fig. 2, Fig. 3).

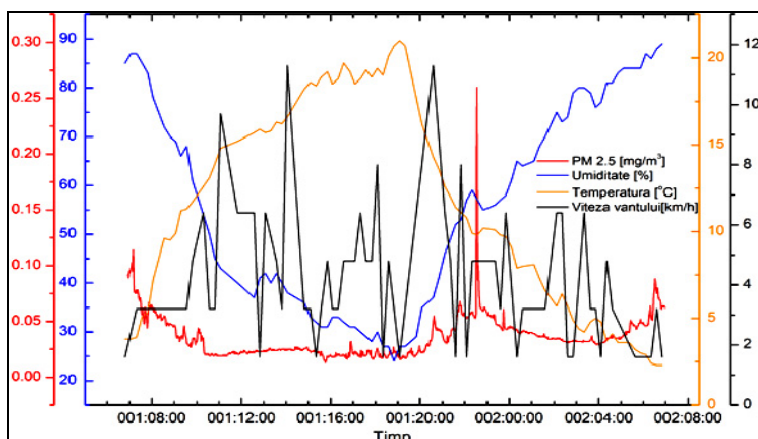


Fig. 3. Variation of PM_{2.5} concentration level and meteorological factors during first measurement in check point no.1.

In this case the resulted correlations were irrelevant because the data collected were not obtained from the same place (the distance between the check point and the weather station is considerable), an exception is that of the wind direction.

Data indicate more emissions in the morning hours. This can easily be observed on both periods of monitoring when the direction of the wind maintained a course from SE and E (see **Fig. 2, Fig. 4**). While the high values related to the W and SW wind, indicate another source of pollution which cannot be determined (see **Fig. 2, Fig. 4**).

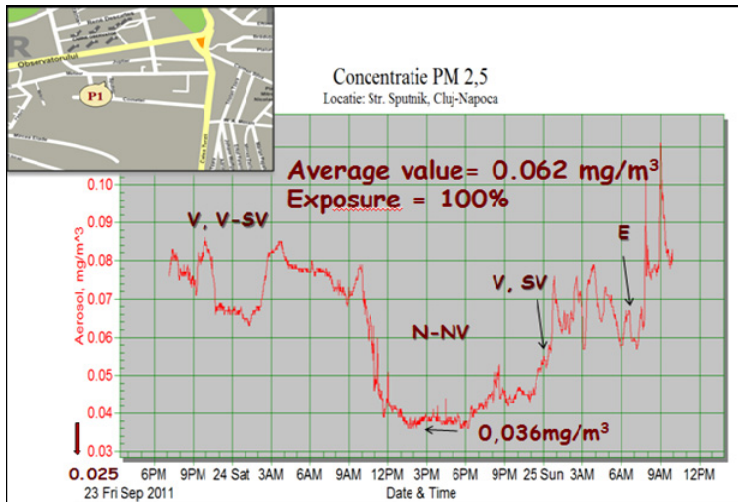


Fig. 4. Variation of PM_{2.5} concentration level during the second day of measurements in sampling point no. 1.

The concentrations obtained during the second amount of measurements highly exceeded the 25 $\mu\text{g}/\text{m}^3$ limit, remaining over 65 $\mu\text{g}/\text{m}^3$ for 24 hours. The high differences between the two sets of data have been explained though by the contribution of the emissions from indoor settings that happened during the measurements in September.

Sampling point no.2- 19 Pajiștei, Zorilor district

In this point there were made two measurements (24 and 12 hours) in the monitoring stages, to emphasize (if the case) the coming into sight of growth risk factors. Regarding the placement of the aerosols monitor, it was placed in the front garden, aprox. 5 meters away from the neighbour's yard (it must be noted that there were deployed construction activities in the first day of surveillance).

Comparing the final results obtained during the first set of measurements, significant differences were observed, but the high level of fine particles (on the 21st of April) and the intermittent contribution, were interpreted on basis of this singular case of pollution. Although the medium value in both cases exceeded, the established value by WHO for health care, the inhabitants being exposed for more than 12 hours to PM_{2.5} concentrations over 25 $\mu\text{g}/\text{m}^3$ (see **Fig. 5, Fig. 6**). Even ignoring the next-door episode, higher values were observed in the morning, due to the traffic.

PM 2.5 CONCENTRATION VALUES IN URBAN ATMOSPHERE OF CLUJ-NAPOCA

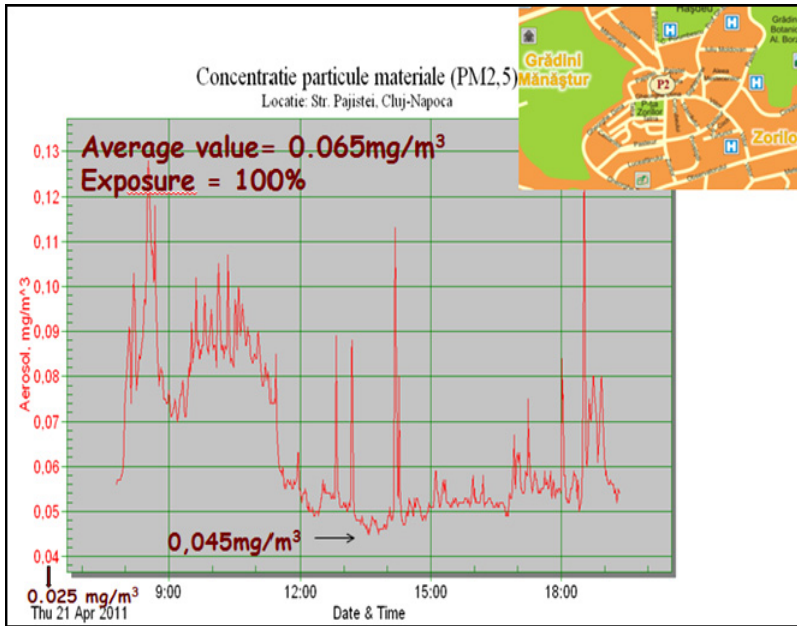


Fig. 5. Variation of PM_{2.5} concentration level during 12hr in first monitoring stage in sampling point no.2.

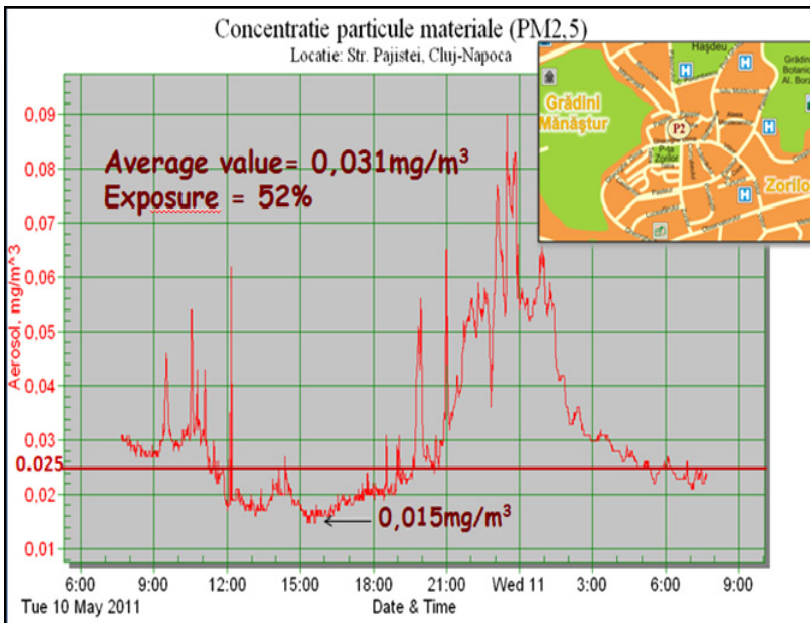
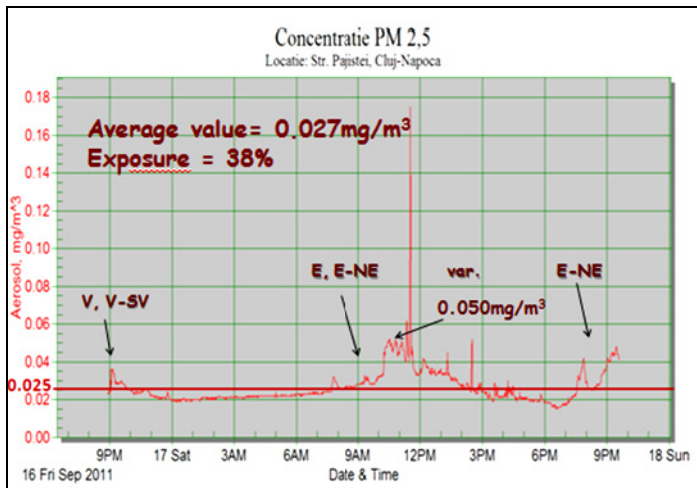


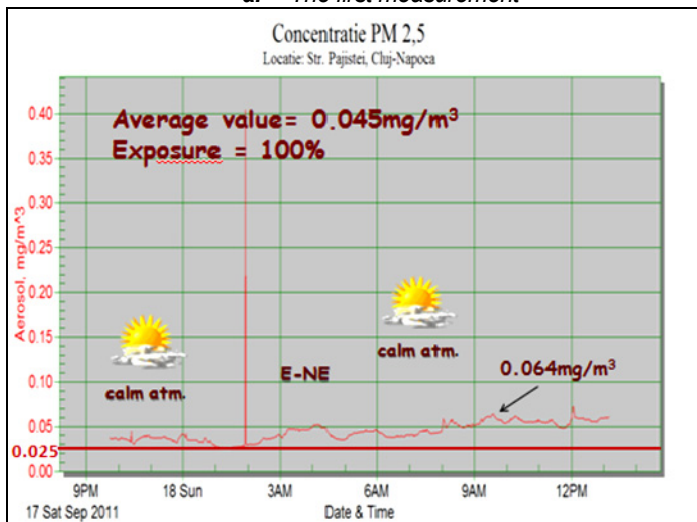
Fig. 6. Variation of PM_{2.5} concentration level during 24hr in first monitoring stage in sampling point no.2.

In order to obtain an image as real as possible regarding pollution in this area, the measured values were correlated with the wind's speed and direction. Thus, concentrations from the first day of measurements were influenced by the low values of wind speed (4.9km/h according to ASPAR weather station) that didn't allow the dispersion of particulates matter. Also, their high level in the evening of the 10th of May was due to the high intensity of the wind caused by the dust that came in that area.

As far as the measurements made in September, average values (27 $\mu\text{g}/\text{m}^3$ respectively 45 $\mu\text{g}/\text{m}^3$) although in the allowed limit, recorded a decrease compared to the first measurements (see Fig. 7).



a. The first measurement



b. The second measurement

Fig. 7. Variation of $\text{PM}_{2.5}$ concentration level during the second monitoring stage in sampling point no.2.

PM 2.5 CONCENTRATION VALUES IN URBAN ATMOSPHERE OF CLUJ-NAPOCA

Due to lack of construction works and high wind speed, during the morning hours it was easily tracked down the concentration of PM_{2.5} because of both high traffic during this time and E-NE wind direction (see Fig. 7).

Sampling point no. 3- 20 E. Ionesco Street, Zorilor district

The third measurement point from Zorilor neighbourhood, was located near an unpaved road, in one of the areas which is still in development, in order to have a direct view of the impact of these factors on the fine particles concentrations. Therefore, the frequency and the size variation of the peaks is very high (see Fig.8, Fig.9), which confirms the presence of nearby PM source (in this case- the unpaved road that emits significant amounts of dust with each passing vehicle).

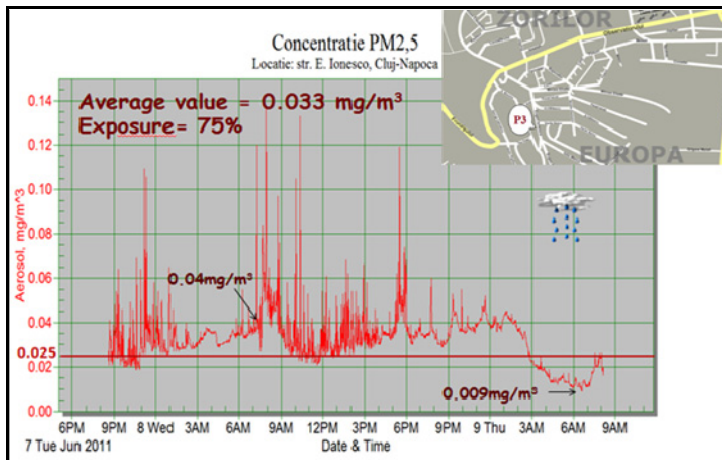


Fig. 8. Variation of PM_{2.5} concentration level during the first measurement in sampling point no.3.

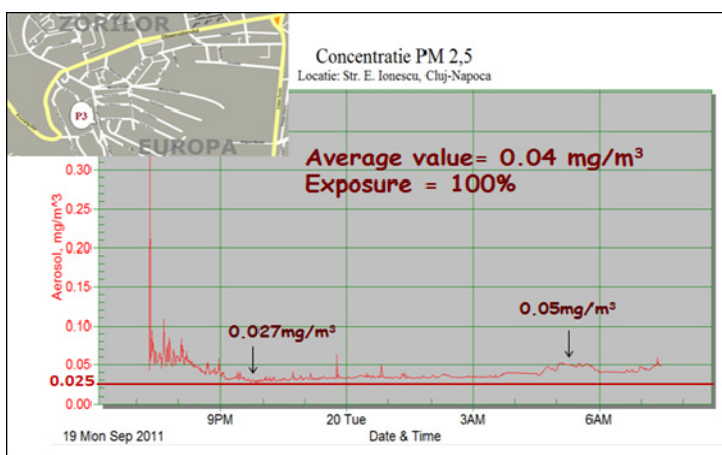


Fig. 9. Variation of PM_{2.5} concentration level during the second measurement in sampling point no.3.

Also, due to traffic increase in the morning and afternoon (the rush hour), there was a rise in the concentrations (see Fig. 8, Fig. 9). This was also present on a small scale in 9th of June, although the values obtained were much lower due to the rain shower recorded around 3:00-4:00 AM.

The limit of $25\mu\text{g}/\text{m}^3$ was not exceeded by far by the average values ($33\mu\text{g}/\text{m}^3$, respectively $40\mu\text{g}/\text{m}^3$), but still the people were exposed to concentrations above the limit of more than 75% of the measured time (see Fig. 8, Fig. 9).

Sampling point no. 4- 9 Predeal Street, Andrei Mureșanu district

In this case, both measurements showed high levels of $\text{PM}_{2.5}$ (see Fig.10, Fig. 11), despite of the fact that they were carried out in a garden located in a more quiet area (the neighborhood of houses), relatively far from the main roads.

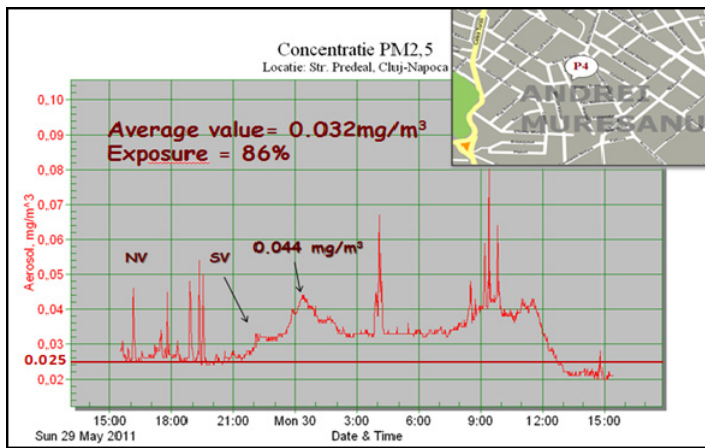


Fig. 10. Variation of $\text{PM}_{2.5}$ concentration level during the first measurement in sampling point no.4.

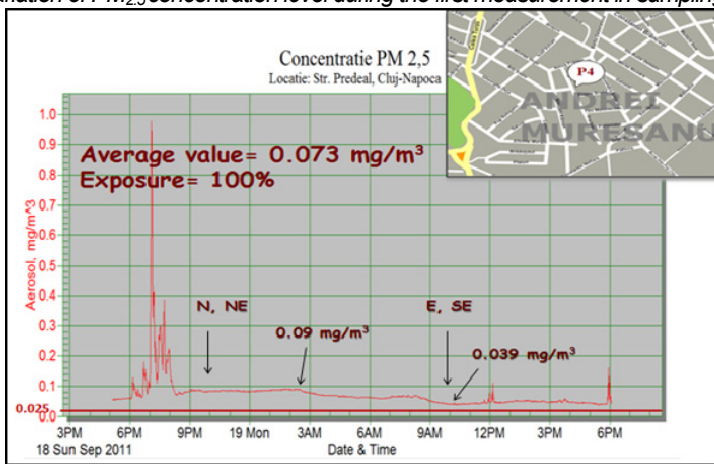


Fig. 11. Variation of $\text{PM}_{2.5}$ concentration level during the second measurement in sampling point no.4.

The concentration remained above the limit set by EU (see Fig.10), even exceeding twice that of USA ($35\mu\text{g}/\text{m}^3$ / 24hr) (see Fig.11). Comparing the two sets of data obtained, it was observed that the wind from the NE and SE had a more important contribution to the fine particles level than the NW or SW wind had. However the emissions from the carpentry workshop located in the same garden should also be considered an important contribution to the values measured in September. This can be clearly seen in the first part of the measurement, when for more than one hour and a half, the concentrations exceeded 15 times the maximum allowed (see Fig. 11). Traffic congestion may be the main cause for the increase in the morning of May 30.

Sampling point no.5- 16 I. Măcelaru Street, Mănăștur district

Unlike the other checking points, this one was located closer to the center of the city, in order to capture the influence of heavy traffic from Moșilor Street (the main gateway for Mănăștur district), as well as one of the brewery Ursus and of the construction works to the stadium that emit significant quantities of pollutants. Like the previous measurements, the results showed an increased concentration of $\text{PM}_{2.5}$ in the morning (see Fig.12, Fig. 13), because of the traffic jams. Regarding the means obtained ($64\mu\text{g}/\text{m}^3$ and $24\mu\text{g}/\text{m}^3$), this highlighted a significant change in the quality of air in the area, due to the brewery closing and the completion of the stadium. The changes in the wind direction can be easily noticed in the variation of the concentrations (see Fig. 12, Fig. 13).

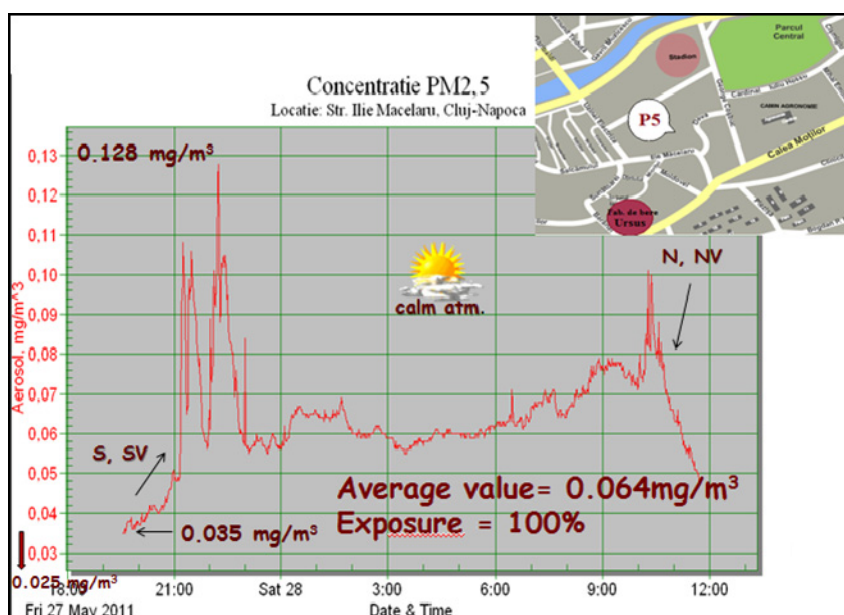


Fig. 12. Variation of $\text{PM}_{2.5}$ concentration level during the first measurement in sampling point no.5.

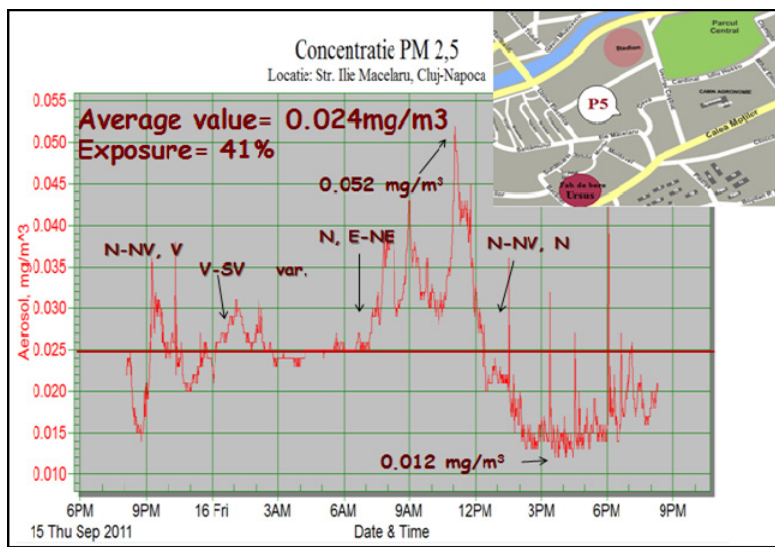


Fig. 13. Variation of $PM_{2.5}$ concentration level during the second measurement in sampling point no.5.

Sampling point no. 6- 60A E. Racoviță, Gruia district

Although it is a residential area, the high frequency of the peaks noted in both graphs indicated the proximity of an intermittent PM source (in this case two important crossings). The air currents coming from these areas lead to higher values of particulate matter (see Fig. 14, Fig. 15).

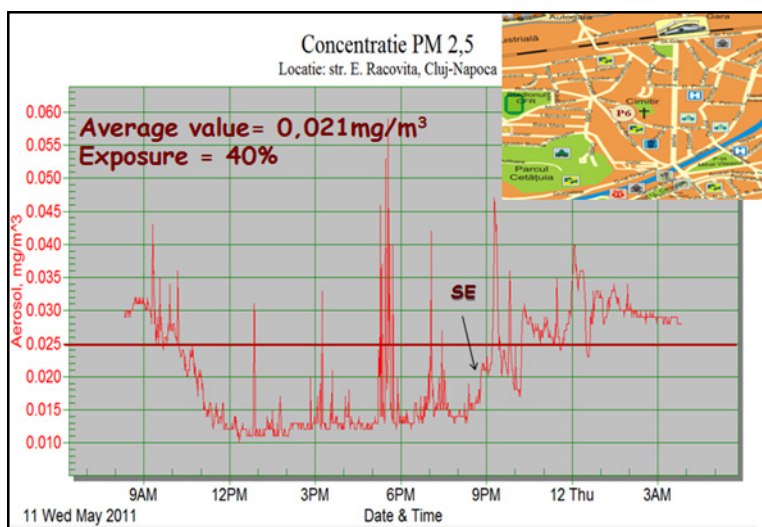


Fig. 14. Variation of $PM_{2.5}$ concentration level during the first measurement in sampling point no.6.

PM 2.5 CONCENTRATION VALUES IN URBAN ATMOSPHERE OF CLUJ-NAPOCA

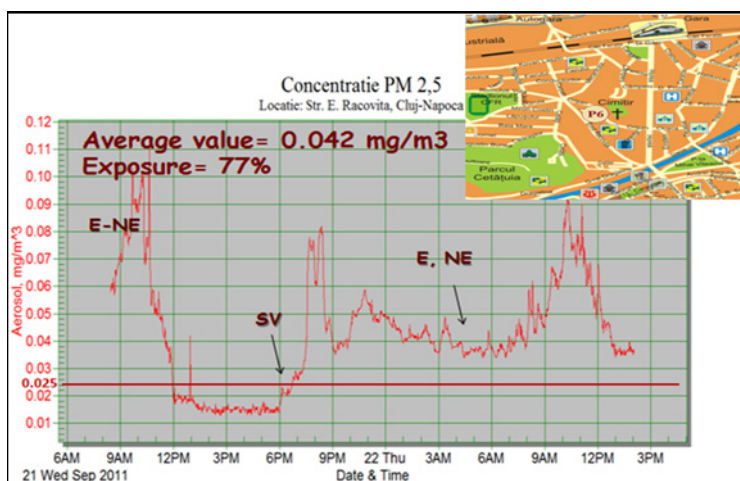


Fig. 15. Variation of PM_{2.5} concentration level during the second measurement in sampling point no.6.

Overall, increases in the level of fine particles were observed as usual in the morning due to the heavy traffic and also with the changes in wind direction (see **Fig.15**, **Fig.16**). Based on the meteorological data it can be assumed that the wind is the main factor that determined the reduction of the values under the limit imposed by law, in the first measurement made.

Time and space distribution of the concentrations obtained in sampling points in Cluj-Napoca

The averages of PM 2.5 obtained during the two monitoring periods made in April-June and September, ranged from 21 $\mu\text{g}/\text{m}^3$ (the first measurement in P6) to 73 $\mu\text{g}/\text{m}^3$ (the second measurement in P4) (see **Fig.16**, **Fig.17**).

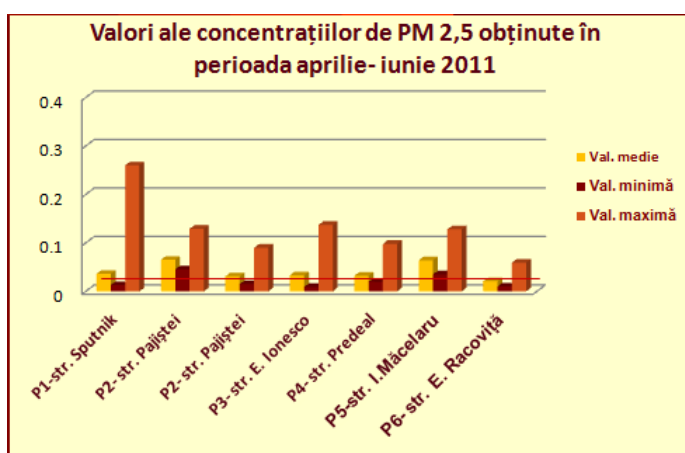


Fig. 16. PM_{2.5} concentrations (average, minimum and maximum) during the first monitoring period in Cluj-Napoca.

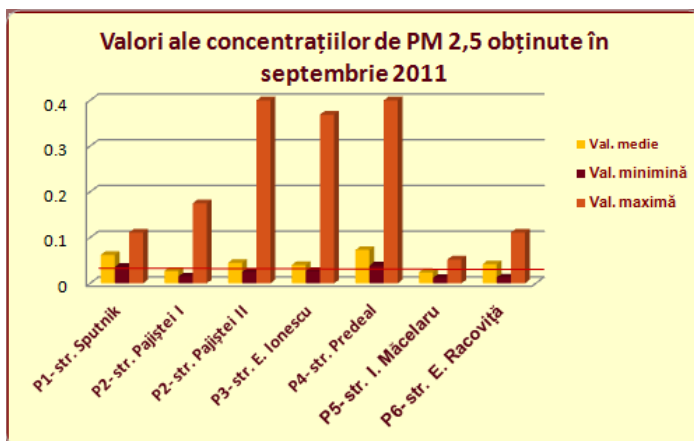


Fig. 17. *PM_{2.5} concentrations (average, minimum and maximum) during the second monitoring period in Cluj-Napoca.*

Only two of the 14 measurements carried out in Cluj-Napoca ranked below the average value of $25\mu\text{g}/\text{m}^3$ (the first measurement in P6 - $21\mu\text{g}/\text{m}^3$ and the second one from P5 - $24\mu\text{g}/\text{m}^3$) (see **Fig.16**, **Fig.17**). Comparing the results, the September concentrations were generally higher than the previous ones, except those registered in the Mănăştur district (due to the closing of the brewery and with the finish of the stadium work) and Pajiștei Street (there were no longer construction works) (**Fig.16** and **17**).

Regarding the distribution of the concentrations, it was seen that their variability in time and space, depending on the influence factors (see **Fig.18**). On these terms one can't tell that pollution is higher near the center of the city.

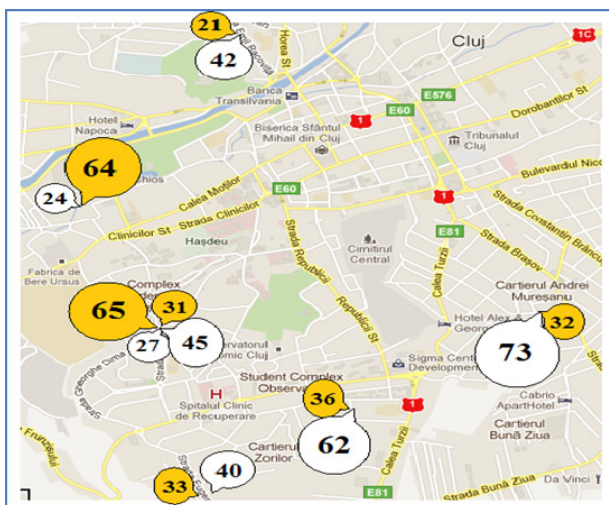


Fig. 18. *PM_{2.5} levels ($\mu\text{g}/\text{m}^3$) over the two monitoring periods in Cluj-Napoca (I-orange, II- white; the size varies with the time measured).*

The evaluation of potential health effects

In terms of health risk in 89% of the measured time representing approximately 242 hours, averages exceeded the standards set by WHO and the EU. This should be remembered that the statistics show an increase in mortality with 1.3-1.7%, even 2.3% (among older people), mainly due to respiratory and cardiovascular diseases associated with exposure of at least 2-4 days at fine particles concentrations which have suffered increases with $10\mu\text{g}/\text{m}^3$ (Schwartz et al., 1996, Borja-Aburto et al., 1998).

In this case each point recorded concentrations that exceeded at least $10\mu\text{g}/\text{m}^3$ the limit set on $25\mu\text{g}/\text{m}^3$ (**Fig. 18**). Epidemiological studies have shown an increased mortality risk of ischemic heart disease by 2.1% (Schwartz et al., 1996), and 4% -8% of lung cancer and all cardiopulmonary causes for each increase with $10\mu\text{g}/\text{m}^3$ in the fine particles concentration (Pope et al., 2002). An exposure of 48 hours or of a longer period of time to such amounts can lead to a significant increase in systolic and diastolic blood pressure, intima-media thickness of carotid artery with 4% and 1.1% in daily mortality (4.5% increase mortality by chronic obstructive pulmonary diseases and 7% due to pneumonia) (Laden et al., 2000; Simkhovich et al., 2008). Also, regarding the cardiovascular system, an increase of $25\mu\text{g}/\text{m}^3$ levels of $\text{PM}_{2.5}$ (obtained for example in the first round of measurements at points located on streets like Sputnik and Predeal, or in the second round, on streets like Pajiștei and I. Măcelaru), registered for a year, would lead to an excess risk of 3 to 8.1% for the occurrence of ischemic heart disease, respectively 4.9 to 6.8% for heart failure (Moldoveanu, 2005).

The results of the study made in Cluj-Napoca, revealed that traffic was the main source of pollution identified. It should be noted that a short-term increase with $10\mu\text{g}/\text{m}^3$ of $\text{PM}_{2.5}$ level occurred from mobile sources was correlated with a 3.4% increase in daily mortality, or 1.1%, if the main source would have been the burning fossil fuels (Laden et al., 2000). Also, studies have showed a high association with coronary atherosclerosis, as the distance between home and the major traffic route was reduced (Hoffmann et al., 2007); based on the former results, in this case, it could be appreciated that most affected residents would be those who lived in the proximity of streets like E. Ionescu, where the unpaved road emits large amounts of dust.

On short period of time the research showed an association of an acute exposure of 2-24 hours to elevated $\text{PM}_{2.5}$ concentrations with a transient risk of acute myocardial infarction onset after the exposure (Peters et al., 2001). Such exposures were recorded so as the first period of measurements (on Pajiștei and I. Măcelaru streets, where the average values obtained were about $65\mu\text{g}/\text{m}^3$), and the second one (on Sputnik and Predeal streets, where the average values obtained for 24 hours, were $62\mu\text{g}/\text{m}^3$, respectively $73\mu\text{g}/\text{m}^3$). However, considering the number of hospital admissions, an increase of $\text{PM}_{2.5}$ with $25\mu\text{g}/\text{m}^3$ led to an 8.7% risk excess for asthma (Chunram et al., 2007).

Considering that each exceeding of $\text{PM}_{2.5}$ concentration with $10\mu\text{g}/\text{m}^3$ was associated to almost a doubling in postnatal mortality risk due to respiratory causes (Pope and Dockery, 2006), maintaining these values obtained in the present study, in long-lasting time it would mean an increased rate of postnatal mortality in the area. After studying the long term effects, researchers observed for each $10\mu\text{g}/\text{m}^3$ an increase of 2.3% in the number of red blood cells and 2.6% in hemoglobin on women (Sorensen et al., 2003), and a 14% increase in the number of non-fatal cardiovascular events, respectively 32% for fatal ones (Pope and Dockery, 2006).

Other studies showed an average increase of 16% per $10\mu\text{g}/\text{m}^3$ of $\text{PM}_{2.5}$ of the mortality risk as well as a decrease of 0.73% per $10\mu\text{g}/\text{m}^3$, but only for cardiovascular respiratory diseases, except for lung cancer (effects can be partially reversible over a period of a decade) (Simkhovich et al., 2008; Laden et al., 2006). Thus, it could be estimated a significant risk reduction for the residents of I. Măcelaru street, where together with the completion of the arena construction and the shutting down of the brewery, concentrations fell below the $25\mu\text{g}/\text{m}^3$ limit. Also, for longer periods of time each decrease of $10\mu\text{g}/\text{m}^3$ in the $\text{PM}_{2.5}$ concentration may indicate a significant reduction of 27% of health risk (Pope and Dockery, 2006).

CONCLUSIONS

The study highlighted the variability in time and space of the concentrations distribution, due to the position of the measurement points from the main pollution sources (traffic and construction works and arrangements) and the influence of certain meteorological parameters. Except for the wind, whose influence was highlighted, the correlation of $\text{PM}_{2.5}$ values with those of the meteorological parameters (corresponding for the monitoring interval), proved to be irrelevant in the present study. Based on these observations, for an effective correlation, it can be assumed that the measurements of the humidity, temperature, wind speed, atmospheric pressure and also those of fine particles must be made at the same point.

Comparing the results, the values from the second monitoring period were higher than the previous ones obtained. In most cases the average values exceeded the $25\mu\text{g}/\text{m}^3$ limit set by WHO for the health protection. Regarding the exposure of the local population to over exceeding concentrations of $\text{PM}_{2.5}$ (40-100% during measurements), it was showed that this can affect the people both short and long term. In order to identify the health effects on the local population, long-lasting periods of monitoring in key locations correlated with observations, and also toxicological and epidemiological studies conducted in the same period are required.

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DETECTION OF IRRADIATED SEAFOOD USING THERMALLY STIMULATED LUMINESCENCE APPLIED ON SHELLS

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ABSTRACT. Treatment with ionizing radiations is one of the most extensively studied technologies and also one of the most effective techniques to preserve food. Thermoluminescence (TL) is one of the physical methods recommended by the European Committee for Standardization for the identification of irradiated food from which silicate minerals can be extracted. Using the TL principle, the aim of our present work was to investigate the luminescence properties of shells in order to be able to use them as dosimeters for a reliable identification for a possible prior treatment with ionizing radiations of seafood.

Key words: *Food irradiation, Thermoluminescence, Shells*

INTRODUCTION

Treatment of food by irradiation is an extensively studied technology that aims at improving microbiological safety and storability of products. However, much of the research has remained of pure scientific interest and this technique is still relatively underutilized commercially. Its application potential is diverse, from inhibition of sprouting of tubers and bulbs to production of commercially sterile foods (Farkas and Mohacsi-Farkas, 2011).

Food irradiation is a physical process in which food is exposed to high doses of ionising radiation. Ionising radiations damage very effectively the DNA so that living cells become inactivated, therefore microorganisms, insect gametes, and plant meristems are prevented from reproducing (Farkas, 2006). According to the Codex General Standard for Irradiated Foods (CAC, 2003) food irradiation is performed with gamma rays emitted by ⁶⁰Co and to a lesser extent ¹³⁷Cs sources, X-rays with energies up to 5 MeV, or accelerated electrons with energies up to 10 MeV. The treatment of foods is generally made after packing in order to avoid the re-contamination of the product.

In 1964, 1969, 1976, and 1980, the Joint FAO/IAEA/WHO Expert Committee on the Wholesomeness of Irradiated Food (JECFI), studied the effects of ionising radiation on the health of consumers of irradiated foods. In 1980, JECFI published the following conclusions: "the irradiation of any food commodity to an overall average

dose of 10 kGy presents no toxicological hazard, hence, toxicological testing of food so treated no longer required” and “irradiation of food up to an overall average dose of 10 kGy introduced no specific nutritional or microbiological problems” (WHO, 1981).

A group of researchers from the Food and Agricultural Organization (FAO), the International Atomic Energy Agency (IAEA) and the World Health Organization (WHO), tested in 1997 the safety of irradiated foods on the health of consumers in the dose range 25-60 kGy, and in 1999 published a report which indicated that food irradiated with a dose above 10 kGy are not toxic (European Communities, 2001).

During the period 1983-2004 the International Consultive Group of Food Irradiation (ICGFI) was established, founded to ensure control and irradiated food trade ensured by the cooperation with governments. According to IAEA, food irradiation is currently approved in 55 countries and 68 centers of irradiation are registered worldwide (Farkas and Mohacsi-Farkas, 2011). RADURA symbol appeared in 1972 and it was made officially by R. M. Ulmann, the manager of the Pilot Plant for Food Irradiation, Wageningen, the Netherlands. The symbol (**Fig. 1**) has the form of a plant surrounded by a circle. The interpretation of the symbol is: the central dot is the radiation source; the two circles segments ('leaves') are the biological shield to protect the workers and the environment; the outer ring is the transport system, the lower half of it is the shielded from radiation by the biological shield, the upper broken half symbolizes the rays hitting the target the target goods on the transport system (Ehlermann, 2009). According to the Codex Alimentarius standard, the usage of RADURA symbol is optional. In USA, there is the obligativity to use the logo while its use is not compulsory in the European Union.



Fig. 1. *The international logo of RADURA according to the Codex Alimentarius (in green) (Ehlermann, 2009).*

The European Union legislation was published in February 1999. The Directive 1999/2/EC and 1999/3/EC became effective in 20 September 2000 and starting with 20 March 2001 all irradiated foods and food ingredients on the Community market were obliged to comply with the provisions of the Directives. The framework Directive 1999/2/EC of the European Parliament and Council on the approximation of the laws of Member States concerning foods and food ingredients treated with ionizing radiation, covers general and technical aspects for carrying out the process, labeling of irradiated foods and conditions for authorizing food irradiation. The implementing Directive 1999/3/EC of the European Parliament and Council on the establishment of a Community list of food and food ingredients authorized for treatment with ionising radiation. This list refers to only one category of foods, namely dried aromatic herbs, spices and vegetable seasonings.

The Romanian law on the irradiation of foods is provided in "Norms concerning foodstuffs and food ingredients treated with ionizing radiation" (CNCAN, 2002) which represents a translation and a combination of the texts of the Directives 1999/2/EC and 1999/3/EC (EC, 1999a, b). The document was published in the Official Gazette on 25 April 2002, and the list of foods and food ingredients from the Directive 1999/3/EC was adopted and published in July 2006 by the Romanian Ministry of Public Health (MSP 2006). In 2007 a study on detection of irradiated foodstuffs from the Romanian market has been published. A wide range of foodstuffs have been studied, such as potatoes, onions, wheat, rice, dried beans, sweet and hot paprika powder, herbal teas, chicken, beef, fish, black pepper, parsley, coriander and shrimps using different detection methods: DNA, ESR and TL (Cutrubinis et al., 2007).

The most recent study on the status of irradiated foods worldwide was carried out by a team of Japanese authors on the results of the research of the Japan Atomic Energy Commission Cabinet Office (Kume et al., 2009). The study presents statistical data relating to irradiated food in 2005. The study referred to four global regions: America, EU, Asia and Oceania, and Africa and others including Ukraine and Israel. The obtained data were organized according to five categories of foods: spices and dry vegetables, grains and fruits, meat and seafood, root crops and bulbs and others. The total quantity of irradiated food worldwide in 2005 was 405000 tons. The most relevant quantity of spices and dry vegetables were irradiated in USA (80000 tons), China (52000 tons), Brazil (20000 tons) and South Africa (16000 tons). For spices and vegetables disinfections using irradiation Ukraine is on the first place with a quantity of 70000 tons and for meat and seafood disinfection, the first positions are occupied by Vietnam (14000 tons), SUA (8000 tons) and Belgium (5500 tons). China is the only country that occupies the first position in the case of two food categories: 80000 tons for the garlic and potato sprout inhibition and 10000 tons for other foods irradiation than the ones already mentioned. China is also the country in which the most relevant quantity of food is being irradiated (146000 tons), followed by USA (92000 tons) and Ukraine (70000 tons).

The consultation paper on food irradiation from year 2000 sent by the Commission services to the European consumer organizations and the European industry associations generated different views (European Communities, 2001). The consumer organizations argue that food irradiation is not necessary in case good hygiene practices are being applied as there might be the danger of using food irradiation as a substitute for good practices of hygiene. On the contrary, the irradiation industry, the FAO/WHO International Consultative Group on Food Irradiation, the USA government and some other research association and institutes declare that food irradiation is a safe process and contributes to the increasing consumer protection by destroying food infectious contaminants. They affirm that if this irradiation process is applied by using good manufacturing practices, it will not substitute the good hygiene practices.

There are a number of methods to detect irradiated foods, including physical, such as Electron Spin Resonance spectroscopy and Luminescence techniques like Thermoluminescence, Photoluminescence or Chemoluminescence, Chemical, DNA and Biological methods.

TL method is suitable for food products such as herbs, spices, bulbs, tubers, vegetables, cereals, shellfish and fruits. This is based on analyzing the luminescence of silicate minerals that can be isolated from these samples, as the dosimetric properties of these minerals are well known and extensively studied (Timar-Gabor, 2012). This is one of the five Codex Alimentarius method approved by CAC and adopted as EN 1788 in 2001 (Chauhan et al., 2009). In the case of shellfish the minerals used for the analysis are generally the silicates present in the intestines, but there are experimental evidences that carbonates that constitute the shells can be suitable for the identification of this kind of food (Cruz-Zaragoza et al., 2012). The aim of our present work was to investigate the luminescence properties of shells in order to be able to use them as dosimeters for a reliable identification for a possible treatment with ionizing radiations of commercialized seafood.

MATERIALS AND METHODS

Food samples

Three types of shellfish have been analysed. Two of the samples have been purchased from different local supermarkets, none of them being labeled as treated with ionizing radiation. The third sample was a natural shell, collected from the Black Sea shore.

Prior to being measured, the samples have been prepared. Organic material has been mechanically removed and the shell was washed with hydrogen peroxide-30% and distilled water. The shells have been gently crushed in a mortar and the fraction ranging from 125 to 250 μm has been isolated by sieving. Discs or cups (9 mm diameter) have been prepared from these samples. In case of discs, the material has been fixed with silicone oil, and in case of cups, these have been filled with a spatula.

Principle of the TL analysis

TL is a method in which heat is applied to release trapped energy from minerals which have been exposed to ionizing radiation. Light emission which occurs on heating is recorded as a first glow curve in a TL reader, a second TL glow of the same sample after exposure to a fixed dose of radiation being recorded to normalize the TL response (Bayram and Delincée, 2003). The method consists in the evaluation of the "TL Ratio" between the first TL glow, and the second TL glow of the same sample after re-irradiation with a certain dose (depending on the type of food). If the TL Ratio is greater than 0.1 the sample has to be considered irradiated (D'Oca and Bartolotta, 2010).

TL measurements

The food samples have been tested using the thermoluminescence detection method (EN 1788-2001). The measurements were carried out by using a Risø luminescence reader, TL/OSL DA-20 model (Faculty of Environmental Science

and Engineering, Cluj-Napoca, Romania) designed to perform measurements of thermoluminescence and optically stimulated luminescence. In case of thermoluminescence, the samples were heated up to 500 °C, with a linear heating rate of 5°C/s. Luminescence was recorded using an EMI 9235QA photomultiplier tube through a thick Hoya U-340 filter, which has an extended UV response with maximum detection efficiency between 300 and 400 nm. The samples irradiation was obtained using the beta irradiator from the reader, with a Sr-90/Y-90 beta source which emits beta particles with a maximum energy of 2.27 MeV. The dose rate in quartz at the sample position is 0.157 Gy/s.

RESULTS AND DISCUSSION

As mentioned, the experiments have been carried out on three different types of shellfish aiming to observe their properties (TL glow curves) in order to use them as potential detectors for a possible treatment with ionizing radiations. **Fig. 2.** shows the TL glow curves of the natural shells from the Black Sea. None of the TL glow curves show peaks at a certain temperature, as expected. In case of the shells purchased from the supermarkets, we can see the TL glow curves in **Fig. 3** and **Fig. 4**. Only one of the samples analyzed shows an intense TL glow peak at a high temperature (shells purchased from a local supermarket – type B). This natural signal has a clear peak in the range of 200-400 °C temperature, which is stable in time.

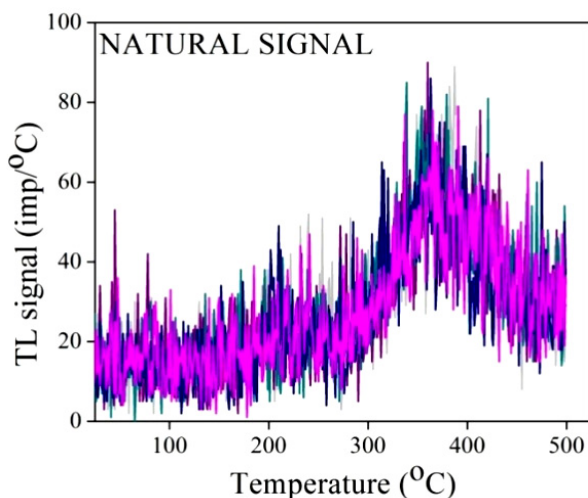


Fig. 2. Natural TL glow curves of the prepared natural shells –type N.

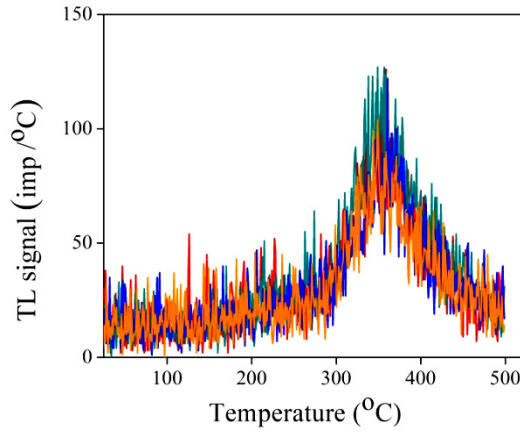


Fig. 3. “Natural” TL glow curves of the shell purchased from supermarket – type A.

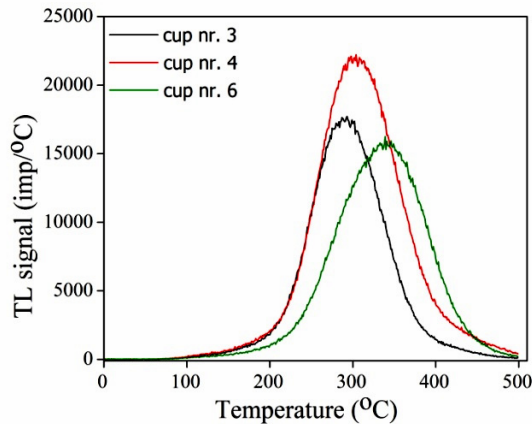


Fig. 4. “Natural” TL signal of three samples in case of the shells purchased from a local supermarket – type B.

Subsequently the same aliquots have been irradiated with an artificial dose of 3000 Gy (an irradiation time of 19000 s). The signal was read immediately after but allowing for the time needed for each aliquot to be individually irradiated, respectively 11 h in case of the first sample, 5 h in case of the second sample, respectively 1 h in case of the last sample. In Fig. 5 we can observe a signal at a low temperature (100-200 °C), which is expected to be unstable in time. The shift of the total signal is explained by the decay of these unstable components.

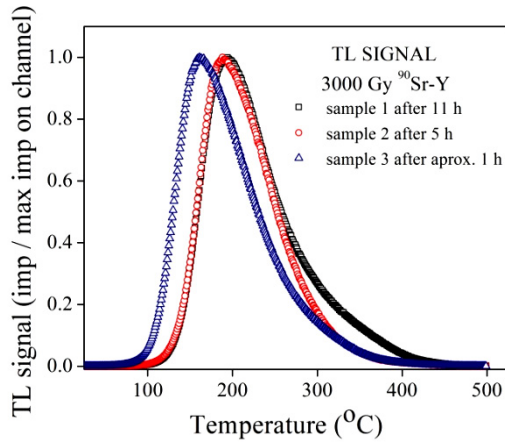


Fig. 5. TL glow curves reported to the maximum impulses on channels of the shell (type B) purchased from supermarket, which was irradiated with an artificial dose of 3 kGy.

Fig. 6 presents the “natural” glow curve of the shell -type B, in comparison with glow curves of the same sample irradiated with a dose of 3 kGy, 15.7 Gy respectively, and the background. It can be easily noticed that the “natural” signal for the as received sample is much higher than expected from normal environmental caused (environmental annual dose being of a few mGys), indicating that this sample has been treated with ionizing radiations.

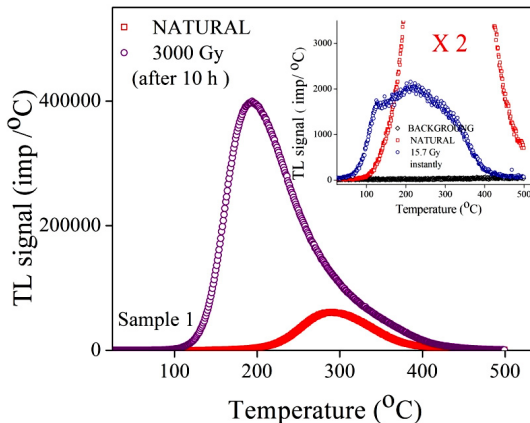


Fig. 6. Comparison of TL glow curves in case of shell (type B) purchased from supermarket, irradiated it with a dose of 3000 Gy, 15.7 Gy respectively the background as well as the “Natural”-as received signal.

For the samples presented above (shell type B, **Fig 4, 5, 6**) the TL integral (calculated as the sum of the counts from 200 to 400 °C), is presented in Table 1, along with the response to a 15.7 Gy artificial dose for the sake of completeness. In columns 4 and 5 the integrated TL signal ratio between the natural TL signal and the signal in case of 15.7 Gy respectively 3000 Gy are presented. In the latter case, the ratio values are greater than 0.1. This can lead us to conclude that this sample was irradiated before, not over the maximum dose (according the Technological dose limits, the maximum dose in case of seafoods is 3 kGy) (IAEA, 2002). Reproducing the same analyses on the same shell samples, but irradiation with a dose of 300 Gy, we can draw the same conclusion, that this sample was treated with ionizing radiation. The Table 2 the TL glow intensity in range of 200-400 °C temperature is presented in case of the natural signal and respectively 300 Gy as artificial dose along with the glow ratios. As we can see, in case of all 5 samples the ratio results are greater than 0.1.

Table 1. *Integrated TL signal in range of 200-400 °C in case of the natural signal of the shell sample -type B and in case of 15.7 Gy and respectively 3000 Gy.*

| Disc number | Glow 1 for natural signal (counts) | Glow 2 in case of 15,7 Gy dose (counts) | Glow 3 in case of 3000 Gy dose (counts) | Glow ratio 1 (Glow1/Glow2) | Glow ratio 2 (Glow1/Glow3) |
|-------------|------------------------------------|---|---|----------------------------|----------------------------|
| 1 | 6397726 | 279268 | 29385831 | 22.9 | 0.21 |
| 2 | 868448 | 83312 | 13804955 | 10.42 | 0.06 |
| 3 | 2970192 | 122051 | 17995252 | 24.33 | 0.16 |

Table 2. *Integrated TL signal in range of 200-400 °C for the natural, respectively 300 Gy dose, and their ratio.*

| Cup number | Glow 1 for natural signal (counts) | Glow 2 in case of 300 Gy dose (counts) | Glow ratio (Glow 1/ Glow 2) |
|------------|------------------------------------|--|-----------------------------|
| 1 | 208773 | 195625 | 1.06 |
| 2 | 559075 | 1178577 | 0.47 |
| 3 | 1853944 | 3253251 | 0.56 |
| 4 | 2535200 | 4293277 | 0.59 |
| 6 | 1886666 | 4129960 | 0.45 |

CONCLUSIONS

Using the thermoluminescence method, we have analysed three different types of shells aiming to observe their properties (TL glow curves) in order to use them as potential detectors for the identification of a possible treatment with ionizing radiations. Our results show that the shells have suitable TL properties that can be used for identification of sea food treated with ionizing radiations.

A shell sample purchased from a local supermarket displayed bright TL natural signals with a clear peak in the range of 200–400°C temperature, which is stable in time. By evaluating the “TL Ratio” between the first TL glow (natural), and the second TL glow of the same sample after re-irradiation different doses up to 3000 Gy, we have concluded that this sample was preliminary treated with ionizing radiations. However, according to our results the sample was not irradiated above the permissive limits, the maximum dose in case of seafoods being 3 kGy (IAEA, 2002). In our country however, only dried aromatic herbs, spices and vegetable seasonings should be commercialized as foods treated with ionizing radiation, according to the Directive 1999/3/EC of the European Parliament and Council.

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A NEW TYPE OF MICROBIAL FUEL CELL - WITH SOLID ELECTROLYTES

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ABSTRACT. The Microbial Fuel Cells (MFC) are usually formed by liquid electrolytes. This study demonstrates that it is possible to realize an MFC two chambers type with both the microbes from anode and cyanobacteria from cathode immobilized onto the electrodes. The anode was filled with sludge collected from the waste water plant, and the cathode was filled with cyanobacteria *Synechocystis C51* in nutritive solution. Three types of cells were realized: liquid-liquid, *gel-gel with Nafion membrane* between the chambers and *gel-gel without membrane*. The bacterial cells were subjected to a two-day cycle of light/darkness - 24 hours light and 24 hours darkness. The power density increased by 50% at 2.5 klux during light compared to that corresponding at 130 klux during darkness. The power density dependence on light shows that the cyanobacteria present in the cathode, even immobilized in gel, produces oxygen through photosynthesis. This means that the cathode aeration, which consumes energy in the case of common MFCs, can be replaced successfully with oxygen produced by the cyanobacteria. The power density of the three types of bacterial cells used in the study have comparable values. The MFC's with immobilized electrolytes works just as well as the classics, with liquid electrolytes.

Key words: *immobilized cyanobacteria, microbial fuel cell, Synechocystis*

INTRODUCTION

The bacteria used in MFC convert the energy into electricity through the catalytic activity (Kim et al., 2007). MFC is made by anode and cathode, separated by a membrane with cationic exchange. The anolyte is represented by the mud containing bacteria that generate electric power, and the catholyte is represented by water, which, most of the times is paddled with air particles. The bacteria oxidate the organic matter, giving protons and electrons.

Oxygen is used as an acceptor of electrons in the cathode reaction, but, by paddling the cathode with air particles, electric power is consumed, reducing the net quantity of energy produced by MFC (Strik et al., 2010). It is considered that the low Coulombic efficiency of MFC is due to the limitation of oxygen in the cathode's room and also due to the diffusion of oxygen in the anode's room through the membrane. Thus, in order to avoid the limitation of oxygen, its concentration

from the cathode must be kept at a high level, which presupposes the increase of consumed power and resulting in a higher diffusion of the oxygen in the anode's room (Pham et al., 2004).

This study proposes the photosynthesis of the cyanobacteria as a source of energy at the cathode without consuming energy from the outside, avoiding the diffusion of oxygen in the anode's room. The study also demonstrates that there is a possibility to build and make work an MFC with the cyanobacteria immobilized on the electrodes. The *Synechocystis* cyanobacteria are used as model microorganisms in studies such as photosynthesis, the assimilation of carbon and of nitrogen, the evolution of plastids and the capacity to adapt to environmental stress. In 1968 it was for the first time separated from freshwater. The photosynthetic machine is similar to that from the plants and it present phototactism (<http://en.wikipedia.org>). In our study, the cyanobacteria comes from The Institute of Biological Research, Cluj Napoca. They have been used as sources of oxygen at the cathode. There have also been used cyanobacteria and algae at the cathode, but under the form of suspension or immobilized in pearls with calcium alginate (Yadav, 2009).

MATERIALS AND METHODS

The mud containing bacteria is found at the anode, while at the cathode we can find *Synechocystis C51* cyanobacteria. The mud comes from The Water Filtering Station Somezeni, Cluj Napoca. The rooms of the cell are spectrophotometric tubs, having a 4.5 cm length and a 1 cm width. The volume of the electrolyte in one room is of 3 ml, and the surface of the hole through which the two rooms of the cell communicate is of 1.4 cm². For this study there have been used graphite spectroscopic electrodes having a stick shape, and a working length of 3.5 cm and a diameter of 0.6 cm. Alfa Aesar naphion membrane, 0.09 mm thick, has been used.

The immobilization of the cells: represents the blocking of the cells in a semisolid mass. An ideal matrix must not permit the dislocation of the cells in the matrix. Still, it has to allow oxygen, nutrients, analytes and products of the cellular metabolism to penetrate inside (Premkumar et al., 2002). This has to be functional at the environmental temperature and to survive the harsh conditions of waste water. It also has to impede other cells from the outside to enter the matrix (**Fig. 1**).

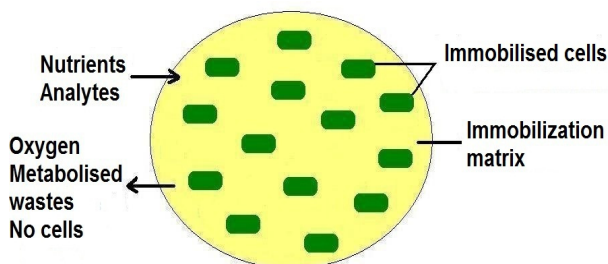


Fig. 1. *The scheme of an ideal immobilization matrix.*

There are several types of matrixes that immobilize cells. These include systems which produce hydrogels as a reaction to the action of some factors (ions, heat, light, or different chemicals with electrophyl action (<http://scholar.lib.vt.edu>). The activation of the immobilizing system has to be considered carefully when building an immobilizing matrix. Excessive heat during the making of the matrix could kill the bacteria, as well as the exposure to different types of chemicals. Ultraviolet light can cause mutations among cells or it can lead to the death of the cells. All these factors can cause premature stress to the bacteria. Hydrogels have an advantage because of their high content of water, flexibility and biocompatibility (Elisseeff et al., 2000, Li 1998, Uludag et al., 2000). In order to immobilize the cells there have been used alginates, (Smidsrod et al., 1990), photopolymers (Bryant et al., 2000, Koh et al., 2002), soil-gels (Livage, 1997, Fennouh et al., 1999), and thermic reversible gels so far (Sun et al., 2003, Sanchez et al., 2004).

The immobilization of the bacteria

- *the immobilization of the bacteria from the anode electrolyte* – we added agar-agar to the water, having a concentration of 1 %, which we brought to the point of boiling; the obtained solution was let to cool down to 30-40 degrees, after that we added the mud and we finally poured the solution into the tubs.

- *the immobilization of the cyanobacteria from the cathode electrolyte* –in order to prolonge the life of cyanobacteria and in order to offer them an appropriate environment, the solvent in which we put agar-agar is a nutritive solution for cyanobacteria, the composition of which is found in (Dragos et al., 1997); in order to immobilize cyanobacteria, we followed the same steps described above at the immobilization of the bacteria from the anode electrolyte, with the exception that the electrolyte is represented by the cyanobacteria found in the nutritive solution.

THE EXPERIMENT

We realized three types of MFC:

- *liquid-liquid*, with naphion membrane between the two rooms; the electrolytes are liquid;

- *gel-gel*, with naphion membrane between the two rooms; the electrolytes are made out of gel;

- *gel-gel*, without a membrane between the two rooms the gel electrolytes are in direct contact with each other.

It has been observed the power density in time of the cells and their reaction to light exposure during two light/darkness 48 h cycles.

RESULTS AND DISCUSSIONS

The obtained cells are given in **Fig. 2** and **Fig. 3**.

The internal resistance of the cells has been measured using the polarisation curves method, **Fig. 4**. The research demonstrated that a high internal resistance decreases the performances of an MFC (Logan & Regan, 2006). It is important to

know the internal resistance in order to be able to apply an external resistance equal to the internal one, so that the cell can function at its maximum capacity. This way, the external resistance chosen for the study was 1 kΩ.



Fig. 2. The bacteria from sludge (up), and cyanobacteria (down) immobilized onto the electrodes.

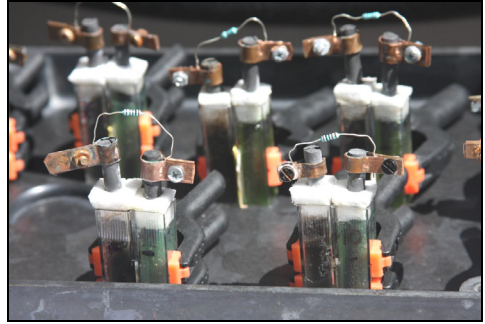


Fig. 3. Assembled cells.

The measurements were made with the PeakTech 3340 DMM multimeter (PeakTech Prüf - und Messtechnik GmbH Germany). The values of the internal resistance for the three types of MFC are 1-1.2 kΩ.

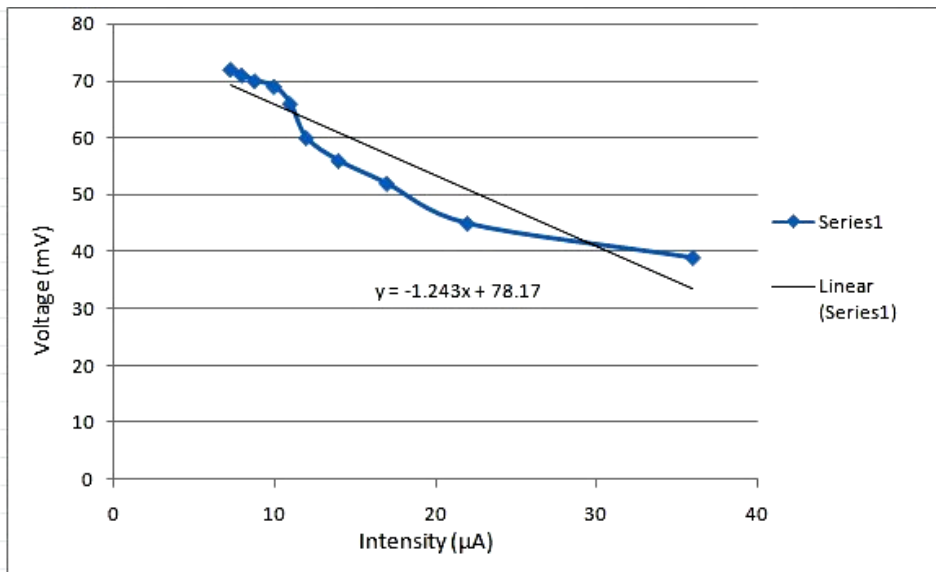


Fig. 4. The diagram of dependance of voltage on intensity.

The cells have passed through some light/darkness cycles, during which the intensity and the voltage of the electric current were measured hour by hour, for four days. The light flow was of 2.5 klux during the period of light and of 130 lux during that of darkness. With these values obtained, there have been made some diagrams of the power density (the power reported to the surface of the section of the electrode), depending on the light/darkness cycles for all the three types of MFC (**Fig. 5**).

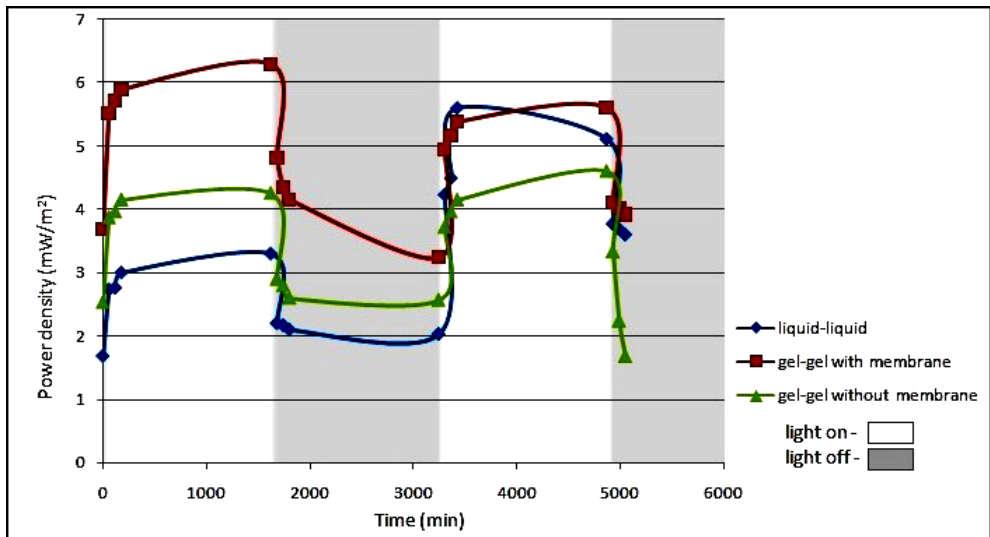


Fig.5. The power density dependence on the light at all three types of MFC.

The power density is dependant on the light; this fact can be noticed at all the three types of MFC. This variation of the power density demonstrates that oxygen is generated through the photosynthesis of the cyanobacteria and it plays a major role in the maximization of the performances of the cell. The power densities of the three types of cells have comparable values. This means that the *gel-gel cells with membrane* and the *gel-gel cells without membrane* function in the same conditions as the classical *liquid-liquid cells*.

CONCLUSIONS

I realized three types of MFC: *liquid-liquid*, *gel-gel with membrane*, and *gel-gel without membrane*. The microorganisms from the anolyte and from the catholyte have been immobilized on the electrodes using agar-agar. I managed to demonstrate that the electric charge and the nutritive substances are transmitted through the matrix. The oxygen produced by the photosynthesis of the cyanobacteria was

evidenced through the cell's reaction to light exposure. The values obtained as a result of the measurements show the dependence of the density of power upon the oxygen generated at the cathode. As shown in (Fig. 5), the values of the power densities are 50 % higher when exposed to light. Obtaining the dissolved oxygen by padding the catolyte using electric power from the outside, can be replaced successfully with the method presented in this study.

The power densities of the three types of MFC have comparable values. Thus, the *gel-gel cells with membrane and those without membrane function in the same way as the classical liquid-liquid cells*. This achievement allows giving up the membrane (the costs are high) and it opens the way to the realisation of some MFC *gel-gel* geometries, impossible to realise with classical *liquid-liquid* cells.

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A NEW TYPE OF MICROBIAL FUEL CELL - WITH SOLID ELECTROLYTES

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DYNAMICS OF THE WHEAT PESTS AND INTEGRATED CONTROL IN RELATION WITH AGRO-ECOLOGICAL CHANGES AND AGRICULTURE SUSTAINABLE DEVELOPMENT, IN TRANSYLVANIA

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ABSTRACT. Elaborated in 2008-2011, at Agricultural Research Station Turda, the paper presents the research concerning the increasing of main wheat pests abundance and extension risk of pests attack on the agro-ecological changes in Transylvania. Entomological study has been carried out under different cultural soil technologies: classical (by plowing) and conservative (by minimum soil tillage and no tillage), in open field agroecosystems with antierosional terraces and in agroforestry belts farming system. The spring months of the last years was characterized by an increased warming and dryness periods, causing the pest abundance and damages growth on wheat. It was pointed out major outbreaks of attack of thrips (*Haplothrips tritici*); wheat flies (*Chloropidae*: *Oscinella frit*, *Meromyza nigriventris*, *Elachiptera cornuta* etc. and *Anthomyidae*: *Delia coarctata*, *Phorbia securis*, *Ph. penicillifera*); stem flea beetles (*Chaetocnema aridula*); bugs (*Eurygaster maura*, *Aelia acuminata*), leafhoppers (*Javesella pellucida*, *Psammotettix alienus*, *Macrosteles laevis*), aphids (*Sitobion avenae*, *Schizaphis graminum*, *Rhopalosiphum padi*, *Metopolophium dirhodum*) etc. The research results proved the importance of integrated pests control and insecticide applications in two different moments: end of tillering phase and spike appearance, in open field with classical soil technology. Also, the integrated pests management (IPM) is a major section of soil no tillage technologies comprising a special pest control strategy, with insecticides application in 2-3 successive treatments, entomophagous conservation and use, environmental protection. The IPM research pointed out the efficiency of biological control, only using the entomophagous natural resources, without insecticides application, in the farming system with protective agro-forestry belts – favorable for the increasing of useful fauna.

Key words: wheat pests, entomophagous, integrated pest control, soil no tillage technology, protective agroforestry belts.

INTRODUCTION

Agricultural entomology and applied ecology researches conducted at the Agricultural Research and Development Station in Turda, in Central Transylvania, have proposed the elaboration of wheat integrated pest control strategy, especially under the conditions of profound agro-ecological changes caused by climate warming and also under the new technological and economical conditions in regional agricultural exploitations (**Fig. 1**). On the last years, the increase of pest damages was registered at the wheat crops intensely affected by climatic unfavorable conditions and by the exploitation system with incomplete or incorrect crop technologies (Malschi 2007, 2008, 2009). The study performed during 1980-2010 has shown the evolution of main cereal pest such as: Diptera, Homoptera, Thysanoptera, Coleoptera etc. (**Fig. 2**), as well as the importance of integrated pest control strategies (Malschi et al., 2011).

Integrated pest management (IPM) is an agro-ecological system approach to crop protection that uses different practices to control the pest and minimize the pesticide applications (Food and Agriculture Organisation/FAO). IPM is an environmentally approach and an economical means of pest management comprising: the environmental and ecological factors involved in pest behaviour, the knowledge on pest lifecycles and their interaction with the environment, biological and chemical pest control methods (Baicu, 1996, Bărbulescu et al., 2001, Malschi Dana, 2009, Malschi et al., 2011, Popov et al., 2009, Wetzal, 1995). IPM is practiced in of the following steps: **1.** Weather forecasting to evaluate the risk of pest outbreaks. **2.** Understanding the pest population and their habitual behaviour, using the pest trapping to analyse the stage of lifecycle and population density; monitoring to spot damaged crops, dynamics and attack level of pest populations; determining the thresholds of economical damage (TED) which refers to the population of pests that can exist on the field with out causing an economical damage, considering that the total eradication of pest is not healthy for the environment. **3.** Culture controls methods: soil preparation, using certified healthy seeds—genetically resistant and tolerant varieties. **4.** Biological controls: entomophagous predators and parasites, biological products and natural resources used to control or to limit the pest population. **5.** Chemical controls: using pesticides to the pest control, only recommended if the biological methods fail and the threshold limit has been surpassed. **6.** Record keeping: used to predict the attack and future investments (Food and Agriculture Organization / FAO, www.fao.org/agriculture/crops/core-themes/theme/pests/ipm/)

Common Agricultural Policy specifying the importance of providing environmental public goods associated with agriculture, mentions the food security, health security, rural vitality and a significant range of public goods also associated with agricultural practices and environment - such as agricultural landscapes, farmland biodiversity, soil, water and air quality, climate stability (greenhouse gas emissions), climate stability (carbon storage), farming practices in order to maintain landscape features and specific habitats, to manage natural resources of water and soils. Special public goods are associated with agriculture practices of integrated crops and pest management - such as the positive impact of integrated pests control technologies, biological pest control, conservation and use of biodiversity of beneficial entomophagous fauna and useful flora, biological agriculture, related to pollution limitation and

sustainable development of environmental factors quality; the positive impact of using technological conservative systems with minimum soil tillage and no tillage, particularly in water stressed areas, etc., related to climate stability (gas emissions, carbon management and storage), (Cooper et al., 2009, <http://europedirect.nord-vest.ro/detaliu>).



Fig. 1. Aspects of culture technology in ARDS Turda fields by comparison with incorrect farming systems in zone little crop fields (Google earth images, 2009).

- A.** Applied IPM on the agroecosystems in open field with land arranged in antierrosion terraces, with classic and conservative no tillage soil technology.
- B.** Applied IPM on the farm with protective agro-forestry belts, in Cean-Bolduț.

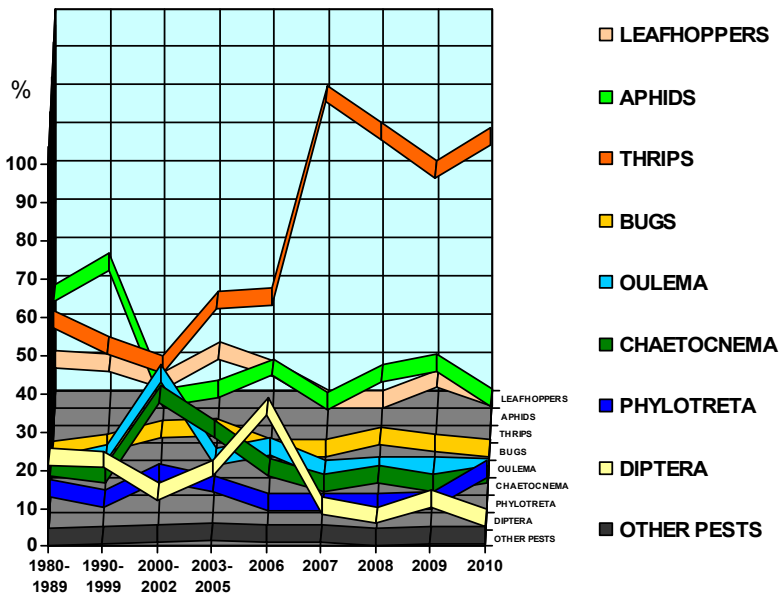


Fig. 2. Dynamics of wheat pests structure (%) (ARDS Turda 1980-2010)

RESEARCH METHODOLOGY

Based on author's 30 year research studies at the Agricultural Research-Development Station Turda of The Romanian Academy of Agriculture and Forestry Sciences, the paper presents an agro-ecological study on the population dynamics and attack evolution of wheat pests and the adequate integrated pest control methods under different cultural soil technologies: classical (by plowing) and conservative (by minimum soil tillage and no tillage), in open field agricultural system with antierosional terraces (**Fig. 3**) and in agroforestry belts farming system.



A.

B.

Fig. 3. **A.** Aspects of classic (plowing) and conservative (no tillage) soil technology, in ARDS Turda fields with land arranged in antierosional terraces; **B.** Aspects of the farming system with protective agroforestry belts in Cean-Bolduț, of ARDS Turda.

The research objectives have comprised aspects of interest such as:

- ◆ the systematic and bio-ecological study of pest species;
- ◆ the danger of attack expansion observed at present in increasing quotas and affecting wheat crop yields in accordance with the agro-ecological conditions;
- ◆ testing the adequate methods of integrated pest management, which comprise preventive and modern pest control methods based on good efficiency, showing reduced side effects and a diminished negative impact on useful entomophagous fauna and environment;
- ◆ elaboration of agro-ecologically integrated pest control strategy by researches of attack diminishing methods in accordance with technological factors such as: - selective, efficient insecticides, agro-technical methods; biotic factors: - natural entomophags, tolerant varieties; and environment protection factors.

During 2008-2011, the study has revealed data on species composition, damage levels and experimental field tests regarding integrated pest control, in wheat crops. Species determination has been achieved based on the abundant samples collected, performed every 10 days. The analyzed samples have been obtained by the method of complex traps, including pitfall soil recipients (the Barber traps for the epigeous arthropod fauna) and captures in 100 double sweep-net catches, for the arthropod fauna at the plant level. The structure and dynamics of the pest species populations interacting with predatory arthropod fauna have been studied in wheat crops.

RESULTS AND DISCUSSIONS

In order to optimize the environment-agriculture-sustainable development relationship, scientific and technological knowledge regarding the modernization of pest control management needs complex research approaches in a systemic, agro-ecologically integrated manner (Malschi 2007, 2008, 2009).

The changes in the level of regional climate, represented by warming and excessive draught, ample alternation of temperatures and the presence of extremely warm periods especially in spring (Fig. 4), have caused the burst of pest populations which may cause unexpectedly important damages to wheat crops. It was pointed out major outbreaks of attack of thrips (*Haplothrips tritici*); wheat flies (*Chloropidae: Oscinella frit*, *Meromyza nigriventris*, *Elachiptera cornuta* etc. and *Anthomyidae: Delia coarctata*, *Phorbia securis*, *Ph. penicillifera*); stem flea beetles (*Chaetocnema aridula*); bugs (*Eurygaster maura*, *Aelia acuminata*), leafhoppers (*Javesella pellucida*, *Psammotettix alienus*, *Macrosteles laevis*), aphids (*Sitobion avenae*, *Schizaphis graminum*, *Rhopalosiphum padi*, *Metopolophium dirhodum*) etc.

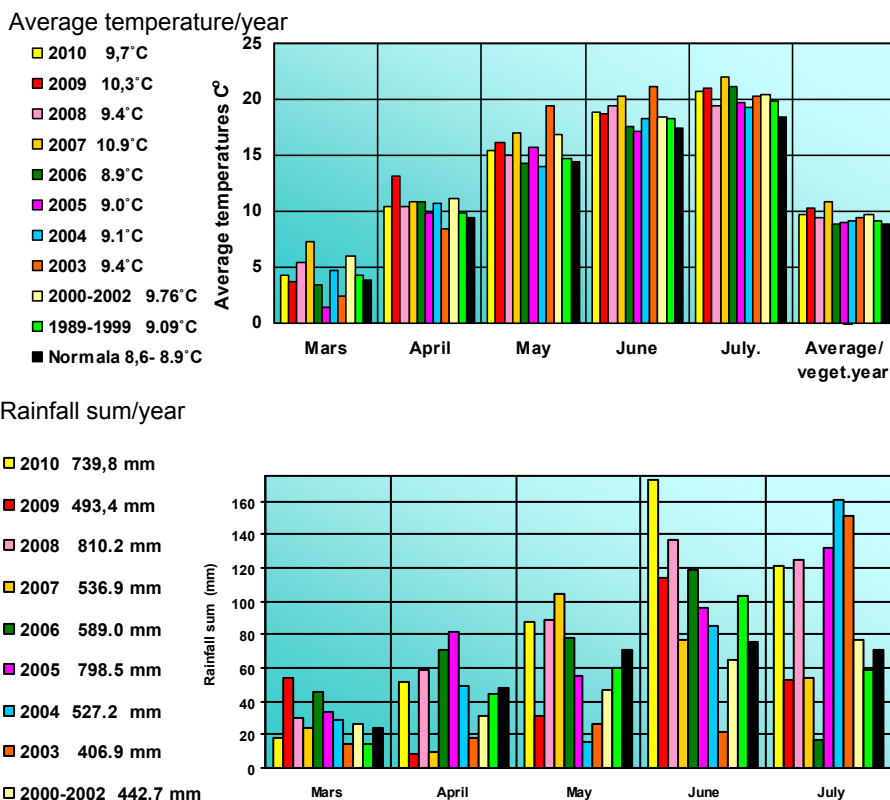


Fig. 4. Average temperatures and sum of rainfall at Turda conditions by month, from March to July and by year, in 1989-2010

During 2008-2011, at the ARDS in Turda studies on the wheat pests such as diptera, aphids, leafhoppers, thrips, bugs, cereal leaf beetles etc, the levels of attack and the present integrated pest control strategy as part of the agro-ecological technological system of the sustainable development of wheat in Transylvania have been conducted (**Tables 1 and 2**).

Table 1. Dynamics of wheat pests structure (%) in 1980-2010, at ARDS Turda

| Wheat pests | 1980-1989 | 1990-1999 | 2000-2005 | 2006-2010 |
|---|-----------|-----------|-----------|-----------|
| Wheat Thrips (<i>Haplothrips tritici</i>) | 30,0 | 23,3 | 26,8 | 69,0 |
| Cereal Aphids (<i>Sitobion avenae</i> etc.) | 32,5 | 40,4 | 6,1 | 9,4 |
| Wheat Leafhoppers (<i>Psammotettix alienus</i> etc.) | 10,5 | 9,4 | 8,8 | 3,6 |
| Cereal Flies (<i>Chloropidae</i> , <i>Anthomyiidae</i> etc.) | 16,5 | 16,0 | 10,6 | 8,4 |
| Wheat Fleas (<i>Chaetocnema</i> , <i>Phylotreta</i>) | 9,0 | 4,1 | 26,0 | 4,5 |
| Cereal Leaf Beetle (<i>Oulema</i>) | 1,0 | 4,0 | 14,1 | 2,0 |
| Cereal Bugs, sunn pest (<i>Eurygaster</i> , <i>Aelia</i>) | 0,2 | 2,3 | 6,2 | 2,0 |
| European Wheat Stem Sawfly (<i>Cephus pygmaeus</i>) etc. | 0,3 | 0,7 | 1,2 | 0,8 |

Table 2. Pests attack and density in wheat crops. ARDS Turda, 2000-2010

| Pests | Attack level | Classic technology, by plowing. Turda 2000-2005 | Conservative no tillage technology, Turda 2006-2010 | Technology with agro-forestry belts. Cean-Bolduț 2000-2010 |
|--------------|---------------------|---|---|--|
| Wheat | adults/ear | 11 | 10,0 | 4 |
| Thrips | larvae/ear | 14 | 18,3 | 4 |
| Aphids | aphids/ear | 21 | 3,7 | 2 |
| Cereal flies | deadheart tillers | 46 % | 40,1 % | 9 % |
| Cereal bugs | bugs/m ² | 5 | 2,0 | 0,5 |

A diminish in the species range and an increase of the population abundance have been recorded in the problematic pests, especially in the monovoltin species or favored by monoculture single crops and regional cereal agroecosystems presence (*Haplothrips tritici*, *Delia coarctata*, *Opomyza florum*, *Phorbia penicillifera*, *Oulema melanopus*, *Chaetocnema aridula*, *Eurygaster maura*, *Aelia acuminata*, *Zabrus tenebrioides* and others, or diptera *Chloropidae* - *Oscinella frit*, *Elachiptera cornuta*, *Meromyza nigriventris* etc. and *Anthomyiidae* polivoltine - *Phorbia securis*, *Delia platura*, leafhoppers, aphids and others). Due to aridization and climate warming, the critical attack moments of different species have been recorded 3-4 weeks earlier than normal, and overlapped (**Table 3**).

The pest achieved 79% and the entomophagous – 21 % in the structure of entomofauna of winter wheat crops in open field agricultural system. *Haplothrips tritici* – reached a 73,5%; flies: 7%; aphids: 8,2%; leafhoppers 4,3%, in the pest structure, showing an important attack potential (**Table 4**).

An entomocenotic balance was maintained in agroforestry belts farming system of Cean Bolduț. The wheat pests had a structural share of 67% and the entomophagous achieved 33% on the favorable conditions due to the forestry belts. Thrips showed 30% only and flies 27,8%, aphids 24%, leafhoppers 3,9% in the pest structure (**Table 4**).

Table 3. *Apartition and dynamics of main pests of wheat (ARDS Turda, 2011) (nr./100 sweepnet catches)*

| Classic technological system (by plowing) | | | | | | | | | |
|---|-------|-------|-------|-------|-------|-------|------|------|-------|
| | 20.04 | 21.04 | 28.04 | 11.05 | 18.05 | 27.05 | 1.06 | 6.06 | 15.06 |
| Thrips | | | 6 | 230 | 29 | 85 | 15 | 7 | 10 |
| Aphids | | 3 | | | 1 | 6 | 34 | 37 | 9 |
| Leafhoppers | 4 | 1 | 10 | 3 | 1 | 10 | 1 | 12 | 5 |
| Cereal flies | 2 | 5 | 7 | 7 | 3 | 10 | | | 3 |
| Wheat fleas | 3 | 3 | 4 | | | | | | 1 |
| Leaf beetle | 2 | 3 | 5 | | | | | | |

| Conservative no tillage soil technology | | | | | | | | | |
|---|-------|-------|-------|-------|-------|-------|------|------|-------|
| | 20.04 | 21.04 | 28.04 | 11.05 | 18.05 | 27.05 | 1.06 | 6.06 | 15.06 |
| Thrips | | | 3 | 150 | 34 | 67 | 25 | 6 | 9 |
| Aphids | 3 | | | 3 | | 16 | 24 | 24 | 21 |
| Leafhoppers | 9 | 4 | | 6 | 1 | 18 | | 5 | 1 |
| Cereal flies | 6 | 5 | 6 | 8 | 13 | 10 | 1 | 3 | 3 |
| Wheat fleas | 1 | | 5 | | | | | | |
| Leaf Beetle | | | 7 | | 6 | | | | |

Table 4. *Abundance and structure of pests and entomophags in wheat crops in open field agroecosystem in Turda and in the farming system with forestry belts in Cean-Bolduț (2010-2011, ARDS Turda. (Nr. / 100 sweepnet catches)*

| | Agroecosystem in open field area. Turda | | | | Agroecosystem with protective forestry belts. Cean-Bolduț | | | |
|---|---|-------------|-------------|-------------|---|-------------|------------|-------------|
| | 2010 | | 2011 | | 2010 | | 2011 | |
| | Total | % | Total | % | Total | % | Total | % |
| Phytophagous | | | | | | | | |
| Thrips (<i>Haplothrips tritici</i>) | 1257 | 84.00 | 756 | 73,5 | 134 | 25.0 | 129 | 30,0 |
| Diptera (<i>Meromyza</i>) | 4 | 0.30 | 10 | 1,0 | 17 | 3.0 | 11 | 2,5 |
| Diptera (<i>Oscinella etc.</i>) | 38 | 3.00 | 52 | 5,1 | 184 | 34.0 | 91 | 21,3 |
| Diptera (<i>Delia, Phorbia</i>) | 7 | 0.45 | 9 | 0,9 | 5 | 1.0 | 16 | 4,0 |
| Col. <i>Oulema melanopus</i> | 2 | 0.13 | 8 | 0,8 | 6 | 1.1 | 20 | 5,0 |
| Col. <i>Chaetocnema aridula</i> | 24 | 3.00 | 26 | 2,5 | 46 | 8.0 | 18 | 4,2 |
| Col. <i>Phyllotreta vitulla</i> | 55 | 4.00 | 3 | 0,3 | 11 | 2.0 | 4 | 1,0 |
| Aphids (<i>Sitobion etc.</i>) | 51 | 3.40 | 84 | 8,2 | 23 | 4.0 | 104 | 24,0 |
| Leafhoppers (<i>Macrostelus</i>) | 12 | 1.00 | 25 | 2,4 | 21 | 4.0 | 12 | 3,0 |
| Leafhoppers (<i>Psammottetix</i>) | 4 | 0.30 | 17 | 1,5 | 17 | 3.0 | 1 | 0,2 |
| Leafhoppers (<i>Javesella</i>) | 3 | 0.20 | 4 | 0,4 | | | 3 | 0,7 |
| Bugs (<i>Eurygaster, Aelia</i>) | 12 | 1.00 | 11 | 1,1 | 46 | 8.0 | 3 | 0,7 |
| Het. (<i>Trygonothylus</i>) | 5 | 0.32 | 14 | 1,4 | 26 | 5.0 | 9 | 2,0 |
| Hym. <i>Cephus, Trachelus</i> | - | | | | 4 | 1.0 | | |
| Orthoptera | 3 | 0.20 | 2 | 0,2 | 3 | 0.5 | 3 | 0,7 |
| Wireworms (<i>Agriotes etc.</i>) | 10 | 0.70 | 7 | 0,7 | 2 | 0,4 | 3 | 0,7 |
| Entomophagous | | | | | | | | |
| Coccinellidae (<i>Coccinella, etc.</i>) | 11 | 5.5 | 9 | 3,4 | 4 | 2,0 | 2 | 1,0 |
| Malachiidae (<i>Malachius bipust.</i>) | 1 | 0.5 | 6 | 2,3 | 1 | 1.0 | 2 | 1,0 |
| Nabidae (<i>Nabis ferus</i>) | 5 | 5.0 | 10 | 3,6 | 17 | 8.5 | 13 | 6,0 |
| Staphylinidae (<i>Tachyporus hypn.</i>) | 4 | 2.0 | 1 | 0,4 | | | | |
| Chrysopidae (<i>Chrysopa carnea</i>) | 1 | 0.5 | 3 | 1,1 | 5 | 3.0 | 3 | 1,5 |
| Syrphidae (<i>Episyrphus, etc.</i>) | 10 | 5.0 | 34 | 13,0 | 4 | 2.0 | 16 | 7,5 |
| Empididae (<i>Platypalpus</i>) | 8 | 4.0 | 27 | 10,1 | 15 | 8.0 | 15 | 7,0 |
| Chloropidae (<i>Thaumatomyia</i>) | 4 | 2.0 | 3 | 1,1 | 4 | 2.0 | 29 | 14,0 |
| Hymenoptera dif. parasites | 4 | 2.0 | 72 | 27,0 | 38 | 19.5 | 60 | 28,5 |
| Hym. <i>Formicidae</i> | 2 | 1.0 | | | 8 | 4.0 | 1 | 0,5 |
| Aranea | 56 | 26.2 | 101 | 38,0 | 95 | 50.0 | 72 | 34,0 |
| Culicidae | 95 | 46.3 | | | | | | |
| Phytophagous Total | 1487 | 88 % | 1028 | 79 % | 545 | 74 % | 427 | 67 % |
| Entomophagous Total | 201 | 12 % | 266 | 21 % | 191 | 26 % | 213 | 33 % |
| Total nr. | 1688 | | 1294 | | 731 | | 640 | |

Haplothrips tritici is the most abundant and important pest of wheat in classical (by plowing) and conservative (by minimum soil tillage and no tillage) technologies. Comparative research on the abundance and structure of wheat pests in classical and conservative soil technologies proved a greater abundance and importance of the populations of flies, aphids, leafhoppers, wireworms reached at conservative no tillage technology, in open field agricultural system (**Table 5**).

Table 5. Dynamics of abundance and structure of pests and entomophags in wheat crops, in two soil technology: classic system (by plowing) and conservative no tillage system, at ARDS Turda, in 2009-2011

| | Abundance (nr./100 sweep net catches) | | | | | | Structure (%) | | | | | |
|------------------------|---------------------------------------|------|------|--------------|------|------|---------------|-------|------|--------------|------|------|
| | Classic | | | Conservative | | | Classic | | | Conservative | | |
| | 2009 | 2010 | 2011 | 2009 | 2010 | 2011 | 2009 | 2010 | 2011 | 2009 | 2010 | 2011 |
| Thrips | 874 | 1896 | 384 | 802 | 970 | 294 | 67.4 | 85.50 | 64,2 | 69.0 | 78.0 | 54,4 |
| Aphids | 106 | 66 | 90 | 162 | 67 | 91 | 8.2 | 3.00 | 15,0 | 14.0 | 5.0 | 17,0 |
| Leafhoppers | 70 | 13 | 47 | 64 | 4 | 61 | 5.4 | 0.63 | 7,8 | 5.5 | 0.3 | 11,3 |
| Cereal flies | 82 | 20 | 38 | 68 | 36 | 55 | 6.3 | 0.92 | 6,5 | 5.8 | 0.9 | 10,1 |
| Fleas and Leaf beetles | 48 | 201 | 26 | 30 | 149 | 19 | 3.7 | 9.13 | 4,3 | 2.6 | 12.2 | 3,5 |
| Cereal bugs | 98 | 12 | 3 | 24 | 7 | 4 | 7.5 | 0.54 | 0,5 | 2.1 | 1.0 | 0,7 |
| Wireworms etc. | 18 | 6 | 10 | 12 | 8 | 16 | 1.5 | 0.28 | 1,7 | 1.0 | 0.62 | 3,0 |
| Phytophags | 1296 | 2214 | 598 | 1162 | 1241 | 540 | 82.7 | 93.00 | 68,7 | 81.6 | 90.0 | 74,0 |
| Entomophags | 272 | 165 | 272 | 262 | 140 | 189 | 17.3 | 7.0 | 31,3 | 18.4 | 10.0 | 26,0 |
| Total nr. | 1568 | 2379 | 870 | 1424 | 1381 | 729 | | | | | | |

In order to provide a sustainable development of winter wheat crop under the present conditions marked by the increase of pest abundance and attack, based on the accumulation of the effects of the unfavorable agro-ecological and technological factors in the agricultural exploitations, the adequate prevention and control measures have been required. Testing the efficiency of the integrated pest control methods, has been carried out under different technological crop systems in open field area: classical system and conservative system (soil minimum tillage and no tillage)-protective against draught, and in the agroforestry belts farming system. Within the testing experiments of economically and ecologically efficient insecticides, optimal application time in an integrated technological system has been studied, including herbicides, fungicides and complex treatments for other wheat pest control, fertilizers applications etc. (**Table 6**).

Table 6. Average effect of conservative system, in wheat (ARDS Turda, 2008, 2009, 2010)

| Tillages | Classic system by plowing | | | Conservative system no tillage | | | % Impact of no tillage technology |
|---|---------------------------|-------|------|--------------------------------|-------|------|-----------------------------------|
| | Grain production (kg/ha) | | | Grain production (kg/ha) | | | |
| Complex treatments Insecticides application moments | Average | % | Dif. | Average | % | Dif. | |
| C1(T1+...+T3+T4) | 4155 | 100.0 | +0 | 4358 | 100.0 | +0 | 104.9 |
| C2 (...+T2+T3+...) | 4046 | 97.4 | -110 | 4419 | 101.4 | +61 | 109.2 |
| C3 (...+T2+T3+T4) | 3883 | 93.5 | -272 | 4250 | 97.5 | -108 | 109.5 |
| C4 (...+T2+...+T4) | 4059 | 97.7 | -96 | 4487 | 103.0 | +129 | 110.5 |
| DL 5% | | | +284 | | | +265 | |

T1 (early spring) - Calypso 480 SC 100 ml/ha; T2 (end of tillering)-Calypso 480 SC 100 ml/ha;

T3 (flag-leaf) - Proteus OD 110 400 ml/ha; T4 (end of flowering) - Proteus OD110 400 ml/ha.

Complex treatments with herbicides, fertilizers or fungicides:

C1(T1 + T3 + T4); C2(T2 + T3); C3(T2 + T3 + T4); C4(T2 + T4).

The integrated pest control methods under **classical** soil technology (by plowing), in open field agricultural system, needs special attention on:

- the analysis of zone and crop climate in interrelation with the periodical observation of attack potential (at crop emergence, in the spring at tillering and in the 2nd decade of May, at flag-leaf apparition and ear emergence);
- the use of agro-technological measures (the sowing in the second half of October, the volunteers wheat destruction, the balanced fertilization, herbicide treatment and others);
- insecticide treatment on seeds or vegetation;
- the multiannual periodical observation of the interactions with auxiliary entomophags, - predator populations enrichment and protection by careful treatment application on vegetation, by protection of entomophag refuge sites (by concentration area development at crop borders, protection of marginal flora diversity, protective agro-forestry belts etc., which ensures the presence and growth of auxiliary species, fast colonization of the crops, and the occurrence of natural efficient biological pest control).

Insecticide application should be carried out when the economic damaging threshold values of pest have been exceeded. Also, insecticide application is recommended taking into account the activity of the natural reserve of predatory and parasite entomophags. Especially, the polyphagous predators diminish actively the main pests in the crops. The natural predators play an important role in decreasing the pests abundance. The well-known systematic groups of entomophagous predators: Aranea; Thysanoptera (Aeolothripidae); Heteroptera (Nabidae etc.); Coleoptera (Carabidae, Staphylinidae, Coccinellidae, Cantharidae, Malachiidae etc.); Diptera (Syrphidae, Empididae etc.); Hymenoptera (Formicidae etc.); Neuroptera (Chrysopidae) etc. were represented in the structure of arthropod fauna (Malschi 2009).

The research proved that the **insecticide treatments** applied on vegetation have been used for the prevention and control of a pest complex, in the last years, in two critical attack moments and risk situations have been reported to require treatment application:

1. The insecticide treatment applied in April, at the same time with the herbicide treatment, for Diptera and wheat fleas control (*Chaetocnema*), bug and *Oulema* adults also to reduce thrips and leafhoppers attack potential. The treatment for diptera larvae control in April, at the end of plant tillering in the 25-33 DC stage (at herbicide treatment), or earlier in some years, has been carried out by using systemic insecticides: neonicotinoids – tiacloprid, thiametoxam; organophosphorous and others, which achieved control efficiencies and yield increases. At present, the entomophagous auxiliary fauna has been at the beginning of its occurrence in the crops and less exposed to insecticides.

2. The treatment in the flag-leaf apparition and ear emergence, in the 45-59 DC stage, in May 10-25 has been applied to control wheat thrips adults (*Haplothrips tritici* Kurdj.), aphids, bugs and others. The pirethroids, neonicotinoids etc. have achieved immediate control of the pest complex with efficiencies against thrip larvae development of the ears and yield increases. At this treatment time the most significant part of the entomophag natural biological control activity has been carried out, most of the species being less sensitive to insecticides as eggs and pupae.

The integrated pest management research on the cereal agro-ecosystems with **conservative no tillage soil technology**, have been conducted in 2008-2011 and have recommended the insecticides chemical control, using 2-3 successive insecticides treatments (Table 6).

The applied integrated pest management on favorable agro-ecological conditions in the **farm with protective forestry belts**, in Cean-Bolduț shows the efficiency of biological control, using the entomophagous natural resources, without insecticides (Malschi Dana 2009, Malschi Dana et al, 2010).

Identification of efficient insecticides in pests control on vegetation, the assessment of optimal application time, the evaluation of insecticide side effects on the auxiliary entomophagous in the crops, the emergence of resistance to insecticide; have been conducted in 2008-2011, in demonstrative experiments and lots where systemic neonicotinoid insecticides (Calypso 480 SC 100 ml/ha), pyrethroids with instant shock action (Decis 25 WG 0,030 Kg/ha) and a mixture of these (Proteus OD 110 400 ml/ha), but also new formula of pyrethroids such as Cylothrin 60 CS 80 ml/ha, Alphamethrin 10 CE 100 ml/ha, Grenade SYN 75 ml/ha have been applied. The research has been showed the value of some quality insecticides adequate to the present high temperatures and abundance of pests and the overlap of attack of several phytophag groups. Identification of adequate, quality seed-applied insecticides, biologically, economically and ecologically efficient has been conducted in experiments using the Yunta 246 FS2 l/t insectofungicide (Table 7 and 8).

Table 7. Effect of insecticide treatments in the wheat flag-leaf and ear emergence stage application (Ariesan variety), ARDS Turda, 2008

| Treatment variants | Ears / m ² | | | Kg / ha | | |
|----------------------------------|-----------------------|-------|----------------------|----------------|-------|---------------------|
| | Average | % | Difer. | Average | % | Difer. |
| V1. Untrated | 463 | 100.0 | - | 5456 | 100.0 | - |
| V2. Yunta 246 FS, 2 l/t TS | 389 | 84.2 | - 74.0 ^{oo} | 5650 | 103.5 | 194 |
| V3. Cylothrin 60 CS 80 ml/ha | 575 | 124.2 | 112.0 ^{***} | 6850 | 125.5 | 1394 ^{***} |
| V4. Alphamethrin 10 CE 100 ml/ha | 504 | 109.0 | 41.0 | 7170 | 131.4 | 1714 ^{***} |
| V5. Decis 25 WG 0,030 Kg/ha | 580 | 125.4 | 117.0 ^{***} | 6793 | 124.5 | 1337 ^{***} |
| V6. Proteus OD 110 400 ml/ha | 488 | 105.5 | 25.0 | 5990 | 109.8 | 534 [*] |
| V7. Calypso 480 SC 100 ml/ha | 567 | 122.5 | 104.0 ^{***} | 6150 | 112.7 | 694 [*] |
| V8. Grenade SYN 75 ml/ha | 556 | 120.2 | 93.0 ^{***} | 5540 | 101.5 | 84 |
| DL p 5% | | 9.4 | 43.7 | | 9.2 | 503.5 |
| DL p 1% | | 13.1 | 60.6 | | 12.8 | 687.9 |
| DL p 0.5% | | 18.2 | 84.2 | | 17.7 | 969.5 |
| | F=21.74 (2.76) | | | F= 15.9 (2.76) | | |

Table 8. Efficiency of insecticides applied in the wheat flag-leaf and ear emergence stage application (Ariesan variety), ARDS Turda, 2008

| Treatment variants | Aphids/ear / 11.06.2008 | | | Thrips larvae/ear / 11.06.2008 | | |
|----------------------------------|-------------------------|-------|--------|--------------------------------|--------|------------------|
| | Average | % | Difer. | Average | % | Difer. |
| V1. Untreated | 2.50 | 100.0 | martor | 3.70 | 100.00 | martor |
| V2. Yunta 246 FS, 2 l/t TS | 2.50 | 100.0 | 0.00 | 3.70 | 100.00 | |
| V3. Cylothrin 60 CS 80 ml/ha | 0.20 | 8.0 | - 2.30 | 0.10 | 2.70 | oo ^{oo} |
| V4. Alphamethrin 10 CE 100 ml/ha | 0.60 | 24.0 | - 1.90 | 0.05 | 1.35 | oo ^{oo} |
| V5. Decis 25 WG 0,030 Kg/ha | 0.40 | 18.0 | - 2.05 | 0.10 | 2.70 | oo ^{oo} |
| V6. Proteus OD 110 400 ml/ha | 0.50 | 20.0 | - 2.00 | 0.05 | 1.35 | oo ^{oo} |
| V7. Calypso 480 SC 100 ml/ha | 5.35 | 214.0 | 2.85 | 4.00 | 108.11 | |
| V8. Grenade SYN 75 ml/ha | 0.05 | 2.0 | - 2.45 | 0.10 | 2.70 | oo ^{oo} |
| DL p 5% | | | 3.171 | | | 1.037 |
| DL p 1% | | | 4.396 | | | 1.438 |
| DL p 0.5% | | | 6.107 | | | 1.998 |
| | F= 3.09(2.76) | | | F= 31.91 (2.76) | | |

Insecticide control using the variety of modern products (pyrethroids, neonicotinoids, plant penetrating systemic products) has been studies in order to test the biological efficiency of the treatments, insecticide remanant capacity, the negative effects on useful entomophag fauna (Table 9 and 10).

Table 9. The side effect of Yunta 246 FS 2 l/t seed treatment on useful entomophagous fauna in winter wheat crops. ARDS Turda, 2008.

| A. Abundance and mortality of auxiliary soil fauna. (Summe of Barber traps catches). | | | | |
|---|------------|---------------|------------|---------------|
| Sampling date | 29.05 | | 24.06 | |
| Variants | V 1 | V 2 | V 1 | V 2 |
| <i>Brachinus explodens</i> | 3 | 1 | 25 | 15 |
| <i>Poecilus cupreus</i> | 84 | 28 | 250 | 150 |
| <i>Pseudophonus rufipes</i> | | | 50 | 30 |
| <i>Pterostichus melanarius</i> | 12 | 1 | 125 | 75 |
| <i>Harpalus distinguendus</i> | 2 | | 15 | 9 |
| <i>Dolichus halensis</i> | 17 | 3 | | |
| <i>Sylpha obscura</i> | 10 | 2 | 25 | 15 |
| <i>Necrophorus vespillo</i> | 2 | | 10 | 6 |
| <i>Aranea</i> | 13 | 2 | | |
| Total | 145 | 37 | 500 | 300 |
| Mortality % - negative impact | | 74.5 % | | 40.0 % |
| B. Entomophagous mortality after Yunta 246 FS (nr./100 sweep net catches) | | | | |
| Sampling date | 14.05 | | 27.05 | |
| Variants | V 1 | V 2 | V 1 | V 2 |
| <i>Coccinellidae</i> | 1 | | 1 | 1 |
| <i>Cantharidae</i> | 17 | 2 | | |
| <i>Malachiidae</i> | | | 2 | 2 |
| <i>Empididae (Platypalpus)</i> | | | 3 | |
| <i>Hymenoptera - parasites</i> | 13 | 6 | 8 | |
| <i>Formicidae</i> | 2 | 3 | 3 | 1 |
| <i>Aranea</i> | 3 | | 2 | 3 |
| Total entomofagi | 36 | 11 | 19 | 8 |
| Mortality % - negative impact | | 69 % | | 42 % |
| Variants of seed treatments: V1 = without insecticide; V2 = with Yunta 246 FS, 2 l/t. | | | | |

Table 10. Dynamics of wheat pests after insecticide application at 30.05.2008. ARSD Turda

A. Phytophags nr/100 sweep net catches. **E%**= insecticide efficiency.

B.Entomophags nr/100 swee pnet catches. **M%**=Entomophagous Mortality.

| | Treatment immediate side effect/after 4 days | | | | | | | | Insecticide side effect after 12 days. | | | | | | | |
|---|--|----|----|----|----|----|----|-----|--|-----|----|----|-----|----|--|--|
| | Sampling date 3.06.2008 | | | | | | | | Sampling date 11.06.2008 | | | | | | | |
| | Mt. | V3 | V4 | V5 | V6 | V7 | V8 | V1 | V3 | V4 | V5 | V6 | V7 | V8 | | |
| A. | 564 | 11 | 38 | 57 | 46 | 53 | 21 | 121 | 42 | 71 | 96 | 35 | 67 | 22 | | |
| E % | | 98 | 93 | 90 | 92 | 91 | 96 | | 65 | 41 | 21 | 71 | 46 | 82 | | |
| B. | 23 | 6 | 11 | 5 | 6 | 11 | 2 | 44 | 11 | 14 | 31 | 7 | 12 | 9 | | |
| M % | | 74 | 52 | 78 | 74 | 52 | 91 | | 75 | 68 | 30 | 84 | 80 | 80 | | |
| | Insecticide side effect after 26 days. | | | | | | | | Insecticide side effect after 34 days. | | | | | | | |
| | Sampling date 25.06.2008 | | | | | | | | Sampling date 3.07.2008 | | | | | | | |
| | Mt. | V3 | V4 | V5 | V6 | V7 | V8 | Mt | V3 | V4 | V5 | V6 | V7 | V8 | | |
| A. | 111 | 28 | 30 | 14 | 40 | 70 | 12 | 141 | 58 | 101 | 80 | 77 | 107 | 44 | | |
| E % | | 75 | 73 | 87 | 64 | 37 | 89 | | 59 | 28 | 43 | 45 | 24 | 69 | | |
| B. | 48 | 15 | 26 | 26 | 18 | 39 | 21 | 96 | 110 | 103 | 89 | 66 | 75 | 82 | | |
| M % | | 69 | 46 | 46 | 63 | 19 | 56 | | | | 7 | 31 | 22 | 15 | | |
| Variants : Mt. (untreated). V1=(seed without insecticidal treatment); V2=Seed treated with Yunta 246 FS, 2 l/t. V3=Cylothrin 60 CS 80 ml/ha; V4=Alphamethrin 10 CE 100 ml/ha; V5=Decis 25 WG 0,030 Kg/ha; V6= Proteus OD 110 400 ml/ha; V7=Calypso 480 SC 100 ml/ha; V8=Grenade SYN 75 ml/ha. SCDA Turda, 2008. | | | | | | | | | | | | | | | | |

The application of special insecticide treatments is required especially under unfavorable agroecological conditions of excessive heat and draught during the critical attack periods and plant growth, in the case of crops with incomplete or incorrect technology related to the use of single crops and early sowing, before the regional optimal time and in no tillage and minimum soil tillage technologies, also (Carlier et al., 2006, Guş, Rusu, 2008, Haş et al., 2008, Malschi et al., 2010, 2011).

CONCLUSIONS

A complex technology as part of the integrated pest control system has been recommended, comprising the use of crop agro-technical measures, having an overall role in the prevention and diminish of the pest attack, virtually achieved by: - crop rotation ensuring the optimum precursory plant and avoidance of monoculture single crops; - soil preparation and maintenance, soil activities (tilling, discing, wheat volunteers destruction, other conservative technology - specific of minimum tillage and no tillage technologies). They diminish mechanically part of the biological pest reserve; - keeping density and optimal sowing time (October 10-20), so that wheat crop emergence avoid massive infestation by pests (diptera, aphids, leafhoppers) and provide good plant growing rhythm and vigor; balanced application of fertilizers, herbicides and disease control treatments which provide a good plant growth.

The integrated control of wheat pests by optimizing the technological factors such as: sowing time, insecto-fungicide seed treatments, insecticide vegetation treatments, fertilization, and by optimizing the biotic factors: natural entomophags, environment protection, preservation and sustainable use of biodiversity has been studied in experimental lots where the optimized technological system has been used (complex phytosanitary treatments with insecticides, fungicides, fertilizers, including preventive seed treatments), in the vegetation year 2008-2011. The economic and ecological efficiency of the integrated wheat pest management system in Transylvania can be achieved by using the prevention and risk control strategy due to the present pest abundance and aggressiveness, by protection and sustainable use of the natural resources of biodiversity, including the activity of auxiliary entomophag activity in the crops.

The thrips, flies, aphids and leafhoppers were dominant in the structure of wheat pests, with abundant populations, well reduced by the applied insecticides.

The IPM research on the cereal agro-ecosystems in open field area with classic by plowing and conservative no tillage soil technology, in ARDS Turda pointed out and **recommended the insecticides** chemical control, using 2-3 successive insecticides treatments. The recommended attack diminishing methods of wheat pests include the application of insecticides, with economic and ecological efficiency, in two different selective moments: 1 - for the control of wheat flies larvae, leafhoppers and other pests, in April, at the end of tillering phase (13-33 DC stage); 2 - for the ear pests control – thrips, aphids, bugs, leafhoppers and other pests at spike appearance in 45-59 DC stage, in the period of May, 10th-25th; the conservation and use of biological factors (tolerant varieties, entomophagous limiters). Yield results have shown that the technological system provided the control of risk factors, and the harvest results at the level of yielding capacity.

Special attention should be given to the farming system with agroforestry belts which provide auxiliary entomophag conservation and development and the natural biological pest limitation, not to mention the antierosion role. The applied IPM on favorable agroecological conditions in the farm with protective forestry belts, in Cean-Bolduț shows the efficiency of biological control, using the entomophagous natural resources, without insecticides.

The knowledge concerning the integrated pest management system achieved in accordance with the contemporary expectations regarding the optimization of the relations between environment, agriculture and sustainable development have been delineated. The integrated wheat pest management has a special significance because it represents one of the priorities of agricultural sustainable development. The objectives are the achievement of yield safety under risky conditions caused by the attack of these pests in relation with the climate and regional agroecological changes, the attaining economic and ecological efficiency of the control methods; the protection of environment and food quality; preservation and use of biodiversity.

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ASSESSMENT OF INDOOR AIR QUALITY BY PASSIVE SAMPLING OF NO₂ AND O₃ IN SCHOOLS OF ALBA COUNTY. ROMANIA

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ABSTRACT. Assessment of indoor air quality by passive sampling of NO₂ and O₃ in schools of Alba County. Romania. This study is performed within the project "SINPHONIE – Schools Indoor Pollution and Health: Observatory Network in Europe, 2010-2012. For this study, in Romania were chosen five schools from Alba County.

This study is important because approximately 20 % percent of the population spend their days in schools. Students are at greater risk because of the hours spent in school facilities and because these are especially susceptible to pollutants. Sampling is done using Radiello cartridges, these will be exposed for a period of five days in three classes during which students operate and in parallel will make a sampling in the schoolyard. The monitoring period is identical to each school. After the cartridges have been exposed will be analyzed in the laboratories of the Faculty of Environmental Science and Engineering. The analysis of NO₂ and O₃ are made with UV-VIZ spectrophotometer.

This study aims to regulate indoor air quality in schools.

Key words: NO₂, O₃, sampling, indoor air, Alba County, school.

INTRODUCTION

The indoor environmental quality, one of which depends essentially the health and well being of people living in space is determined by the composition of the air (with reference to chemical pollutants, physical, biological or otherwise) and comfort (the main components: acoustic, thermal, visual).

Indoor air quality (IAQ) is a term that refers to air quality in and around buildings and construction, especially as it relates to health and comfort of building occupants.

Recent studies shows that in today's society, people spend about 80% of their time indoors (home, in offices, vehicles, etc.). Hence the need to control indoor air quality. In the table below are given sources for NO₂ and O₃.

Table 1. Indoor sources of pollution for NO₂ and O₃.

| Polutant | Source | Possible conc. | Ci/Co ¹ | Domain |
|-----------------|--|-------------------------------|--------------------|-------------------|
| NO ₂ | Combustion, stoves, dryers, engines, cigarettes | 0.013 – 0.062 ppm* | >>1 | indoor |
| O ₃ | electric arc, light sources (UV), copywriters, ion-generating air cleaners | 0.03 – 0.4 ppm** 0.3 ppm** | <1 >1 | outdoor indoor |

[¹] Indoor/outdoor concentration * WHO air quality guidelines **EPA

In ambient air, heating power stations, motor vehicles, industrial and buildings heating systems are the most important emission sources of NO₂ (ISO 16000-15 / 2008)

A global image shows the European mean tropospheric nitrogen dioxide (NO₂) between January 2003 and June 2004, as measured by the SCIAMACHY instrument on ESA's Envisat. The scale is 1015 molecules/cm⁻². The image is produced by S. Beirle, U. Platt and T. Wagner of the University of Heidelberg's Institute for Environmental Physics (E.O., 2004).

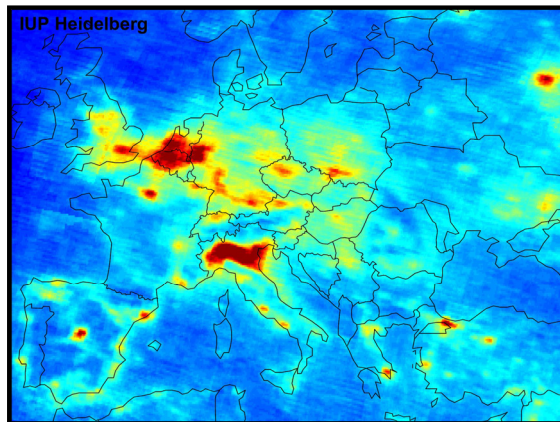


Fig. 1. NO₂ levels over Europe (by S. Beirle, U. Platt and T. Wagner, in E. O, 2004)

The indoor concentrations for NO₂ is in the range 13 –62 µg/m³ (7 -32 ppb), but the concentration of concern is above 200 µg/m³ for 1 hour mean (105 ppb) (WHO guidelines for indoor and ambient air). The guideline for ambient air is at 40µg/m³ for annual mean (21 ppb) (WHO air quality guidelines)

Ozone is normally created in the upper atmosphere by sunlight or electrical charges (i.e. lightning) on normal oxygen. It can also form in the lower atmosphere when hydrocarbons (such as evaporating fuel, paint, and dry cleaning fluids) and nitrogen compounds mix with sunlight or electrical charges.

Ozone Levels in Europe. In the light green areas, the pollution levels are under the critical value of 3000 ppb/hours). In the dark green areas, the critical level is exceeded up to two times. In the yellow areas the critical level is exceeded from two to three times. In the orange areas the critical level is exceeded from three to four times. In the most polluted areas of Europe, the red areas, the critical level is exceeded by more than four times.

The results are obtained by running the Danish Eulerian Model (DEM).

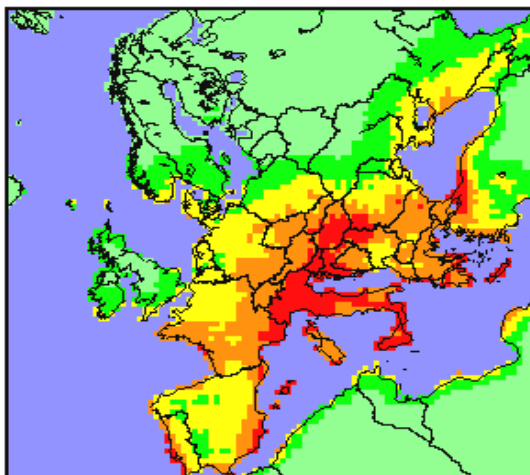


Fig. 2. Ozone Levels in Europe

(Source: <http://www2.dmu.dk/atmosphericenvironment/staff/zlatev.htm>).

The indoor concentrations of O₃ are depending on ambient air introduction and range between 10 to 80% of outdoor concentration, usually between 0 and 60 µg/m³, but the outdoor concentration are very variable, from 30 to more than 400 µg/m³ (15 and 200 ppb) (WHO air quality guidelines). In the indoors, in the presence of an internal source, could peak up 600 µg/m³ (300 ppb) (EPA). The ambient air guideline = 100 µg/m³ for 38-hour mean (50 ppb) (WHO air quality guidelines).

Health effects

Long-term exposure to NO₂ at concentrations above 40 – 100 µg/m³ causes adverse health effects. The epidemiological studies provide some evidence that long-term NO₂ exposure may decrease lung function and increase the risk of respiratory symptoms.

Available evidence suggests that long-term O₃ exposure reduces lung function growth in children. There is little evidence for an independent long-term O₃ effect on lung cancer or total mortality. (WHO report; McElroy et al., 1997).

MATERIALS AND METHODS

The sampling was made in five schools from Alba County during a week, when were hold classes and during the sampling we monitor the temperature, humidity which can influence the results.

In Alba County were selected five secondary schools for the monitoring of NO_2 and O_3 and in each school are monitored 3 classes and also is monitored the outdoor air quality from the school yard (see Fig. 3).

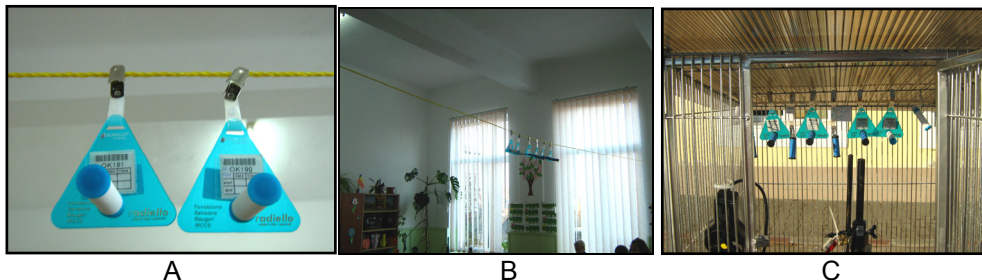


Fig. 3. Exposed Radiello passive samplers for NO_2 and O_3 (A, B –indoor, C –outdoor).

For the determination of NO_2 and O_3 were used Radiello passive samplers. The passive samplers are small, silent, and reliable; do not need electricity; and are less expensive. They can be used for indoors and outdoors monitoring in rural, urban, arctic, and tropical environments where they can provide exposure profiles with high quality (Gorecki and Namiesnik, 2002). Samplers do not need field calibration, air volume measurements, and technical demands at the sampling site (Salem et al., 2009).

NO₂ analysis

The sampling of air to determine the NO_2 concentration were made with Radiello passive samplers (see Fig. 4) with a detection limit of $2 \mu\text{g}/\text{m}^3/\text{week}$.



Fig. 4. Radiello passive samplers, blue diffusive body code 120-1 and supporting plate.

The samplers are composed of an inert bed coated with moistened Tri-Ethanol-Amine (TEA) and the NO_2 reacts with TEA to form nitrite (NO_2^-) ions. The derivatization is made with Sulphanilamide and N-(1-naphtyl)-ethylendiammine for the spectrophotometric analysis or the direct analysis of eluted with Ion Chromatography. We used the spectrophotometric analysis.

Sampling rate of NO_2 varies from the value at 298 K on the effect of temperature (in Kelvin) following the equation (1):

$$Q_K = Q_{298} \left(\frac{K}{298} \right)^{7.0} \quad (1)$$

where Q_K is the sampling rate at the temperature K ranging from 263 to 313 K (from -10 to 40 °C) and Q_{298} is the reference value at 298 K.

The concentration C_{NO_2} is calculated according to the equation 2:

$$c_{NO_2} = \left(\frac{m_{NO_2}}{Q_K \cdot t} \right) \quad (2)$$

where m_{NO_2} is nitrite mass in μg found on the cartridge, t is exposure time in minutes and Q_K is the sampling rate value at the temperature K in Kelvin.

For the analysis it was added 5 ml of distilled water in the plastic tube and stirred. After this it was transferred a volume of the cartridge solution in a plastic tube along with *sulphanilamide* reactive and *NEDA* reactive. This extract solution was analyzed with a spectrometer by measuring the absorbance of samples at 537 nm using water to zero the spectrophotometer.

O₃ analysis

The sampling of air to determine the O₃ concentration was also made with Radiello passive samplers with a detection limit of 2 $\mu\text{g}/\text{m}^3/\text{week}$.

The O₃-MBTH passive samplers principle of functioning is: Ozone reacts with 1,2-di(4pyridyl)-ethylene (DPE) from the adsorbing cartridge which is formed by a micropore polyethylene tube, to form an ozonure which cleavage yields stoichiometrically 4-pyridylaldehyde (Fig.5). The following step is to determine the aldehyde by derivatization with Methyl-Benzotiazolinone (MBTH) to yield the corresponding azide, yellow colored and the spectrophotometric analysis. The absorbance of the solution was measured at 430 nm.

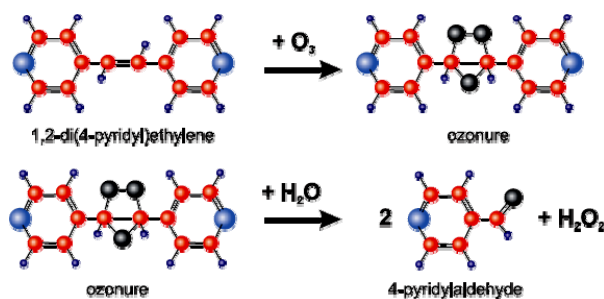


Fig. 5. Reactions inside an exposed O₃ cartridge

Sampling rate varies from the value at 298 K on the effect of temperature (in Kelvin) as expressed by the following equation (3):

$$Q_K = Q_{298} \left(\frac{K}{298} \right)^{1.5} \quad (3)$$

where Q_K is the sampling rate at the temperature K and Q_{298} is the reference value at 298 K. Sampling rate is not influenced by humidity or wind speed.

The average concentration over the whole exposure time is calculated according to the equation 4.

$$C[\mu\text{g} \cdot \text{m}^{-3}] = \frac{m[\mu\text{g}]}{24.6 \cdot t[\text{min}]} 1,000,000 \quad (4)$$

where **m** is ozone mass in μg sampled by radiello and **t** is exposure time in minutes.

CONCLUSIONS

The data collected from the participant schools, in the project SINPHONIE, will be put in a European data base. This data base will help to create European directives, which do to the improvement of the indoor air quality in the schools. 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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INTERNATIONAL INTERCOMPARISONS OF RADON DEVICES AND SOLID STATE NUCLEAR DETECTORS, IN CZECH REPUBLIC

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ABSTRACT. During the 6th Conference on Protection Against Radon at Home and at Work which held in September 2010 in Prague, the 1st Intercomparison of Continuous Radon and its Short-lived Decay Product Monitors was organized and held by the National Radiation Protection Institute (SURO, Prague), and an International Intercomparison of Solid State Nuclear Track Detectors was organized by the National Institute for Nuclear, Chemical and Biological Protection (SUJCHBO, Czech Republic). The Environmental Radioactivity Research Group of the Faculty of Environmental Science and Engineering from Babeș-Bolyai University was an active participant at these intercomparisons, obtaining good results in accordance with reference values of the organizers. We intended to intercompare and tests the RADIM EMAN 3A continuous radon monitor, a DOSEMAN PRO radon and short-lived decay products monitor, RAMON 2.2 simple radon monitors, and the purchased CR-39 track detectors. Results of the radon monitor measurements show 10 % difference from the NRPI reference continuous monitor for the RADIM 3A continuous monitor. Regarding to the EEC results shows an underestimation by a factor of four for the DOSEMAN PRO, and for RAMON 2.2 were about 10% overestimated then the reference value. Results of the solid state nuclear track detectors intercomparison was approx. the same than the reference values of the organizers.

Key words: *radon and short-lived radon decay products, continuous monitor, equivalent equilibrium concentration, solid-state nuclear track detector, international intercomparison.*

INTRODUCTION

Radon is a natural radioactive gas which is produced in different levels in rocks and soils. It migrates from the ground to the atmosphere, and is quickly diluted to low concentrations. However, the radon can reach high concentrations in closed spaces, such as caves and mines, and also in buildings. Radon and mainly its short-

lived decay products are the largest contributors to the radiation dose to the public. The exposure to high radon concentrations leads to an increased risk of lung cancer. Most of the risk comes not from the radon gas itself, but from its short-lived decay products. The radon decay products can get attached to all surfaces including the surfaces of airborne particles in the atmosphere. Their behavior in the atmosphere is also influenced by their deposition on larger surfaces, especially in the lungs during inhalation. This deposition is strongly determined by the size distribution of the aerosol (Cosma and Jurcut, 1996; Cosma et al., 2009).

For measuring radon levels in homes by integral methods, passive detectors like solid state nuclear detectors (SSNTD) are predominantly used. These methods permit the determination of an annual average concentration of indoor radon. Continuous monitoring permits the study of temporal variation of radon concentration, and is useful in indoor radon diagnostic and testing radon mitigation techniques. Many of the continuous monitors measure beside radon concentration, meteorological parameters (i.e. temperature, atmospheric pressure and relative humidity). The testing and calibration of measuring devices for radon and decay products require stable conditions (first of all radon and the decay products concentrations) (WHO, 2009).

During the 6th European Conference on Protection Against Radon at Home and at Work held in autumn 2010 in Prague, the 1st Intercomparison of Radon and its short-lived decay products Continuous Monitors was organized by the National Radiation Protection Institute (SURO, Prague). Closed to this, an International Intercomparison of solid state nuclear track detectors was organized by the National Institute for Nuclear, Chemical and Biological Protection (SUJCHBO, Kamenná, Central Bohemia). The National Radiation Protection Institute (NRPI) plays the key role in the Czech National Radon Programme, carrying out special radon diagnostic measurements. Since 2004 it was established a big radon chamber there. Eight laboratories submitted eight continuous radon monitors (ALPHA GUARD PQ 2000, RADIM 3A, RAD7, EQF 3220 and TESYS MR1), two electronic monitors (RAMON 2.2), and three continuous radon short-lived decay product monitors (Fritra 4, EQF 3120, DOSEMAN PRO). The intercomparison included exposures to both the radon gas concentration and equivalent equilibrium radon concentration (EEC) under different ambient conditions, in particular, by the influence of the equilibrium factor F , unattached fraction (fp) of EEC and absolute air humidity. The results of all monitors were compared with the reference NRPI monitors. (Jílek and Marušíaková, 2011).

The National Institute for Nuclear, Chemical and Biological Protection (SUJCHBO) ensures for the Czech Republic the metrological traceability for devices which measure the radon concentration and the equivalent radon concentration (EEC) connected with the radon decay products. Five laboratories used different types of track detectors (LR 115 and CR 39), attended to the inter-comparison (Burian et al., 2011).

MATERIAL AND METHODS

Intercomparison of Radon and its Short-lived Decay Product Continuous Monitors

The NRPI radon chamber having a volume of 48 m³ and walls similar to dwellings provides the quantities of interest which can be varied, held stable and controlled, as radon concentration, equivalent equilibrium radon concentration (EEC) including its unattached fraction (*fp*), air exchange rate, temperature and relative humidity, aerosol spectra around 100 nm and its total concentration. The chamber contains radon gas which concentration can be adjusted and held stable from about 100 to 8000 Bq/m³.

The calibrated level of radon concentration during the whole exercise was ~ 8 kBq/m³ that was held constant by means of known and constant both air exchange rate and radon entry rate. Due to this high radon concentration the contribution of the thoron gas and decay products could be neglected. Radon concentration in the chamber was on-line hourly monitored continuously by means of the NRPI reference monitor (Alphaguard PQ 2000 PRO) and twice a day the chamber interior air was sampled by the NRPI reference scintillation cells. The combined standard uncertainty of measured radon concentration was estimated better than 5 % in case of both the Alpha Guard monitor and scintillation cells (Jílek et al., 2008; Jílek and Marušiaková, 2011).

Air exchange rate was adjusted in the chamber by means of the built-in ventilation system, which can be varied in the chamber from about 0.05 h⁻¹ to 2 h⁻¹. Standard uncertainty of air exchange rate was estimated better than 5%.

The estimated time of the intercomparison was taking only ~ 75 hours, in order to be able to compare all the participating both passive integral detectors and continuous monitors and at the same time to avoid problems with different adjusted sampling times and limited measurement capability of some of the exposed monitors. As results, the integral average values during properly selected time periods were estimated only. During properly chosen time periods, the influence of the absolute air humidity and the variation of the ratios between radon decay products were monitored, since the principle of the exposed types of instruments could be affected by the changes of both parameters.

Equivalent equilibrium radon concentration (EEC) and unattached fraction *fp* were on-line continuously monitored each two hours in the chamber during the whole exercise by means the NRPI reference continuous monitor (Fritra 4). Besides on-line EEC monitoring of the chamber air was also twice a day a one-grab sampling was taken through a 0.8µm filter placed behind of a diffusion screen, to estimate unattached and attached activity of each short-lived radon decay product. The standard uncertainty of measured EEC in the chamber was estimated better than 10%. The standard uncertainty of the unattached fraction (*fp*) of EEC was estimated 15 %. Different values of equilibrium factor (*F*) between radon concentration and its decay products were obtained for the two exposures in the intercomparison. To obtain a high value of *F*, an aerosol generator was used to maintain a higher aerosol concentration, and a low equilibrium factor was obtained by running an electrostatic precipitator including fan which both removed aerosol concentration and attached decay products by filtering and increase plate-out of decay products attached to aerosols onto chamber surface.

The total ambient aerosol concentration and particle size distribution measured in the chamber ranging from 5 to 1100 nm. The used aerosol generator produced in the chamber particles of the regular spherical shape, by total aerosol concentration of the order 10^4 p/cm³.

The absolute humidity and the in the chamber was changed and held stable during the exposure.

The instruments of our Radon Research Group participated at the intercomparison are: a RADIM 3A continuous radon monitor, a DOSEMAN PRO radon and short lived decay products monitor and two RAMON 2.2 simple radon monitors. The detection principle of the RADIM 3A and RAMON 2.2 monitors are based on counting of proper alpha particles coming from alpha radon decay collected on surface of semiconductor detector by an electric field, and of the DOSEMAN PRO radon decay product monitor are based on the estimation of the activity from each short-lived radon decay product collected on an open face filter (see Fig. 1).



Fig. 1. *The placement of the instruments at the 1st Intercomparison of continuous radon and its short-lived decay product monitors (NRPI, Prague) (RADIM 3A - left-down, DOSEMAN PRO - right top and the two RAMON 2.2 - center top).*

At the beginning of the exercise the absolute humidity in the chamber air was adjusted to lower values by means of dehumidifier and air handler. At the same time the equilibrium factor F was reduced to lower values by means of a powered electrostatic precipitator. Due to reduction of aerosols the unattached fraction (*fp*) was increased. These conditions then timely corresponded to **situation A (13.9. 13:00 - 15.9. 17:00)** in case of radon gas and to **situation C (14.9. 9:00 -**

15.9. 9:00) in case of EEC. In the second part of the exercise corresponding to **situation B (15.9. 17:00 - 16.9. 16:00)** the electrostatic precipitator was un-powered and by means of an aerosol particle generator short-time injection of aerosols was introduced into the chamber, by which the total aerosol concentration and explicitly equilibrium factor F was increased and the unattached fraction (fp) decreased. At the same time absolute humidity in the chamber was increased to higher values. The situation A+B involved all the above mentioned time periods A, B and C, where the period C was part of the situation A (see Table 1) (Report 1, 2010).

Table 1. *Exposure conditions at the Intercomparison of radon and its short-lived decay products continuous monitors (Report 1, 2010).*

| Exposure situation | A | B | A + B | C |
|--------------------------------|----------|----------|--------------|----------|
| Duration (h) | 52 | 23 | 75 | 24 |
| Exposure conditions | | | | |
| Air exchange rate (h^{-1}) | 0.1 | 0.1 | 0.1 | 0.1 |
| RH (%) | 27 | 57 | 39 | 27 |
| Temperature ($^{\circ}C$) | 22 | 22 | 22 | 22 |
| Abs. humidity (g/cm^3) | 5.2 | 11.1 | 7.6 | 5.2 |
| F | 0.06 | 0.52 | 0.20 | 0.18 |
| fp | 0.65 | 0.03 | 0.18 | 0.67 |
| Aerosol conc. (p/cm^3) | 600 | 13000 | 2100 | 600 |

Intercomparison of Solid State Nuclear Track Detectors

The exposure of the SSNTD's was performed in a radon-aerosol chamber, as a part of the Czech primary radon measurement equipment situated in the SUJCHBO. The construction of chamber consists from the walk-in testing chamber with the inner volume of 10 m^3 and of the moving handling box with the inner volume of 0.3 m^3 . The handling box makes it possible to put some measuring devices or some other equipment into the chamber without disturbance of parameters. The use of handling box could decrease the radon concentration in the chamber less than 3%. The maximum radon concentration in the chamber air is $\sim 2\text{ MBq}\cdot\text{m}^{-3}$. The relative humidity is controlled by a vaporizer and a condenser which allow the level of a relative humidity in the range of 20-90 %. The concentration and the size distribution of aerosol particles are controlled by a generator, which principle of creation of aerosol particles based on the wax vapour condensation at a well-defined temperature (Burian et al., 2011).

Intercomparison conditions. For exposure to radon gas the track detectors, it was applied two levels of time integral radon concentrations. For the first case, the exposure (EER) was $3.1\text{ MBq}\cdot\text{h}\cdot\text{m}^{-3}$, and for the second case $0.69\text{ MBq}\cdot\text{h}\cdot\text{m}^{-3}$. In both cases the climatic conditions were the same, $15\text{ }^{\circ}C$, RH 75%, 925 hPa, and the moving of the air in the chamber was negligible. All these conditions may not influence the measurement results. The time of exposures were about 7 h and after applications detectors were 16 h in room characterized by radon concentration about $300\text{ Bq}\cdot\text{m}^{-3}$ and afterwards in outdoor air (about $20\text{ Bq}\cdot\text{m}^{-3}$). This over-exposure is first of all negligible and probably was subtracted with help of "background" detectors (Report 2, 2011).

RESULTS AND DISCUSSIONS

Intercomparison of Radon and its Short-lived Decay Product Continuous Monitors

Before it was informed about the given exposures at the NRPI radon chamber, participants submitted measurement results of their instruments. The measurement data series performed by RADIM 3A continuous radon monitor are shown in fig.2, with the DOSEMAN PRO radon and short-lived decay products monitor are shown in fig.3. A summary of the results for both radon gas and EEC measurements during the investigated time periods A, B, C and the overall exposure (A+B) are given in table 2 and table 3. Measurement results with the RAMON 2.2 simple radon monitor for the overall exposure period (A+B) are given in table 4.

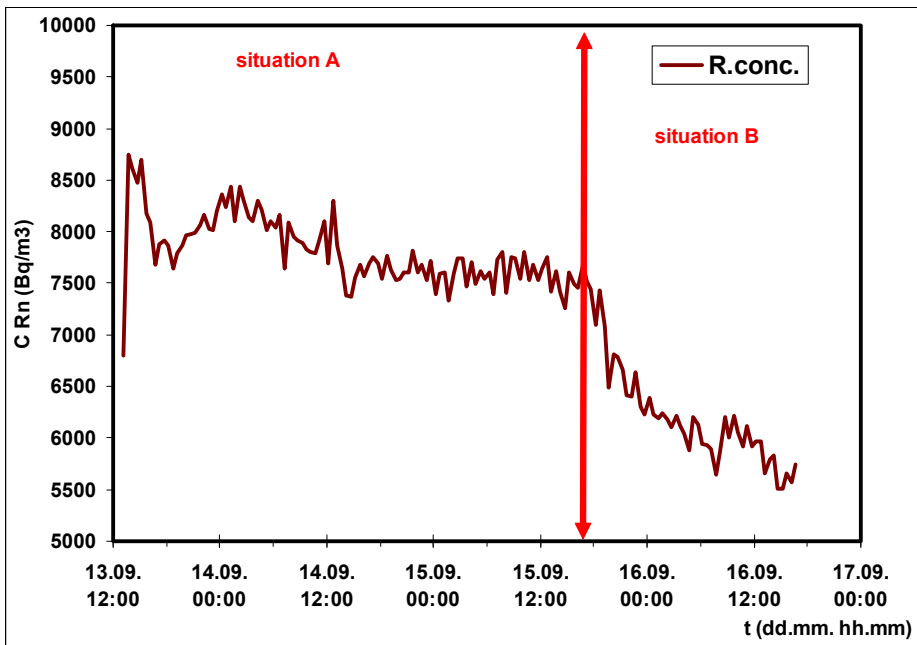


Fig. 2. Radon concentration measured by RADIM 3A continuous radon monitor all the exposure period (including situation A and B).

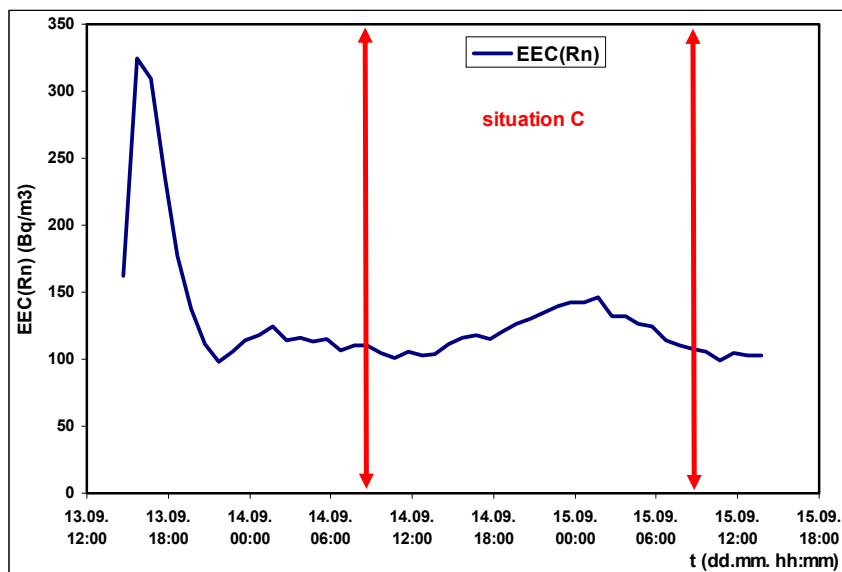


Fig. 3. Equivalent equilibrium radon concentration (EEC) measured by DOSEMAN PRO radon and short lived decay products monitor.

Table 2. Summary statistics of radon measurements by RADIM 3A and the NRPI reference monitor, and the intercomparison results (mean values of radon concentrations related to the reference NRPI mean (R) and the 95% CI).

| Parameter/monitor | A | B | A + B |
|------------------------------------|-------------|-------------|-------------|
| REF. Alphaguard PQ 2000 Pro | | | |
| Mean Rn (Bq/m^3) | 8378 | 7839 | 8215 |
| SD (Bq/m^3) | 608 | 259 | 587 |
| SEM (Bq/m^3) | 84 | 54 | 67 |
| VC (%) | 7.3 | 3.3 | 7.1 |
| Radim 3A S/N 06/32 | | | |
| Mean Rn (Bq/m^3) | 7808 | 6221 | 7314 |
| SD (Bq/m^3) | 326 | 485 | 831 |
| SEM (Bq/m^3) | 32 | 71 | 68 |
| VC (%) | 4.2 | 7.8 | 11.4 |
| Intercomparison | | | |
| R | 0.932 | 0.794 | 0.890 |
| 95% CI | 0.912-0.952 | 0.772-0.815 | 0.869-0.912 |

To avoid expected higher radon gas exhaustion from the chamber during the introduction of monitors before the exposure, the initial radon concentration in the chamber was adjusted to be a little bit “higher” than “working”. Thus the mean radon concentration during the investigated period A was measured systematically higher compared with the one during the period B.

Table 3. Summary statistics of the EEC measurements by DOSEMAN PRO and NRPI reference monitor (for situation C) and the results of the intercomparison (mean values of EEC related to the reference NRPI mean (R) and the 95% CI).

| Parameter/monitor | REF. Fritra 4 | Doseman Pro |
|-------------------------------|---------------|-------------|
| Mean EEC (Bq/m ³) | 489.2 | 117.8 |
| SD (Bq/m ³) | 22.9 | 12.5 |
| SEM (Bq/m ³) | 5.9 | 2.1 |
| VC (%) | 4.7 | 10.6 |
| Intercomparison | | |
| R | 0.241 | |
| 95% CI | 0.229-0.253 | |

Table 4. Summary statistics of radon measurements by RAMON 2.2 and the NRPI reference mean value, and the results of the intercomparison (mean values of radon concentrations related to the reference NRPI mean (R)).

| Parameter/monitor | RAMON 2.2 a | RAMON 2.2 b | NRPI ref. value |
|------------------------------|-------------|-------------|-----------------|
| Mean Rn (Bq/m ³) | 8604 | 8550 | 8018 |
| Intercomparison | | | |
| R | 1.098 | 1.091 | - |

For each continuous monitor were calculated the mean, standard deviation (SD), standard error of the mean (SEM) and variation coefficient (VC) using input data with sampling times of 30 minutes for RADIM 3A and of 1 hour for the DOSEMAN PRO.

The key results of the evaluation of intercomparison for both radon gas and EEC are the ratio (R) between the mean values of radon concentrations related to the NRPI mean reference and the corresponding 95% confidence interval (CI) for the ratio (R). These results are included in the tables 2, 3 and 4, respectively.

Intercomparison of Solid State Nuclear Track Detectors

The *reference value* of the radon concentration measured by AMS with help of Lucas cells of relatively high volume (1 litre), was **4.73 MBq·h·m⁻³** for the first exposure (by an exposure time of **7.6 hours**), and **0.77 MBq·h·m⁻³** for the second exposure (by an exposure time of **7.4 hours**). After these exposures, our results were **4.11 ± 0.00 MBq·h·m⁻³** for the first exposure, and **0.76 ± 0.02 MBq·h·m⁻³** for the second exposure. In conclusion, for the first exposure, the ratio (R) between the reference value and our results was **R₁ = 1.15**, and for the second exposure was **R₂ = 1.01**.

CONCLUSIONS

Following the Intercomparison of Continuous Radon and its Short-lived Decay Product Monitors, organized by the National Radiation Protection Institute (SURO, Prague), conclusions with respect to our instruments, are:

- RADIM 3A continuous radon monitor shows an approx. 10 % under-estimative difference to the NRPI reference continuous monitor. This systematic underestimation was caused probably by the calibration of the instrument.
- Regarding to the EEC results, the DOSEMAN PRO monitor indicated a systematic underestimation by a factor of 4, which was caused probably by either inadequately high pump flow rate or air leakage around the filter holder.
- Both the exposed radon electronic dosimeters Ramon 2.2. were about 10% over-estimated.
- The investigated influence of changes of both the absolute humidity and the equilibrium factor F was most remarkably observed for RADIM 3A monitor during the period B. Here the difference was larger than 20%.

About the International Intercomparison of Solid State Nuclear Track Detectors, organized by the National Institute for Nuclear, Chemical and Biological Protection (SUJCHBO, Czech Republic), radon concentration results with CR-39 track detectors was 15% lower than the reference values in the first case, and are approx. equal in the second case.

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ELECTRONIC COMPONENTS AS FORTUITOUS DOSIMETERS

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ABSTRACT. This study investigated the optically stimulated luminescence (OSL) dose response of electronic components and chip-cards found within cell phones. The analysis of components extracted from these ubiquitous devices was proposed for applications regarding rapid accident dose reconstruction. The majority of the investigated components displayed bright OSL signals upon irradiation, a functionality between given dose and signal being observed. The dose response of the surface-mount resistors with alumina porcelain card chips was linear up to 6 Gy, thus making these electronic components suitable candidates as dosimeters in the case of a nuclear accident or attack.

Key words: *Retrospective dosimetry, Accident dosimetry, Fortuitous dosimeters, Optically stimulated luminescence*

INTRODUCTION

Retrospective dosimetry is a technique that measures overexposure doses, either chronic or acute, using common materials available for public domain. The aim is the after-the-fact determination of an overexposure dose from a radioactive source. Overexposures could be due to fallout from a nuclear accident or terrorist attack, or could be the result from a direct exposure to ionising radiation from a stolen or lost source or an unshielded source while being operated. (Cauwels and Vanhavere, 2008).

Probably the main contribution of luminescence technique to dosimetry and certainly the most applications can be found in the field of retrospective assessment of external exposures of a settlement (Göksu and Bailiff, 2006). In a review of luminescence for retrospective and accident dosimetry Woda et al. reported that the feasibility of using fired building material consisting of quartz and feldspar for luminescence dose reconstruction was shown over 40 years ago, and one of the first attempts at luminescence dose reconstruction was made using roof tiles in the Dosimetry System 86 for Hiroshima and Nagasaki (Woda et al., 2009). The authors also mentioned the successful use of luminescence methods for determining the external dose at the Nevada and Semipalatinsk Test Site, Chernobyl and in two former settlements of the Techa River valley, in the Southern Urals. Measured doses in the

near surface layer of the bricks ranged from high values of 2 - 4 Gy for bricks from the highly contaminated former village of Meltino at the upper Techa River to comparatively low values of 100 - 300 mGy for bricks from settlements in the middle Techa River valley (Muslyumovo) and the fallout area of the Semipalatinsk Test Site (Woda et al., 2009). It is important to specify that by measuring height profiles along building walls and dose-depth profiles into the brick, information on the source distribution and photon energy can be obtained (Meckbach et al., 1996).

The possible risk of an unexpected nuclear accident or terrorist attack necessitates proper methods and processes applicable in emergency situations. The so-called “view back” dosimetry is one of the most important tools of accidental dosimetry where no dose data is available (Mesterházy et al., 2011). So, it is important to have the possibility of rapidly measure the effects that arise from nuclear radiation incidents. Also, activities to identify the people at risk of significant acute radiation effects into the health care system are needed too. A crucial step towards this goal is to rapidly estimate the external radiation dose to which members of the public have been exposed (Bernhardsson et al., 2008). Today, however, only personnel within rescue teams assigned to nuclear emergency response organisations have ready access to dosimeters, normally thermoluminescent (TL) and/or electronic dosimeters. To make accurate predictions of the radiological consequences in an emergency situation, and to give correct information to the public, alternative methods to retrospectively estimate ultra low absorbed doses (<10mGy) are needed, as the conventional personal dosimeters are not in widespread public use (Bernhardsson et al., 2008).

Ideally, a “fortuitous dosimeter” should be carried by a large percentage of the population, positioned close to the body, and be enough sensitive to detect doses below the threshold for deterministic health effects (Inrig et al., 2009). Many objects can be applied as natural dosimeters, having suitable thermoluminescent (TL) and optically stimulated luminescent (OSL) properties. Common salt (NaCl) is recognized to have strong retrospective capabilities in the case of ionising radiation. Some of these refers to high sensitivity to radiation, high stability of the TL signal during the storage of the material (low fading), high linearity of the TL emission with the dose in the range of interest (up to 5 Gy) and thermal stability (Rodriguez-Lascano V., et al, 2012). It has been studied in various form: analytical one (Bailey, 2000, Bulur, 2001, Tanir et al., 2006), in the form of halite (mined rock salt) (Zhang j.f., et al, 2005) and household salt for cooking purposes (Thomsen et al., 2002; Zacharias et al., 2007). Several studies have reported the use of dust for individual dosimetry by collecting it from personal objects that people usually wear such as watches, keys, coins, jewels and also tobacco and investigated (Bortolin et al., 2010). Human calcified tissues (as bones and teeth – tooth enamel) are also of special interest to retrospective dosimetry. They can provide very useful information on exposure to ionising radiation many years after the event, since the signal is stored in these materials (Brady et al., 1968; Driessens, 1980; Callens et al., 1998; IAEA, 1998).

Regarding electronic devices, intensive research efforts were undertaken to find materials with appropriate radiation sensitivity that are carried close to the human body and which are also ubiquitously available and can be used as fortuitous dosimeters in a large scale emergency situation. Earlier, in 2003 and 2007 several studies have shown that certain types of chip cards, that find use as health insurance,

ID, cash and credit cards have high potential to be used as individual dosimeters in the case of radiological accidents (Mathur et al., 2007; Göksu, 2003). Woda and Spöttl investigated the potential of OSL for retrospective and accident dosimetry for wire-bond chip card modules. They demonstrated that this kind of dosimeters have a unique and reproducible signal response to doses up to several Gy, no signal in the unexposed state, a low detection limit of tens of mGy and also allow a dose assessment of reasonable accuracy up to several days after the exposure (Woda and Spöttl, 2009).

There are also various electronic components based on ceramics such as resistors, resonators, capacitors and transistors. And this is important because of the useful luminescence dosimetry properties of alumina-rich contained in these ceramics (Beerten et al., 2009). The authors presented the results from TL measurements of these electronic components (ceramic resonators and substrates of electrical resistors taken from the circuit board of a USB flash drive); and, for comparison, the OSL of the components was investigated as well (Beerten et al., 2009). According to this study, the magnitude of an irradiation event can be determined by analysing a ceramic resonator from a portable electronic device using advanced OSL equipment and conventional TLD one.

This present study investigates the optically stimulated luminescence (OSL) dose response of electronic components and chip-cards found within personal commonly used electronic devices in our country in order to characterise them as dosimeters for applications regarding rapid accident dose reconstruction.

MATERIALS AND METHODS

The present work discusses the investigation of OSL characteristics of both chip-cards and various electronic components found within mobile phones such as resistors, capacitors, resonators, inductors, diodes in order to prove if these components can be used as fortuitous dosimeters. There were also investigated two microchips removed from wrist watches and a chip card module used in credit cards. Samples selected for analysis consisted of a representative selection of electronic components removed from the circuit boards of nine different used mobile phones (Siemens C60, Nokia 6101, Orange SPV C 100, Nokia 3310, Ericsson1101401BV, Siemens A50, LG Z525I, Alcatel BG31G, Sony Ericsson W660i), seven used cell phone chip-cards (Orange SIM-2, Orange PrePay, Connex, Vodafone, Dialog, ALO-DA) and one unused (Vodafone), two microchips removed from Citizen and Casio Beside wrist watches, and an ING chip card. The total number of samples investigated is 45.

All measurements were performed using a TL/OSL Luminescence Reader, model Risø TL/OSL-DA-20. It is equipped with 28 blue LEDs emitting at 470 nm with a total power of 36 mW/cm², which were used as an optical stimulation source for our aliquots. Unless otherwise stated the stimulation power of the diodes was set to 30% of the maximum power in order to prevent the saturation of the PMT. The light detection system consists of a bialkali EMI 9235QA photomultiplier tube (PMT), and a detection UV detection filter (Hoya U-340; 270-370 nm). The irradiations were performed using the integrated ⁹⁰Sr/⁹⁰Y beta source (dose rate of 0.1 Gy/s).

In preparation for analysis, each device was disassembled and the electronic components were removed from the circuit boards using a small screwdriver. The cell phone cards, as well as the credit card were taken apart in order to expose the

crystalline component of the chip. Afterwards, the components were arranged by type, size and manufacturer and placed bottom-up on a stainless steel cup.

In order to investigate the OSL specific luminescence and dose response, signals have been collected under continuous wave (CW) stimulation. The data processing procedure consisted of a small OSL integration interval to which an early background subtraction had to be applied in order to avoid apparent sensitivity changes and signal recuperation. Therefore, the net signal is the signal integral of the first 6 channels (0.4 s of blue light stimulation) from which a background (last 6 channels of stimulation) has been subtracted in order to correct for slow OSL components and the photomultiplier dark counts.

RESULTS AND DISCUSSION

OSL signal

The OSL decay curve represents the gradual depletion of electrons from traps, usually starting with a pronounced signal that drops in a certain amount of time to the background level. A series of typical OSL decay curves, measured for 100 s at room temperature after irradiation with 1 Gy are depicted in **Fig. 1** and **Fig. 2**. The OSL decay curve of most the samples showed a complex shape with a dominating “fast component”, which has a decay time similar to the decay time of the “fast component” in quartz, but also marked “medium components” and an approximately constant background signal was reached during the stimulation time. The stimulation time selected for the experiment procedures was sufficient to completely readout the fast and medium components. **Fig. 1** presents the samples no OSL response, respectively not a very bright OSL signal, **Fig. 2** illustrates the most representative electronic components removed from cell phones in terms of luminescent response provided after irradiation. Therefore in **Fig. 2** is presented a selection with the brightest electronic components, providing both the most pertinent examples of analysed resistors, inductors and capacitors, and the investigated cell phone chip cards.

All the surface-mount electronic components consistently exhibited OSL following irradiation, the brightness of the signal varying widely between the type and for the relevant cases the size of the samples. The most luminescent component was a resistors bridge found in Siemens A50 mobile phone, while the resonator removed from Siemens C60 registered the lowest value. In comparison to alumina-rich resistors the radiation sensitivity of capacitors and inductors is about one and in some cases two orders of magnitude smaller. This is due to the dark-colored barium and calcium titanate out of which they are made. Although, this is not the case for two capacitors removed from Siemens A50, respectively LG Z525I mobile phones which both had the same order of magnitude as the resistors bridge. Regarding mobile phones chip cards, newer generations SIM cards whether PrePay or subscription based presented a significantly higher OSL response in comparison to older ones. It is important to specify that all the cell phone chip cards were covered with a transparent plastic cover, in contrast to the credit card chip module which was encapsulated using a black plastic layer and thus it gave little OSL response. In most cases protective layer removal damages the chip integrity, thus invalidating any further tests.

Dose response

Integrating the signal in the OSL decay curve as function of given dose one can estimate the number of excited traps and thus determine the equivalent dose of a sample. For constructing the dose response, the samples were exposed to alternating cycles of irradiation and OSL, starting with an optical stimulation bleaching (removing background signal). For each samples, five doses were applied using the integrated $^{90}\text{Sr}/^{90}\text{Y}$ beta source, namely 0.5 Gy, 1 Gy, 2 Gy, 4 Gy and 6 Gy, followed by the measurement of the signal for a nil dose and a repeat dose (2 Gy). The experiment procedure refrained from any preheat treatment and measured the OSL at room temperature, immediately after irradiation. Most tested samples showed a zero-dose signal considerably smaller than the 1 Gy dose signal. Usually the zero-dose signal was 2-3 orders of magnitude smaller than the 1 Gy dose signal indicating negligible recuperation. The response was also found to be repetitive as it can be seen from the recycled dose of 2 Gy, represented as a star in **Fig. 3**. The resistors substrates and the newer generation SIM cards described a linear dose response curve for doses up to 6 Gy, meanwhile the remaining electronic components response showed either cubic or exponentially saturating behavior. **Fig. 3** presents one typical example of each.

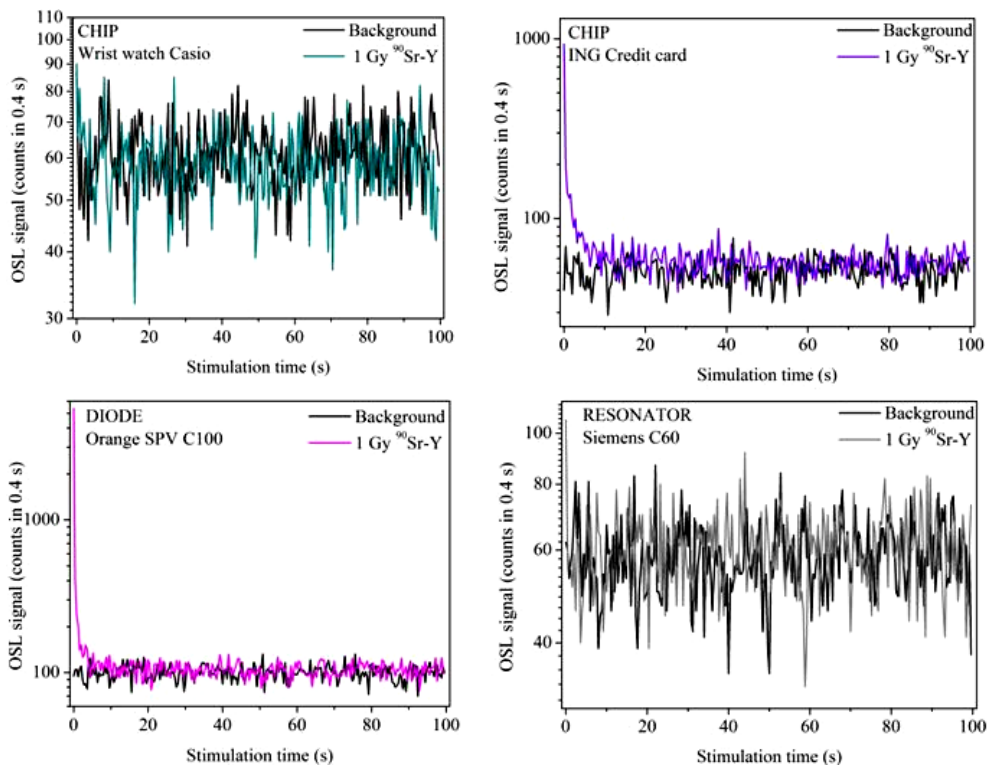


Fig. 1. Comparison of OSL decay curves. The background response is compared to the response recorded after irradiation with a dose of 1Gy.

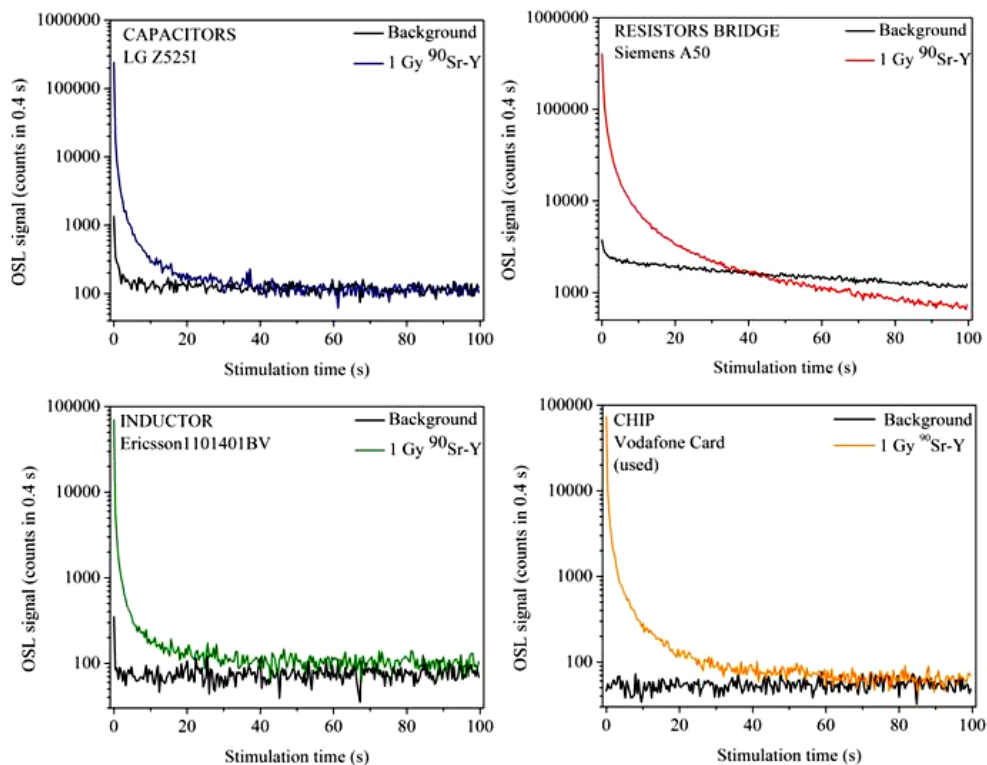


Fig. 2 Comparison of OSL decay curves between the most representative samples with a bright OSL response. Please note the logarithmic scale.

CONCLUSIONS

Cement, mortar, ceramics or bricks, traditionally used in retrospective luminescence accident dosimetry need complex, tedious and time consuming sample preparation in order for quartz grains to be extracted from these materials for reconstructing the dose absorbed, in order to relate it to the dose the victims have been exposed to. Moreover, given that accidental exposures are localized or highly heterogeneous, one can easily understand the difficulties in converting the dose measured in the materials to the dose distribution of the victim's organism. Chemical products such as cleaning agents are also characterized by the same disadvantages. Unlike the previously described materials, the dose measured in both the electronic components and the chip cards found within mobile phones is more pertinent and can be related to the victims, due to the fact that those devices are usually worn close to the body.

ELECTRONIC COMPONENTS AS FORTUITOUS DOSIMETERS

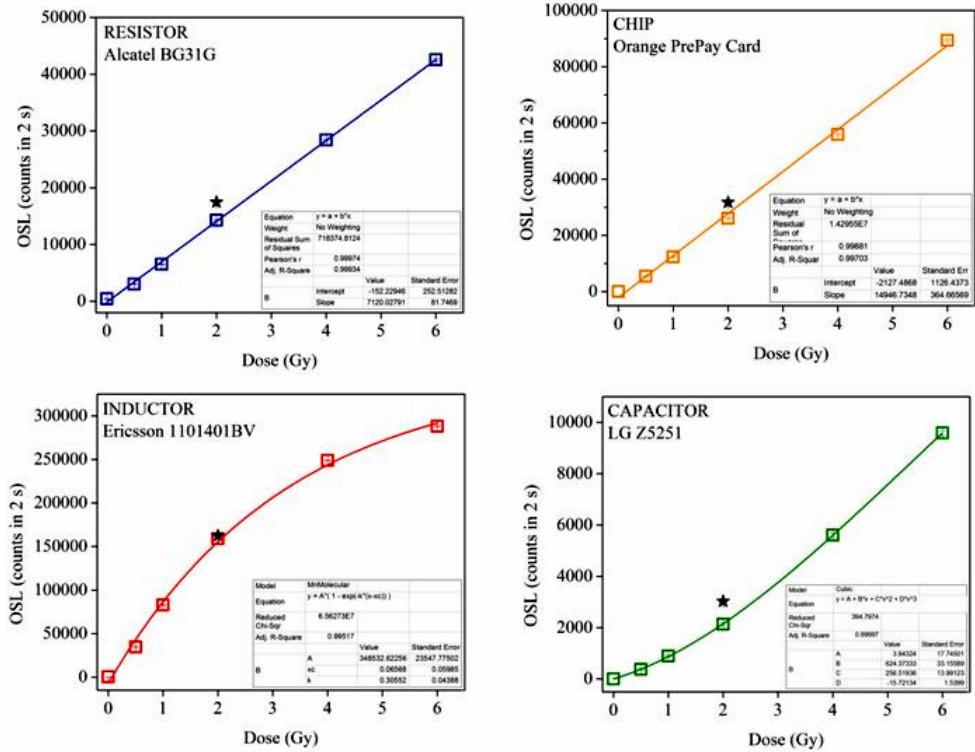


Fig. 3. Typical dose responses of analysed electronic components. A good linear OSL response ($R^2 > 0.99$) can be observed in the case of resistors and card chips.

The components investigated in this study were sufficiently sensitive to detect doses below the threshold for deterministic health effects, respectively 1 Gy. Moreover, the dose response of resistors and chip card was found to be well approximated by a linear function (with determination coefficients better than 0.99). Further investigations regarding the lower limit of detection as well as time delayed response (fading) are in progress. Given these characteristics, both electronic components and chip cards removed from cellular phones can function as a fortuitous dosimeter in an emergency response.

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LIFE CYCLE ASSESSMENT (LCA) OF MUNICIPAL SOLID WASTE MANAGEMENT IN CLUJ COUNTY, ROMANIA PRELIMINARY RESULTS

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ABSTRACT. Life cycle assessment (LCA) is a tool which can be used to evaluate the environmental performance of municipal solid waste (MSW) management systems. The aims of the study were to identify the environmental “friendly” system in applying this methodology at Cluj County level. In this study, two different municipal solid waste (MSW) management scenarios were developed and compared for the Cluj County.

Scenario 1 represents the current MSW management status in Cluj County, involving comingled collection, transport and landfilling, while scenario 2 was incorporated a mechanical-biological treatment unit for the wet part of the MSW before landfilling.

The Life Cycle Assessment (LCA) methodology was applied in order to determine the most environmentally friendly system scenario. The Life Cycle Inventory (LCI) analysis was carried out with the aid of GaBi4 software for universities. Impact categories dealt with were: Global Warming Potential (GWP), Acidification Potential (AP), Eutrophication Potential (EP), Human Toxicity Potential (HTP) and Photochemical Ozone Creation Potential (POCP).

The lowest contribution to the global warming category was calculated for the Scenario 2.

Key words: *LCA, Municipal Solid Waste (MSW), Global warming potential, waste.*

INTRODUCTION

Solid waste management is important to ensure human health and safety and for this reason it must to be reduced as much as possible the environmental impacts of waste management. (White et al., 1999). Life cycle assessment is a tool which can be used to predict and compare the environmental impact of waste management systems. Comparing impacts for different options, allows environmental improvements to be identified.

The study focuses on the assessment of environmental performance of alternative solid waste management options that can be used in an area of Cluj County, Romania.

The area of Cluj County has about 690.406 of inhabitants and a production of municipal solid wastes (MSWs) equal to about 707 t per day. These were all sent to land filling until 2010, without any significant recourse to separate collection and thermal treatment. This solution fast made exhausted the landfill volumes of the area, so that since 2010 no more space for restwaste dumping was available.

METHODOLOGY

Life Cycle Assessment (LCA)

ISO 14040 (2006) describes the life cycle assessment (LCA) phases including: definition of the goal and scope, the life cycle inventory analysis (LCI) phase, the life cycle impact assessment (LCIA) phase and the life cycle interpretation phase.

Scope and goal definition

Two different scenarios of Municipal Solid Waste Management Systems (MSWMSs) that include different MSW processing and/or disposal methods were developed. It's were compared with respect to their environmental burdens and total fuel consumption. The MSWMS scenarios were developed based on the current MSWMS of Cluj County.

The MSWMSs were compared in a LCA context, which considered the following components: collection and transportation of MSW, biological (aerobic digestion) treatment and landfilling. Boldrin et al. (2011) considered that biological treatment is a common option for management of organic municipal solid waste, and a complete waste management system can be modeled with LCA tool and biological treatment is one of the available options. The composting part was included into the scenario 2, because the composting process reduced moisture and stabilized the waste (Pognani et al., 2012)

The functional unit and system boundaries

The functional unit in this study has been defined as the amount of MSW generated in Cluj County. The system boundaries selected for the life cycle was defined as the moment when material ceases to have value, becoming labeled as waste.

The scenarios

The two scenarios considered in this study with the system boundaries are represented in Fig.1. The first scenario (Fig.1a) consists of three main steps: collection, transport and landfilling of MSW. This case represents the current status in Cluj County. Scenario 2 (Fig.1 b) was fed to the model in order to assess the possibility of improving the current MSWMS. In scenario 2, a MBT (Mechanical-Biological Treatment – aerobic digestion or composting) treatment was added to the bio-waste, before landfilling.

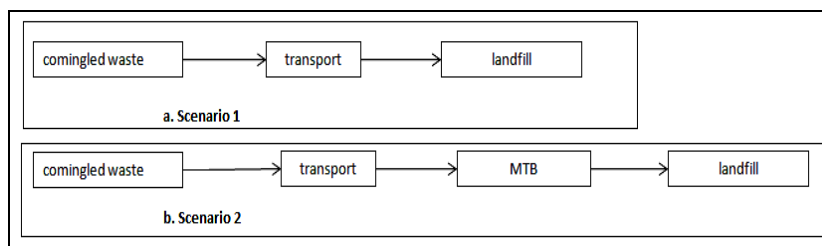


Fig. 1. The scenarios of MSWMS used in this study

Life Cycle Inventory (LCI)

The data used in this study were secured by REPA (Regional Environmental Protection Agency) and by the regional project from an integrated waste management system in Cluj County (Medana Company, 2010): waste characteristics and composition by weight and operational data of landfill sites.

In this LCA study, it is assumed that the waste was transported to the open dumps landfills in the Cluj County.

The main tool used in this study was the software GaBi4, the version for universities, developed by the Institute for Polymer Testing and Polymer Sciences (IKP) of the University of Stuttgart in collaboration with PE Europe GmbH Company, Germany. The GaBi 4 software system is a tool to create life cycle balances, and helps to analyze and interpret the results.

RESULTS AND DISCUSSION

Input amounts of waste were similar in each of the scenarios developed (198,081.736 tons/year) In the case of scenario 1 (representing the current status of MSWM in Cluj County), landfilling was the only disposal method for MSW resulting in an amount over 95% of the generated MSW), since the average percentage of waste being landfilled in the EU was 62% in 1995 and it has dropped to 44% in 2005. (ETC/RWM, 2008)

Table 1 shows a comparison of the different scenarios in terms of environmental burdens.

Table 1. Comparison of scenarios results

| Impact categories | Unit | Scenario 1 | Scenario 2 |
|--------------------------|---|-------------------|-------------------|
| EHP | kg PO ₄ equiv./ton waste managed | 2.3363 | 2.2664 |
| AP | kg SO ₂ equiv./ton waste managed | 0.6101 | 0.2022 |
| POCP | kg ethene equiv./ton waste managed | 0.2844 | 0.2499 |
| HTP | kg DCB equiv./ton waste managed | 5.4455 | 1.1766 |
| GWP | kg CO ₂ equiv./ton waste managed | 909.9900 | 902.7900 |

It can be seen in the Table 1, in terms of global warming, that the contribution of the scenarios is important. About the other contributions at the environmental impacts, the scenario 1 has higher values than the scenario 2, excepting the eutrophication potential impact. The values for the human toxicity potential are much higher for the scenario 1 than for the scenario 2.

Table 2 shows the contributions of each part of the cycle of waste management in Scenario 1, in terms of environmental burdens.

Table 2. Contributions of Scenario 1 at the environmental impacts

| Scenario 1 | | | | | |
|-------------------|--------------------------------|--------------------------------|--------------------------------|-----------------------------------|---------------------------------|
| | AP | EHP | HTP | POCP | GWP |
| Unit | kg SO2 equiv./ton waste | kg PO4 equiv./ton waste | kg DCB equiv./ton waste | kg ethene equiv./ton waste | kg CO2 equiv./ton waste. |
| EU Diesel | 0.0473 | 0.0031 | 0.7326 | 0.0061 | 7.1615 |
| Transport | 0.2613 | 0.0677 | 1.5262 | 0.0280 | 59.0370 |
| Landfill | 0.1777 | 2.2663 | 1.1741 | 0.2498 | 902.7200 |

As can be seen in Table 1, the contributions of the landfill are higher than transport and diesel, for the follow impact categories: global warming potential, eutrophication potential and photochemical ozone creation potential. The transport has the higher values for acidification potential and human toxicity potential.

Table 3 shows the contributions of each part of the cycle of waste management in Scenario 2, in terms of environmental burdens.

Table 3. Contributions of Scenario 2 at the environmental impacts

| Scenario 2 | | | | | |
|-------------------|--------------------------------|--------------------------------|--------------------------------|-----------------------------------|--------------------------------|
| | AP | EP | THP | POCP | GWP |
| Unit | kg SO2 equiv./ton waste | kg PO4 equiv./ton waste | kg DCB equiv./ton waste | kg ethene equiv./ton waste | kg CO2 equiv./ton waste |
| EU Diesel | $0.0529 \cdot 10^{-3}$ | 0 | $0.8187 \cdot 10^{-3}$ | $0.0068 \cdot 10^{-3}$ | $8 \cdot 10^{-3}$ |
| Transport | $0.0805 \cdot 10^{-3}$ | $0.0567 \cdot 10^{-3}$ | $0.0171 \cdot 10^{-3}$ | $0.0002 \cdot 10^{-3}$ | $49.432 \cdot 10^{-3}$ |
| Landfill | $17.856 \cdot 10^{-3}$ | $13.95 \cdot 10^{-3}$ | $1.116 \cdot 10^{-3}$ | 0 | $383,090 \cdot 10^{-3}$ |
| MBT | $177.71 \cdot 10^{-3}$ | $2,266.3 \cdot 10^{-3}$ | $1,174.1 \cdot 10^{-3}$ | $249.8 \cdot 10^{-3}$ | $902,720 \cdot 10^{-3}$ |

As can be seen in Table 1, the contributions of the MTB are higher than the other parts of the cycle, for all the impact categories, followed by the landfill.

Comparison of environmental impact categories

Figure 2 shows the comparison between the contributions at the environmental impact categories of the two scenarios.

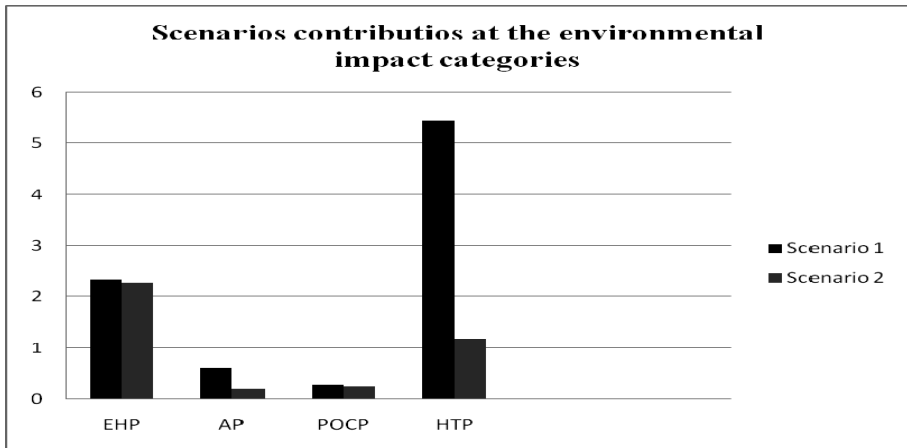


Fig. 2. Comparison between the contributions of the scenario1 and scenario2 at the environmental impact categories

Figure 3 shows the comparison between the contributions at global warming of the two scenarios.

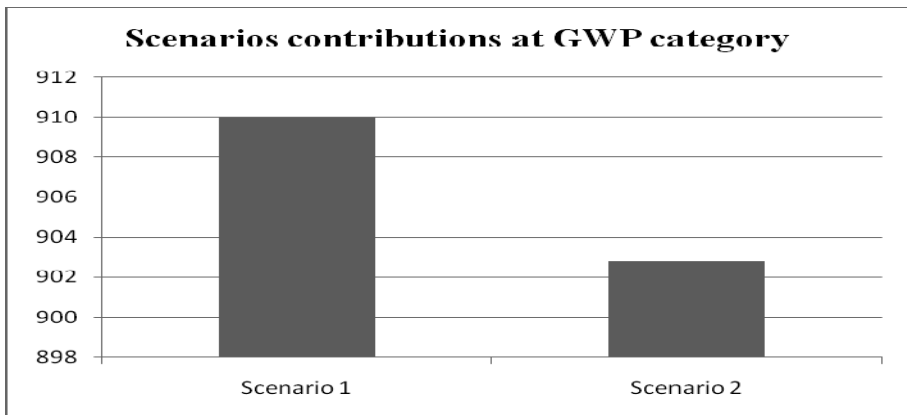


Fig. 3. Comparison between the contributions of the scenario1 and scenario2 at global warming potential

From figure 2 and 3 result that the highest contribution to all environmental impact categories belongs to scenario1.

In the case of global warming impact category, scenario 2 originated the least burden. This is due to the reduction of greenhouse gas emissions by added the aerobic treatment of the bio-waste.

The human toxic potential is higher in the scenario 1, and this is due to the presence of heavy metals and halogenated hydrocarbons emissions from the waste in the environment, which present a risk for the human health. The scenario 1 originated the highest values for HTP due to the transport and landfilling of all amount of collected waste.

CONCLUSIONS

This study was conducted to determine the most environmental friendly municipal solid waste management system, out of two scenarios developed for the Cluj County. This was executed by using Life Cycle Assessment (LCA) as a tool to compare different treatment and/or disposal options.

The main findings of the study can be summarized that Scenario 2 was the best option for all of environmental impact categories.

Even the life cycle assessments are always associated with uncertainties (Ekvall et al, 2007) and there is still a lack of consensus about methodology on how to determine data quality and investigate the range and impact of uncertainties (Bernstad & Jansen, 2011), the results obtained from this study support the conclusion that LCA, as an environmental tool, can be successfully applied in an Integrated Solid Waste Management System (ISWMS) as a decision support tool, and should be implemented for waste management activities.

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LIFE CYCLE ASSESSMENT (LCA) OF MUNICIPAL SOLID WASTE MANAGEMENT IN CLUJ COUNTY

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PASSIVE SAMPLING OF INDOOR AIR FORMALDEHYDE IN FIVE ROMANIAN SCHOOLS IN ALBA COUNTY

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ABSTRACT. In this work, a passive sampling method for formaldehyde determination in air samples is described. The method is based on the derivatization of formaldehyde with 2,4-dinitrophenylhydrazine, followed by liquid chromatography coupled to UV-Vis detection analysis.

Key words: formaldehyde, passive sampling, indoor air pollution

INTRODUCTION

Aldehydes, especially formaldehyde, are indoor and outdoor chemical pollutants of particular interest due to their recognized mutagenic and carcinogenic nature and their toxic activity associated with eyes and respiratory tract irritations, nausea, headache, tiredness and thirst (WHO, 2002). Formaldehyde is usually the most abundant aldehyde in air and also the most studied since it is classified as Group 1 (human carcinogen) by the International Agency for Research on Cancer (IARC) due to its carcinogenicity (IARC, 2004).

In humans, transient and reversible sensory irritation of the eyes and respiratory tract has been observed in clinical studies and epidemiological surveys. The recent increased prevalence of childhood asthma has brought into question the contribution of aldehydes to this problem. The odor threshold for most people ranges between 0.5 and 1 ppm. In general, eye irritation, the most sensitive endpoint, is associated with airborne concentrations beginning in the range of 0.3 to 0.5 ppm (INCHEM, 2002). Eye irritation does not become significant until about 1 ppm, and rapidly subsides. Moderate to severe eye, nose and throat irritation occurs at 2 to 3 ppm (INCHEM, 2002). Sensory irritation has also been reported at lower exposure levels, but is then difficult to distinguish from the background. Formaldehyde causes skin irritation and has corrosive properties when ingested. In some individuals, contact dermatitis may occur at concentrations as low as 30 ppm. Formaldehyde is weakly genotoxic and was able to induce gene mutations and chromosomal aberrations in mammalian cells (INCHEM, 2002). DNA-protein cross-links are a sensitive measure of DNA modification by formaldehyde.

Formaldehyde is ubiquitous in the environment. It is formed naturally in the troposphere during the oxidation of hydrocarbons, which react with hydroxyl radicals and ozone to form formaldehyde and other aldehydes as intermediates in a series of reactions that ultimately lead to the formation of carbon monoxide and dioxide, hydrogen and water (IARC, 2004). Among the hydrocarbons found in the troposphere, methane is the most important source of formaldehyde. Because of their short half-life, these sources of formaldehyde are important only in the vicinity of vegetation. Formaldehyde is one of the volatile compounds that are formed in the early stages of decomposition of plant residues in the soil, and occurs naturally in fruit and other foods (WHO, 1989; IARC, 1995).

The most extensive use of formaldehyde is in the production of resins with urea, phenol and melamine, and of polyacetal resins. Formaldehyde-based resins are used as adhesives and impregnating resins in the manufacture of particle-board, plywood, furniture and other wood products; for the production of curable moulding materials (appliances, electric controls, telephones, wiring services); and as raw materials for surface coatings and controlled-release nitrogen fertilizers (IARC, 2004). They are also used in the textile, leather, rubber and cement industries. Further uses are as binders for foundry sand, stonewool and glasswool mats in insulating materials, abrasive paper and brake linings (WHO, 1989; IARC, 1995; IARC, 2004). Another major use of formaldehyde is as an intermediate in the synthesis of other industrial chemical compounds, such as 1,4-butanediol, trimethylolpropane and neopentyl glycol, that are used in the manufacture of polyurethane and polyester plastics, synthetic resin coatings, synthetic lubricating oils and plasticizers. Other compounds produced from formaldehyde include pentaerythritol, which is used primarily in raw materials for surface coatings and explosives, and hexamethylenetetramine, which is used as a cross-linking agent for phenol-formaldehyde resins and explosives (IARC, 2004). Formaldehyde is also the basis for products that are used to manufacture dyes, tanning agents, precursors of dispersion and plastics, extraction agents, crop protection agents, animal feeds, perfumes, vitamins, flavourings and drugs (WHO, 1989; IARC, 2004).

The resulting indoor contribution to the average human daily intake of formaldehyde was found to be higher than 98% of the total human exposure (Hanoune et al. 2006). Some of the sources of formaldehyde in homes are presented in Fig.1 (Andreini et al., 2000) and include building materials, hardwood, plywood, laminate floorings, adhesives, paints and solvents, smoking and the use of unvented fuel-burning appliances, like gas stoves or kerosene space heaters (Hanoune et al., 2006).

Formaldehyde is an important indoor and outdoor chemical pollutant of particular interest due to its potential impact on human health. The indoor formaldehyde concentrations are usually 2–10 times higher than the outdoor ones, indicating the presence of significant indoor sources such as direct emissions and indoor chemical formation (Hanoune et al., 2006). Formaldehyde concentration levels in domestic air vary from ambient level (1–25 ppbv) to 4 ppmv in newly constructed houses (Piyante et al., 2005).

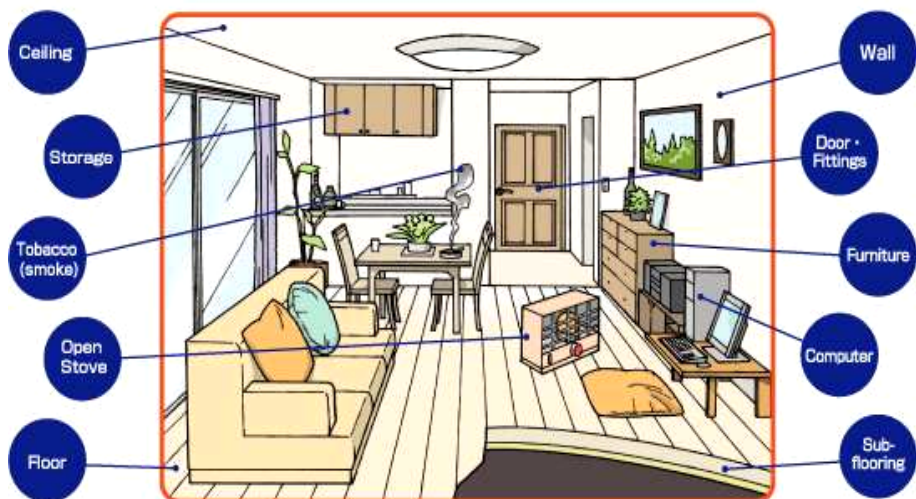


Fig. 1. Common Household Sources of Formaldehyde (Andreini et al., 2000).

The guidelines set by the World Health Organization (WHO) for formaldehyde in indoor air are $100 \mu\text{g}\cdot\text{m}^{-3}$ (0.08 ppmv) based on the levels that have been shown to cause nose and throat irritation in humans (WHO, 1999). The reference concentration of formaldehyde in the atmosphere was recommended to be 0.01 ppm based on carcinogenic effects (Naya and Nakanishi, 2005). The Health Canada, Canada's federal department of health, recently revised its residential indoor air quality guideline for formaldehyde: 1 and 8-h exposure limits were set at $123 \mu\text{g}\cdot\text{m}^{-3}$ (0.1 ppmv) and $50 \mu\text{g}\cdot\text{m}^{-3}$ (0.04 ppmv), respectively (Health Canada, 2006). At higher concentrations, formaldehyde causes headache and itchiness of the skin.

MATERIALS AND METHOD

Reagents and materials

- Acetonitrile (Sigma-Aldrich, Code 27.071.7), HPLC Grade
- Volumetric pipettes (2 mL) class A
- Disc filters ($0.45 \mu\text{m}$) solvent resistant (Millex HV)
- Radiello passive sampling devices (Fig. 2) composed by blue polycarbonate microporous polyethylene cylindrical diffusive body (RAD 1201), polycarbonate supporting plate with clip and transparent label pocket (RAD 195) and adsorbent cartridge (RAD 165) which consisted on 900 mg florisil (35-50 mesh) covered with 2,4-dinitrophenylhydrazine. The passive samplers were purchased by Supelco/Sigma Aldrich (RAD 195).



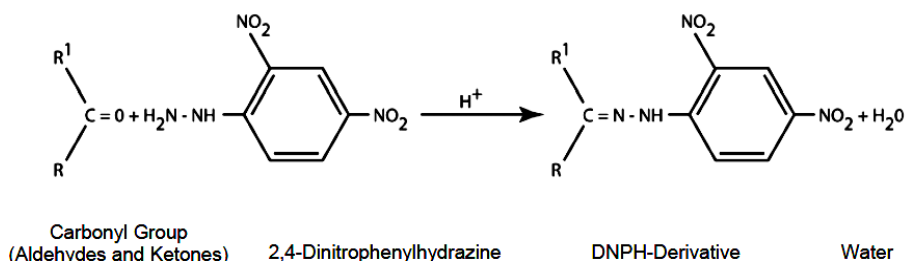
Fig. 2. Radiello passive sampling device.

Formaldehyde passive sampling procedure

In this work, a passive sampling method for formaldehyde determination in air samples is described. The method is based on the derivatization of formaldehyde which is then analyzed by liquid chromatography coupled to UV-Vis detection.

The adsorbent cartridge, containing florisil sorbent impregnated with 2,4-dinitrophenylhydrazine (2,4-DNPH), is placed into the diffusive body which is screwed onto the supporting plate. Each sampler is labeled and the location, starting date/time and ending date/time are mentioned. The samplers are then installed in an appropriate position, according to ISO 16000-2 protocol. The samplers are installed only in one location per room, 2 m from walls, at a height of 1.5 m from the ground. They should not be installed in the vicinity of a suspected emission source, or in a place where they are exposed to direct sunshine, or nearby a heating or a ventilation system. The passive sampler devices are exposed for approximately 5 days, from Monday to Friday to indoor/outdoor air.

The formaldehyde present in the air sample reacted with 2,4-DNPH to form the corresponding 2,4-dinitrophenylhydrazone, according to the following equation:



where R and R¹ are alkyl or aromatic groups (ketones) or either substituent is a hydrogen.

Temperature is the only parameter to be kept under control, because the outdoor value can be very different from 25°C used to calibrate Radiello. If the temperature falls below 20°C or arises over 30°C, it is advisable to correct the sampling rate value. Sampling rate is invariant with humidity in the range of 15-90% and with wind speed between 0.1 and 10 m·s⁻¹. After the exposure the adsorbent cartridge is removed from the diffusive body and is placed into a glass vial well tight. The exposed cartridges are kept in a dark place at 4°C and remain stable and unaltered for 60 days.

The so trapped and derivatized formaldehyde is then eluted with acetonitrile. The tube is closed with its stopper and shaken for 30 min. The obtained solution is filtered through a 0.45 µm filters. The solution can be directly injected into the HPLC system. If is well capped and stored at 4 °C, the resulting solution is stable for at least 42 days. The analyses were performed in the laboratory from Environmental Science and Engineering Faculty, Babes-Bolyai University.

Applicability

The method was used to analyze indoor formaldehyde in 5 schools in Alba county, Romania, included in the SINPHONIE (Schools Indoor Pollution and Health: Observatory Network in Europe) Project study. Two of the schools included in this study are located rural areas, and three are located in urban. The sampling will be performed during the cold season, from the end of October 2011 to the beginning of January 2012.

The results of the sampling campaign and analyses will set the basis for a comprehensive risk assessment study regarding the impact of indoor air quality in classrooms on children's health and performance.

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HEALTH RELATED TO ENVIRONMENTAL EXPOSURE TO IONIZING RADIATION: LUNG CANCER BETWEEN CAUSE AND POSSIBLE MEANS FOR EARLY DIAGNOSIS

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ABSTRACT. Lung cancer is a major health concern, being the second leading cause of death after heart disease and the most common of all cancers, with 1.61 million new cases diagnosed in 2008. Radon is the primary cause of lung cancer among non-smokers and is much more likely to cause lung cancer in people who smoke. The most significant natural exposure to ionizing radiation, over 55% of all sources, comes from inhalation of radon (^{222}Rn), thoron (^{220}Rn) and their progeny. On the other hand, analysis of exhaled breath gains more attention in the diagnosis of pulmonary diseases and the assessment of their activity. The development of non-invasive and highly discriminating diagnostic tools is desirable in correlation with breath VOC analysis that proved to be a non-invasive test which may potentially detect lung cancer at an early stage and reduce the high mortality of the disease. The present study aims to the task of relating the leading cause of lung cancer (after smoking) with its management, including risk assessment, fraction of lung cancers attributed to radon and possible means for early diagnosis. Thus, the latest radiation biologic, experimental and epidemiologic data available in the related literature was reviewed and Ion Mobility Spectrometry (IMS) proved to be the most convenient and appropriate method for breath analysis for detecting any follow-up parameters (such as PSA in prostate cancer) that could serve as lung cancer biomarkers.

Key words: *lung cancer, radon, IMS*

INTRODUCTION

Ionizing radiation arises from both natural and man-made sources and at very high doses can produce damaging effects in human tissue that can be evident within days after exposure. In the low-dose exposures, so-called late effects are produced many years after the initial exposure. Although low dose radiation exposure can potentially generate different kinds of biological risk, the risk of most concern is cancer (Mitchel and Boreham, 2000), which is the end-point that will be addressed here. Lung cancer is a major health concern, being the second leading

cause of death after heart disease and the most common of all cancers, with 1.61 million new cases diagnosed in 2008 (Ferlay et al, 2006; IARC, 2008). Radon-induced lung cancers are mainly caused by low and moderate rather than by high radon concentrations, because of the large number of people exposed to indoor radon in homes with such low concentrations (WHO, 2009). BEIR VII Report (2006) developed the most up-to-date and comprehensive risk estimates for cancer and other health effects from exposure to low-level ionizing radiation (particularly radon) and concluded that the current scientific evidence is consistent with the linear non-threshold (LNT) model. This model assumes that, at low doses (in the range of near 0 up to 100 mSv) there is a linear dose-response relationship between exposure to ionizing radiation and the development of solid cancers in humans, the risk continuing in a linear fashion at lower doses without a threshold and that the smallest dose has the potential to cause a small increase in risk to humans (BEIR VII, 2006). It has been proved that lung cancer is induced primarily by smoking and then by exposure to radon and its progeny (NRC, 1999). Radon is the main radioactive element that contaminates the human environment. It is an inert, colorless, insipid and inodorous gas, which occurs naturally from the decay of radium - in the uranium radioactive series - found in varying proportions in all rocks and soils in the world. Radon seeps out easily from the soil into outdoor air and also indoors, where it can become trapped and builds to dangerous concentration levels. Its most stable isotope, ^{222}Rn (commonly referred as radon) has a half-life of 3.8 days, and decays into its short-lived products called radon daughters or progeny. Radon and its short-lived progeny are inhaled and, while radon itself is generally exhaled immediately after inhalation, its short-lived progeny- which are solid elements - deposit on the surfaces of the bronchial epithelium. While decaying, radon and its progeny deposited in these sites emit alpha particles (high Linear Energy Transfer radiation) that may directly affect the cell components or indirectly, causing water-derived radicals. The interaction between alpha particles, which have high energy – and cellular DNA may generate mutations in genes that control certain behaviors, such as the growth of transformed cells and its uncontrolled division, leading to cancer. Based on risk estimates from studies of underground miners, it has been calculated that between 6.600-24.000 lung cancer deaths per year in the United States may be attributable to exposure to radon progeny (Lubin et al., 1989). The dose due to the inhalation of radon gas is low, compared to the one due to the short-lived radon progeny, which are isotopes of polonium, lead and bismuth. The greatest dose contribution is from alpha irradiation of the bronchial epithelium. The most significant natural exposure to ionizing radiation, over 55% of all sources, comes from inhalation of radon (^{222}Rn), thoron (^{220}Rn) and their progeny (Iacob and Botezatu, 2000; ICRP, 1981). Radon is estimated to cause between 3% and 14% of all lung cancers, depending on the average radon level in a country (WHO, 2009). These facts, together with the experimental and epidemiological data prompted the International Agency for Research on Cancer (IARC) – in 1988, as well as the U.S. Environmental Protection Agency (EPA) and other regulatory bodies to classify radon as being carcinogenic to humans. In 1986, the USA Environmental Protection Agency (EPA, 1992) established an "action level" for indoor radon exposures of 4 pCi/ Litre of air (160 Bq/m³). To develop appropriate public policy for indoor radon, decision makers need a characterization

of the risk of radon exposure across the range of exposures people actually receive. In response, carcinogenesis models for the assessment of lung cancer risk attributed to radon have been developed (e.g. BEIR VI models, Darby's model, the Transformation Frequency-Tissue Response model). Radiation protection guidelines for human health safety state rules and regulations based on risk estimations such as the ones that will be shortly reviewed below, but were more detailed in previous works (Truta-Popa et al., 2010; 2011 a, b).

QUANTIFICATION OF LUNG CANCER RISK

There is a great uncertainty and research is being developed for studying the health effects of low dose exposures to high LET radiation (e.g. alpha particles emitted by radon and radon progeny decay). Alpha particles are at least as carcinogenic as electrons. A single alpha particle track can deposit tens of cGy while a single ^{60}Co - gamma ray (low LET) will deposit, on average, about 1 mGy (Mitchel and Boreham, 2000). The biological effects caused by exposure to ionizing radiation, particularly radon, are the result of a complex series of physical, biological and physiological interactions (Kotecki, 1998). These interaction may depend upon factors such as the type of radiation, the duration and intensity of exposure and the nature of the biological system implied (Mebust et al., 2002). One of the fundamental tools of radiation biology is a formalism describing these interactions as dose-response and time-dose relationships (Fleishman, 2004). During the last decade, the carcinogenesis theory was marked by the report of an interactive relationship between experimental observations and modeling efforts (Fleishman, 2004). Cancer formation is a multi-step process and although we usually consider radiation as acting on normal cells, it may act on cells which are at any point in that process. The underlying genetic and molecular determinants for each step and pathway remain still undefined. Since cancer is considered to be monoclonal (single cell) in origin, this suggests that the dose-response is linear at low doses with no threshold. However, it is possible that the whole organism may be more capable of repairing damage at low doses and low dose rates, which would modify the dose-response to a sub-linear curve (NCRP, 2002). The magnitude of the mutagenic effect (per unit dose) varies with dose rate. In this respect, the Transformation Frequency-Tissue Response (TF-TR) model developed recently (Truta-Popa et al., 2011 a, b) could be used to simulate the dose-effect relationship for low radon exposures, typical for the general population. This model is a mechanistic, biology-based model, that includes the initiation-promotion of cancer, and biophysical/oncogenic parameters (e.g. cellular hit, cell cycle duration, cell killing/cell survival, absorbed dose, cellular dose, oncogenic transformation) that successfully predicts lung cancer risk for different exposure conditions - from very high to very low doses, and for different dose-rates. The TF-TR model was described in detail elsewhere (Truta-Popa et al., 2011 a, b), but the following capture illustrates the excellent agreement between the TF-TR model predictions and the epidemiological data of Darby and colleagues (2006), for 13 European residential studies:

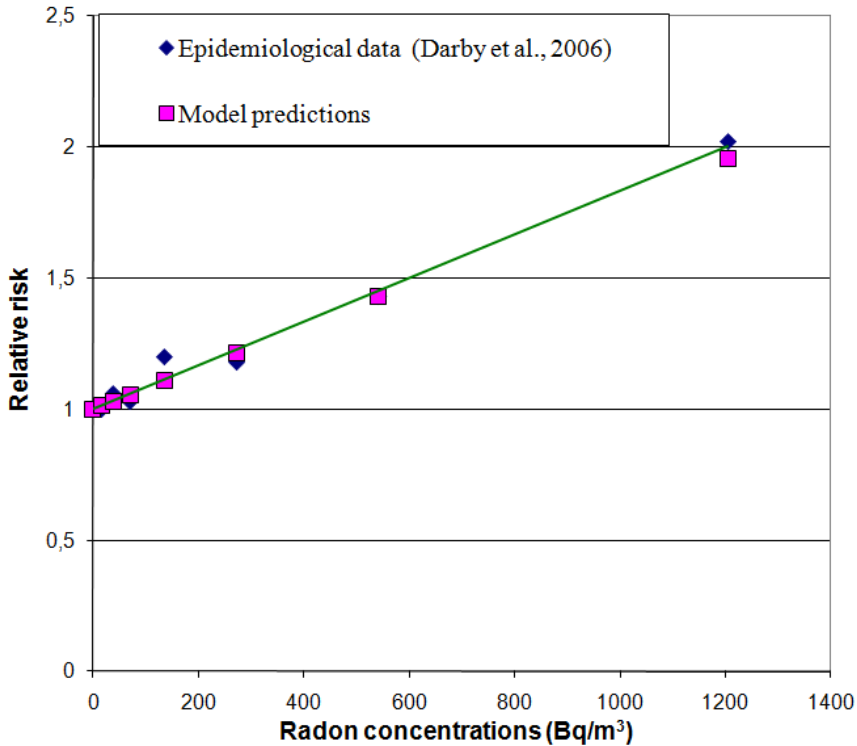


Fig. 1. TF-TR model predictions compared to the epidemiological data of Darby and colleagues (2006)

Compared to other carcinogenic models (e.g. Darby's model, BEIR VI models), the TF-TR model has the advantage that it meets the necessity reported by the BEIR VI Committee, i.e. the assessment of lung cancer risk based on biology and mechanistic concepts. Moreover, it successfully simulates the dose-effect relationship for different exposures (even the inverse dose-rate effect occurring at very high cumulative exposures) and also the hot spots effect (due to the inhomogenous pattern of alpha particle deposition in the bronchial airways), correlating the events from *in vitro* induction of oncogenic transformation to the tissue response *in vivo*, from cell hit to tumour formation.

FRACTION OF LUNG CANCERS ATTRIBUTED TO RADON

The number of total lung cancer deaths due to indoor exposure to ^{222}Rn ($N_{Rn,a}$) could be estimated with the following relation, derived from the available studies (Catelinois et al., 2006; Pirard et al., 2007):

$$N_{Rn,a} = \frac{(RR - 1)}{RR} \cdot N_{T,a} \quad (1)$$

where $\frac{(RR - 1)}{RR}$ is the fraction of risk attributed to radon (FRA), a is the area where the investigated population is exposed, RR is the relative risk, predicted by the selected carcinogenesis model, and $N_{T,a}$ is the total annual number of lung cancer deaths in the area a , where radon concentrations were measured (Truta-Popa et al., 2010). The demographic data could be provided by the National Institute of Statistics. For such calculations, it should be assumed that the populations of the different regions as well as the measured sites are homogeneously distributed among the investigated regions (Truta-Popa et al., 2010). The percentage of lung cancer deaths attributed to radon exposure (%LC) could be derived in two ways:

- a) either from the total, average annual number of lung cancer deaths for the areas where Rn-222 concentrations were measured ($N_{T,a}$) and the number of lung cancers deaths attributed to radon ($N_{Rn, a}$). The average annual lung cancer mortality rates per 100,000 inhabitants could be provided by the National Institute of Statistics for the investigated areas.;
- b) or from the fraction of risk attributed to radon (FRA), i.e.:

$$\%LC_{Rn} = (FRA) \times 100 \quad (2)$$

The second method (Eq. 2) proposed for assessing the percentage of lung cancers attributed to radon has the advantage that it requires only the RR value, but this must be very precisely estimated. This method is particularly relevant in cases where the demographic data (regarding the number of total lung cancer cases or deaths, the number of inhabitants) are not available, are difficult to get from medical records or National Institutes of Statistics, or where not all persons who die of lung cancer are registered accordingly, especially in the rural sites. Hence, the quantitative estimates of the lung cancer risk caused by radon will no longer be affected by the uncertainties from the demographic and lung cancer data, a fact that is really important in using the risk projections as a basis for making risk-management decisions (BEIR VI, 1999). The proposed method for the assessment of the percentage of lung cancers attributed to radon exposure was validated by comparison with the epidemiological data reported by Darby et al. (2006). In her study, RR values, frequency and radon concentrations, as well as the number and percentages of lung cancers for each concentration interval were presented. Based on this information and equation for N_{Rn} , the absolute number of lung cancer cases corresponding to the measured radon concentration and frequency of measurements was computed and then plotted in Figure 2:

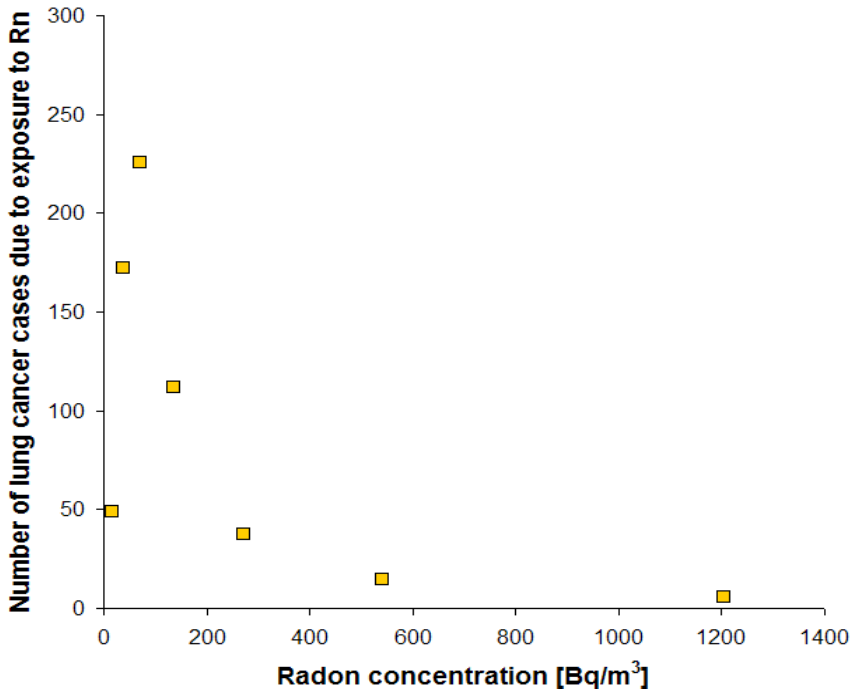


Fig. 2. *Number of lung cancers attributed to radon exposure for the epidemiological study of Darby and colleagues (2006).*

The highest number of lung cancer cases due to radon exposure occurred below 100 Bq/m³, because 72.5% of the total number of lung cancers also occurred in this range. Based on the weighted average RR of 1.094, predicted with the carcinogenic model for the entire population, and applying the original formulation of Catelinois et al. (2006), the number of lung cancers attributed to radon is 616, out of 21,356 people, for the whole exposure time considered. This corresponds to a percentage of lung cancers due to exposure to radon (%LC_{Rn}) of 8.6%. The same number was also predicted by using the proposed simplified formulation (for %LC_{Rn}), which if rounded, is exactly the 9% of lung cancers attributable to indoor radon exposure reported by Darby et al. (2006), thus exhibiting excellent agreement with this but also with other epidemiological studies, too (Catelinois et al., 2006; Lubin and Steindorf, 1995).

POSSIBLE MEANS FOR EARLY DIAGNOSIS OF LUNG CANCER

Lung cancer is mostly detected when it is already too late for surgery. But even when tumours can still be operated, there has not been a simple, convenient way of observing any follow-up parameters such as PSA in prostate cancer (Kurth

et al., 2011). Investigating possible means for early diagnosis of lung diseases (particularly cancer) could improve prognosis and treatment and could reduce their high mortality. Inflammatory and metabolic changes associated with lung diseases may lead to differences in the production and processing of VOCs within the body (Mazzone, 2010). These differences might be expressed in the exhaled breath. If these differences are robust and unique, and a sensing technology is able to accurately and consistently detect them, then the sensing technology could be developed into a useful clinical test. Such a test could be capable of diagnosing a lung disease, or identifying the nature and activity of this disease (Mazzone, 2010). Results of therapeutic interventions are particularly discouraging when the disease is discovered in an advanced stage. Early diagnosis is limited by the fact that the disease usually develops asymptotically and available screening methods do not fulfill the requirements for reliable discrimination between patients with lung cancer and subjects not suffering from the disease (Horváth et al., 2009). With the non-invasive analysis of Volatile Organic Compounds (VOCs) in exhaled breath using Ion Mobility Spectrometry (IMS) we could step up in the development of a new, non-invasive method not only for early diagnosis of lung cancer (Baumbach et al., 2011; Westhoff et al., 2010), but also for treatment monitoring (Kurth et al., 2011). In this respect, the study of Kurth and colleagues (2011) is relevant, because they reported differences between the peaks before and after lung surgery. Recently, it has been scientifically proved that breath sampling/analysis is completely noninvasive and provides a potentially useful approach to screening lung cancer (Horváth et al., 2009). It represents a new diagnostic technique that is without risk for the patient, even if repeated frequently, and can provide information beyond conventional analysis of blood and urine (EC). Tumor markers are normally present in small amounts in the blood or other tissues. Cancer cells can sometimes make these substances. When the amount of these substances rises above normal, cancer might be present in the body.

Previous finding shown that the composition of the breath of patients with lung cancer contains information that could be used to detect the disease. These volatiles organic compounds are mainly alkanes and aromatic compounds (Di Natale et al., 2003; Phillips et al., 1999). Phillips and colleagues (1999) investigated whether a combination of VOCs could identify such patients and observed that a combination of 22 breath VOCs, predominantly alkanes, alkane derivatives, and benzene derivatives, discriminated between patients with and without lung cancer, regardless of stage. Exhaled biomarkers contain both volatile and nonvolatile molecules. Horvath and colleagues (2009) also observed that the profile of volatile organic compounds is different in patients with lung cancer than in control subjects. In exhaled breath condensate, the proteomic profile of breath from cancer patients differs from that of healthy smokers. They reviewed the scientific evidence demonstrating that a unique chemical signature can be detected in the breath of patients with lung cancer and that the exhaled breath biomarker profile could aid clinical decision making (Horvath et al., 2009). Besides the *in vivo* studies mentioned above, there have been performed *in vitro* studies that represent the first step towards a better understanding of the release of VOCs from cancer cells. Compared to the *in vivo* one, the advantage of *in vitro* studies is that the experimental conditions could be

more accurately tested and controlled. Thus, Sponring and colleagues (2009) found that at least two substances, 2-methylpentane and 2-ethyl-1-hexanol, can be released from the NCI-H2087 lung cancer cell line, while Smith and colleagues (2003) discovered that acetaldehyde is released by the lung cancer cell lines SK-MES and CALU-1. The work of DeSouza and colleagues (2005) reported that Calgizzarin was one of two proteins that exhibited significant upregulation in colorectal and lung carcinoma cell lines over normal colorectal mucosal cells.

All these findings showed that the composition of the breath of patients with lung cancer contains information that could be used to detect this disease. Since radon is the second leading cause of lung cancer, after smoking, we consider that a pre-screening of the population - living in radon-prone areas (i.e. Stei) or in dwellings where indoor radon concentration exceeds the recommended Action Level (AL) of 200 Bq/m³ (CEC, 1990; WHO 2009) – could possibly result in detection of persons with lung diseases. Once a health disorder is detected –by using a method for analyzing the exhaled breath (e.g. IMS), further clinical investigations should be performed, at physician's recommendation and thus, there is great chance that lung diseases are early diagnosed and easier to be treated, saving the life of thousands people, every year. For the use of breath tests in clinical praxis it is essential to know origins of marker molecules as well as potential confounding variables (EC). The lung cancer biomarkers have to be reliable, measurable, specific and predictive. The recognition of relevant and determining substances is of main importance. Therefore, an overview about the composition of human exhaled breath is necessary, to come to a detailed analysis of specific substances proposed as biomarkers (Westhoff et al., 2007). In comparison to other analytical methods, **Ion Mobility Spectrometry (IMS)** provides a detailed separation of volatile organic substances detected especially in very low concentrations as relevant for human breath analysis (Westhoff et al., 2007). But, unfortunately, there is only little knowledge about this gas analysis method, especially concerning applications for medical questions (Westhoff et al., 2007). This is particularly important in cases where such substances may be used as disease markers, e.g. in cancer. Using GC-MS, substances in exhaled breath gas samples can be identified and quantified. Nevertheless, online measurements with this technique are impossible because the origin, biochemical pathways and distribution of the most volatile organic marker molecules are still unknown (EC). Unlike the study of a single protein, it enables a systematic overview, leading to a better understanding of the disease. Indeed, lung cancer is a heterogeneous disease at the cellular and molecular level, resulting in the expression of various proteins, so that looking for a combination of protein alterations (or *profile*) is likely to have greater utility than focusing on a specific tumor marker (Ocak et al., 2009).

CONCLUSIONS AND DISCUSSIONS

Ionizing radiation can induce all types of mutations commonly seen in human cancers. There is a great uncertainty and research is being developed for studying the health effects of low dose exposures to high LET radiation (e.g. alpha particles emitted by radon and radon progeny decay). Radon concentration measurements

would not have a significant outcome for the general population if they weren't processed, analysed and interpreted through some radiation carcinogenesis models, so that the health risk induced by a certain exposure be assessed as rigorous as possible. The correct quantification of this risk is of vital importance, both for occupational and residential exposures, for radioprotection purposes and the consequences on human health. The estimated 15,400 or 21,800 of annual lung cancer deaths, in the United States, attributed to radon in combination with cigarette smoking, and radon alone in never-smokers represent a serious public-health problem (BEIR VI, 1999). Based on the Transformation Frequency-Tissue Response and Darby's model predictions of relative risk, we estimated a fraction of 9% lung cancers attributed to radon, out of the total lung cancers, for the 13 European indoor radon study of Darby and colleagues (2006) which is in excellent agreement with the percentage of 3 to 14% that the World Health Organization (WHO, 2009) estimated from the available epidemiological studies. Since radon is responsible for so many thousands of deaths, every year, it is very important to improve the screening and analysis methods so that they will accurately detect lung cancer at early stages, or/and monitor the efficiency of the lung cancer therapy. Breath VOC analysis is a non-invasive test which may potentially detect lung cancer at an early stage and reduce the high mortality of this disease. The desired improvement would represent a great accomplishment in the management of lung cancer and particularly in its control and death prevention. Regarding the breath analysis by analysis of breath condensate, there are several questions that have to be addressed. One question is of whether breath analysis allows diagnosing a distinct disease or whether disease activity or prognosis can be estimated (Westhoff et al., 2007). Another question would be whether the discovered protein profiles that could serve as biomarkers and that could identify new molecular therapeutic targets are independent from other clinical factors (Ocak et al., 2009). In order to assess the diagnostic value of new techniques in breath analysis it is useful to test them in healthy persons and in diseases which can be proven or excluded with high certainty (Westhoff et al., 2007). In future research it would be interesting to carry out further investigations on long-term patient observations after defined time intervals. Even though analysis of exhaled breath for recognition of human diseases using endogenous volatile organic compounds (VOCs) offers the possibility of noninvasive diagnosis, the cellular and biochemical origin of endogenous VOCs is only poorly known and has to be further elucidated (Sponring et al., 2009).

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