STUDIA UNIVERSITATIS
BABEŞ-BOLYAI

AMBIENTUM

1/2017

STUDIA
UNIVERSITATIS BABEŞ-BOLYAI
AMBIENTUM

1 / 2017
January – June
ISSUE DOI:10.24193/subbambientum.2017.1

STUDIA
UNIVERSITATIS BABEŞ-BOLYAI
AMBIENTUM

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Cover 1: *Taxodium distichium* with *Tillandsia usneoides* (moss). Photo: Graeme Mattews

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Dedicated to Professor Dr. Iovanca Haiduc
on the Occasion of Her 75th Anniversary

YEAR Volume 62 (LXII) 2017
MONTH JUNE
ISSUE 1

S T U D I A

UNIVERSITATIS BABEŞ-BOLYAI

AMBIENTUM

1

Dedicated to Professor Dr. Iovanca Haiduc on the Occasion of Her 75th Anniversary

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(RECOMMENDED CITATION)

ON ANNIVERSARY

This year marks the 15th anniversary of the establishment of the Faculty of Environmental Science and Engineering, at Babeş-Bolyai University of Cluj-Napoca. The Faculty was established in 2002 to unify in a single coherent academic structure the different forms of environmental education that had appeared since 1990 at other faculties of the Babeș-Bolyai University (Geography, Biology-Geology, Physics, Chemistry and Chemical Engineering). The Faculty of Environmental Science and Engineering promotes a modern and dynamic education in national and international context, in one of the most attractive and most important areas at present: study of the environment and environmental protection. The Faculty of Environmental Science and Engineering is the only faculty in the country offering study programs in this field, at bachelor, master and doctorate level. The educational offer of the faculty includes two major directions, namely: Environmental Science and Environmental Engineering.

Mrs. Iovanca Haiduc was part of the team of founding members who initiated the establishment of the Faculty of Environmental Science, later becoming the Faculty of Environmental Science and Engineering (in 2011).

The continual development of the image of the institution and mostly of the qualitative content of didactic and scientific research activities carried out within our faculty was achieved with the support of outstanding personalities of the Romanian higher education in our university, including Ms. Iovanca Haiduc, to whom we dedicate this special issue of the scientific journal Ambientum, at a time when we celebrate together the anniversary of her birthday.

This homage is not one of complaisance, dictated by the double conjuncture moment mentioned above, but is based on the acknowledgement of the fact that some personalities of the academic environment of Cluj deserve not only the attention of their contemporaries but also of younger generations, representing models to follow. Professor Iovanca Haiduc is a member of this category.

As a remarkable academic person and a reputed scientist, Professor Iovanca Haiduc is one of the academic personalities of higher education in chemistry and environmental science with special professional, scientific and managerial skills, who managed to put her mark on the formation of our faculty at that time. She started her academic career at Babeş-Bolyai University from 1962 until 2009. At first she was a member of the Faculty of Chemistry, and since 2002 he has strengthened the teaching staff of the newly established Faculty of Environmental Science, whose dean she was between 2002 and 2008.

Throughout her career, she has carried out intensive didactic and research activities, publishing alone or in collaboration 9 books and 4 collections of problems and practical works of analytical chemistry and environmental analysis, and about 90 scientific papers (65 in the country and 25 abroad). Professor Iovanca Haiduc benefited from internships abroad at renowned universities: University of Iowa (USA), University of Nottingham (England), Lehigh University (USA), University of Singapore, which allowed her to open up her vision of research and teaching activities supported by our faculty.

Her vast and complex activity with 47 years of dedication and passion devoted to the study and scientific creation, her academic pursuit, the seriousness and the conscientiousness with which she performed her mission everywhere she worked, were acknowledged and appreciated by everyone in the academic environment. We are glad that we have the opportunity to pay homage to Professor Iovanca Haiduc, to honour her properly, and to thank her for all that she has given us throughout the years in our faculty. Happy anniversary, Mrs. Professor Iovanca Haiduc! May you have happiness, fulfillment and much health!

On behalf of the faculty of Science and Environmental Engineering

Professor Eng. Alexandru Ozunu PhD,
Dean of Faculty of Environmental Science and Engineering

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CURICULUM VITAE - PhD Professor IOVANCA HAIDUC

Professor **Iovanca HAIDUC** was born on 6 October 1941 in the village of Soca, Timis County. Between1954-1957 she attended the courses of High School no. 8, actual Dositeje Obradovici from Timisoara. Iovanca HAIDUC graduated from the Faculty of Chemistry of the Babeş-Bolyai University, Cluj-Napoca, and in 1971 she obtained her doctorate degree at the same institution in the field of electroanalytical chemistry with the doctoral thesis titled "Electrozi de Pt, Pd și Au cu suprafață chimic modificată în determinări potențiometrice (Pt, Pd and Au electrodes with chemical modified surface in potentiometric determinations)" under the guidance of distinguished Prof. PhD. Candin Liteanu.

Teaching activity:

From 1962 until 2009 she is employed by Babeş-Bolyai University as follows: 1962 - 2002 at the Faculty of Chemistry and Chemical Engineering, Department of Analytical Chemistry and between 2002 - 2009 at the Faculty of Environmental Science and Engineering, Physics, Chemistry and Environmental Engineering Department, where she occupies various teaching positions: Preparator (1962), Assistant Professor (1965), Lecturer (1976), Associate Professor (1990), Professor (1998-2009).

Between 2002 and 2009 she worked at the Faculty of Environmental Science and Engineering, at Babeş-Bolyai University, Cluj-Napoca, being among the founding members of the faculty and between 2002 and 2008 she was vice-dean at the Faculty of Environmental Science and Engineering.

Throughout her career, she has been involved in intensive didactic activities, besides the classical courses of Analytical Chemistry she held for the first time at the Faculty of Chemistry courses related to Environmental Science such as Water Quality Control (1984) and Environmental Chemistry (1990).

At the Faculty of Environmental Science and Engineering she introduced courses of Environmental Chemistry, Dangerous Chemical Pollutants and Green Chemistry - all being new courses.

She has published on his own and in collaboration with various authors, 9 books and 4 exercise books and practical issues of analytical chemistry and environmental analysis on the themes of the courses.

We only report:

1. Chimie Analitică (Analytical Chemistry) (Part I) - UBB, Cluj-Napoca (1981).
2. Chimia Verde și poluanții chimici (Green chemistry and chemical pollutants) - EFES, Cluj-Napoca (2006) - Iovanca Haiduc.
3. Analiza Mediului (Environmental Analysis) (Part I) - Napoca Star Publishing, Cluj-Napoca (2002) - Iovanca Haiduc, Simona Cobzac.
4. Chimia Verde. Principii și aplicabilitate (Green chemistry. Principles and Applicability) - Cluj University Press (2013) - Beldean-Galea M.S., Iovanca Haiduc, Roba C.A.

Scientific activity:

Fields of interest:

- Analytical electrochemistry
- Extraction of elements: U, Th with dithiophosphoric acids (collaboration with the collective of prof. Ionel Haiduc through the International Atomic Energy Agency in Vienna, 1983-1985)
- Water quality control
- Control of greenhouse gases (CO_2 , CO, CH_4)
- PMs control from air

She has published around **90 papers in these scientific areas** (65 in the country and 25 abroad).

Mention only:

- Pretreated bright Pd electrode in potentiometric redox titration, Talanta, 1972, 50, pp. 55-65, co-author (Liteanu C., Haiduc Iovanca)

- Ultraviolet spectra of some polyhaloaromatic organosilicon derivatives, J. Organomet. Chem.,1968, 11, pp. 459-462, co-author (Ionel Haiduc, Iovanca Haiduc and Henry Gilman)
- Solvent extraction of Th (11) with dialeyldithiosphoric acids, J. Radioanal, Nucl. Chem. Letters, 1986, 99, pp. 257-163.
- Solvent extraction of U, Th and rare earth with dithiophosphoric acids. Vol. Chemical Aspects of Nuclear Methods of Analysis, IAEA TEC-Doc. Vienna, 1985, pp.101-172.
- Uses of ozone in the detoxification of cyanide – heaving waste-waters (R. Roum. Chem. Quant. Rev. 1998 (Iovanca Haiduc, G. Katona)
- Comments on a controversial gold mining project in Western Carpathians. Environmental and other aspects. In vol. "Sustenability for Humanity and Environment" Politehnica Timișoara Publishing, 2005, pp. 53-60.
- Variations of Greenhouse Gases in Urban-Areas. Case Study: CO_2, CO and CH_4 in three Romanian Cities. In Vol. Air Quality Model and Applications ed. By D. Popovici, Intech open 2011, chapter 15 Rijeza, Croatia.

Documentation / Research

Internships abroad:

- 1968 (May - July) Iowa, USA
- 1994 (September- October.) University of Nottingham, England
- 2000 (August - September) Lehigh University, USA
- 2002 (December) University of Singapore

Diplomas obtained:

- Merit Diploma for the contribution to the development of BBU, 2005;
- Didactic Excellence Diploma awarded by UBB in 2006;
- "Omul, natura și schimbările climatice (Man, Nature and Climate Changes)" Diploma, 2007, awarded by the Ecological Action Foundation, Craiova.

Member of professional associations:

- Romanian Society of Chemistry;
- Balkan Environmental Association (B.EN.A.).

Conf. dr. Simion Mihail Beldean-Galea
Prof. dr. ing. Cristina Roșu

STUDIA UBB AMBIENTUM, LXII, 1, 2017, pp. 9-27
(RECOMMENDED CITATION)
DOI:10.24193/subbambientum.2017.1.01

TESTING OF INDIVIDUAL SENSITIVITY TO RADON AND THORON EXPOSURE BY *IN VITRO* IRRADIATION OF LYMPHOCYTES CULTURE

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ABSTRACT. Identify the factors that affect individual sensitivity is a very important step in cancer risk assessment at low doses or low doses rates, according with study of dose-response relationship. DNA damage response processes are likely to play an important role in radiation by cancer risk association. This paper tries to quantify the individual sensitivity to alpha particles exposure using an in vitro exposure model. Quantify of DNA lesions by comet assay, in lymphocytes cultures exposed to the same doses of radiation was made. The irradiation was performed using the pitchblende ore during a 72 hours period, intermittent exposure with dose rates of 89.15 kBq/m^3. The lowest and highest Radon Thoron concentrations computed in this study were 89.15 kBq/m^3 and 212.9 kBq/m^3, respectively.

The study was done for healthy donors, comparatively with chronic obstructive pulmonary diseases donors. Ageing in vitro of lymphocytes cultures exposed to low doses of ionizing radiation is the biological model used, which are presented here. Based on these results, a standard test should be develop and applied for study of sensitivities in average population groups.

Key words: *individual sensitivity; low doses exposure model*

INTRODUCTION

Radon is a ubiquitous gas and an indoor air pollutant in homes (Darby et al., 2005; PHE, 2014). Based on the evidences from human and animal exposures, the International Agency for Research in Cancer (IARC) has classified the radon as a group 1 carcinogen (IARC 2001). When is inhaled, radon 222 can have a carcinogenic effect on lung tissue, because of the emission of alpha particles upon decay (Hofmann et al., 1986; Fabrikant, 1990).

Our disease donors were patients with chronic obstructive pulmonary diseases (COPD). Individuals with respiratory diseases like COPD are especially sensitive to air pollution, and should be a vulnerable group to radon exposure, when the concentrations of the alpha particles from air are increased. When lung cancer cases were compared with controls, history of any previous lung disease was associated with a significant increased risk of lung cancer. Several lung diseases, including asthma, chronic bronchitis, pneumonia, and tuberculosis, were reported more often by lung cancer cases than by controls, and the difference was statistically significant for asthma, and chronic bronchitis (Wu et al.,1995; Turner et al., 2007).

Usually, the individual sensitivities were treated in relation with genetic factors, age, sex, nutrition, disease, and drug. As could be observed, the epidemiology studies, means the most directly way to estimate human risks to Radon, and often, is masked by confounding factors such as age, smoking, life style (Muirhead, 2008; Greenland, 2001; Stram and Kopecky, 2003) etc. Testing of individual sensitivities to Radon exposure could be a good point in environmental Radon studies, because the Radon toxicity is a certainty (Au et al., 1995; ATSDR, 2010). While the main low-dose risk is currently assessed to be from cancer induction and, to a lesser extent hereditary effects, some non-cancer effects may also be of concern even at low doses (NAS, 1999).

Although high radon concentrations are associated to increased risk of lung cancer by both experimental studies and investigations of underground miners, epidemiologic studies of residential radon exposure display inconsistencies. In many cases, such extrapolations may either over or underestimate the risk (Barros-Dios et al., 2002; Sa`inz et al., 2008).

In order to have a real risk of environmental assessment to low doses and low dose rates of radon exposure, it is very important to know the individual susceptibility (HLE, 2008). In the low-dose region it is easily to assume that each increment of dose produce a directly proportionate increment in biological and/or health effect. Knowing of the dose – response relationship is necessary for testing of individual sensitivity to ionizing radiation. An in vivo exposure test couldn't be available direct, through human model exposure, so, in vitro methods, must be more efficiently for risk estimation in radiation protection, and need arose to conduct experiments using in vitro irradiation methods.

The cells human radiosensitivity was observed not only for a series of genetic disorders (Friedberg, 1978), but also for a wide range of cancers as a consequence of exposure to different genotoxic agents from environment (Ron, 1998; Scott et al., 1999; Leong et al., 2000).

In the present rapid and reliable tests are used for prediction of normal tissue responses to radiotherapy (Burnet et al., 1994; Barbera et al., 2000). The comet assay is a simple technique for quantification of low levels of DNA damage in individual cells, very sensitive, using the fluorescence microscopic method (Fairbairn et al., 1995; Singh et al., 1988; Pereira et al., 1988; Tice, et al., 2000; Møller et al., 2000; Brock and Tucker, 2000; Rossler et al., 2006).

The present study tries to classify the individual sensitivity, by in vitro exposure method of the lymphocytes cultures, according with individual susceptibility to radiation. The exposure marker will be DNA damage, quantified by comet head and comet tail. The irradiation was performed using the pitchblende ore during a 72 hours period, intermittent exposure with dose rates of 89.15 kBq/m^3. The lowest and highest activities computed in this study were 89.15 kBq/m^3 and 212.9 kBq/m^3, respectively.

MATERIAL AND METHOD

The study took place during May-July 2008.

In vitro Irradiation System using Pitchblende Ore

Pitchblende ore (UO_3, U_2O_5, U_3O_8), is a uranium ore. Is a radioactive ore, which contain also oxides of lead, thorium, and rare earth elements. The name came from pitch, because of its black color, and blende, a term used by German miners to denote minerals whose density suggested metal content, but whose exploitation was, at the time they were named, either impossible or not economically feasible. The natural airborne radioactivity results by disintegration of “parent-progeny”, so-called "radon-thoron" (RnTn). These radioactive isotopes are the main contributors to the dose from natural radiation sources.

Using the Hamza’ example (Hamza et al., 2008), we have done our particularly exposure system, figure 1.

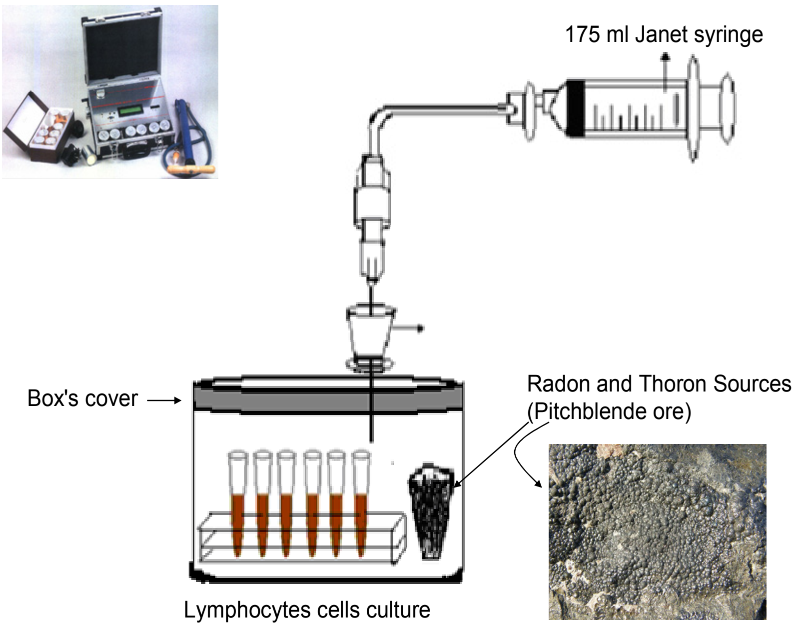

Fig. 1. *Assembly for in vitro irradiation, using pitchblende ore*

Estimation of radon activity

The Radon-Thoron gas radioactivity inside the experiment box, having 1000 ml capacity, figure1, was measured with Lucas cell scintillation, according with the recommended methodology (Plch, 1997; Eappen et al., 1980). The structure of this instrument is based on the Lucas cell principle, and can be used for Radon and Thoron content determinations in soil, water and for medium or high indoor RnTn concentrations (more than 200 Bq/m^3).

A quantity of gas from the chamber (50 ml) was extracted using a Janet syringe and then this air was introduced in the Lucas cell of the LUK 3A, figure 1, device previously empted and calibrated (Cosma et al., 2008).

The extracting operation was possible due a special valve in the upper part of the radon exposure boxes. The radon activity estimation was very well done, because in 2007, this method was included an intercompared experiment between laboratories, Chiba (Japan), when was apply for two different concentrations (Janik et al., 2009).

The airborne radioactivity was monitored after each day of exposure, during 72 h, when lymphocytes cells culture was kept inside of the experimental box, at 22^{0}C. After 24 hours an exact volume of radon gas was counted immediately as well as after 3 h, being the time when radon progeny build-up is roughly completed and a state of transient equilibrium reached. The alpha particle counted was converted in Bequerel/m^3, by using the equation 1:

$$C_{Rn} = N/V_s \cdot k, \quad \text{(eq. 1)}$$

where: C_{Rn} – radon concentration for indoor experimental box's air

N – counted number of scintillation / second

Vs – Janet syringe volume (175 ml capacity)

k – means a constants, according with the used apparatus (1.38)

Radon, Thoron and their progeny, comprise a complex radiation source emitting alpha, beta and gamma particles, but when compared to the alpha dose, the others are negligible (Jostes, 1996). So, we assuming that the majority of exposure is due to alpha particle emitted to radon rather than the rest of progeny. The measured activity of pitchblende ore are presented in the next table 1 (figure 2).

Irradiation sample

10 ml of blood was taken from 3 healthy donors and 3 diseases donors by venipuncture, and were collected in heparin's vacuette tubes (Greiner Labortechnik, Austria). Blood donations come from volunteer donors and a safety protocol has been respected, according with Medical College Recommendations.

Lymphocytes are separated using the density gradient protocol, on Histopaque-1077. Briefly, blood is diluted 1:1 with PBS and layered over 600 µl Histopaque and centrifuged at 800 X g for 20 minutes. The 'buffy' coat, an opalescent layer containing mononuclear cells is aspirated into 3-5 ml of PBS and centrifuged at 250 X g for 10 minutes to pellet the lymphocytes and counted over a haemocytometer and viability tested. The pellet is resuspended in 1 ml of (RPMI + 15% fetal serum, + 10% glutamine + antibiotics) in test tubes. Aliquots of 2 X 10^6 cells per 100 μL of medium are taken for each dose of the test material.

Table 1. *The irradiation doses during in vitro exposure, t = 22 ^{0}C, constant*

Time of exposure (hours)	Radon Concentrations ($kBqm^{-3}$)
24	89.15
48	162.6
72	212.9
96	220

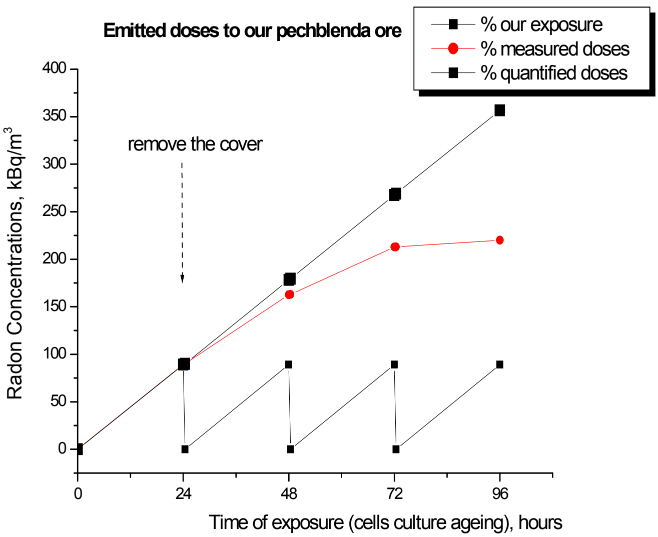

Fig. 2. *Simulate of exposure doses during 24, 48 and 72 hours. Theoretic cumulate of the first measured doses (89.15 kBq/m^3-24 hours) during 96 hours are represented with black, and the measured doses during 96 hours are represented with red, in our exposure system. We have a "chronic" irradiation, in each day with 89.15 kBq/m^3.*

Aliquots containing lymphocytes were diluted with PBS 1:10 and tubes are inverted to mix the cells and test material in order to obtain a homogenous suspension.

The cells cultures suspension was distributed equally, in three test tubes, for each sample donor (healthy respectively diseases). Than, were closed to irradiation in our experimental box, at room temperature (22^{0}C). In each day, one test tube from each sample was analyzed.

Study of genotoxicity using (SCGE, "comet assay")

We performed the single cell gel electrophoresis after each day of irradiation, 24, 48, 72 hours respectively. The comet assay is a relatively novel technique based on electrophoresis migration of damaged DNA. With this assay, effects such as DNA single-strand breaks, incomplete excision repair sites and alkali-labile sites can be easily analyzed. The alkaline comet assay was performed according to Tice's protocol, 2000; Collins, 2004 and modified after Brie et al., 2004.

Inducted DNA damage quantification: Cells were scored with a Zeiss AxioImager M1 Microscope using an image program acquisition with automated integration time adjustment, automated thresholding of cells ('head') and Comet tails, and measurement of cell features.

RESULTS

DNA damage response processes are likely to play an important role in radiation-associated cancer risk. Also, a variety of less well understood epigenetic factors and non-targeted effects may also be involved.

After 24 hours of irradiation

Could be observed the significantly increased number of Score1 lesions, both for healthy and disease donor with exposure, but not an important difference between, figure 3.

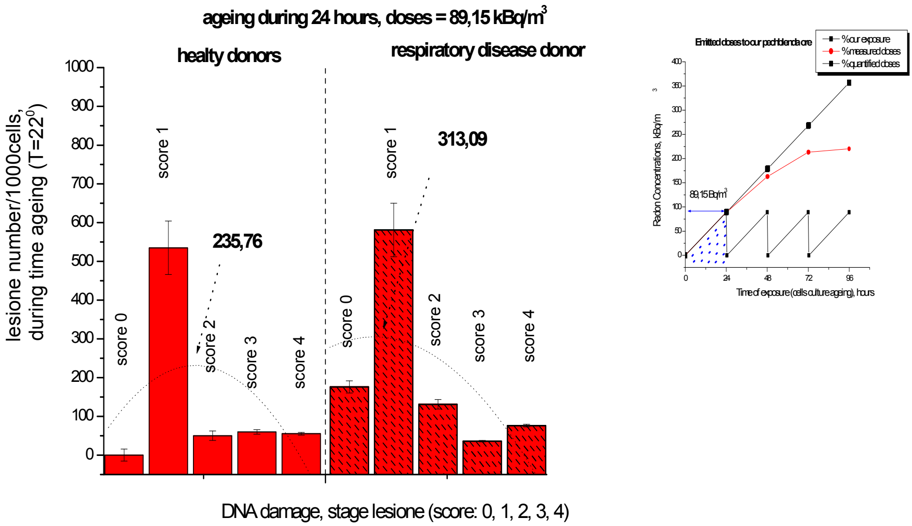

Fig. 3. *Representation of cells number according with stage lesions (Score 0, 1, 2, 3, 4) after 24 hour of irradiation and fit polynomial analysis of the data points represented.*

After 48 hours of irradiation

Could be observed the significantly increased of lesions number with Score 1, both for healthy and disease donor with exposure, figure 4. Also, are presented the increase of the lesions with Score 2 and 4 for disease donor.

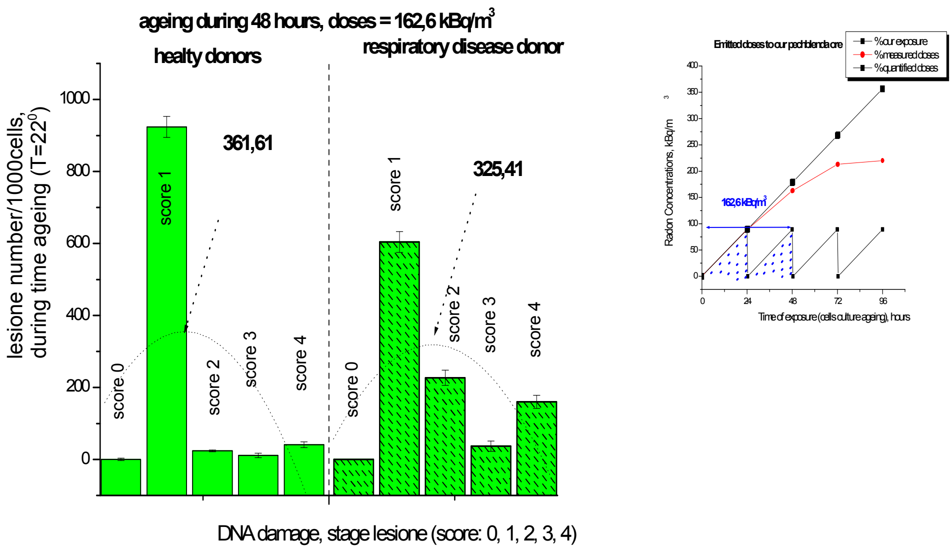

Fig. 4. *Representation of cells number according with stage lesions (Score 0, 1, 2, 3, 4) after 48 hour of irradiation and fit polynomial analysis of the data points represented.*

After 72 hours of irradiation

We observed the significantly increased of lesions number with Score 1, both for healthy and disease donor with exposure, figure 5. Also, are presented the increase of the lesions with Score 2 and much more Score 4 for disease donor. The increased score 0, for healthy donor could be an artifact and must be verified again.

The overall evaluation of DNA damage was made through two parameters: lesions score (SL), figure 7, 8, 9 table 2, 3 and tail factor (TF), figure 10, 11, 12 and table 4, 5. The results are presented below.

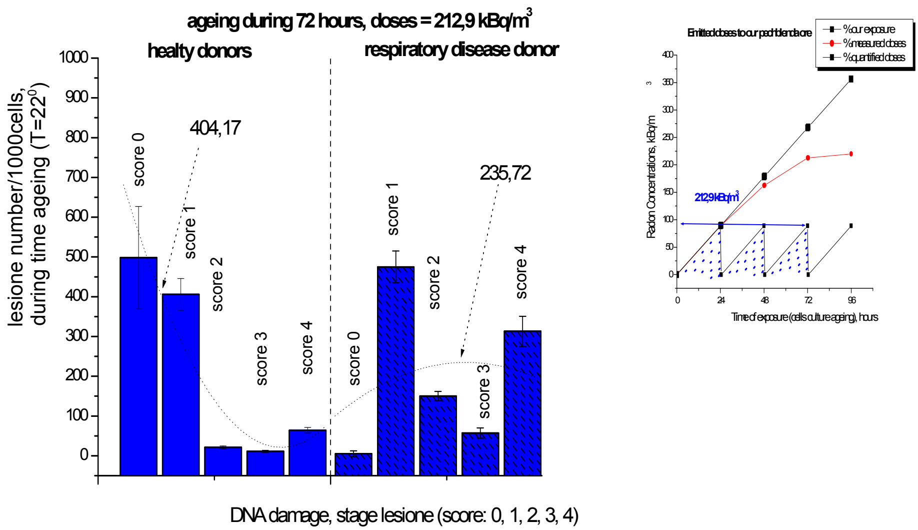

Fig. 5. *Representation of cells number according with stage lesions (Score 0, 1, 2, 3, 4) after 72 hour of irradiation and fit polynomial analysis of the data points represented.*

A) Score Lesions (SL) and Individual Sensitivity

Have been registered the significantly increase of Score Lesions of DNA for the donors with chronic obstructive pulmonary diseases, figure 6. The individual sensitivity was estimated by inducted DNA damage to lymphocytes cells, which has quantified according with the percent of inducted effect, table 2.

Table 2. *Inducted effects in time, according with individual sensitivity, using as exposure marker the Score Lesion, SL*

Score Lesions Healthy Donor (H)	Score Lesions Disease Donor (D)	Time of exposure	Radon Concentrations kBq/m³	Effect (%) (D-H)/H x 100
103.5	125.5	24 hour	89.15	21.25
116.9	169.7	48 hour	162.6	45.16
73.7	219.8	72 hour	212.9	198.23

Representing the best linear fit of inducted effects, figure 7 and overlapping the graphic representation of score lesions, figure 8, was possibly to classify the individual sensitivity.

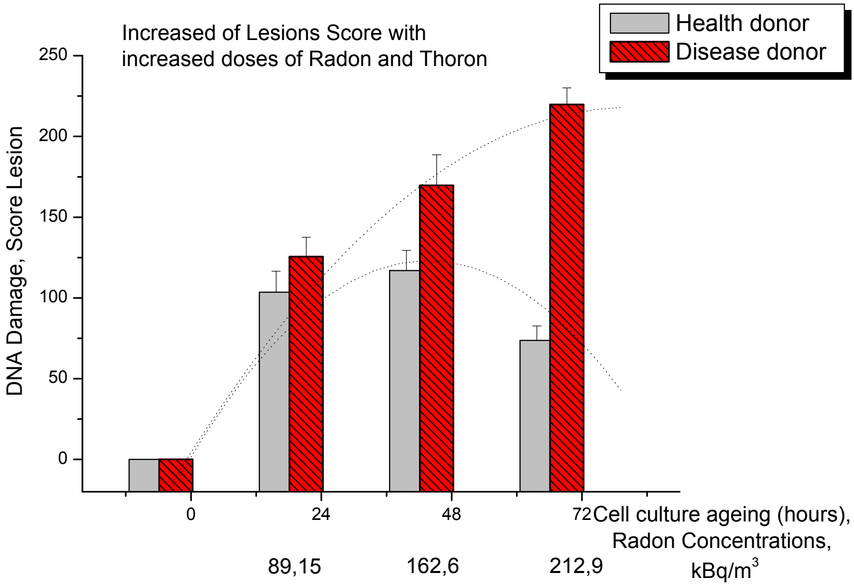

Fig. 6. *The overall dependence of the Score Lesions with in vitro exposure doses of Radon and Thoron, and the fit polynomial analysis of data points represented.*

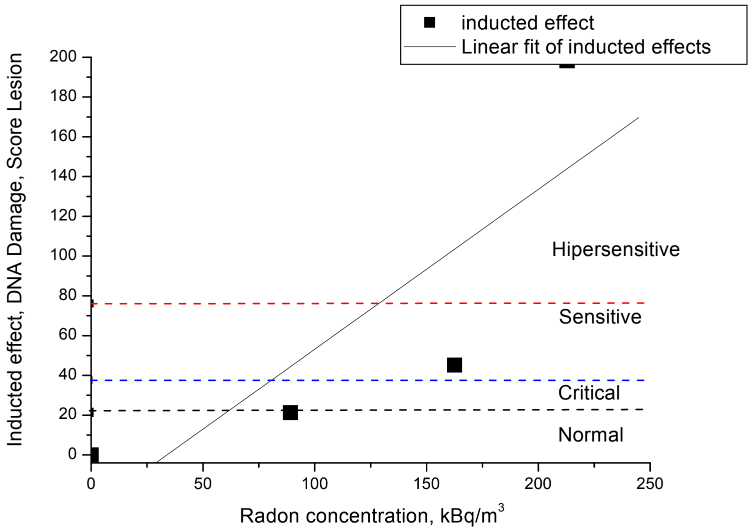

Fig. 7. *Dependence of Individual Sensitivity according with exposure doses for in vitro cells culture, by quantify of Score Lesions. (Data points are the mean for two independent experiments; best linear fit is drawn. * Statistically significant difference from control at p = 0.05.)*

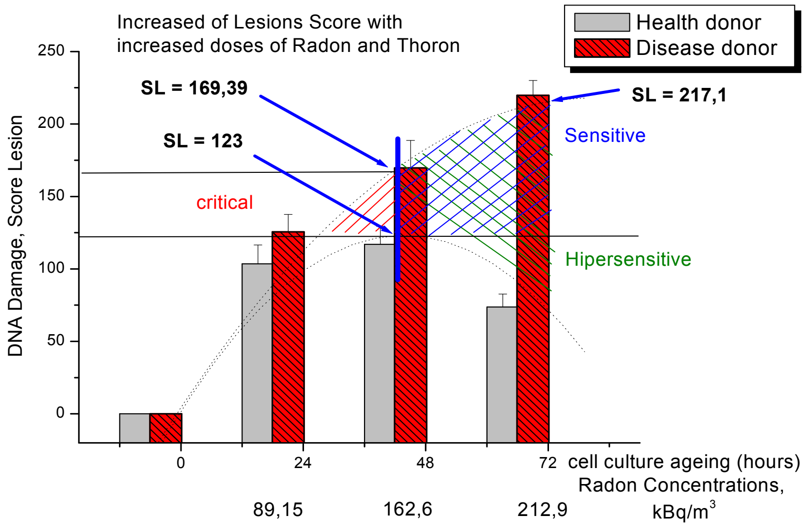

Fig. 8. *Overlapping the linear fit of inducted effect with overall representation of score lesions*

From figures 6, 7, 8 and table 2 have been possible to quantify the individual sensitivity, according with Score Lesions, which are represented in the below table 3.

Table 3. *Inducted effect in time, according with individual sensitivity, using as exposure marker the Score Lesion, SL*

Time of exposure	**Inducted Effect, %**	**Individual Sensitivity Characterization according with Score Lesions**
24 h	21.25	Normal
	> 21.25	Critic
48h	21.25 – 37.71	Critic
	> 37.71	Sensitive
	>76.50	Hipersensitive

B) Tail factor (TF) and Individual Sensitivity

In a similar way, we quantified the individual sensitivity using as exposure marker the Tail factor. In figure 10, have been represented the overall dependence of Tail Factor with *in vitro* exposure doses of Radon and Thoron. Have been registered the significantly increase of Tail Factor to donors with chronic obstructive pulmonary diseases, figure 9.

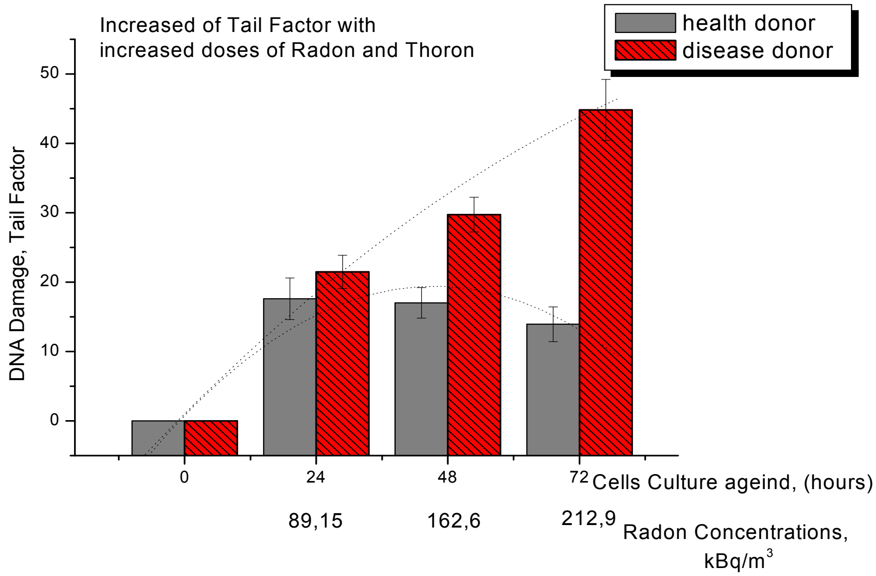

Fig. 9. *The overall dependence of Tail Factor with in vitro, exposure doses of Radon and Thoron and the fit polynomial analysis of data points represented.*

The individual sensitivity was estimated by inducted damage effects to DNA, for lymphocytes cells irradiated, quantification being in accord with the percent of inducted effects, table 4.

Table 4. *Inducted effects in time, according with individual sensitivity, using Tail Factor (TF) as exposure marker*

Tail Factor Healthy Donor (H)	**Tail Factor Disease Donor (D)**	**Time of exposure**	**Radon Concentrations kBq/m^3**	**Effect (%) (D-H)/H x 100**
17.6	21.47	24 hour	89.15	21.98
17.01	29.73	48 hour	162.6	74.77
13.93	44.82	72 hour	212.9	227.516

Representing the best linear fit of inducted effects (TF), figure 10 and overlapping the graphic representation of tail factor, figure 11, was possibly to classify the individual sensitivity, table 5.

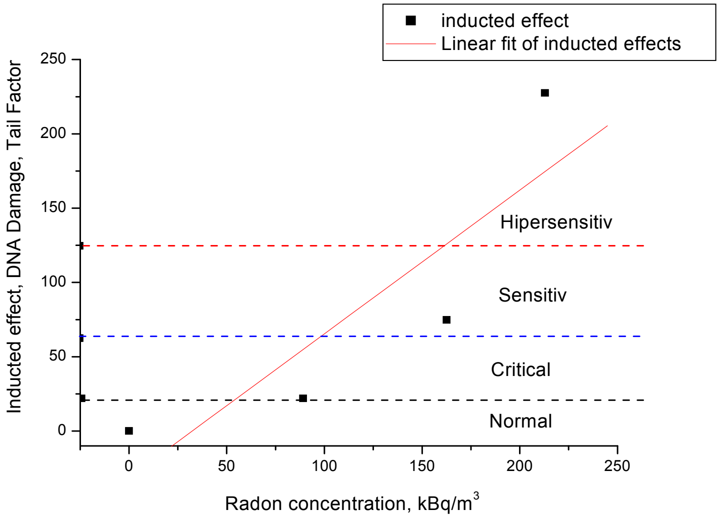

Fig. 10. *Dependence of Individual Sensitivity according with exposure doses of in vitro cells culture, by quantify of Tail Factor. (Data points are the mean for two independent experiments; best linear fit is drawn. *Statistically significant difference from control at p = 0.05.)*

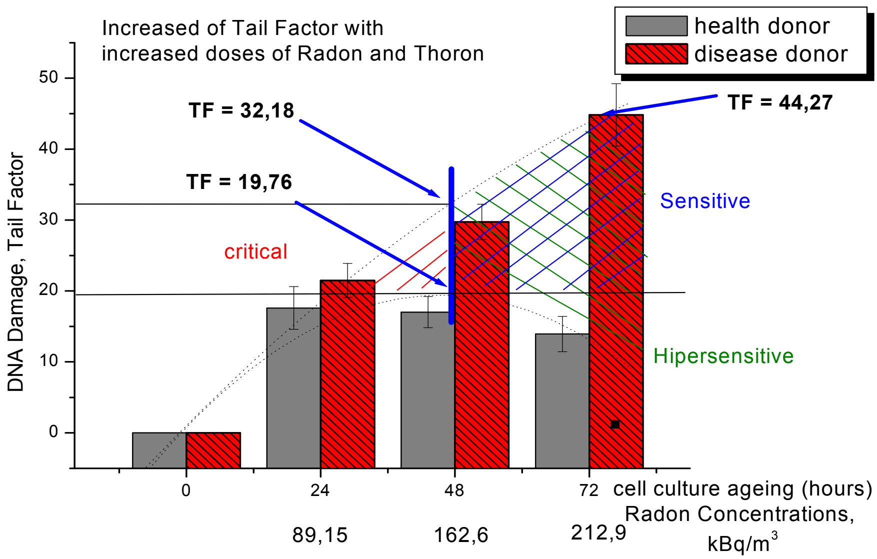

Fig. 11. *Cell sensitivity representation according with Tail Factor. Overlapping the linear fit of inducted effect with overall representation of Tail Factor*

From figures 10, 11, 12 and table 4 have been possible to quantify the individual sensitivity, according with Tail Factor which are represented in the below table 5.

Table 5. *Inducted effect in time, according with individual sensitivity, when the exposure marker is the Tail Factor*

Time of exposure	**Inducted Effect (%)**	**Individual Sensitivity Characterization according with Tail Factor**
24 hour	21.98	Normal
	> 21.98	Critic
48 hour	21.98 – 62.85	Critic
	62.85 – 124.03	Sensitive
	> 124.03	Hipersensitive

The individual sensitivity, using in vitro exposure to alpha particle emitted from Radon and Thoron, should be appreciated, already after 48 hour, from A) and B), when have been registered, the significantly effects.

DISCUSSION

Studies in vitro, about Radon toxicity, were often signaled (Purrot et al., 1980; Edwards et al., 1980; Pohl-Ruling and Pohl, 1990; Jostes et al., 1991; Jostes 1996; Petitot et al., 1997; Pohl-Ruling et al., 2000; Hamza et Mohankumar, 2009). Hamza Z and her collaborators in 2009, using a similar in vitro model has observed the dicentric aberrations in lymphocytes, healthy donors, from the irradiated blood with Radon, for the next doses, table 6:

Table 6. *Our results (irradiation with alpha particle emitted to pitchblende ore) comparative with Hamza results (irradiation with alpha particle from a Radium sources, with an 98.6 kBq activity)*

Our Conc. of alpha particle, kBq/m^3	Hamza's Conc. of radon, kBq/m^3,	Radon Dose Estimated (Hamza) (mGy)	DC/cells yield dicentrics Hamza's Experiment	Our Inducted effect (%), DNA Damage, SL Score Lesions	Our Inducted effect (%), DNA Damage, TF Tail Factor
89.15	89.3	7.14	0.0052	21.25	21.98
	112.34	8.98	0.0057		
162.6				45.16	74.77
212.9	216.10	17.288	0.0073	198.23	227.516
	424. 132	33.93	0.01020		

Correlate, our DNA damage could be associated with induction of chromosome aberrations, in irradiated sample. DNA damage after the irradiation must be more prominent because the cells ageing, was amplified at 22^0C, a temperature not properly, for cells divisions process, even the cells was kept in a culture medium. According with our experiment, the dose–response should be different between donors, due to interindividual variations. Also, a significantly difference was observed between healthy and diseases donors, for low irradiation doses of Radon, by association, between 7.14 mGy -17.28 mGy respectively. We consider that donors with respiratory diseases, are especially sensitive to radon exposure, and represent a vulnerable group, with an increased lung cancer risk. The increased of lymphocytes lesions number reflected between Score Lesions (45.16 %, after 48 hours) and Tail Factor (74.77%, after 48 hours) represent a really evidence of their vulnerability.

Personal exposure to Radon varies, depending on the concentrations present in homes or in the occupational environment. Bauchinger et al., in 1994 has done a biodosimetric study about environmental exposure. According with their research, the domestic exposure to radon, in some houses was possible to induce an increased number of chromosomes aberrations at very low doses and dose-rates (Bauchinger et al., 1994). The similarly studies was reported to Zhou et al., 2001, and Mihalache et al., 2007.

Although high radon concentrations are associated to increased risk of lung cancer by both experimental studies and investigations of underground miners, epidemiologic studies of residential radon exposure display inconsistencies. In many cases, such extrapolations may be either over or underestimate the risk (Stram and Kopecky, 2003; Muirhead, 2008).

Comparing our in vitro irradiation Radon concentrations, with those from database, Darby and his col., 2005, has estimate the lung risk cancer, for lower concentrations, ~104 Bq/m^3. Radon concentrations around 60 and 330 Bq/m^3, have been reported to Friedmann et al.,1996, for Austrian people exposure, also, 280 Bq/m^3, Cosma and col., 2007 in Stei region (Bihor county) Romania, in association with risk lung cancer incidence, or 4.6 kBq/m^3, Lubin et al., in 1997, like an association with lung cancer mortality residential radon exposure.

Lettner and colab. in 1996, have been reported similarly Radon concentrations, up to 100 kBq/m^3, in a thermal gallery.

Results obtained from ecologic studies have the inherent problem that conclusions are subject to the ecologic fallacy. The validity of individual risk estimates based on group data is not known and cannot be reliably determined from an ecologic study design. The ecologic study is primarily designed for generating hypotheses. Testing the hypothesis, assessing the validity of the association, and obtaining reliable estimates of the exposure-response relationships require independent testing by individual-level study designs having personal exposure measures, as well as individual health data.

The lowest radiation dose associated with statistically significant increased risk remains controversial. Current understanding and quantification of risk at low doses is limited by the uncertainties of the available scientific methods and by a lack of understanding of the basic biological mechanisms. Epidemiological studies are not powerful enough to detect risks at doses approximating 1 cGy in the general population, because the necessary large populations are not available. The published data that have been used to estimate low-dose risks are often equivocal. In evaluating risks at small doses, all published studies need to be considered unless there are scientifically defensible reasons for exclusion. Although unequivocal evidence of risk is unavailable at very low doses, this does not mean that increased risks do or do not exist. However, if there is a risk below 1 cGy, it is very small for any given individual – the controversial issue being the risk to a large population potentially exposed to these small risks (Brenner and Mossman, 2005.

Studies based on individual sensitivities in estimates of exposures should generally be more informative if the aim is to quantify a dose-response relationship, in radiation protection dosimetry. According to Mezei and Kavet (2002) risk estimates are applicable only to subjects or groups of subjects with various characteristics who are at risk of developing cancer rather than to cases that already developed cancer (Mezei and Kavet 2002).

Four basic model options on low dose response tend to be considered following exposure of the whole body or of individual tissues: linear-no-threshold, linear but with a zero-effect interval below a given threshold dose, supralinear (hypersensitivity), or more complex bi-modal relationships (including beneficial health effects or hormesis at low doses) (UNSCEAR, 2000; CERRIE, 2004; NRC, 2006; French Academy, 2005; ICRP, 2007). According with our results, studies about Low-Dose Risk Extrapolation should be associated with individual sensitivities, so: normal – hormesis; critic – threshold; Sensitive – LNT and hypersensitive – Hypersensitive.

The setting of dose constraints can take account of individual variability in radiation response. So, understanding the cellular mechanisms of carcinogenesis is increasingly important to assess the biologic risks.

The next appeared problem will be to correlate the observed sensitivities between the individuals, or groups. Only knowing the spread of sensitivities in average population groups, could have realistic estimates of radiation risk.

CONCLUSION

The result of cell's irradiation combined with ageing process is an increase of DNA damage. For estimation of inducted DNA lesions, the comet assay is a very properly and sensitive test.

A great difference in response to irradiation has been observed between healthy and chronic obstructive pulmonary diseases donor, using comet head and comet tail as exposure markers. The quantifications of DNA damage on the lymphocytes cultures expose in vitro, to different concentrations of Radon and Thoron, intermittent exposure with dose rates of 89.15 kBq/m^3 revealed a significantly increasing of inducted lesions, for disease donors, which has been classified as hypersensitive. Also, this donors represent a vulnerable group with an increased risk in lung cancer apparition, according with our results, the aspects of dose–response relationship being a really evidence.

In conclusion, the individual sensitivity could be assessed after 48 hours, using our in vitro model. The sensitivity was proportional estimated with individual susceptibility to radiation, by inducted effects to DNA level. This sensitivity has been classified as: normal, critic, sensitive and hypersensitive individuals.

This model must be combined with analysis of environmental Radon concentrations (exposure assessment) and epidemiologic studies, epidemiological cohorts of populations (uranium miners, nuclear workers, medically exposed groups, residential radon exposures, etc.) potentially informative for low dose risk research. At present there is insufficient information to establish how large these various differences in sensitivity may be between individuals or between groups of individuals both in the sizes of the variations and also in the proportions of the population that are affected with consequent on risk estimates at low dose.

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STUDIA UBB AMBIENTUM, LXII, 1, 2017, pp. 29-42
(RECOMMENDED CITATION)
DOI:10.24193/subbambientum.2017.1.02

PRELIMINARY DATA REGARDING THE CONTENT OF PETROLEUM PRODUCTS IN WATER AND SOIL SAMPLES FROM SUPLACU DE BARCĂU AREA, ROMANIA

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ABSTRACT. The main objective of the present study was to perform a general screening study regarding the quality of surface water, underground water and soil in Suplacu de Barcău area. In some of the investigated sampling points, the concentration of the analyzed parameters reflects the impact of the anthropic activities carried out in the area. Based on petroleum hydrocarbons content, the surface waters can be classified as 1st and 2nd quality class. For some of the analyzed underground water and soil samples, the petroleum hydrocarbons content exceeded the intervention level, while the majority of the analyzed underground waters had the petroleum hydrocarbons content below the alert level.

Key words: *oilfield, in-situ combustion, petroleum hydrocarbon, water, soil*

INTRODUCTION

Rapid economic development of modern society and dramatic population growth is accompanied by a continued high demand of energy sources, especially hydrocarbons. Simultaneously, the conventional oil reserves have recorded a constant decline due to the problems in locating new oil fields. Therefore, oil industry started to focus on the remaining oil recovering in old reservoirs and the unconventional oil resources, such as heavy oil, extra heavy oil, oil sand, tar sands, oil shale and bitumen. These unconventional resources are equivalent to about 70% of all fossil fuels resources in the world.

The main characteristics of unconventional oil are: high viscosity, high density, high content of nitrogen, oxygen, sulfur and heavy metals and increased quantity of heavier oil fractions (Santos et al., 2014). In order to recover this unconventional oil, as well as to recover the remaining oil in conventional reservoir after primary operation, different enhanced oil recovery (EOR) can be applied: thermal methods, chemical methods and gas methods (Manrique et al., 2010). In the case of thermal methods, the heavy oil production is accomplished by viscosity reduction with the aid of a heat source. The local raising of the reservoir temperature is made by either injection of hot water, hot steam, or in-situ (Butler, 1991).

In the case of in-situ combustion (ISC), also known as fire-flooding, the thermal energy necessary for viscosity reduction is achieved by chemical reaction between the heavy fraction of the crude oil and injected oxygen. The compressed air at the surface is the most common way to introduce oxygen in the reservoir. In addition to oil viscosity decreasing, gas drive and thermal expansion maintain the production. The combustion front propagates through the reservoir, with the reaction components displacing vapors and liquids ahead toward production wells (Sarathi, 1999).

Haynes et al. (1979) based on the environmental assessments for EOR pilot projects implemented in USA, have revealed a number of potentially important environmental impacts on land, vegetation, surface water, groundwater and air. More specifically for ISC operation, the water quality problems could be associated with:

- formation of water-soluble, secondary chemical compounds (e.g., metals and metal oxides) in the reservoir during the high temperature combustion process;
- corrosion and erosion of well casings, particularly by hot sand, resulting in fluid leaks;
- improper disposal of low pH produced water containing small amounts of oil and residues of metallic substances from the crude oil.

The combustion of large quantities of oil during the development of ISC process potentially can release SO_2, NO_x, hydrocarbons, CO, CO_2, and other combustion products as fugitive or uncontrolled emissions (Zoveidavianpoor and Jalilavi, 2014). Subsidence can also occur as a result of the oil extraction form sandy reservoirs.

Petroleum hydrocarbons represent a common environment contaminant class, being in some cases regulated as hazardous wastes. It is a complex mixture of hundreds of compounds, ranging from light to heavy volatile hydrocarbons, with very different physico-chemical and toxicological properties. The total petroleum hydrocarbons (TPH) parameter generally includes hazardous substances from C10 to C40 (ISO, 2004).

There are a variety of spectroscopic and nonspectroscopic techniques used to analyze the presence of petroleum hydrocarbons in environmental samples. The most frequently used methods include immunoassay, general gravimetry, gas chromatography with flame ionization detection or mass spectrometry, infrared spectroscopy, Raman spectroscopy, and fluorescence spectroscopy (Okparanma and Mouazen, 2013). In the present study the presence of petroleum hydrocarbons in water and soil samples was analyzed by fluorescence spectroscopy.

STUDY AREA

Suplacu de Barcău geologic structure is situated in the northeastern part of Bihor County, at about 75 km northeast of Oradea town, under the village of the same name. Studied area, with a hilly terrain features (maximum altitude of 570 m), belongs to the north-eastern part of Pannonian Basin, bordered by Plopiș Mountains on the south, Șimleu Basin on the southeast and Barcău River (a left tributary of Crișul Repede

River) on the north and east (Fazecaș et al., 2011). Suplacu de Barcău village has an area of 2.735 ha and a population of 2.554 inhabitants.

The geology of Suplacu de Barcău area is represented by a Precambrian metamorphic basement (mica schists and gneiss) covered by Pliocene and Quaternary sedimentary deposits (Petit et al., 1990, Carcoana, 1990, Turta et al., 2007). A succession of clastic rocks characterize Pliocene deposits (Sarmatian and Pannonian age), while Quaternary formations are composed by alluvial sediments (sands and gravels).

Geological exploration made before 1960 has discovered an oil reservoir in the Pannonian formation. This sedimentary deposit formed by the moulding of the underlying metamorphic basement, represents an east-west oriented anticline upfold, the dips ranging between 4 and 8 degrees. The major Suplacu de Barcău fault has cut axially the tectonic structure, which limits the field to the south and east. The north and west borders of the field are represented by an aquifer (Petit et al., 1990, Carcoana, 1990, Turta et al., 2007, Ruiz et al., 2013).

The length of the oil bearing structure (western limb of the anticline) is approximately 15 km. Both depth and thickness of Pannonian formation increase from the east to west and the north to south. The depth is in the range of 35 m to 200 m and the net pay thickness varies between 4 m and 24 m. The reservoir rock is poorly sorted unconsolidated slightly marly sand with an average to coarse grain size (Petit et al., 1990, Carcoana, 1990, Panait-Patică et al., 2006, Ruiz et al., 2013). The total area of oilfield is 1700 ha (Panait-Patică et al., 2006).

Geological surveys have indicated the presence of asphalt-base-oil (Panait-Patică et al., 2006). Considering the features of this unconventional play (table 1), the Suplacu de Barcău structure can be classified as tar sand accumulation (Popescu and Anastasiu, 2017).

Table 1. *Main reservoir characteristics of Suplacu de Barcău structure (after Petit et al., 1990, Carcoana, 1990, Panait-Patică et al., 2006, Turta et al., 2007, Ruiz et al., 2013)*

Parameter (measurement unit)	Values
Initial reservoir pressure (bar)	4-22
Initial reservoir temperature (°C)	18
Average effective porosity (%)	32
Initial oil saturation (%)	85
Absolute permeability (mD)	1700-2000
Oil dynamic viscosity (mPa·s)	2000
Oil density (kg/m^3)	960
Connate water saturation (%)	15

Carcoana (1990) have estimated the original volume of oil zone at 46.9 × 10^6 stock-tank m^3. The oil production started in 1960, the dissolved gas expansion and pumping being the main mechanism. Based on initial oil rates of 2-5 m^3/day/well, which very rapidly decreased at 0.3-1 m^3/day/well, the final oil recovery was estimated at 9% (Carcoana, 1990). In these circumstances, thermal methods were considered the only way to increase the oil recovery and production rate. These types of enhanced oil recovery (EOR) are appropriate to be applied to heavy oil reservoir with high oil viscosity such Suplacu de Barcău. In order to use the best technological and economical method, a steamdrive (SD) and in-situ combustion (ISC) field tests were conducted during 1963 to 1970. The initial pilot was an inverted 5-spot pattern of 0.5 ha located in the upper (southern) part of the structure, followed by a semi-commercial operation consisting of six adjacent patterns of 2 – 4 ha. Based on data collected during the progress of the operations, several conclusions has emerged (Panait-Patică et al., 2006, Turta et al, 2007):

- a cyclic steam stimulation (CSS) has to be used in order to prepare the production wells;
- for better results was necessary to convert the pattern exploitation to line drive exploitation (continuous combustion front);
- gradually sweeping the reservoir from the uppermost part to the lowest part of the structure was the adequate strategy for exploitation.

The ISC line drive exploitation started in 1979 moving progressively downstructure, parallel to isobaths (figure 1). The air injection well are located on the East-West line of more than 10 km, the distance between two adjacent wells within a row ranging between 50 – 10 m. Data regarding the oil wells production have been used to forecast an ultimate oil recovery of 55% and to estimate an ultimate oil recovery for the entire structure higher than 50% (Panait-Patică et al., 2006, Turta et al, 2007). By the beginning of 2010, more than 2700 wells were drilled in the field. The oil production at that time was 1200 m^3/day from about 700 active wells, 80 wells were used for air injection and 20 to 24 wells per day were receiving CSS (Ruiz et al., 2013). Using monitoring data of the ISC combustion process, it can be predicted that the combustion front will cover the entire surface of the oil field in about 10 years and the commercial operation will last for more than 40 years (Turta et al., 2007).

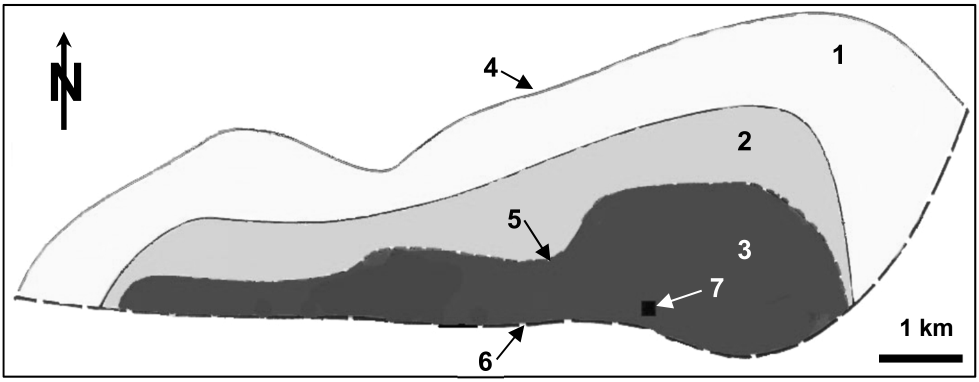

Fig. 1. *Schematic map of Suplacu de Barcău ISC operation (after Păduraru and Pantazi, 2000). Legend: 1 – combustion unaffected area, 2 – combustion affected area, 3 – swept zone, 4 – water-oil contact, 5 – combustion front, 6 – Suplacu de Barcău fault, 7 – initial pilot ISC*

During the exploitation process, some temperature measurements taken in the wells recorded maximum values of around 600°C. As a result of the combustion process, an increase of concentration in natural emulgators in the produced oil, such as asphaltene, resins, naphthenic acids and finely dispersed solid particles, have been observed (Turta et al., 2007). Carcoana (1990) noticed some peculiarities of the water extracted from the production wells: yellow color, decreased values of pH and salinity, increased values of sulfate and iron content. The produced gases from the same wells have 11-15% CO_2, nitrogen, traces of CO, possible unreacted O_2 and sometimes H_2S. Panait-Patică et al. (2006) presented additional data regarding the composition of produced gas: the presence of unsaturated hydrocarbon and up to 17 – 19%CO_2. Saturated and some unsaturated and aromatic hydrocarbon were found in the fluid processing.

Almost since the beginning of the application of the ISC technique, leakage to the surface of combustion gases was observed as mud and steam volcanos-like phenomenon which appeared high structurally through or between adjacent wells to air injectors. These events were still appearing even after the advancement of the combustion front down the structure. Moreover, hazardous gases were detected in the basement of some houses located above the combustion zone (Carcoana, 1990). The most likely cause of the escaping gas would be whether the very small depth of the reservoir or the improper sealing of some old production wells (Turta et al., 2007).

Despite the long history of oil production from Suplacu de Barcău structure (nearly 60 years), very few data are published about the environmental impact of exploitation operations. Pavelescu et al. (2008) analyzed ten surface soil samples for total petroleum hydrocarbons (TPH) using two analytical techniques: infrared and fluorescence spectroscopy. The aim of the study was a preliminary evaluation of soil pollution with petroleum products in order to establish the appropriate method for bioremediation. The TPH concentrations in soil samples varied between 3000 and 27000 mg/kg, high above the intervention level (2000 mg/kg) for industrial sites according to Romanian legislation (MAPPM Order no. 756/1997). Grec and Maior (2008) performed a more detailed study regarding the negative impact produced by the oil extraction on the air, soil and water quality in Suplacu de Barcău area. Soil samples were collected from 10 drillings at a depth of 0.2 m and 0.5 m and 6 groundwater samples were taken from wells used by population for drinking water. The values of TPH in soil samples ranged between 2074.10 mg/kg and 112154.90 mg/kg. The petroleum products concentrations in groundwater were very high, from 0.2 mg/L to 0.7 mg/L.

MATERIALS AND METHODS

Sampling

In order to make an up to date assessment of the petroleum products concentration in Suplacu de Barcău area, surface water, groundwater and soil samples were collected during two field campaigns carried out in 4th November 2015 and 10th May 2016. Despite the preliminary nature of this assessment, the main objective in selecting sampling sites was the best possible coverage area of the oilfield. Surface water samples were collected from 2 points: a small creek (W1) at the roadside located in the northern part of the Suplacu de Barcău area, close to air compression station and Borumlaca Valley (W2), a left tributary of Barcău River, which is crossing the village, being the main collector of the runoff water (figure 2). Groundwater samples were taken from 11 wells used by the population as drinking water, positioned on the whole surface of the Suplacu de Barcau rural area (figure 2). The samples from W3 to W13 were collected during the first campaign, while the samples W4.1, W5.1 and W6.1 were taken in the second. The waters were sampled in polyethylene containers of 500 ml.

Soil sampling was made in multiple sites (figure 3) of the oil field trying to characterize the impact of different type of oil well: productive, decommissioned and abandoned. The land use was also various, from farmland to land areas close to the active or abandoned well pad. In the first campaign, 4 soil samples (S1, S2, S3, S5) were taken, the other 6 samples (S1.1, S2.2, S2.3, S4, S6, S6.1) being collected in the second campaign. In the case of two sites, two samples were taken at different depths: S2.2 at 10 cm and S2.3 at 30 cm, respectively S6 at 10 cm and S6.1 at 30 cm. The other samples were collected from the depth of 10 cm. A blank sample located at about 1 km to the south of Suplacu de Barcău village, in an unaffected area of oil exploitation, was taken also from the depth of 10 cm. Soil samples (500 g) were collected with a stainless hand auger, after removing the vegetation and the sand/stones from the surface (Pinedo et al., 2014). The soil samples were stored in labeled polyethylene bags.

All the samples were transported to the laboratory in cold (4°C) and dark conditions.

The water pH, redox potential (ORP), electrical conductivity (EC), total dissolved solids (TDS), and salinity were measured in situ using a portable multiparameter (WTW multi350i, Germany).

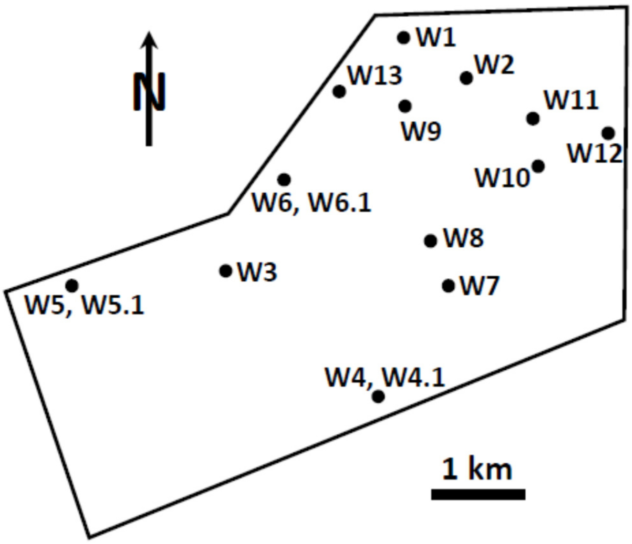

Fig. 2. *Location of water samples in the Suplacu de Barcău oilfield*

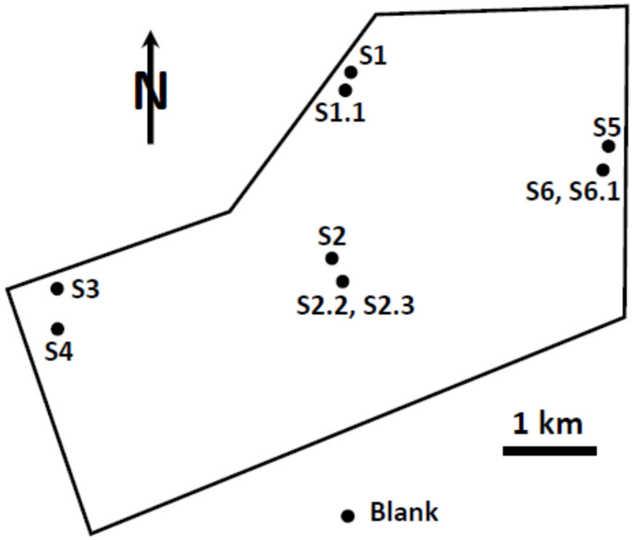

Fig. 3. *Location of soil samples in the Suplacu de Barcău oilfield*

Water samples processing

The water samples used for anions analysis were previously filtered through 0.20 µm pore syringe filters in order to remove the impurities.

For petroleum hydrocarbons analysis, a sample volume of 100 ml was transferred into pre cleaned glass containers, the sample was acidified to pH < 2, by adding HCl 37%. Then the extraction solvent (n-hexane) was added and the bottles were vigorously stirred for 5 min. The solvent was allowed to separate for 5 minutes and the bottles were allowed to depressurize. The organic suspension was collected separately and filtered through 0.20 µm pore syringe filters in order to remove the impurities (Brost et al., 2011), (www.oilinwatermonitors.com). The extraction method, known as *fastHEX* is adapted to US EPA Method 1664 (1996) used for the extraction of petroleum hydrocarbons from aqueous matrix impurities (Brost et al., 2011), (www.oilinwatermonitors.com). Hexane is an organic solvent with a density lower than water, non-fluorescent, which extract all types of crude oil with high efficiency.

Soil samples processing

The soil pH, electrical conductivity (EC) and salinity were measured in a aqueous suspension 1:5 (*v:v*) using a portable multiparameter (WTW multi 350i, Germany) (SR ISO 10390:1999).

For petroleum hydrocarbons analysis, the soil samples were air dried, homogenized, grounded and sieved (< 2 mm). An amount of 10 g soil sample was transferred to a glass container, mixed with the extraction solvent (n-hexane), and vigorously stirred for 5 min. The solvent was allowed to separate for 5 minutes and the bottles were allowed to depressurize. The organic suspension was collected separately and filtered through 0.20 µm pore syringe filters in order to remove the impurities (Brost et al., 2011), (www.oilinwatermonitors.com).

Ion chromatographic analysis

The analyzed anions included F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, and SO_4^{2-}. These parameters were analyzed by ion chromatography using an IC 1500 Dionex system (SUA).

Fluorometric analysis

The processed samples were analyzed by fluorescence spectrometry using a Turner TD-500 fluorometer, designed to analyze the content of oil, condensate gas and refined hydrocarbons in water and soil samples. The fluorometer has two analysis channels operating at different wavelengths: (1) with fluorescence excitation in the UV spectrum and (2) with fluorescence excitation in the VIS range (typically used for high concentrations, over 100 ppm and up to 10000 ppm) (Belore et al., 2009, Brost et al., 2011), (www.oilinwatermonitors.com).

Before analysis, the fluorometer was calibrated using a blank (n-hexane) and a set of standard solutions. Calibration once performed will be stored in the device memory. According to information provided by the supplier, the linear domain is between 0 and 100 ppm (www.oilinwatermonitors.com).

RESULTS AND DISCUSSION

Water samples

The analyzed water samples were generally neutral having the pH within the national limits for surface (6.5 – 8.5) and drinking water (6.5 – 9.5). Three underground samples (W3, W4, W4.1) proved to be more acidic than the national limits. Both surface and underground water had relatively low levels of electrical conductivity (624-663 µS/cm, respectively 672-1970 µS/cm). All the underground waters had the EC within national standards (2500 µS/cm) for drinking water (Law 458 from 8th July 2002) (table 2 and 3).

The F^-, Br^- and PO_4^{3-} were not detected in the analysed waters, while NO2- was detected only in sample W11 (0.2 mg/l), within the national limit (0.5 mg/l) for drinking water (Law 458 from 8th July 2002). Based on Cl^-, NO_3^-, and SO_4^{2-} content, the surface waters belong to 3rd quality class, exception for W1 sample which can be classified as 2nd quality class, considering the NO_3^- content (table 2).

The concentrations for petroleum hydrocarbon (PH) in surface water samples are presented in table 2. These values have been compared with acceptable limit from national legislation regarding the surface water quality (MO 1146/2002).

Based on petroleum hydrocarbons content, the surface waters can be classified as 1st quality class (SW2) and 2nd quality class (SW1).

Table 2. *The quality parameters for the analyzed surface water samples*

	pH	ORP (mV)	EC (μS/cm)	salinity (‰)	Cl^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)	PH (μg/l)
W1	7.2	-36.8	624	0	87.1	4.64	121.9	170
W2	6.7	-21.1	663	0	101.18	19.4	134.6	35
1st quality class	6.5-8.5	-	-	-	25	4.4	60	-*
2nd quality class		-	-	-	50	13.3	120	100*
3rd quality class		-	-	-	250	24.8	250	200*
4th quality class		-	-	-	300	49.6	300	500*
5th quality class		-	-	-	>300	>49.6	>300	>500*

**Order no. 161 / 16th February 2006 for the approval of the Normative on classification of surface water quality for establishment of water bodies ecological status; ** Order no. 1146/2002 for the approval of the Normative regarding the reference objectives for the classification of surface water quality*

The underground waters have higher levels of dissolved ions (table 3), ranging between 46.1 and 348.5 mg/l for Cl^-, between 7.6 and 156.1 mg/l for NO_3^- and between 81.2 and 385.3 mg/l for SO_4^{2-}. Some of the analyzed samples exceeded the limits regulated by national legislation for NO_3^- (50 mg/l), Cl^- (mg/l) and SO_4^{2-} (mg/l) content in drinking water (Law no. 458 of 8 July 2002).

The PH contents of groundwater samples are displayed in table 3. Highest concentrations have been recorded for the samples taken in the central part of the oilfield (W9, W11, W12, W13). This samples are located in a narrow elongated area, oriented approximately from west to east, the samples at the western (W13) and eastern (W12) ends of the alignment, having higher concentrations than the two central samples (W9, W11).

Table 3. *The quality parameters for the analyzed groundwater water samples*

	pH	ORP (mV)	EC (μS/cm)	salinity (‰)	Cl^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)	PH (μg/l)
W3	6.4	2.6	678	0.1	89.9	20.9	140.5	184
W4	5.9	34.2	720	0.1	214.3	76.5	148.1	15
W4.1	6.1	18.5	1156	0.5	170.2	23.3	124.1	17
W5	6.9	-32.5	672	0.1	62.8	79.4	125.1	16
W5.1	7.2	-43.0	1005	0.4	74.4	58.8	100.7	17
W6	6.6	-6.4	1234	0.6	125.4	23.7	121.1	11
W6.1	7.0	-20.0	1452	0.5	238.7	20.1	119.8	33

	pH	ORP (mV)	EC (µS/cm)	salinity (‰)	Cl^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)	PH (µg/l)
W7	6.7	-18.5	1178	0.5	124.5	49.8	243.5	ND
W8	7.1	-29.0	1095	0.5	46.1	8.1	87.9	ND
W9	7.0	-26.2	996	0.4	113.2	7.6	125.1	2399
W10	7.1	-28.1	1970	1.0	348.5	106.3	153.2	5
W11	7.1	-28.0	1755	0.9	101.5	156.1	385.3	3463
W12	7.1	-26.3	1218	0.6	122.8	24.8	115.8	1878
W13	7.0	-15.7	1048	0.5	144.7	28.3	81.2	1107
underground water_alert level*								100
underground water_intervention level*								600
drinking water **	6.5-9.5		2500		250	50	250	

**Decision no. 449/2013 regarding the amendment and completion of the annex to the Government Decision no. 53/2009 approving the National Plan for the protection of groundwater against pollution and deterioration; **Law no. 458 of 8 July 2002 on the quality of drinking water*

Nine of the analyzed underground water (64%), had a low level of petroleum hydrocarbons (5 – 35 µg/l), below the alert level (100 µg/l) for underground water (HG 449/2013). Considerably higher concentrations were detected in samples W9 (2399 µg/l) and W11 (3463 µg/l), where the petroleum hydrocarbons content exceeded the intervention level for underground water regulated by national legislation (600 µg/l) (HG 449/2013).

Soil samples

The analyzed soil samples proved to be neutral to slightly basic, having the pH between 7.7 and 8.0, with relatively low levels of electrical conductivity (28.8 – 163.7 µS/cm) and salinity (0‰), reflecting the low content of dissolved salts.

The values of TPH concentrations in soil are very variable due to the specific nature of sampling sites (table 4).

Table 4. *The quality parameters for the analyzed soil samples*

Soil samples		Depth (m)	pH	EC (µS/cm)	PH(mg/kg)
S1	close to air compression station	0.10	7.7	124.0	12460
S1.1		0.10	7.9	163.7	5135
S2	agricultural	0.10	7.8	100.5	2460
S2.2		0.10	7.7	121.1	282
S2.3		0.30	7.6	114.2	225

S3	vicinity of abandoned oil wells	0.10	7.7	39.0	24105
S4		0.10	7.9	77.4	610801
S5	vicinity of active oil wells	0.10	7.8	107.0	5092
S6		0.10	8.0	83.6	347
S6.1		0.30	8.0	80.6	277
Blank	background	0.10	7.6	28.8	ND*
Normal concentration (mg/kg)**					100
Alert level - soil for sensitive use (mg/kg)**					200
Alert level - soil for less sensitive use (mg/kg)**					1000
Intervention level - soil for sensitive use (mg/kg)**					500
Intervention level - soil for less sensitive use (mg/kg)**					2000

**ND-Not Detected; **Order no. 756 of 3 November 1997 for the approval of the regulation on environmental pollution assessment*

The highest values of petroleum hydrocarbons are recorded for the samples taken close to the abandoned wells (S3, S4) from the western part of the oilfield. Technical accidents or uncontrolled extraction operation on the well pad can be the cause of oil spilling affecting surrounding area. No rehabilitation actions have been noticed in this area. High values of PH in uncultivated soil samples (S1, S1.1) have been found in the northern part of the oilfield, close to the air compressed station and other industrial facilities. Soil samples (S5, S6, S6.1) taken from the eastern zone of active oil wells are showing high to moderate values, caused by the extraction operations. On vertical profile, a slight decreasing trend has been noticed comparing the concentration of S6 and S6.1 samples. Moderate and high PH concentrations have been identified on soil samples (S2, S2.2, S2.3) collected from the people farmland located on the west-central part of the village. On this site, the downward decreasing trend of recorded values on surface versus deep sample (S2.2 vs. S2.3) has been also observed. This contamination probably is due to the adjacent location of some oil wells to tested farmland. The blank sample contains virtually no petroleum products.

Two PH values recorded for farmland samples (S2.2, S2.3) are above alert level, and one value (S2) is exceeding by more than four times the intervention level, indicating a seriously contaminated soil. Two samples (S6, S6.1) collected from an area close to a new active well are below alert level for industrial areas, indicating a good management of oil extraction. The other soil samples have PH concentrations high above intervention level for industrial sites, the contamination source being either the uncontrolled historic production activities specific to the abandoned wells (S3, S4), either the poor management of active wells (S5) or other industrial facilities (S1, S1.1).

CONCLUSIONS

For some of the investigated sampling points, the obtained results reflect the impact of the anthropic activities carried out in Suplacu de Barcău area. Based on petroleum hydrocarbons content, the surface waters can be classified as 1st and 2nd quality class. The content of petroleum hydrocarbons for some of the analyzed groundwater's was higher than the intervention level, regulated by national legislation. High levels of petroleum hydrocarbons were detected in some soil samples, especially for those taken close to the abandoned wells, which could be correlated with possible oil spilling caused by technical accidents or uncontrolled extraction operation on the well pad.

For some ground waters, the level of NO_3^-, Cl^- and SO_4^{2-} exceeded the limits mentioned by national legislation.

In some of the analyzed soil samples, collected from an area close to a new active well, the petroleum hydrocarbons content was below the alert level for industrial areas, indicating a good management of oil extraction.

Acknowledgments

This work was supported by the PN II – Parteneriate grant (PCCA-2013) „Innovative technology for ex-situ bioremediation of soils polluted with hydrocarbons (BIORESOL)", contract no. 91/2014.

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STUDIA UBB AMBIENTUM, LXII, 1, 2017, pp. 43-51
(RECOMMENDED CITATION)
DOI:10.24193/subbambientum.2017.1.03

ASSESSMENT OF PHYSICO-CHEMICAL PARAMETERS OF SOILS IN ZOOTECHNICAL FARMS AREA FROM TICHILEȘTI AND TUFEȘTI LOCALITIES (BRĂILA COUNTY)

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ABSTRACT. Two growing-fattening pig farms – non-organic and organic - have been chosen in order to estimate the potential environmental impacts of heavy pig production. The above mentioned farms are situated in Tichilești-Tufești area, Brăila County, Romania. This area is situated in the north-eastern part of the Romanian Plain, which is delimitated by the Danube River in the southern part. Is one of the highest agricultural potential areas, reflected in a development of the economical sector based on zootechnical farms. Using the electrochemical methods, the nitrites and sulphides, from soil and water, together with physico-chemical parameters have been analyzed. The obtained results indicate the presence of the above mentioned chemical compounds in a small amount, excepting one location, situated near the organic farm. The maximum permissible limits imposed by the Romanian legislation are exceeded only for drinking water, being in normal values for all analyzed soil samples. In addition, a positive correlation between clay and nitrite/sulphides content can be observed.

Key words: *organic and non-organic pig farms, physico-chemical parameters, nitrites, sulphides, Tichilești-Tufești area*

INTRODUCTION

Considering environmental problems in Romania and across the world, significant changes have been occurring at zootechnical farm (Sutherland, 2011).

Intensive pig farming is usually concentrated in large production units, which increases the risks of air, water and soil pollution and represents a serious environmental problem. As could be expected, the environmental impacts of pig farming can be direct (due to the farming and manure management systems) or indirect (due to the impacts associated to produce inputs like feed and electricity).

The main pollution sources of pig farming arises from the production of crop based ingredients for feed production and from the emissions of methane (CH_4), ammonia (NH_3), carbon dioxide (CO_2) and hydrogen sulfide (H_2S) of pig housing and of the manure management systems (Gutierrez et al., 2016).

Nitrate (NO_3^-) can reach the underground and surface waters, increasing eutrophication and reducing drinking water quality. The EU Nitrates Directive 91/676 (EEC, 1991) requires member states (MS) to introduce measures to reduce NO_3^- losses to underground and surface waters from agricultural sources. The loss of nitrates can also contribute to indirect emissions of nitrous oxide, (N_2O) where NO_3^- is reduced into the underground and surface water bodies (Webb et al., 2014). Drinking water is also one of the major sources for nitrate/nitrite exposure. Nitrate is a source of nitrite due to it's endogenously conversion (Thomson et al., 2007).

The aim of this study was to highlight the difference between two types of pig farms - non-organic and organic - situated in Tichilești-Tufești area, Brăila County, Romania. The main objective was to evaluate the quality of environmental factors in the study area by determining the physico-chemical parameters (pH, redox potential, electrical conductivity, total dissolved solids, salinity, dissolved oxygen) and the concentrations of NO_2^- and S^{2-} in drinking water and soil samples.

MATERIALS AND METHODS

Study area

The studied area is represented by Tichilești-Tufești villages, located in the north-eastern part of the Romanian Plain, which is delimitated by the Danube River in the Southern part. This area has a very high agricultural potential (figure 1).

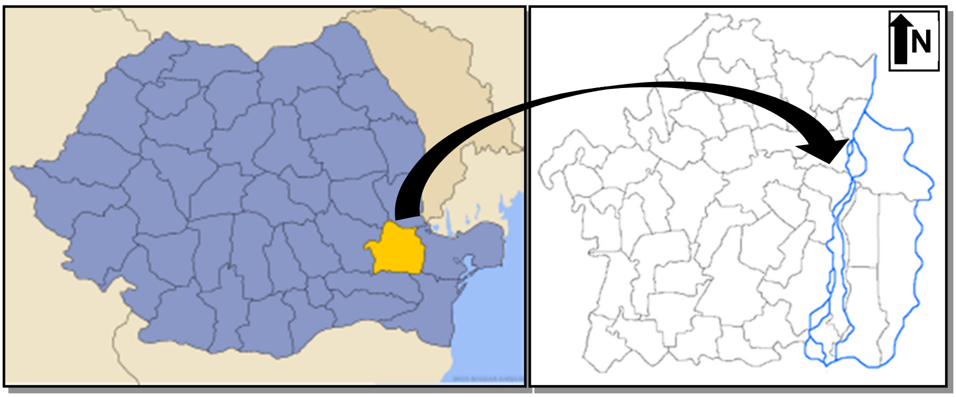

Fig. 1. *Location of the Tichilești-Tufești area on the (https://ro.wikipedia.org/wiki/Listă_de_comune_din_județul_Brăila)*

Total surface of the non-organic pig farm from Tichilești is about 175.240 square meters, while the organic pig farm from Tufești has a total surface area of 120.400 square meters. Both farms are delimitated by no.212 County Road in the western part and agricultural land in northern, eastern and southern part (figure 2).

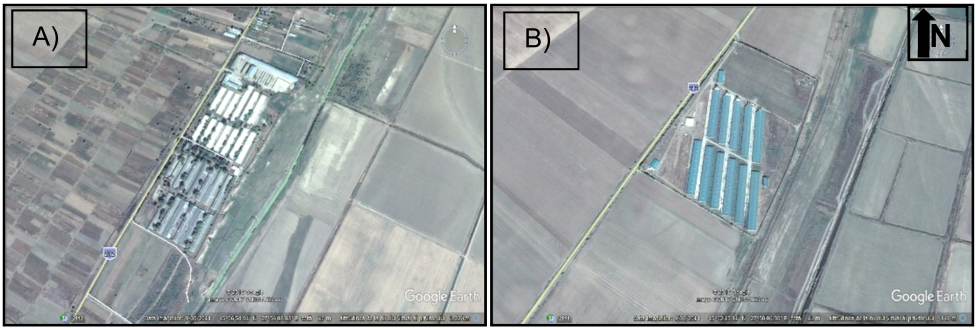

Fig. 2. *Location of the Tichilești non-organic farm (A) and Tufești organic farm (B) (GoogleEarth)*

A continental steppe climate with excessive influences and high thermal amplitudes characterizes the studied area. The average annual temperature is 11°C, summer average being 22.2°C. Annual relative humidity is 70% (in winter – over 80% and in summer – under 60%). Average annual precipitation does not exceed 450-500 mm during the summer, around 20 rainy days being registered (Ganea, et al., 2017).

Sampling and analytical methods

In order to evaluate the impact of the organic and non-organic growing pig farms, samples of soil and water have been collected using the methodology from the Order of the Ministry of Agriculture and Rural Development no. 278, published in the "Romanian Official Law Monitor" No. 928/28 December 2011 (OM 278/2011).

The soil physical parameters were determined according to the current national and international standard protocols, as follows: determination of organic matter - STAS 7107/1-76; determination of grain size-sedimentation and sift method - STAS 1913/5-85 and SR EN 14688-2:2005, and determination of free swell index of soil - IS-2720-PART-40-1970.

The physico-chemical parameters (electrical conductivity, salinity, pH, total dissolved solids) of the water and soil have been measured using a WTW Multi 350i multiparameter device. The electrochemical determination of nitrites (in water and soil) was performed using carbon paste electrodes (CPEs) modified with zeolite adsorbed with Toluidine Blue (CPE-Z-TB) and the sulphide determination used carbon paste electrodes modified with zeolite adsorbed with Methylene Blue (CPE-Z-MB). All electrochemical experiments were carried out using an AUTOLAB electrochemical analyzer (Autolab-PGSTAT10, Eco Chemie, Utrecht, Netherlands); all measurements were performed at room temperature.

The obtained sensors CPE-Z-TB and CPE-Z-MBs were used for the detection of nitrite and sulphide, respectively, using the standard addition method. In order to evaluate the pollution degree of the environment in the area and the potential effects upon human health, the concentrations have been compared to the maximum permissible limits imposed by Romanian legislation for drinking water (Law no.458 of 8 August 2002), and soil (Order no.756/3 November 1997) maximum limits issued by the US Environmental Protection Agency (US-EPA).

RESULTS

Physical parameters of the soils are characterised by the silty clay texture, with an adsorption capacity between 50% and 60%, excepting one sample with a clayey silt grain-size content having an adsorption capacity slightly larger (80%). Organic matter content is between 2% and 5% for most of the samples, overcoming 5% in one silty clay sample. A positive correlation between clay content and nitrites/ sulfides concentration can be pointed out as a general pattern. One exception appeared in the case of the sample with the highest content of nitrites/sulfides where the content of clay are not respecting this pattern.

The analyzed soil samples are included in the sensitive soils category, referring to the type of usage. The differences of physico-chemical parameters between non-organic pig farm and organic pig farm are not obvious (figure 3).

Physico-chemical parameters of the soil are characterised by the following values: pH between 7.7 and 8.1, the electrical conductivity between 156.8 and 185.1 μS/cm, salinity 0 ‰, total dissolved solids between 94.04 and 111.06 mg/L and redox potential between -72.8 and -57.3 mV. A correlation between electrical conductivity, total dissolved solids (TDS) and redox potential (Eh)can be observed. High concentration of the TDS have lead to a high electrical conductivity and also to a low redox potential.

Regarding NO_2^- level in soils, the average of all samples falls around 0.313 mg/kg (Fig. 3). A visible difference between the level of nitrites, between two analyzed pig farms, can be pointed out. Nitrites concentration in non-organic pig farm soils range between 0.206 and 0.222 mg/kg (average 0.214 mg/kg) while in organic pig farm varies between 0.260 and 0.558 mg/kg (average 0.379 mg/kg). Thus, the activity of the studied pig farms doesn't influence the quality of the soil due to the fact that the nitrite concentrations are low. It is necessary to mention that nitrites are not normalized by the Romanian legislation.

The concentrations of S^{2-} in soil samples are following the same pattern as nitrites concentration, a visible difference couldn't be noticed. The average concentration of S^{2-} in all samples is around 0.220 mg/kg except one value of 1.496 mg/l identified in one of the samples collected at the organic farm (figure 4). According to the Romanian legislation regarding the maximum limits allowed (MLA) for sulfides, the identified concentrations are falling into these limits.

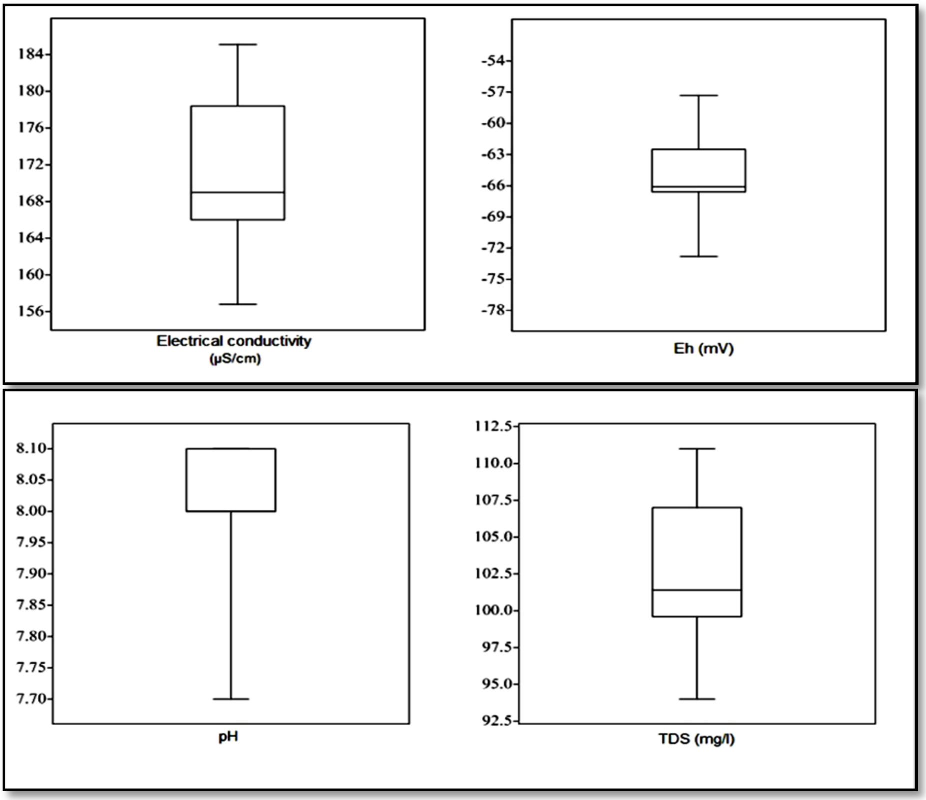

Fig. 3. *Physico-chemical parameters of soil samples*

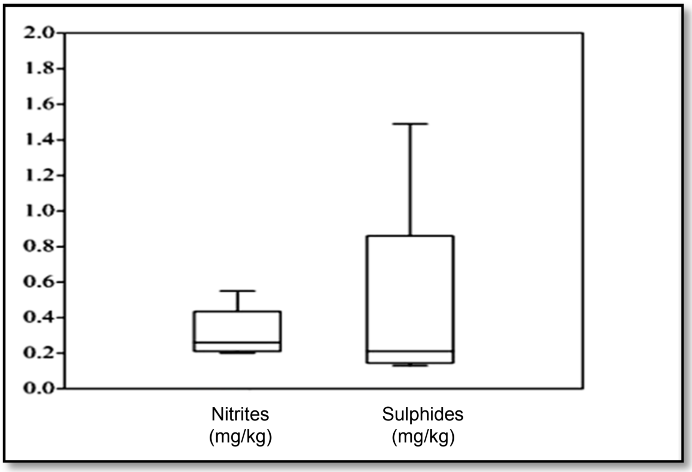

Fig. 4. *Nitrites and sulphides concentrations into the soil samples*

Regarding the drinking water samples, the concentration of nitrites are exceeding the MLA in one sample while the concentration of sulfides are exceeding these limits in all analyzed samples. The average values obtained for NO_2^-concentrations in drinking water is 0.290 mg/l with an exceedance of 0.518 mg/l (MLA 0.50 mg/l) and for S^{2-} the registered concentrations were361.5 µg/l (MLA 100 µg/l) (figure 5).

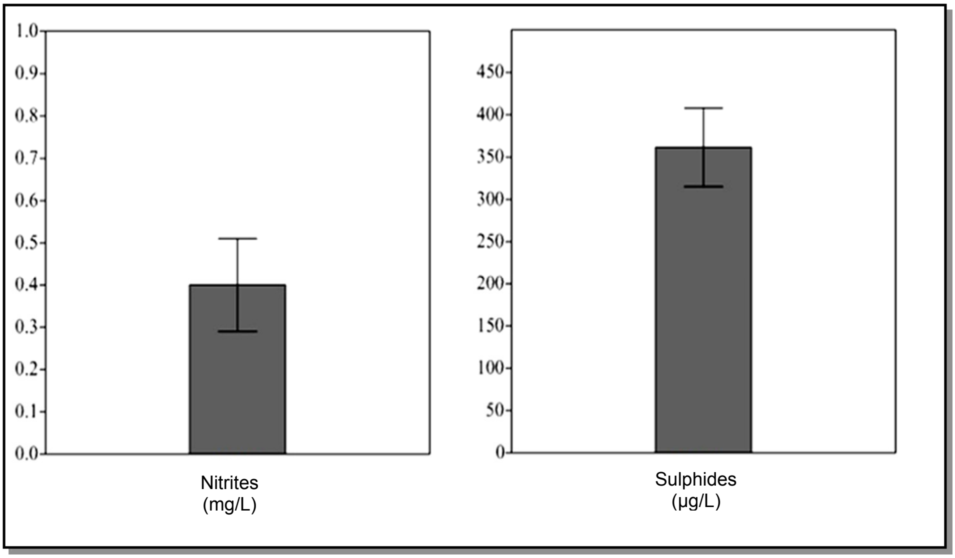

Fig. 5. *Nitrites and sulphides concentrations into the drinking water samples*

The physico-chemical parameters in drinking water are all in normal values according to the Romanian legislation no. 458/08.07.2002. pH between 7.55 and 7.86 (MLA 6.5-9.5), TDS between 864.6 mg/l and 2382 mg/l, salinity between 0.7 ‰ and 2 ‰, Eh between -39.5 mV and -58 mV, dissolved oxygen between 6.470 mg/l and 7.150 mg/l (MLA >5 mg/l) and an average value for electrical conductivity of 2705 µS/cm with an exceedance in one sample of 3970 µS/cm (MLA 2500 µS/cm) (figure 6). This exceedance pointed out the presence of a high dissolved salt content in water.

The obtained data indicates that the activity of the two analysed pig farms does not affect the soil but affects groundwaters, from nitrites/sulfides content point of view. Some other studies pointed out the exceeding of the MLA for many other chemical compounds (MST, CBO_5, CCO-Cr, SET, NO_3, NH_4, Nt, Pt, phenols) including the nitrites, in the case of the non-0rganic pig farms. In recent years many studies are focused on environmental impacts of organic farming (Cobb et al., 1999; Hole et al., 2005; Petersen et al., 2006; Wood et al., 2006; Sandhu et al., 2008) concluding that this type of agriculture offer environmental benefits, such as: an efficient nutrient cycles, an increasing of biodiversity across the farm, etc. These benefits are due to the fact that organic farming is characterised by the prohibition of the synthetic chemicals in both crop and livestock production (Lampkin, 2002). Instead, some other studies are contesting these benefits (e.g. Colman, 2000).

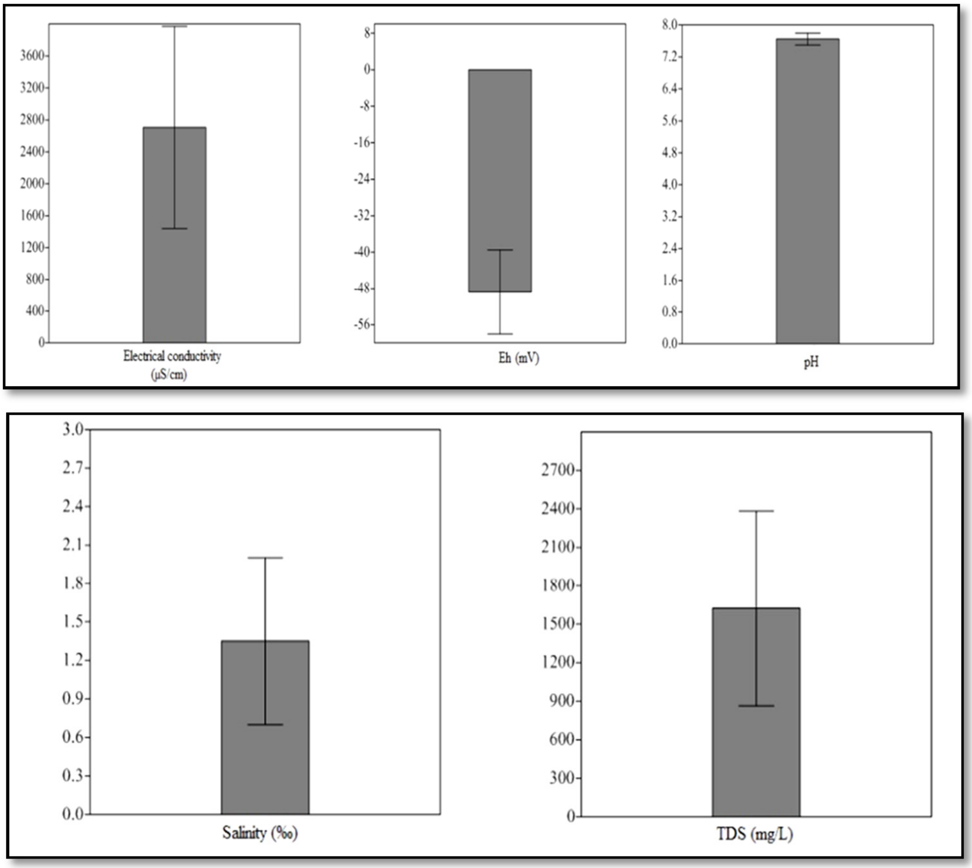

Fig. 6. *Physico-chemical parameters of drinking water samples*

To reduce the N excretion and NH_3 emissions, who can further pollute the soil and groundwater, farmers can adopt a series of best practices, such as changing the feeding system together with the reduction of crude protein content (Pirlo et al., 2016) and optimizing the amino acid profile in the different physiological phases (Xiccato et al., 2005). Thus, the role of feed chain in the environmental load of pork production is the most important factor regarding the impact on the environment together with farm size and reproductive efficiency (Bava et al., 2017. A source for sulf related compounds linked to pig production is the emission of hydrogen sulfide (H_2S) from pig housing and from the manure management systems (Stone et al., 2012; Reckmann et al., 2013). Thus, a proper management of the manure can be the solution to reduce the negative environmental impact (Vu et al., 2007).

CONCLUSIONS

In the current study the concentrations of NO_2^- and S^{2-} have been investigated in Tichilești-Tufești area. High levels of NO_2^- and S^{2-} were identified in all the drinking water samples investigated, exceeding the maximum permissible limits recommended by the Romanian legislation. However the concentrations of NO_2^- and S^{2-} in the soil samples were very low, being in the normal values recommended by the national legislation.

Considering the obtained results, the agricultural activity in the investigated area is not a source of pollution, from NO_2^- and S^{2-}concentrations point of view. To sum up, both farms have no significant environmental impact and do not represent a potential harm for the local community.

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STUDIA UBB AMBIENTUM, LXII, 1, 2017, pp. 53-62
(RECOMMENDED CITATION)
DOI:10.24193/subbambientum.2017.1.04

ASPECTS RELATED TO THE INTERPRETATION OF DISASTER MANAGEMENT AT OPERATIONAL LEVEL

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ABSTRACT. With the transformation of the disaster management system in Hungary also the alerting system has changed fundamentally. The alerting and deployment nowadays is based totally on informational systems. The deployment of special-purpose trucks in disaster management interventions is often wrongly associated with the words “special” or “extraordinary” by the public, media or even within the disaster management system. In order to clarify the situation, it is important to define the circumstances when special-purpose trucks are deployed in a mission. The authors start with the description of ordinary fire interventions, requiring less forces and resources, and gradually arrives to the interventions with special-purpose trucks, exemplified with case studies. Furthermore, the factors that classify alerts as rescue situations requiring special interventions are also analysed. The paper highlights how the effectiveness of rescue activities can be increased starting with the alert and continued by the intervention. The paper offers insight into the alarm levels and special rescue activities and describes which events demand special-purpose units at the site.

Key words: *disaster management, firefighting and technical rescue, intervention, special, extraordinary*

INTRODUCTION

Despite the efforts taken during the last decades for the reduction of fire prevention and fire suppression costs many problems can be identified in these fields. Several studies are discussing the higher level of fire safety of the society, focusing on the structures of the buildings (Majoros and Balázs, 2004; Czoboly et al., 2015; Lublóy et al., 2015), the safety of the intervention (Pántya et al., 2014; Restás, 2014a), more effective decision making (Cohen et al., 1996; Klein, 1999; Restás, 2015), economical efficiency (Gould, 2009; Restás, 2014b; Vincent et al., 2014) etc. In this paper the authors focus on the experimental or professional part of the effectiveness of the special interventions.

Professional interventions require minimum intervention time, minimum losses, but maximum quickness for starting the intervention and maximum saved goods. These requirements strongly correlate with the effectiveness of decision making. Many studies reflect on the fact that decision making at the fire scene is totally different from what we usually know or learn during trainings (Cohen et al., 1996; Klein, 1999; Restás, 2013a). Therefore, several studies modelling firefighter's decision making methods focusing on theoretical parts (Klein, 1999; Killion, 2000) or practical side (Restás, 2013b, Restás, 2014c) can be found. Even if different models can be very helpful and important, the real experiences are not avoidable.

With the restructuring of disaster management system in Hungary significant changes took place in the operation of the organization. Although several years since this restructuring have already passed, there are still regular misunderstandings from the part of society in connection with the operation of disaster management system. The change not only affected the legal environment, but also organizational restructurings took place and different measures have been introduced in terms of task execution. As a result of the restructuring in several cases the intervention staff took different actions in occasions of incidents with identical characteristics. There were also cases when laws applied according to the new system gave a reason for dispute among the experts.

With the restructuring of disaster management system, the work of the intervention staff has been transformed changed as an effect of the new laws. The classification and processing of alarms, the regulations of operation control are all made in accordance with the new stipulations (OKF, 2014). In public awareness and in media priority alarm degrees are often confused with special interventions. The difference between general intervention and special intervention is determined by the type of equipment and vehicles commanded to the site. There are incidents where the technical equipment of disaster management is not sufficient for carrying out the rescue, therefore it is necessary to involve the assistance of special units, equipment.

The paper also presents the laws which regulate the work of intervention staff in case of incidents, especially those related to the special interventions of fire fighters, as well as the organizations and units carrying out the special rescue tasks. The authors describe in detail the power-tool system applied by fire fighters. The study is based also on personal experiences of the authors and opinions of the special rescue teams' managers and staff.

Primary activities for intervention

Primary intervention lasts until the direct emergency situation is not over or the control of the event is taken over by a higher disaster management organization (defence committee).

The intervention is an activity for protecting human health and life, as well as protecting material goods. It is performed using the permanent tools and equipment of the fire brigade and it only lasts until it is considered primary intervention.

Statement of competence

Although laws exactly define the notion of competence, it is worth explaining it because the fire brigade are entitled to (or must) intervene in the situation if the legal competences can be defined.

The chain of responsibility starts from the operator who gets the call, through the person who evaluates the call and finally the commander of the rescue team. The notion of technical rescue and the acceptance of the call should be subjects of periodical trainings. The person who evaluates the call has to be able to decide if the emergency situation necessitates technical rescue.

Primary calls are accepted by the operation controllers of the County Disaster Management Headquarters Main Control Department. Their tasks are to evaluate the calls/alerts.

As the operation controller decides that the situation is a technical rescue, he has to apply the regulations which require the commander of the rescue team to follow a continuous investigation, during which he has to analyze not only what kind of operations he has to accomplish, but also whether the conditions of technical rescue are available.

INTERPRETATION OF DEFINITIONS REGULATING BASIC OPERATION

In order to clearly see the work of intervention staff carried out for incidents it is important to interpret the basic laws regulating operation.

We distinguish two types of incidents: A) Fire event and B) Technical rescue.

The paper describes especially technical rescue during the operation of the system, because during technical rescue special tools and organizations are more often applied. Basic definitions on intervention are interpreted precisely in the Fire-Fighting Tactical Regulation No. 5/2014. (II.27.) BM OKF (hereinafter: Fire-Fighting Tactical Regulation). The knowledge of the following definitions is essential for the correct execution of rescue.

Fire (fire event)*: burning process which is dangerous to life, physical safety or material assets, causing damages* (Law XXXI/1996).

Definition of technical rescue: *natural disaster, accidents, incidents, abnormal technological process, technical failures, dangerous substance released or other plot-induced emergency during which protection of human life, physical safety and material assets is carried out by fire department as primary intervention activity with the available and utilized equipment (*Regulation 39/2011. (XI. 15.)*).*

Fire trucks: *standby vehicles of the fire department which are available together with the built in and mounted equipment, extinguishing and auxiliaries specialized for the enforcement of firefighting and technical rescue (*Order no. 5/2014. (II.27.)*).*

Fig. 1. *Vehicle water hose (Photo: Authors)*

Squad: *tactical part of firefighting and technical rescue organization which is capable of independent intervention with its own tools, staff comprising 1+5 people* (Order no. 5/2014. (II.27.)).

If necessary, several fire trucks can be commanded to the incident site at the same time, as there can be two or sometimes three fire trucks during the same period of time at certain fire stations. In these cases we cannot speak about special rescues (figure 1 and 2).

Fig. 2. *Fire trucks during intervention (Photo: Authors)*

In case of interventions for fire events, as well as technical rescue, in many cases special, specific fire trucks are required on site. The special fire trucks can be handled by a person who has performed a specific operator course. Special fire trucks are used in special situations. In cases of fire events the most often used equipment are the aerial ladder and the pumper vehicles. Several fire trucks are used during technical rescue as well. The most commonly commanded fire trucks are the rescue trucks as well as the regional crane vehicles.

The *rescue squad* commonly called the *„field”,* is a speedy light truck less than 3500 kg. Due to its capabilities, it reaches a higher speed, thus delivering very quickly the special tools (hydraulic cutter, aggregator) stored in the cargo space.

For interpretation of special fire truck, it is worth becoming familiar with the definition.

Definition of special fire truck: *All fire fighting vehicles which differ in construction and in equipment from the general fire engine constructed for multipurpose use. Its special construction and equipment makes it suitable for single-type fire extinguishing or technical rescue tasks (*Order no. 102/2012*).*

Fig. 3. *Egerszeg / Crain*
Photo: Zalaegerszeg Deparment for Disaster Management

According to the definition above, there are several types of special fire trucks (figure 3):

- Tanker
- Ladder truck
- Forest fire truck
- Rescue squad
- Hazardous material rescue container

Equipment found on the firefighting trucks are determined by the 29/2012 BM OKF General Director Measures. Interventions which can be carried out with this equipment are called *general firefighting interventions.* All members assigned to the vehicle should have qualification for using these tools.

The area of operation

Nowadays, it can regularly happen that in certain cases, several cooperating organizations are responding together. These organizations include disaster management organizations, fire brigades, as well as the workers of the National Ambulance. Of course, there could be some cases where other institutions, such as the National Tax and Customs Office, also have to intervene in the processes.

In case of a road accident which involves human injuries, the ambulance, the fire brigade and the police all have to participate in the rescue. However, it can happen that on arrival at the scene of the accident the commanders of the rescue teams cannot agree on the size of the area of operation, and also they cannot agree on the person with major responsibility. As soon as the ambulance crew arrive, they start saving lives, while the fire brigade actively take part in the rescue. If needed, they use their special equipment (tightening cutter) to cut cars and change the scene.

This operation disturbs the works of the crime scene investigators. The scene of the damage (the so-called area of operation) can be modified, that is why the investigators would like to start the examination on the spot as soon as possible, by securing the position of the vehicles and by taking photos. This can pose several threats, as the fire brigade has not finished the technical rescue and the intervention can cause further human injuries.

In several cases, during the rescue, the fire brigade had to give their own equipment (helmet) to the ambulance men, so that the doctors working on the scene would not be injured (by glass- or metal splinters).

Imagine a hazardous event, when a vehicle carrying dangerous chemicals is involved in an accident. The fire brigade arrives at the scene and they have to cope with this situation. The investigation requires special equipment and protective clothes. In such a case the police arriving at the scene enter the area of operation without protective clothes and do not take the danger into consideration, which can lead to arguments between the commanders. The fireman in charge instructs the policeman to leave the area of operation, but the policeman refuses to do so as he refers to the "60/2010, ORFK Instruction: in case of road accidents and in case of any criminal acts happening on the roads there is a regulation to be followed" which defines the main tasks and responsibilities of the police and entitles him to be present on the scene.

However, there are several laws in favor of the fire brigade entitling the firemen to perform operations independently considering protection of human life and property.

These problems frequently occur in interventions. As there are often arguments between the cooperating organizations, in our opinion a unified law should be introduced to define who should be considered the commander in the area of operation. In case of a more serious damage it could become a disadvantage and it could affect the rescue operation if the commanders of the different organizations cannot agree on the execution of the rescue.

ALARM DEGREES

We distinguish five degrees of alarm applied by the disaster management chief duties which are marked with roman numerals (I-V). If a special truck is commanded to the site then it qualifies as *special alarm* (figure 4). Commanding a special truck to the site does not mean that the incident is a special incident. Most of the branches have some kind of special vehicles i.e. ladder, tanker which are frequently used. In these cases, like in all cases, the rescue of lives and material goods are the priorities. According to this the question of efficiency arises.

Fig. 4. *Special alarm degree: 2 vehicle water hoses, 1 ladder (Photo: Authors)*

The definition of efficiency may have different meanings. One of these is the so-called professional efficiency which can be found when fulfilling the operative task of all organizations. To a fire department chief efficiency means saving lives with all available forces, equipment, eliminating fire and incidents, and reducing damages. The statement includes a rather serious restrictive factor, namely the words "with all available forces, equipment". The mentality of the fire department chiefs naturally adjusts to this statement. Thus, they strive to decrease this restrictive factor in the interest of increasing efficiency. That means they require more and more special and – who would dare to disagree – automatically, more expensive equipment. This is clearly a correct endeavor from the point of view of the fire department chiefs and this ensures the increase of professional efficiency (Restás, 2012a).

The regional technical rescue stations established in the country have special vehicles (regional crane, dry powder or foam containers, chemical or technical containers).

Vehicles belonging to the rescue stations are only commanded to incidents requiring special intervention. The regional crane is only commanded once or twice or not at all during summer as the weather is ideal for transport.

In the winter period the monthly commanding increases considerably due to the weather conditions. In case of heavy snow or frost the number of daily incidents may multiply. The chemical containers are used in case of chemical accidents. Containers are used to deliver special equipment (protective clothing, storage containers). These are used once or twice or not even once throughout the year. Further corner stones can be formulated as conditions influencing decision or determining professionalism such as the priority of saving lives, the importance of safety and technicality (Restás, 2012b).

Due to the construction practice in Hungary the height of buildings in the cities generally does not exceed ten floors. A ladder or skylift vehicle can be found in each of these cities. The occurrence of these vehicles can be considered common in the country.

THE ACTIVITY OF SPECIAL RESCUE ORGANIZATIONS IN EMERGENCY SITUATIONS

The fire department frequently asks for assistance from special rescue organizations to mitigate incident consequences. In most cases, external assistance is required as the fire departments do not have the special equipment or staff needed for rescue. In most cases they require the assistance of special rescue organizations established at county level because these have diving, aerial and deep rescue equipment (figure 5). Different prime movers are also required for traffic accidents. These rescues can be called special in almost every case as efficient intervention could not be carried out by the fire department alone.

Fig. 5. *Searching of missing person*

Zala Special Rescue Team is employed in most cases in the course of deepwater rescue. The skilled divers can efficiently intervene even in extreme weather conditions. Their intervention was successful in several cases within Zala County.

CONCLUSION

The authors pointed out the characteristics of the general technical rescues and afterwards described the special units which are used during a special rescue procedure. Civil rescue organizations taking part in rescue missions were introduced, which ensures great assistance for fire departments.

Today the range of technical vehicles and machines is so broad that it is almost impossible for the staff of the fire department to be prepared for comprehensive rescue and also this is not possible from the economic point of view. There are certain interventions which occur only very rarely or not even once annually, such as gas outburst. Therefore, these are dealt with by the help of external assistance. The rescue organizations form an organic part in rescues and more and more special units will be required together to keep up with the industrial development.

Missions are regarded as special in every case as the solution can only be carried out with coordinated, special work. Incidents occur on a daily basis, but the fire departments have to cope in every case and, if necessary, they have to adapt to special interventions.

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STUDIA UBB AMBIENTUM, LXII, 1, 2017, pp. 63-74
(RECOMMENDED CITATION)
DOI:10.24193/subbambientum.2017.1.05

THE RECYCLING OF THE RUBBER WASTE BY INCORPORATION INTO THE CEMENT MATRICES

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ABSTRACT. The rubber wastes result mainly from the automobiles, but may also result from the construction or from other industrial activities as well as from households. Increasing the use of the rubber has generated an increase of the amount of rubber waste resulted. Thus, the increasing of the amounts of the rubber waste produces important environmental issues, especially when they are stored. The degradation of the tires take long times, by comparison, we can even say that rubber wastes have an unlimited lifetime compared to other organic wastes. In addition, in the case of an accidental ignition of the stored tires, their combustion releases gases containing hazardous chemical compounds, and fine particles, into the environment. Some of that gases produced by ignition are dangerous not only for the environment but also for the human health. These are some of the reasons why the European legislation prohibited the storage of rubbers in the landfills. In this context, the recovery and the recycling of the rubber waste to the detriment of their storage become very important.
This paper studies the possibility of the recycling of the rubber wastes by incorporating the crumbs of rubber in the cement. The rubber crumbs were added to the cement, partially replacing the fine aggregate in the cement matrix, in various proportions (10, 20, and 30% weight units). The characteristics of the resulting types of cement were evaluated from their mechanical and physical properties.

Key words: *rubber waste, recycling, sustainable waste management, cement*.

INTRODUCTION

The amounts of the wastes produced in the world are constantly increasing, and then it is very important to find different ways to recover or to recycle them. The first reasons are the significant environmental impact of the waste and too often to use the storage of the waste in the landfills, that is a solution that seems to be cheap at the moment, but it is an expensive and a polluting one in time. Also, it important to understand the fact the non-renewable resources decreasing in time and an efficient recycling of the waste could provide a balance between the resources consumed and the wastes produced.

The rubber wastes have certain characteristics that give them a special place in the waste management that recommend them for the recycling. Some of these characteristics are: the rubber wastes are produced in enough large quantities annually, especially from the industrialized countries, they have large dimensions, and they have a different chemical composition, they do not break down in the nature, and their accidental combustion produce a lot of toxic and dangerous gases for the environment and for the human health (Downard et al., 2015).

Many of the dangerous gases produced by the burning of the tires are toxic, carcinogenic and mutagenic, being more dangerous than those produced by the burning of plastics or the fossil fuels in the combustion boilers. If the combustion of the tires occurs with oxygen deficiency, as in the case of dumped tires in the higher piles, the amount of the polycyclic aromatic hydrocarbons (PAH) in the combustion gases are increasing. In addition to the PAHs, the combustion gases can also contain SO_2, PM-2,5, black carbon, acrolein, formaldehyde and CO, all of these compounds having a high risk for the health (Downard et al., 2015; Demarini, 1994).

The main source of the rubber waste is generated by the used tires resulted from the motor vehicles. Sienkiewicz et al. (2012) estimate at 17 million tons per year the world production of the used tires. Tiwari et al. (2016), estimate that 1.5 billion tires are produced annually in the world, and around 1,000 million tires complete their lifetime, and half of them are stored in the uncontrolled landfill without any prior treatment. He also estimates that at this rate, by 2030, the amount of dumped tire will increase and will reach about 1200 million tons annually, and the total number of the tires inadequately dumped may reach 5,000 million.

In the Europe, the Landfill Directive (1999/31 / EC) prohibits the storage of the used tires in the landfills. The End of Life Vehicle Directive (2000/53 / EC), also, proposes to reuse, to recycling or to do other different treatments of the waste resulted from the old vehicles (including the rubber waste). The End of Life Vehicle Directive proposes to use various methods for the rubber waste as: tires retreading, reuse, recycling or energy recovery in the cement kilns to the detriment of storage. Those legislative measures helped to promote the research into the field of the recycling of the rubber wastes, and also the monitoring the uncontrolled storage of the rubber waste. Also, the producers were directly involved in the rubber waste reuse or recycling process applying the principle of "producer responsibility" in the field of rubber waste management (Sienkiewicz et al., 2017).

The storage of the old tires may pollute the water and the soil due to the substances they may be containing (lead, zinc, mineral oils) or tire landfills located in the vicinity of the inhabited areas can be the shelters for the reproduction of some harmful insects or micro-organisms (Layachi et al., 2016).

The recycling of used tires is not very simple because they have a complex structure and composition. Sienkiewicz, M. et al. (2017) show that there are 8 types of natural rubber and 30 types of high-quality synthetic rubber and there are some various chemical compounds used to vulcanise them. The tires also contain steel wires or polyester and cellulose wires that need to be separated for recycling (Ramarad et al., 2015; Schnubel, 2014). Sienkiewicz et al., (2017) shows that the tires are resistant to biodegradation, and they also withstand at the high temperatures (100°C) and low temperatures (-30°C), so their recycling is complex and requires various technologies and equipment (Sienkiewicz, M. et.al, 2017).

Due to the large amounts of the resulted rubber waste every year, their recycling is welcome and their mixing into the concrete matrix has been studied by several researchers. It was shown the advantages of the rubber recycling in the concrete matrix as well as which is the impact of the addition of the crumbled rubber to the quality of the concrete.

It is important to recycling the tires after separating the other components of their structure, each component being recycled specifically then to produce suitable products according to the composition and the structure of each of them (Girskas and Nagrockiene, 2017).

The results of the experimental studies and the literature available have shown that recycling of the rubber by incorporating into the concrete matrix can be a viable solution in the areas where the mechanical strength of the concrete is not a major concern (Gupta et al., 2017). Sienkiewicz et al. (2012) shows that adding of the crumbled rubber wastes into the concrete reduces the compressive strength, the tensile strength and the elastic modulus of the concrete, but improves the energy absorption, the abrasion resistance, the freeze-thaw resistance, and the performance at the high temperature of the concrete with crumbled rubber compared to the regular concrete.

The other possibilities for the use of the rubber wastes in buildings sector may be for the sound insulation of buildings (Bujoreanu et al., 2017; Pitre, 2000), in the asphalt to increase the elasticity and the freeze-thaw resistance (Rezaifar et al., 2016) or to produce the rubber protective rugs (Rafique, 2012). The waste tires may also be used to produce the culverts, bricks, blocks and paving slabs, acoustic panels, sidewalks, running tracks, roller compacted concrete, self-compacting concrete, high strength concrete, masonry walls (Rezaifar et al., 2016).

The literature shows that, for some specific cases, the use of the crumbled rubber in the concrete matrix for the recycling of the rubber wastes may improve some properties of the concrete such as freeze-thaw resistance, the fatigue performance, the tear resistance, the deformation capacity (Rezaifar et al., 2016) or the resistance of the concrete at the high temperatures (Layachi et al., 2016).

MATERIALS AND METHODS

Shredding of the rubber wastes

Shredding of the rubber wastes reduces the volume of used tires. The crushed rubber has applications in different areas, depending on the dimensions to which it has been shredded, or the cost of shredding. The cost of shredding increases with the need to obtain pieces as small as possible (Rafique, 2012).

For the grinding of the rubber wastes are initially used mechanical cutters, roll crushers and screw shredders. To obtain the finer particles, shear crushers and granulators are further used. The final processing of the rubber wastes should be carried out on high-temperature shredding equipment such as rotary shredders where the degradation occurs during the compression with simultaneous shear and wear (Mikulionok, 2015).

In the initial phase, the shredding of rubber wastes is made at the dimensions approximate of 7.62 x 10.16 cm. The pieces resulted are then placed in the cutters that can cut them to the sizes of 0.63 x 0.63 cm (Rafique, 2012).

Incorporating the crumbled rubber into the concrete

The crumbled rubbers are incorporated into the mortar by replacing the aggregates in different weight percentages (10, 20, and 30%). The production of these types of concrete is done for certain types of concrete matrix structures, depending on the desired properties of the concrete at the end. It is possible to call for the removal of textile pieces and the metal wires, or could be used the complete the tires, including the metal and textiles wires (Sgooba et al., 2010).

For the experiment in this paper were used only the crumbled rubbers without metal insertions.

By incorporating the rubber granules in the mortar, some mechanical and physicochemical properties of the concrete have changed. There was a decrease in the specific weight of the final product as the amount of rubber used was increased. Also, the workability of the mortar has become more difficult than in the case of conventional concrete recipes, the difficulty of mixing increasing with the size of the rubber granules. The other research in the field has also shown that it is harder to work with large or coarse rubbers crumbs than with the medium, fine or superfine rubber crumbs (Girskas and Nagrockiene, 2017).

The durability of a concrete is characterized by the ability to withstand to the water absorption. Regardless of the degree of homogeneity of the mixture, the concrete will always have waterborne voids in its mass (Sgooba et al., 2010). The lowest possible presence of voids in the concrete mass ensures a lower permeability for it. For the concrete containing rubber, the permeability is reduced as the percentage of rubber used is higher. The result is probably due to the ability of the rubber to reject water (Oikonomou and Mavridou, 2009). Also, the concrete with rubber incorporated ensures a lower weight and a lower density of the concrete (Sgooba et al., 2010).

The mechanical strength of the concrete is the unitary effort to which the concrete is subjected, as long as the material retains its properties so that the structure or construction made of that concrete is not affected in terms of stability. The mechanical strengths differ on the concrete depending on the requirements to which the concrete are subjected (Manea, 2006).

Thus, the compressive strength is defined by the relationship:

$$R_c = \frac{N}{A} \text{ [N/mm}^2\text{]}, \qquad [1]$$

where: R_c – the compressive strength; N – the compressive force; A – the area of the samples.

For the other types of the mechanical resistances this equation is similar. In the case of the torsion resistance or bending resistance, the force (N) from the fraction counter is replaced with the torsion moment or the bending moment (M), and the surface from the fraction denominator is replaced with the resistance modulus (W). The Equation will become:

$$R_T = \frac{M}{W} \quad [\text{N/mm}^2], \qquad [2]$$

where: R_T – the torsion or bending resistance; M – the torsion or bending moment; A – the resistances modulus.

The mechanical strengths of the concrete are affected by the percentage of embedded crumbed rubber from the concrete, the type of cement that was used, and the size and the texture of the crumbled rubber mixed in the mortar.

The concrete specimens for the mechanical tests

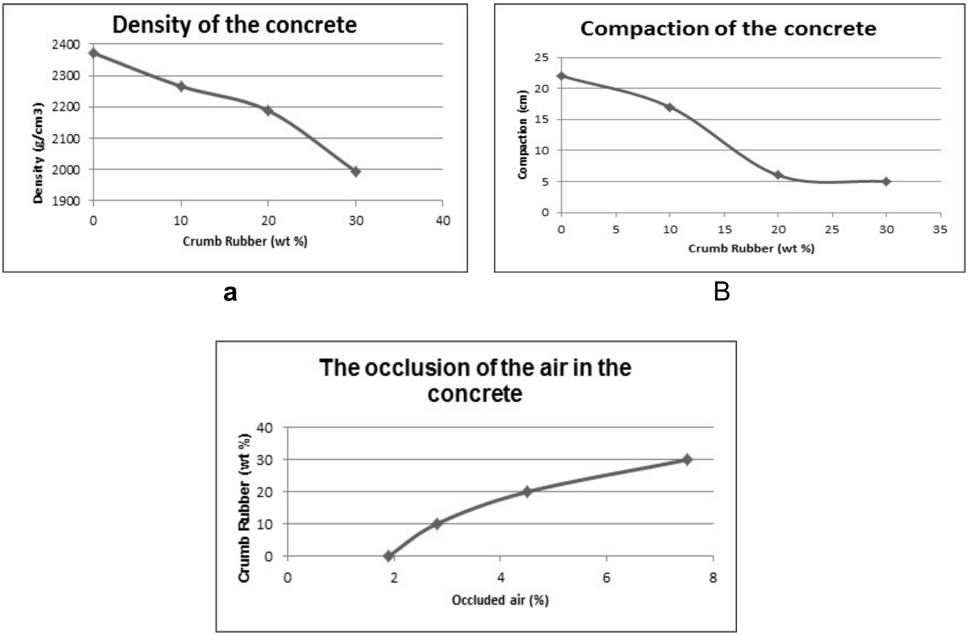
It was accomplished the concrete specimens in the cubes form with the 15 cm edge using concrete of the resistance class C25 / 30 without the addition of rubber, and specimens of the same shape and strength class with addition of crumbled rubber 10 to 20 and 30 (weight) %, that replacing a part of the fine aggregate from the concrete matrix. It has been noticed that if was adding more than 30% (by weight) of the rubber in the concrete it was is affected the workability of the concrete, their properties and also the posibilty to putting into concrete work.

The aggregates used to make the concrete have the maximum size of 16 mm. The rubber granules were shredded to have a size between 2 and 5 mm. The cement was made using a suitable mixture of water, coarse aggregates, fine aggregates, and sand. The concrete specimens were made and deposited in molds according to the practice standard for the concrete production CP 012 / 1-2007 and were kept under suitable temperature and humidity conditions for the 7 days and 28 days. The mechanical determinations were performed according to the same standard of practice, CP 012 / 1-2007.

The physical and the mechanical tests of the specimens containing crumbled rubber

The specific parameters of the concrete workability (the compaction and the air occlusion) and the mechanical compressive strengths of the concrete specimens with and without rubber addition were studied in the laboratory (figure 1.a, b, c). The compressive strength was determined by using a hydraulic press.

In the case of the concrete made with crumbled rubber, a constant increase in the concrete workability was observed proportional with the percentage of rubber addition that increase from 0% to 30% (wt). Another factor that can influence the workability of the mortar is the size of the used granules of the rubber.



c.

Fig. 1. *Density, compaction and occluded air in the concrete specimens with adding of the 0, 10, 20, 30 % (wt) crumb rubber*

It has been noticed that if more than 30% of the weight of the natural aggregates in the concrete is replaced with crumbled rubber, the concrete will be no longer workable and the density of the samples has decreased as the more crumbled rubber are added to the mortar.

The granulometry of the aggregates is useful to separate the aggregates based on their size and to calculate the frequency with which particles in the different classes are present in mix to getting the mortar.

Theoretically, depending on the size of the aggregates used, the aggregates mixture that was obtained has an ideal granulometric curve to which it tends, based on the mode of the preparation of the concrete and the aggregates used to made the concrete (figure 2).

To investigate whether a mixture of aggregates can be used at the practical level, it is compared the granulometric curve with the accepted intervals for that type of the recipes.

On the basis of the sieve analysis curve, it can be noticed that the concrete without rubber addition (figure 2) complies with the provisions of standard CP 012 / 1-2007; Its sieve analysis curve being located within the accepted limits.

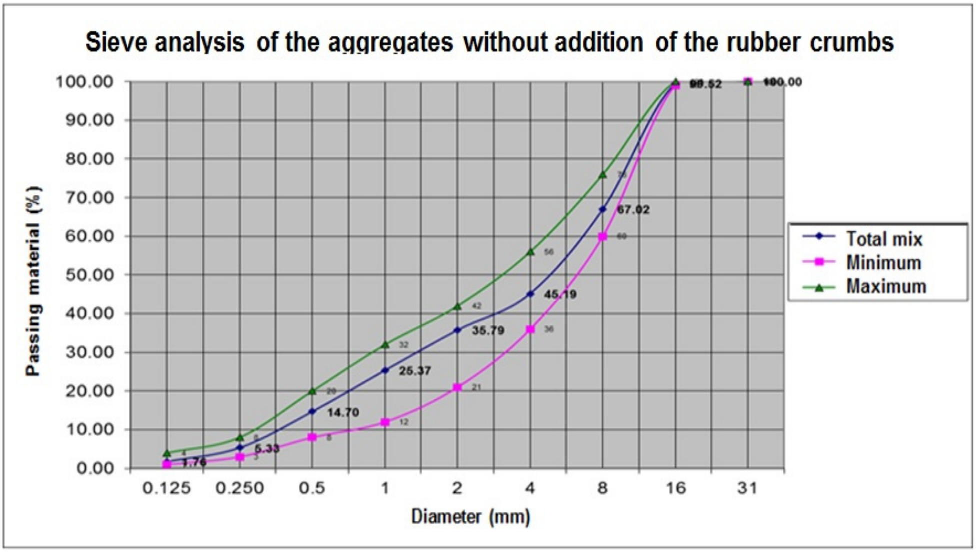


Fig. 2. *Sieve analysis of the aggregates without addition of the rubber crumbs*

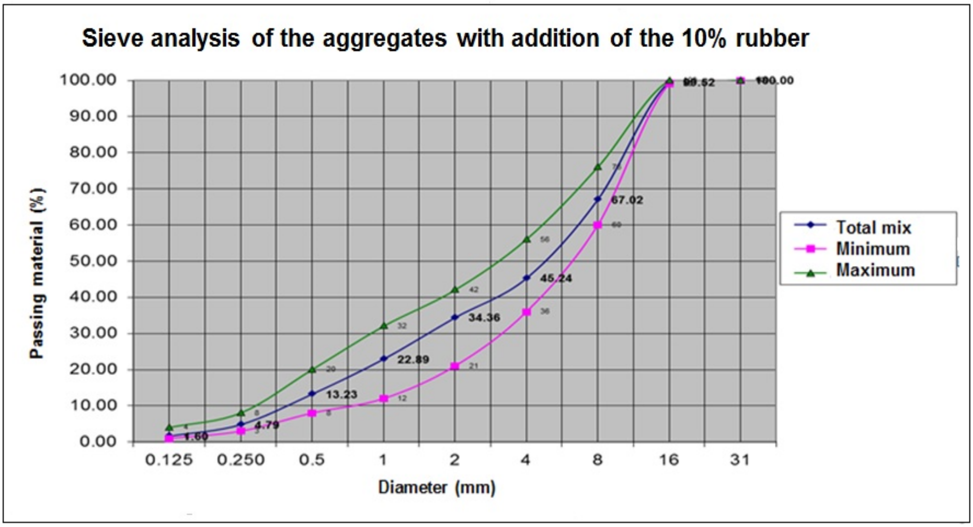


Fig. 3. *Sieve analysis of the aggregates with addition of the 10% of the rubber crumbs*

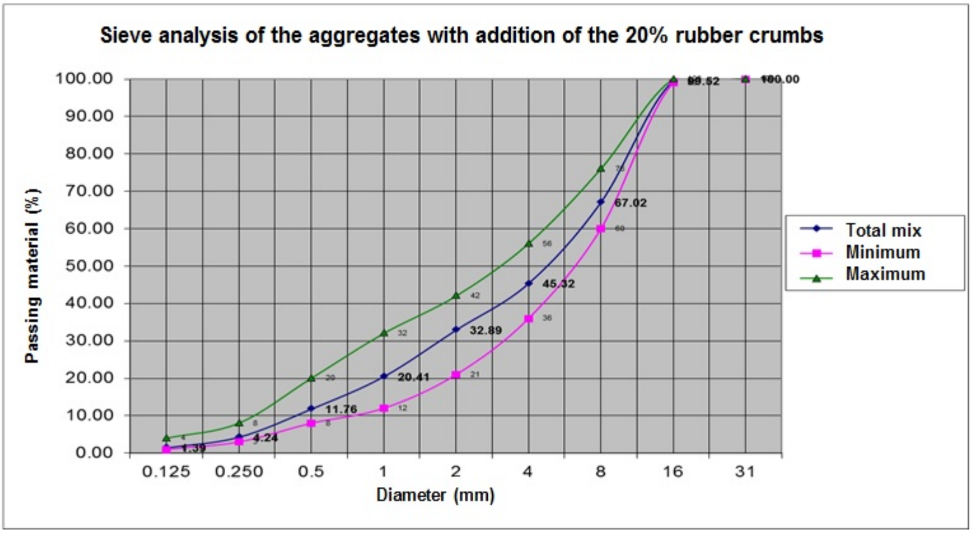


Fig. 4. *Sieve analysis of the aggregates with addition of the 20% of the rubber crumbs*

By partially replacing of the fine concrete aggregate with rubber crumbs (10, 20 and 30% by weight), the sieve analysis curve of the resulting mixture it remains within the acceptable limits (figure 3, 4, 5). This confirms that the concrete prepared by the partial replacement of the mineral aggregates with the rubber crumbs can be used for some certain types of construction.

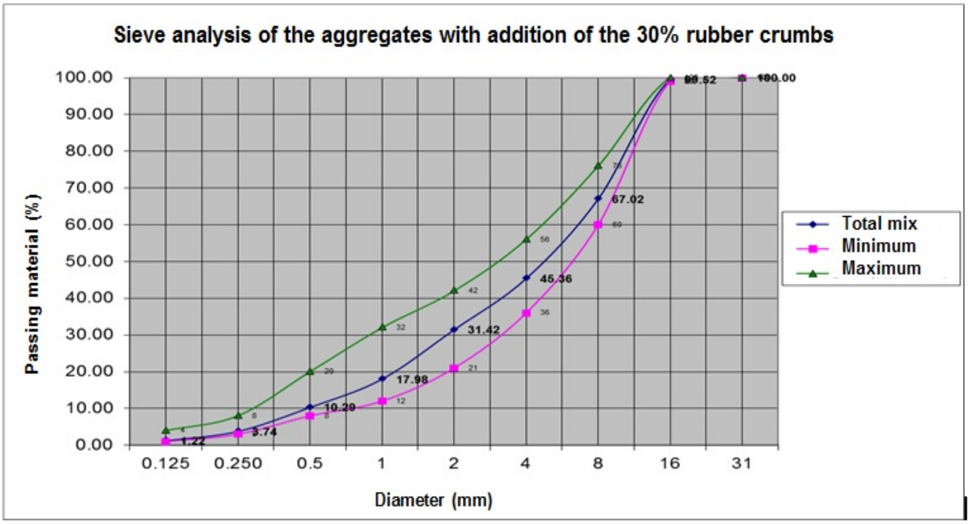


Fig. 5. *Sieve analysis of the aggregates with addition of the 30% of the rubber crumbs*

The resistance to compression of the samples (figure 6) was determined using a hydraulic press which was compressed on the side the cubic specimens with an edge of 15 cm. The samples were inserted between two slides platens and were pressed with an increasing force until the cracking or even the breaking the sides of the specimens occurred; The samples resulting after determining the compressive force have reaching a form of the hourglass.

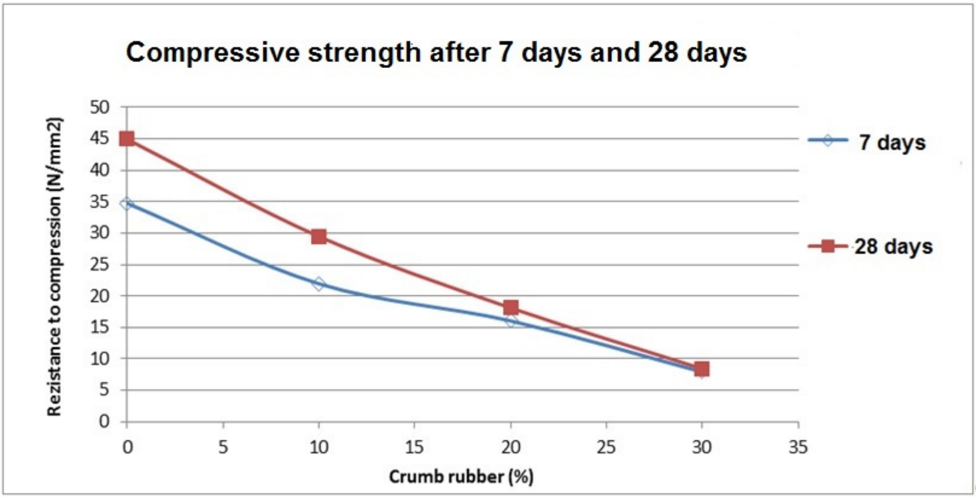


Fig. 6. *The compressive strength of the concrete samples with and without added of the rubber crumbs, after 7 days and after 28 days*

It can be noticed that the compressive strength of the specimens with rubber crumbs (figure 6.) is less influenced by the time passing than the compressive strength of the specimen that uses only mineral aggregates.

RESULTS AND DISCUSSIONS

From the sieves analysis of the aggregates, it can be noticed that the concretes in which the mineral aggregates are partially replaced with the rubber crumbs may be used for certain types of construction. Although the resistance to compression of the concrete containing rubber crumbs is lower than that of the concretes containing exclusively mineral aggregates, the resistance to compresion of the concrete with rubber crumbs is less influenced by the time. Thus, in time the specimens of the concrete made with rubber crumbs suffer less changes if they are subjected to compressive forces than the specimen made of traditional concrete. This was also emphasized by the compaction curve wich illustrating that the concrete with the addition of rubber suffers a lower compaction.

The literature shows that the tensile strength and the bending strength decrease in the case of the rubber additions to the concrete. The tests that were trying to introduce latex into the concrete matrix with rubber crumbs did not improved the mechanical properties of the concrete (Ling et al., 2009).

There are other studies is suggesting that the strength of concrete with embedded rubber may be superior to conventional concrete using certain methods of conditioning the used rubber before it is added into the mortar. Sodium hydroxide (NaOH) for example is proven to be effective for conditioning the rubber tires by improving the bond between the rubber particles and concrete paste (Al-Nasra and Torbica, 2013).

Rezaifar et al., (2016) proposes the use of the metakaolin in the concrete matrix, where the rubber crumbs replace partially the aggregates, and the metakaolin replaces partially the cement in the mortar mixture. He concluded that the optimal mix is about 3.3 vol.% for the sand replacing by the rubber crumbs and 19.5 vol.% for the cement replaced by the metakaolin.

The studies show that the modified concrete samples with the rubber crumbed from wastes provide a satisfactory hardness and an effective reduction in brittleness risk, which is beneficial to the materials which are subjected to the impact and for the dynamic tests (Xiaovei et al., 2017).

Mendis et al. 2017 shows that in addition to the compressive strength, the crumbed rubber concrete also offers an increased capacity of energy absorption that could be advantageous into the designing of the structures that are subjected to the dynamic loading and to the impact. Recently, the research in Australia has investigated the performance of the crumbed rubber concrete columns under seismic loads, and has shown that the crumbed rubber concrete use will increases the damping ratio of energy dissipation (Youssf et al., 2015). In the same study, Mendis et al. 2017, shows that because of the lack of the design rules it is hard to accept to use the crumbed rubber in the structure of the construction.

And other researchers have also shown that the use of the crumbed rubber in the concrete products improves the behaviour at the freeze-thaw cycles, the fatigue performance, the brittleness index and the kinetic of fracture processes, as well as the flexural impact strength, the deformation ability, and the explosive spalling resistance. However, the use of crumbed rubber in the concrete and the other cement-based products has also some important disadvantages such as the reducing of the mechanical properties of the concrete (Rezaifar et al., 2016).

It is also worth to mention that the inclusion of the recycled rubber crumbs in the concrete can reduce the risk of explosion of the concrete at elevated temperatures (Layachi et al., 2016).

CONCLUSIONS

From the available data from the present work, as well as from the literature, it can be noticed that the use of the crumbed rubber in the concrete has both, some advantages and also some disadvantages. One of an important advantage is the recycling of the rubber wastes, which can generate some specific environmental problems, but also the replacement of mineral aggregates that are a natural resource. The qualities that the embedded crumbed rubber it gives to the concrete could not to be neglected. Thus, the concrete with the embedded crumbed rubber has increased the fire resistance; it is respond better to the successive freeze-thaw cycles, it is increased the energy absorption capacity of the concrete, the flexural strength and the performance under the seismic loads. At the same time, the mechanical properties of the concrete with crumbed rubber are reduced, compared to the traditional concrete produced with the mineral agglomerates and drops even more, as the amount of the embedded rubber in concrete is increasing.

Whereas there are no specific normative and the standards for designing for the concrete with crumb rubber, the possibility to use it in the construction sector is now difficult to do.

The extensive research in the field, including the blending of the concretes with crumbed rubber with other substances used as binders for a better homogenization of the mixing paste are expected in the near future

Acknowledgments

Thanks to the Laboratory for Analysis and Testing in Construction from Simeria Veche - S.C. POMPONIO S.R.L from Simeria Veche, Hunedoara County, for the help with tests for the concrete samples.

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STUDIA UBB AMBIENTUM, LXII, 1, 2017, pp. 75-82
(RECOMMENDED CITATION)
DOI:10.24193/subbambientum.2017.1.06

DETERMINATION OF THE CHLORINATED PESTICIDES RESIDUES IN SOILS TREATED WITH MODERN PESTICIDES

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ABSTRACT. The potential for pesticide soil contamination is a worldwide concern, due to the intensive use of organochlorine compounds. The use of pesticides has offered significant economic benefits by increasing the production of food and preventing different form of diseases, therefore their use has affected not only the health of human population, but the environment as well. Organochlorine pesticides like Aldrin, Chlordane, DDT, Dieldrin, Endrin and Heptachlor have been banned after the 2001 Stockholm convention. That is why many jurisdictions try to control human exposure by specifying the soil's maximum allowable concentration. 12 soil samples were collected from different parts of Romania, aiming to evaluate the organochlorine concentration in order to study if the soils have been treated with this type of pesticides. Each sample was dried, extracted with hexane by ultrasonication and analyzed by GC-ECD. The results of the analyzed samples showed low concentrations, ranging between 28.36 and 73.19 µg/kg. The most identified compounds were Alpha HCH, Beta HCH, Heptachlor, Aldrin, Heptaclhor epoxide, trans-Clordane, Endosulfan I, 4,4` DDE and Dieldrin+Endrin.

Key words: *Organochlorine pesticides, modern agriculture, soil*

INTRODUCTION

Organochlorine pesticides (OCPs) are chemical compounds which have been widely used in agriculture for controlling the pests and vector borne diseases (Abhilash and Singh, 2009; Zhang et al., 2011). After the beginning of the 20th century pesticides have been widely spread having traces in all areas of the environment. The use of pesticides has offered the world significant economic benefits by enhancing the production and yield of food and fibers and the prevention of different diseases, evidence suggest that their use has adversely affected the health of human populations and the environment. They are liposoluble compounds and are capable of bioaccumulating in the fatty parts of biota such as breast milk, blood and fatty tissues (William et al., 2008). As a result, human beings are exposed to the effects of these micropollutants by eating foods in contact with contaminated soil or water (Belta et al., 2006; Raposo and Re-Poppi, 2007). These pesticides not only cause serious diseases in humans but are also highly toxic to most aquatic life (Aiyesanmi and Idowu, 2012) and soil microflora (Megharaj, 2002). They represent the most hazardous class of pesticides. OCPs are very stable compounds and their half-lives can range from a few months to several years in some cases decades (Cremlyn, 1991 cited by Yadav et al., 2015). It has been estimated that the degradation of DDT in soil ranges from 4 to 30 years, while other chlorinated OCPs may remain stable for many years after their use (Afful et al., 2010). OCPs have been used worldwide for over 60 years in different countries around the world. Due to the widespread use of agricultural and residential pesticides, the potential for pesticide soil contamination is a worldwide concern (Cheng et al., 2008). Thus, at least 54 nations have promulgated guidance values to specify the maximum allowable concentration of pesticides in soils. In 2001 under the Stockholm Convention the use of eight OCPs such as aldrin, hexachlorobenzene, chlordane, dieldrin, endrin, heptachlor, mirex, toxaphene) were eliminated because they showed persistence, toxicity and capability of long-range transport. After the Stockholm Convention, many of the organochlorines had been banned and restricted in several countries.

The aim of this study is to evaluate the OCPs concentration in different type of soils treated with modern pesticides in order to evaluate the degree of contamination with these compounds. The study was focused on different regions of Romania.

MATERIAL AND METHODS

Sampling area

The samples were obtained from 12 points from the country, from Transylvania to the southern part of Romania. The sampling points (P1-P12) are presented in the figure 1 and the locations that corresponded to each point are presented in table 1. The samples were obtained from a vegetation-free soil using a shovel to dig about 15 centimeters to avoid getting surface soil that might be contaminated with dust and other suspension particles.

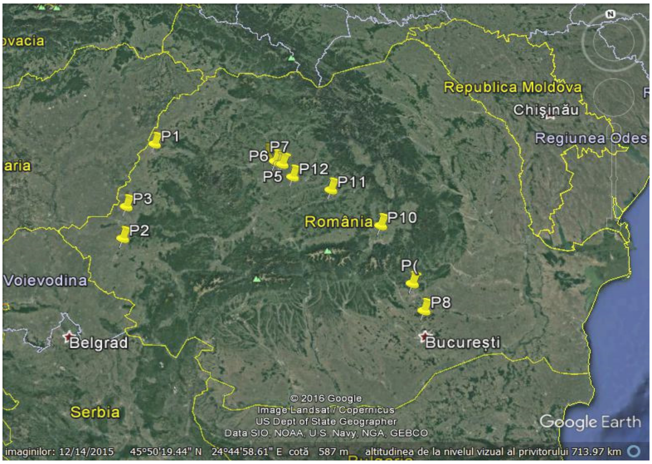

Fig. 1. *The map of the sampling points*

Table 1. *Sampling point and code of the samples made in Google Earth*

Sample cod	Sampling point	County	Coordonates
P1	Oradea, Airport	Bihor	47°1’46.96"N 21°53’37.29"E
P2	Giarmata,	Timiş	45°50’49.98"N 21°18’12.05"E
P3	Arad, entrance from Oradea	Arad	46°14’46.86"N 21°22’27.28"E
P4	Cojocna	Cluj	46°45’12.34"N 23°48’56.63"E
P5	Ceanu Mare	Cluj	46°40’15.79"N 23°57’5.61"E
P6	Valea Largă, entrance from Cluj	Mureş	46°37’50.92"N 24°1’38.14"E
P7	Valea Largă, central	Mureş	46°37’26.17"N 24°3’50.68"E
P8	Săftica, Ilfov	Ilfov	44°37’46.34"N 26°4’13.77"E
P9	Ploieşti, entrance from Braşov	Prahova	44°58’18.51"N 25°56’58.10"E
P10	Braşov, exit to Sighişoara	Brașov	45°43’20.81"N 25°34’39.55"E
P11	Albești, Sighișoara	Mureș	46°14’8.49"N 24°50’3.38"E
P12	Iernut, entrance from Luduș	Mureş	46°26’58.06"N 24°13’2.77"E

Sample processing

Each sample was dried at the room temperature for at least 10 hours. After that, the samples were slowly crushed using a mortar with pestle. 30 grams of the sample were weighted and transferred into an Erlenmeyer flask of 200 mL. The samples were extracted with 40 mL of hexane by ultrasonication for 15 minutes at the room temperature. After decantation, the supernatant was removed, filtered through a PVDF sample filter with pore size of 0.45 μm (Merck Milipore) and evaporated to dryness at the room temperature. Subsequent the residue was redisolved in 2 mL hexane and analyzed by GC-ECD under the conditions described below.

Analysis conditions

Analysis of OCPs was performed using a Thermo Trace Focus GC gas chromatograph equipped with an electron capture detector (ECD) (Thermo Electron Corporation). Nitrogen of high purity at a constant flow rate of 2 mL min^{-1} was used as carrier gas. The inlet temperature was set at 320 ºC and the injection was made in splitless mode. The temperature of ECD detector was set at 320°C and the auxiliary gas (nitrogen) was set at 40 mL min^{-1}.

For the separation of the tested compounds a TRB-35 column (30 x 0.25 mm, 0.25 μm film thickness) purchased from Teknokroma, Spain was used. The separation of compounds was performed with a gradient temperature program, starting by heating of 15ºC min^{-1} from 180ºC to 250ºC, and from 250ºC to 320ºC, 3ºC min^{-1}, 5 minutes final hold time.

The data acquisition was performed using the Chrom-Card software. The identification of the compounds was done based on the retention time of a standard mixture of 20 OCPs, purchased from Restek. The chromatogram of the tested compounds is presented in figure 2.

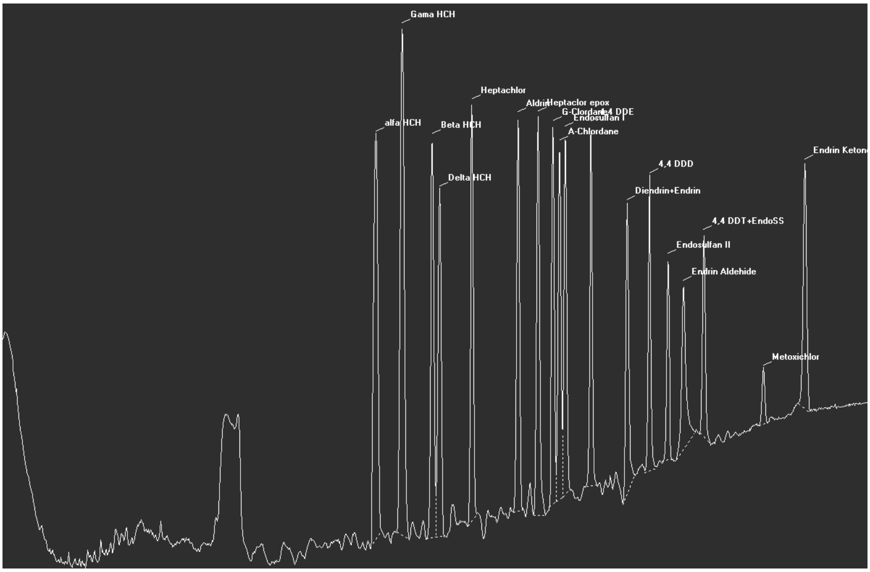

Fig. 2. *The chromatogram of a standard mixture in concentration of 0.2 ppm*

RESULTS AND DISCUSSIONS

The analysis of the target compounds were performed using the method described above. The performances of the optimized method are presented in the table 2.

As can be seen in table 2 the method has a good linearity, repeatability and a limit of quantification able to quantify the compounds at the concentration level expected in the real soil samples. Thus, the method can be applied for the analysis of real soil sample.

Table 2. *The performance of the optimized GC-ECD method*

Compounds	Calibration curve equations	Correlation coefficients	Repeatability RSD %	LOQs mg kg^{-1}
Alpha HCH	y = 2E+06x + 165438	1	0.42	0.90
Gamma HCH	y = 2E+06x + 22938	0.996	0.76	1.29
Beta HCH	y = 2E+06x + 49276	0.9297	2.39	1.94
Delta HCH	y = 1E+06x + 86323	0.9325	1.18	1.42
Heptachlor	y = 1E+06x + 287363	0.9971	7.01	1.79
Aldrin	y = 2E+06x - 114664	0.9624	5.27	1.81
Heptaclor epoxide	y = 2E+06x + 87527	0.9564	4.06	1.28
trans-Chlordane	y = 1E+06x + 101095	0.94	5.43	1.51
cis-Chlordane	y = 899744x + 163458	0.9725	0.77	1.81
Endosulfan I	y = 985702x + 97260	0.9502	6.06	1.94
4,4` DDE	y = 1E+06x + 109135	0.9079	7.77	1.80
Dieldrin+Endrin	y = 2E+06x - 25722	0.9543	5.60	2.46
4,4` DDD	y = 1E+06x + 48338	0.9996	1.27	2.15
Endosulfan II	y = 671002x + 6225,5	0.9948	6.89	2.71
Endrin Aldehide	y = 388136x + 65817	0.9132	9.53	2.85
4,4` DDT+EndoSS	y = 742300x + 33344	0.9915	1.56	2.75
Metoxichlor	y = 175739x + 6111	0.9574	1.43	2.56
Endrin Ketone	y = 1E+06x + 28014	0.9885	1.99	3.25

The results of the analyzed soil samples showed that the concentrations of OCPs are low varying between 28.36 and 73.19 µg kg^{-1} (table 3). A total of 20 OCPs were identified with concentration varying in the range of not detected to few micrograms per kilogram soil. The highest concentrations were detected in the areas near Cluj-Napoca (P4, P5) and Târgu-Mures (P10, P12), meaning that in these areas OCPs were widely used in the past for agriculture. The lowest detected concentration was in sample P1, sample collected near Oradea, Bihor County. On the other hand, the highest concentration was found in sample P10, collected near Iernut, Mureş County which has a long history in the cultivation of industrial plants. The most identified OCPs were Alpha HCH, Beta HCH, Heptachlor, Aldrin, Heptaclhor epoxide, trans-Clordane, Endosulfan I, 4,4` DDE and Dieldrin+Endrin.

The most prevalence of alpha-HCH isomer may lead to the conclusion that technical HCH (60–70% alpha-HCH, 5–12% beta-HCH and 10–12% gamma-HCH), was used in agricultural practices in the majority of locations instead of pure lindane (gamma-HCH). Moreover high incidence of 4,4` DDE instead of 4,4` DDD and 4,4` DDT may suggest that it originated from old usage of this insecticide in agriculture (Ene et al., 2012).

By comparing the obtained data with the reference values for traces of chemical elements in soils (O.M. No. 756/03.11.1997) it can be observed that the only Alpha HCH and Beta HCH concentrations exceed the normal values stipulated by legislation. For Heptachlor, Chlordane, 4,4` DDE, 4,4` DDD and 4,4` DDT the concentrations are very low or not detected.

Table 3. *The concentrations of OCPs in the analyzed soil samples*

Compounds	Concentration (μg kg^{-1} dry soil)													
	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	NV	AL
Alpha HCH	2.96	nd	3.07	3.44	3.53	3.83	4.19	3.91	3.50	4.14	7.32	1.01	<2	100
Gamma HCH	nd	1.64	nd	nd	1.27	nd	1.02	nd	nd	nd	1.23	nd	<0.1	50
Beta HCH	4.14	1.83	3.57	3.91	7.25	3.00	6.24	8.67	4.12	4.28	8.40	4.16	<1	20
Delta HCH	nd	nd	nd	nd	2.82	nd	nd	3.18	nd	nd	3.19	8.11	-	-
Heptachlor	nd	14.90	7.24	1.75	8.47	5.15	1.79	1.89	11.79	10.89	nd	nd	-	-
Aldrin	2.38	2.87	1.13	5.51	9.51	2.62	3.75	3.02	3.38	3.24	3.01	16.10	-	-
Heptaclor epoxide	4.75	5.30	5.99	5.93	6.75	5.00	6.29	7.49	6.00	7.37	7.28	2.26	-	-
trans-Chlordane	4.51	5.57	5.75	6.90	5.33	4.57	6.17	6.89	6.03	7.72	6.68	7.74	-	-
cis-Chlordane	1.19	4.65	3.74	nd	nd	nd	nd	nd	nd	5.58	nd	10.55	-	-
Endosulfan I	nd	nd	1.21	8.74	2.37	2.59	2.01	2.11	2.27	2.24	1.80	9.72	-	-
4,4` DDE	nd	nd	1.13	6.04	1.14	1.23	1.91	1.60	nd	1.54	2.00	2.95	<50	500
Dieldrin+Endrin	7.15	6.84	7.76	5.27	8.11	7.26	8.51	nd	8.39	nd	14.37	1.71	-	
4,4` DDD	nd	nd	nd	3.87	nd	nd	nd	1.31	nd	nd	nd	3.11	<50	500
Endosulfan II	nd	nd	nd	nd	nd	nd	nd	1.34	nd	nd	nd	2.73	-	-
Endrin Aldehide	nd	nd	1.14	2.39	1.81	nd	nd	4.02	nd	nd	nd	nd	-	-
4,4` DDT+EndoS	nd	1.29	nd	nd	nd	2.36	nd	nd	nd	nd	nd	1.98	<50	500
Metoxichlor	1.29	1.38	nd	1.09	nd	nd	nd	1.57	1.76	2.31	3.85	1.06	-	-
Endrin Ketone	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	P12sigh	nd	-	-
Total OCPs	28.37	46.27	41.72	54.83	58.37	37.59	41.88	47.01	47.25	49.30	7.32	73.19	-	-

nd- not detected, NV-normal value, AL – alert level established by O.M. No. 756/03.11.1997

CONCLUSIONS

The results of the performed studies shows that in all sampling sites the concentration of OCPs are low and do not exceed the alert level and intervention threshold in the sensitive (agricultural/residential) area.

These concentrations are the results of their use in the past and not in this time.

The prevalence of alpha-HCH isomer may lead to the conclusion that technical HCH was used in agricultural practices in the majority of locations instead of pure gamma-HCH.

High incidence of 4,4` DDE instead of 4,4` DDD and 4,4` DDT may suggest that it originated from old usage of this insecticide in agriculture.

Acknowledgements

The authors thanks to the Faculty of Environmental Science and Engineering, Babeș-Bolyai University, for the technical support given in this research.

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STUDIA UBB AMBIENTUM, LXII, 1, 2017, pp. 83-92
(RECOMMENDED CITATION)
DOI:10.24193/subbambientum.2017.1.07

STRATEGIC ASSESSMENT OF THE IMPACT OF INDUSTRIAL AND ECONOMIC ACTIVITIES IN THE DEVA-HUNEDOARA CONURBATION USING THE RIAM METHOD

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ABSTRACT. Deva-Hunedoara conurbation is a bipolar structure located in central-western Romania composed of 49 settlements. It is located in the center of Hunedoara County. The long history of industrial activities in the area resulted in an abundance of environmental impacts which has significant negative consequences on the local population. Intense industrial activity, regarded as the base for the urban development of the conurbation, dates back to the 1840's when the first steel mill was constructed in the region.

The main sources of environmental impact are represented by the decaying industrial centres of Hunedoara, Simeria and Călan and the newly developed industrial sites located on the major transport networks. A secondary source of environmental impact is represented by the various small enterprises.

Coupled with various other human activities and with the general state of the environment, the impact generated by industry and other economic activities represents a great threat to overall development of the conurbation.

In assessing the environmental impact on within the conurbation we proposed the use of the RIAM method with a modified matrix which is best suited for our area of study. With this matrix we assessed the environmental impact of industrial and commercial areas, transportation and utility systems and several other aspects related to human activities (health and safety, unemployment, human density, etc.). For the final interpretation of the environmental impact we used the IDWIM - Inverse Distance Weight Interpolation Method to generate maps of impact.

Key words: *conurbation, RIAM, matrix, environmental impact, industrial area.*

INTRODUCTION

Environmental impact assessment can be performed by multiple methods and techniques derived from numerous scientific disciplines. Among the most used methods are the matrices. The major use of matrices is to indicate cause and effect by listing activities along the horizontal axis and environmental parameters along the vertical axis. The simplest matrices use a single mark to show whether an impact is predicted or not. However it is easy to increase the information level by changing the size of the mark to indicate scale, or by using a variety of symbols to indicate different attributes of the impact. The greatest drawback of matrices is that they can only effectively illustrate primary impacts.

One of the cheapest, fast and well tested matrices is Leopold’s matrix. This matrix creates the connection between environmental factors and human activities and ensures that no type of user impact has been omitted. Assessment of magnitude and importance of impacts involves partially subjective judgments, which diminishes the accuracy of knowing those beneficial and adverse impacts (Leopold et al., 1971). The Leopold matrix was conceived by geologist Luna B. Leopold and his colleagues in 1971, as a response to the US Environmental Policy Act of 1969, which didn’t give clear instructions to the Federal Government agencies for preparing an impact report or for examining the environmental effects of the projects that an agency plans. According to the Leopold matrix method, EIA should consist of three basic elements: listing of the effects on the environment; evaluation of the importance of each of listed effects; a summary evaluation, which is a combination of magnitude and importance estimates.

The best adaptation of Leopold’s matrix is the RIAM method (Rapid Impact Assessment Matrix) developed by the Pastakia and Jensen. The RIAM method essentially preserves Leopold’s matrix structure but offers the possibility of restricting the number of analyzed components. RIAM is a matrix method developed to bring subjective judgments in a transparent way into the EIA process. The method was developed by Cristopher Pastakia (Pastakia and Jensen, 1998) at the end of the 1990s, and since then it has been widely tested in many assessment situations and case studies. RIAM is based on the standard definition of concepts used in the EIA process. With the help of the method different impacts and their significance can be evaluated using commonly defined criteria, each of which has its own ordinal scales. The results of the assessment are placed on a simple matrix, which leaves permanent and reasoned records about the judgements made. In the original RIAM method five evaluation criteria are used, namely impact importance (A1), magnitude (A2), permanence (B1), reversibility (B2) and cumulatively (B3) (Pastakia, 1998).

METHODOLOGY AND RESEARCH AREA

Out of the existing industrial and economic activities in Deva-Hunedoara conurbation, the current paper analyses only the most important and significant components with RIAM – Rapid Impact Assessment Matrix.

RIAM methodology applied in this study complements earlier stages (field research) of the impact assessment enabling a broader approach in the context of human pressures on the environment. In this context, environmental impact assessment is seen as a procedure designed to ensure that potential significant environmental impacts are assessed satisfactory and are considered in the planning, design, approval and implementation of all relevant types of human activities (Glasson et al., 1994).

The adaptation the method and matrix's components were performed taking into account the environmental specificities of the studied territory and their anthropogenic significance. The evaluation is based on official information and detailed observations made in the field, which allows an increase in the objectivity of the assessment itself.

As shown in table 1 the considered economic activities mainly relate to: health, transport, utility networks, population density, waste management and industrial areas. Depending on the specificity of each of them, these activities cause various impacts, which determine that in some areas the presence of economic activities is evident, while in other less significant. For example, on industrial sites, activities have a more obvious impact compared with transport activities.

Table 1. *Analyzed components*

Economical and Operational Components				
Human Health and Safety	Unemployment Rate	Tourism	Population Density	Waste Storage
Transport Networks	Utility Networks	Residential Areas	Commercial Areas	Industrial Areas

Table 2. *Classification and description of categories of environmental impact based on assessment scores*

Environmental Score	Impact Categories	Category Description
over +101	+E	Major Positive Changes / Impacts
+76 la +100	+D	Significant Positive Changes / Impacts
+51 la +75	+C	Moderate Positive Changes / Impacts
+26 la +50	+B	Positive Changes / Impacts
+1 la +25	+A	Slightly Positive Changes / Impacts
0	N	Lack Change of the Status Quo / Not Applicable
-1 la –25	-A	Slightly Negative Changes / Impacts
-26 la –50	-B	Negative Changes / Impacts
-51 la –75	-C	Moderate Negative Changes / Impacts
-76 la –100	-D	Significant Negative Changes / Impacts
under -101	-E	Major Negative Changes / Impacts

In order to determine the environmental impact of each component analyzed, the fallowing formulas are used:

$$(A1) \times (A2) = (At) \quad (1);$$
$$(B1) + (B2) + (B3) = (Bt) \quad (2);$$
$$(At) \times (Bt) = (SE) \quad (3);$$ where SE is total evaluation score.

Finally, based on the evaluation scores and notes obtained (factorial and total) impact categories are created (table 2).

Graphical representation of impacts (sectorial and general) was done using ArcGIS 10 software, specifically with IDWIM - Inverse Distance Weight Interpolation Method. The method is based on the principle that the magnitude of the impact is directly proportional to the source location of impact. This method literally takes the concept of spatial autocorrelation, based on the presumption that the more a standard point is closer to the place to be determined, the value to be determined will be closer to standard point value (IDW - Spatial Analyst ArcGIS Resource Center).

Also, the IDW method determines individual values for each cell using a point system whose "weight" and role in the interpolation varies linearly starting from a set of determined point values. The values for each cell are estimated from the average value of the sampling points in the vicinity of each cell (Lu and Wong, 2008; Shougeng et al., 2013; Mueller et al., 2004). Because this method is based on the average values of sample points and the distance between them, the result cannot include values greater than the maximum or lower than the minimum.

This method is best suited when it is applied to a dense network of points, as is our case with 49 locations distributed over 420 square km. In order to reach objective results based on existing methodology we used a formula for weighting locations based on their rank in the settlement system of the conurbation. The final impact score (FIC) resulted after the application of the formula:

$$FIC = SE \times (10-R/10);$$

where: SE = impact score; R = settlement rank; 10 = constant

Deva - Hunedoara conurbation is a bipolar structure located in central - western Romania. In the county of Hunedoara the conurbation is located at the confluence of Cerna and Mureş rivers, at the contact the four major geographical units: in the north Apuseni Mountains with subdivision Metaliferi Mountains, in the west Poiana Ruscă Mountains, in the south the Haţegului Depression and in the east the Orăştiei hills (Dobrei, 2013). Deva - Hunedoara conurbation is formed by the union of 49 settlements, 4 towns and 45 villages (table 3).

Table 3. *Statistical data of Deva-Hunedoara conurbation*

Administrative Unit	Number of Settlements	Population in 2002	Administrative Surface (sq. km)	General Density (inh. /sq. km)
Deva	5	69257	61.85	1119.75
Hunedoara	6	71257	104.05	684.83
Simeria	7	13895	48.59	285.96
Călan	13	13030	93.54	139.22
Băcia	4	1797	29.04	61.88
Peştişu Mic	9	1290	49.95	25.82
Cârjiţi	5	798	45.82	17.41
Total	49	171324	432.84	395.81

From a hierarchical point of view the top position is occupied by Deva, Hunedoara occupies the second place, Simeria and Călan share the 3rd position while the remainder of 45 settlements are spread out over another 4 ranks. Given the high number of urban settlements in the area and considering the fact that most economic and industrial activities are located in urban areas we have decided to also apply RIAM to the urban areas. In doing this we divided each of the 4 urban settlements in 5 zones with similar characteristics and analyzed each separately.

RESULTS

As expected, the vast majority of results are located in the negative scale (47 out of 49) (table 4). This is due to intense urbanization and industrialization of the area which created intense anthropogenic pressure on the analyzed components. The lowest score is recorded in Călan (-86) while the only two positive results are registered in Cîrjţi and Mânerău (+2). Major deficiencies in Waste Storage, Utility and Transport Networks, high Unemployment Rate, abandoned or poorly structured industrial areas are the main causes of the high negative impact scores.

The graphical representation from figure 1 reveals in a clear and suggestive manner the distribution of the environmental impact in the conurbation. We observe a clear clustering: significant negative, negative and moderate negative results tend to cluster along the Călan – Hunedoara – Peştişu Mare – Cristur – Deva alignment, slightly negative and slightly positive results on the other hand tend to occupy the western and eastern (rural) parts of the territory.

Clustering of the major negative impacts in the central of the conurbation is a consequence of the positioning of major economic, industrial and transportation activities along the main lines of force of the territory.

Comparing the results obtained for each of the 4 urban centers, shown in table 5 and in figures 2, 3, 4 and 5 we conclude the fallowing: in the central area/CBD of each city we encountered numerous and varied activities, thus the varied scores from -32 to -1; on average environmental impact in house residential areas is lower than in apartment residential areas; the lowest impacts are recorded in the ecological/ recreational areas (from -9 to +2) do to strict control of activities and low human density; in the dedicated industrial/commercial areas we have registered the biggest impact scores (-7 to -33); in Deva and Simeria the transport activities have the biggest impact while in Călan and Hunedoara the biggest impact is generated by the steel industry.

Table 4. *RIAM method - Economical and Operational Components*

Name	Impact Score	Impact Class	Name	Impact Score	Impact Class
Deva	-69	-C	Mânerău	+2	+A
Hunedoara	-57	-C	Nădăştia de Jos	-6	-A
Simeria	-56	-C	Nădăştia Sus	-6	-A
Călan	-86	-D	Nandru	-10	-A
Almaşul Mic	-12	-A	Ohaba Streiului	-8	-A

Name	Impact Score	Impact Class	Name	Impact Score	Impact Class
Almaşul Sec	-14	-A	Peştişu Mare	-31	-B
Archia	-3	-A	Peştişu Mic	-9	-A
Băcia	-3	-A	Petreni	-8	-A
Bârcea Mare	-23	-A	Popeşti	-6	-A
Bârcea Mică	-19	-A	Răcăştia	-17	-A
Batiz	-11	-A	Sâncrai	-9	-A
Boş	-10	-A	Sântămăria de Piatră	-5	-A
Călanu Mic	-16	-A	Sântandrei	-12	-A
Cârjiţi	+2	+A	Sântuhalm	-26	-B
Cărpiniş	-8	-A	Săuleşti	-17	-A
Chergheş	-8	-A	Simeria Veche	-26	-A
Ciulpăz	-3	-A	Strei	-5	-A
Cozia	-12	-A	Strei-Săcel	-6	-A
Cristur	-11	-A	Streisângeorgiu	-10	-A
Cutin	-10	-A	Tâmpa	-22	-A
Dumbrava	-6	-A	Totia	-3	-A
Grid	-7	-A	Uroi	-10	-A
Groş	-6	-A	Valea Nandrului	-9	-A
Hăşdat	-12	-A	Valea Sângeorgiului	-8	-A
Josani	-9	-A			

Table 5. *RIAM - Economical and Operational Components in urban areas*

	Deva		Hunedoara		Simeria		Călan	
	impact score	impact class	impact score	impact class	impact score	impact class	impact score	impact class
central area/CBD	-32	-B	+1	+A	-12	-A	-20	-A
residential area (houses)	-18	-A	-5	-A	-8	-A	-16	-A
industrial/commercial area	-7	-A	-33	-B	-31	-B	-20	-A
residential area (apartments)	-10	-A	-26	-B	-7	-A	-21	-A
ecological / recreational area	-2	-A	+6	+A	+2	+A	-9	-A

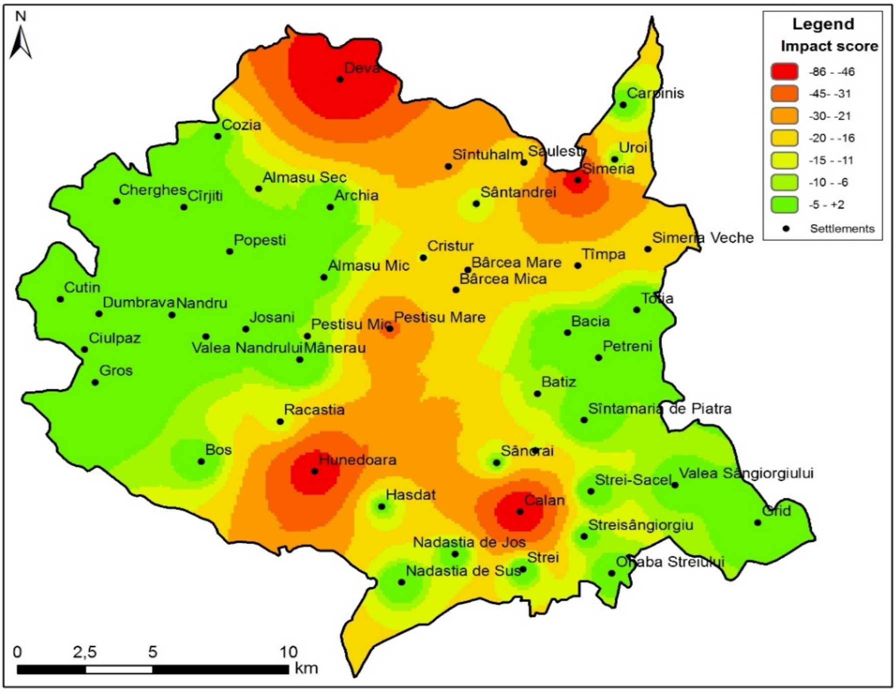

Fig. 1. *Environmental impact – IDWM – Economical and Operational Components*

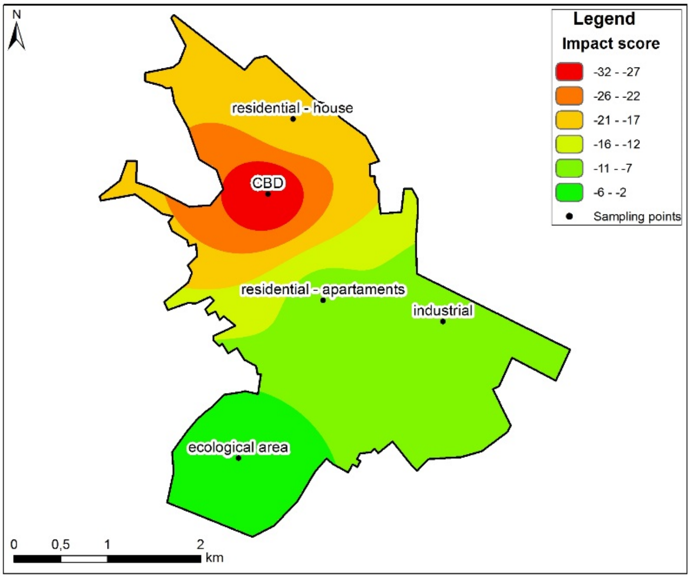

Fig. 2. *Environmental impact – IDWM – Economical and Operational Components in Deva*

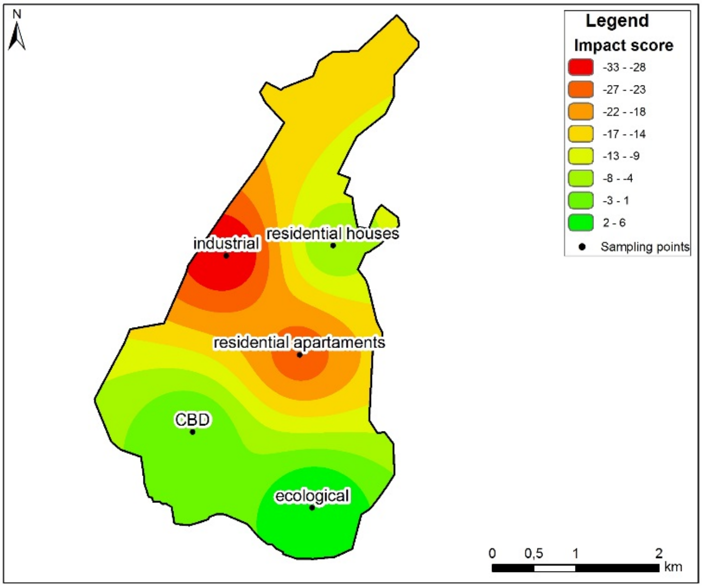

Fig. 3. *Environmental impact – IDWM – Economical and Operational Components in Hunedoara*

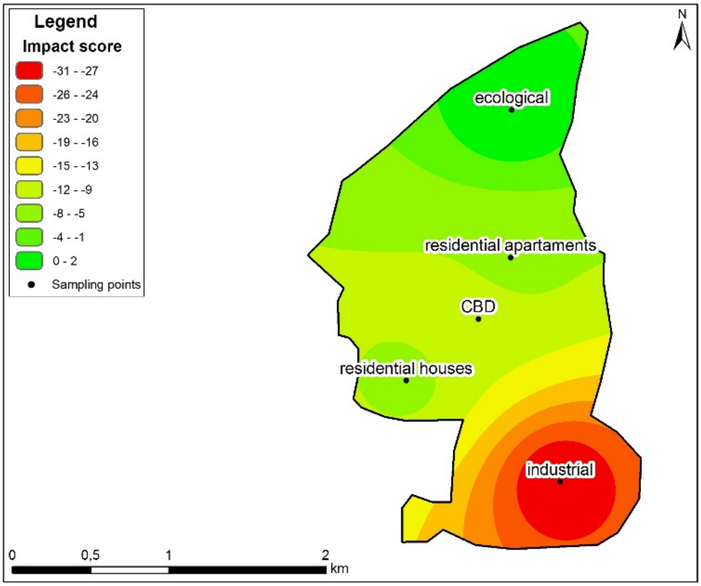

Fig. 4. *Environmental impact – IDWM – Economical and Operational Components in Simeria*

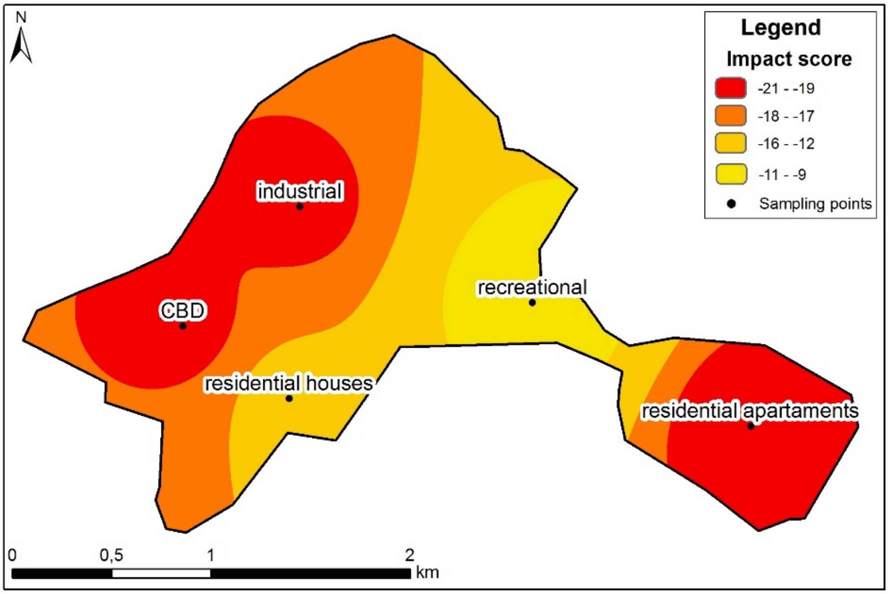

Fig. 5. *Environmental impact – IDWM – Economical and Operational Components in Călan*

CONCLUSIONS

RIAM and IDWM applied as the last stage of the Environmental Impact Assessment study generates satisfactory results given that the prior stages (fieldwork, documentation, physical-chemical analyses) are conducted with responsibility and precision.

The flexibility offered by RIAM in choosing the components analyzed allows this method to be successfully applied to multiple areas of study. In our case it proved to be the ideal method combining the authors knowledge of the area with data gathered from local and regional authorities. The method was easily and quickly adapted to the area's particularities.

The graphic representation performed with IDWM further enhanced the results obtained with RIAM by adding weight to the impact point. Maps created with this method are suggestive and easily understandable.

The limitations of the method are well known and discussed and refer to the subjectivity of the person applying the method. We consider that the authors meticulous and varied information gathering process combined with some of the results being validated by local experts created a high degree of subjectivity in this study.

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STUDIA UBB AMBIENTUM, LXII, 1, 2017, pp. 93-102
(RECOMMENDED CITATION)
DOI:10.24193/subbambientum.2017.1.08

IDENTIFICATION THE SOURCES OF PAHS IN CLUJ-NAPOCA'S CITY ATMOSPHERE USING MOSS AS BIOMONITORS

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ABSTRACT. This study aims to determine the concentrations of PAHs in Cluj-Napoca`s city atmosphere using moss as biomonitors. Samples from different neighborhoods of Cluj-Napoca city were collected and analyzed by gas chromatography coupled with mass spectrometry. The concentrations of individual PAHs ranged from 0.61 μg kg^{-1} (chrysene) to 353.6 μg kg^{-1} (Indeno(1,2,3 -cd)pyrene), and the ΣPAHs ranged from 92.61 μg kg^{-1} to 353.6 μg kg^{-1} with a mean value of 329.23 μg kg^{-1}.Residential areas characterized by both low population density and traffic intensity had the lowest concentration levels of ΣPAHs in moss samples, below 200 μg kg^{-1}. Levels of concentration between 200 and 300 μg kg^{-1} were obtain in similar residential areas, but with more intense traffic. The locations that had PAHs concentration levels in moss exceeding 300 μg kg^{-1} are either industrial areas or neighborhoods with intense traffic. In all the study's locations the main emission source, according to PAHs diagnostic ratios, is pyrogenic, mainly originating from traffic emissions. The FL/ (FL+PYR) and FLA/ (FLA+ PYR) ratios indicate that in some cases there also is a petrogenic source. In a cross examination however, it can easily be seen that the main apportion for all the location is from pyrogenic sources.

Key words: *Polycyclic aromatic hydrocarbons, urban atmosphere, moss, biomonitors*, *Cluj-Napoca*

INTRODUCTION

Air quality is generally monitored with physicochemical detectors that offer quantitative data, however these are limited by analytical difficulties (such as detection limit), by costs and maintenance equipment (Marć et al., 2015), and the measurements provide only the concentration levels that are present in the environment at the moment of sampling (Wu et al., 2014). On opposite, biomonitoring is easier to apply, has no need for electrical energy, is cheaper and can provide a larger number of samples for a larger number of pollutants, and can provide a better coverage (Iodice et al., 2016; Vukovi et al., 2015, Marć et al., 2015; Ares et al., 2012). Yet, the lack of standardized procedure prevents the usage of this technique on a large scale (Marć et al., 2015; Ares et al., 2012).

The biomonitors are define as the living organisms that are used with the purpose to obtain quantitative and qualitative information regarding a certain aspect of the environment (Forbes et al., 2015). Mosses are capable to quickly absorb pollutants due to the fact that they rely on air for the most important nutrients uptake because of the lack of reticular system. In addition, the lack of waxy cuticle allows the direct contact of the foliar cells with the pollutants (Wu et al., 2014), and the poorly developed vascular system and the large exposed surface ratio compared with the total mass allow a better assimilation of atmospheric polycyclic aromatic hydrocarbons (PAHs) (Forbes et al., 2015, Thomas and Simon, 1985). Mosses are often used in biomonitoring studies because they are isolated from the ground, and so, they are less exposed to contamination with soli particles (Forbes et al., 2015; Liu et all, 2005), can be found all over the world, and their slow growth allows the study of contaminants accumulation over a long period of time (Vuković et al., 2015; Wu et al., 2014).

The moss usefulness in air quality assessment was promoted by many scientists in a large variety of studies (Capozzi et al., 2016a; Lazić et al., 2016; Iodice et al., 2016; Ares et al., 2009, Liu et al., 2005; Viskari et al., 1997; Wang et al., 2009, Wegener et al., 1992, Thomas et al., 1984, Wu et al., 2014, Thomas, 1986, Holoubek et al., 2000). Of course, not only PAHs were studied, but also many other chemical contaminants with negative health effects, such as, persistent organic pollutants (POP): polychlorinated biphenyls - PCB, dioxins and furans - PCDD/F, or polybrominated diphenyl ethers - PBDE (Harmens et al., 2013), heavy metals (Capozzi et al., 2016b; Iodice et al., 2016, Wegener et al., 1992), radioactive compounds (Capozzi et al., 2016a), nitrogen oxides, carbon monoxide, volatile organic compounds (VOC), particulate matter (Iodice et al., 2016) etc.

PAHs are a family of chemical compounds made from hydrogen and carbon atoms that forming at least two fused aromatic nuclei links. After the emission, volatile PAHs remain in the gas phase, while less volatile PAHs (with five or six nuclei) are adsorbed on solid particles in the atmosphere. The deposit in the vegetal material occurs from the absorption of lipophilic compounds both in gas phase and in solid phase (Harmens et al., 2013). Due to their toxic effects on human health PAHs concentration in the environment are regulated by the European Union (Directive 2004/107/CE).

In Romania only two studies were made on pollutants concentration from air that can be found in moss. The first one studies the chlorinated pesticides (Tarcău et al., 2013), and the second one studies heavy metals, rare earths and some other microelements in the proximity of Ploiesti city (Oprea and Mihul, 2003). According to our knowledge, there are no studies in the scientific literature for the PAHs air pollution assessment by using moss in Romania.

MATERIAL AND METHODS

Sampling

The study was carried out in Cluj-Napoca, one of the largest cities of Romania, situated in the central north-western part. Eleven samples of common moss were collected from the neighborhoods presented in figure 1: Someșeni, Mărăști, IRA, Grigorescu, Mănăștur, Gheorgheni, Iris, Zorilor, Andrei Mureșanu, Parcul Central and Gruia.

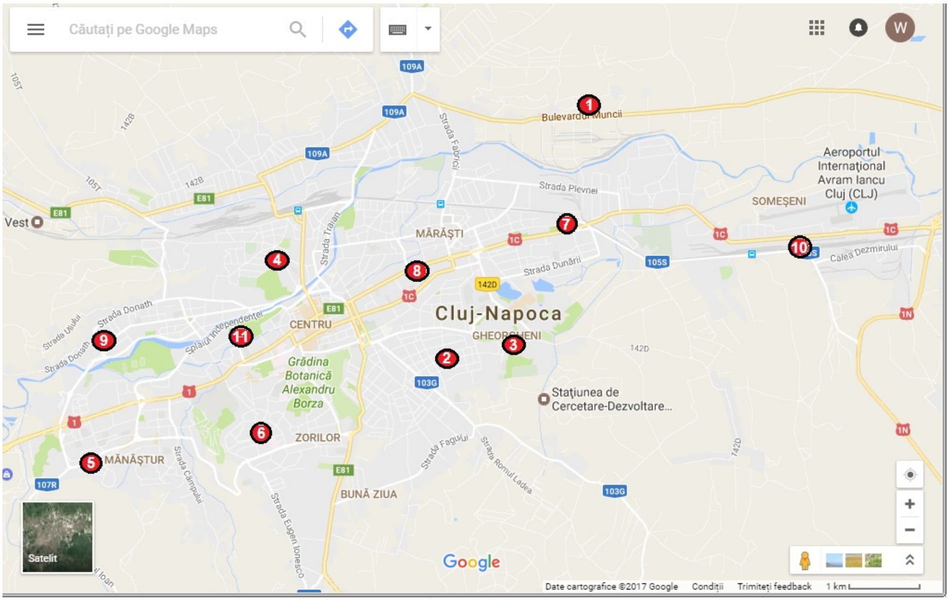

Fig. 1. *Map showing the eleven sample locations in Cluj city.*
1. Iris, 2. Andrei Mureșanu, 3. Gheorgheni, 4. Gruia, 5 Mănăștur, 6. Zorilor, 7. IRA, 8. Mărăști, 9. Grigorescu, 10. Someșeni, 11. Parcul Mare

All of the samples (table 1) were collected, when possible, at distances of more than 5 m from roads and houses. Whenever possible the samples were collected from parks and gardens, and when this was not possible, from the green areas that separated the block of flats from the sidewalk, maintaining of course the same distance limit.

Table 1. *Samples abbreviation and location coordinates*

Sample location	Abbreviation	Latitude	Longitude
Iris	S1	46°47'46.1"N	23°37'49.4"E
Andrei Mureșanu	S2	46°45'43.1"N	23°36'22.6"E
Gheorgheni	S3	46°46'05.2"N	23°37'29.4"E
Gruia	S4	46°46'33.0"N	23°34'38.9"E
Mănăștur	S5	46°45'10.5"N	23°32'56.3"E
Zorilor	S6	46°45'25.9"N	23°34'43.9"E
IRA	S7	46°46'55.0"N	23°38'09.3"E
Mărăști	S8	46°46'36.7"N	23°36'27.8"E
Grigorescu	S9	46°46'04.0"N	23°32'59.3"E
Someșeni	S10	46°46'48.2"N	23°40'47.2"E
Parcul Mare	S11	46°46'04.7"N	23°34'30.8"E

Sample processing

Due to the fact that, when the objective of a biomonitoring study with terrestrial mosses is to determine the bioconcentrated fraction, washing is ineffective (Aboal et al., 2011), and the option of dry-cleaning with a nitrogen jet is not available, the moss was cleaned by manually physical removal of contaminants: other plant remains, hair, soil, withered leafs, roots etc. The apical segments (3-4 cm long) were cut from the moss shoots and then left to dry on paper sheets at room temperature, 22º C, for 72 hours and milled afterwards.

Chemical analysis

For extraction of PAHs, 3 g of milled moss were weighed. Thirty milliliter of a mixture of n-hexane/dichloromethane (1:1 *v/v*) was then added. For extraction, the samples were placed in ultrasonic bath for 15 minutes. After extraction, the solvent was decanted and, filtered through a PVDF sample filter with pore size of 0.45 μm (Merck Milipore)). The extracts were then left to evaporate for 24 hours at room temperature and afterwards the residue was disolved with 2 milliliter of n-hexane/ dichloromethane (1:1) and kept in the freezer until they were analyzed.

The PAHs were analyzed by gas chromatography-mass spectrometry using a gas chromatograph model Thermo Electron Corporation (Focus GC; DSQII; TriPlus Autosampler). The separation of target compounds was performed on DB-5 column (25 m x0.25 mm x 0.25 μm i.d.). The MS had the ion source heated at 200º C, and was set on selected ion monitoring (SIM) mode. The separation was performed with two gradient of temperature as follows: from 120ºC, up to 220ºC with 10ºC min^{-1}, and from 220ºC to 300ºC with 3ºC min^{-1}. Injection volume was 1 μL, splitless, using Helium as carrier gas at a constant flow of 1,2 mL min^{-1}. The autosampler was set to have a 3 cycles pre-injection cleaning with 2 μL of solvent, and a 3 cycles post-injection cleaning with 2 μL of solvent.

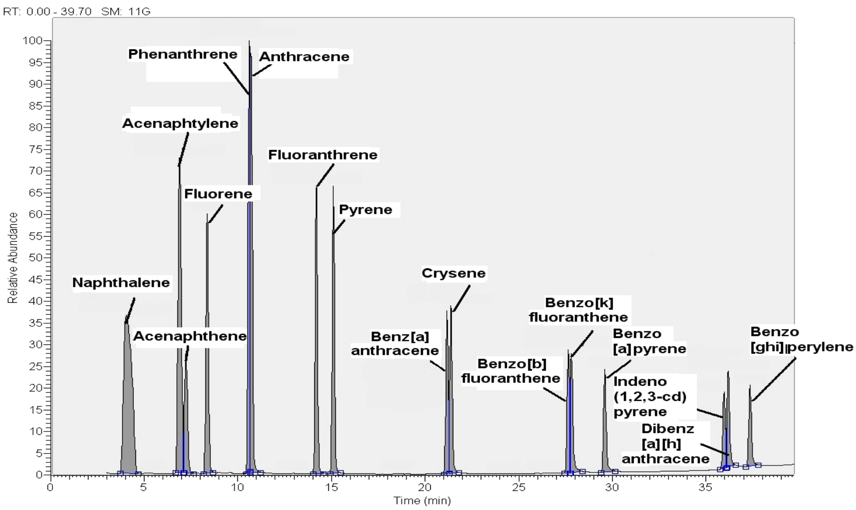

Fig. 2. *Chromatogram of the PAHs standard mixture*

For the qualitative and quantitative analysis a PAH standard mixture containing 16 compounds purchased by Supelco was used. The PAHs determined were: naphthalene, acenaphthene, acenaphtylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, crysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno(1,2,3-cd)pyrene, ibenz[ah]anthracene and benzo[ghi]perylene (figure 2).

RESULTS AND DISCUSSION

The concentrations of individual PAHs (table 2) ranged from 0.61 ng g^{-1} (chrysene – S3) to 353.6 ng g^{-1} (Indeno(1,2,3 -cd)pyrene – S1), and the ΣPAHs ranged from 92.61 ng g^{-1} (S8) to 353.6 ng g^{-1} (S1) with a mean of 329.23 ng g^{-1}. In all samples the sum of high molecular PAHs, with a mean of 284.73 ng g^{-1}, was much higher than the sum of low molecular PAHs, with a mean of 44.51 ng g^{-1}, indicating that for all locations the main source is of pyrogenic origin.

Locations comparison

Residential areas characterized by both low population density and traffic intensity, like S3 – Gheorgheni, S4 – Gruia and S6 Zorilor neighborhoods, had the lowest concentration levels of ΣPAHs in moss samples, in all of these location the concentration level was below 200 ng g^{-1}. Mărăști and Grigorescu, although quite similar residential areas, obtained levels of concentration between 200 and 300 ng g^{-1} due to the more intense traffic.

The locations that had PAHs concentration levels in moss exceeding 300 ng g^{-1} are either industrial areas or neighborhoods with intense traffic. The highest concentration levels were in S1 - Iris and S2 – Andrei Mureșanu. Iris is the most developed industrial area of Cluj-Napoca city and the obtained results in this study are consistent with the expectations. Concentration levels in S7 – IRA (figure 3) was also consistent with the industrial activity, in a proportional ratio with the intensity of the activity, and in S10 location – Someșeni, the international airport of Cluj-Napoca city is located.

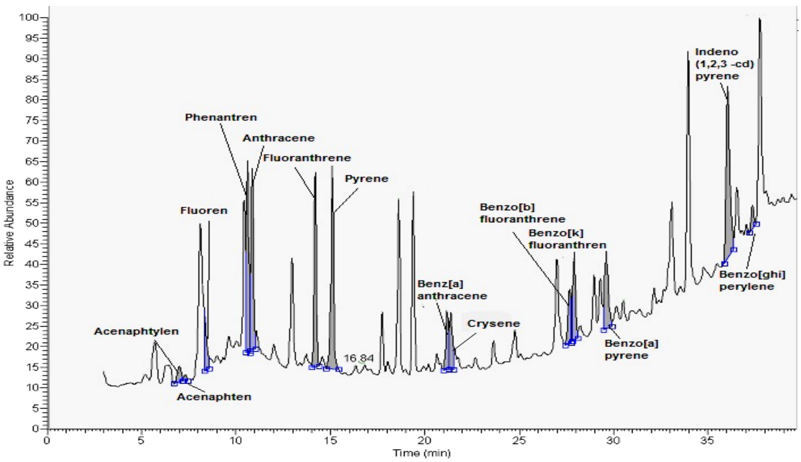

Fig. 3. *Cromatogram of a real moos sample – S7 – IRA*

On the other hand Andrei Mureșanu is a residential area, but the moss sample was collected from a central area of the neighborhood, in the close proximity of a busy intersection. High levels were also obtained in S11 – Parcul Mare and S8 – Mănăștur. Mănăștur is the neighborhood most densely populated from Cluj-Napoca city, so the high concentration levels are easily explained by the intense traffic and a large number of diverse heating systems. The intense traffic is also the reason why Parcul Central has high concentration levels, being situated in the city centre, witch represents the access point from one neighborhood to another, also it is the subject of transitory vehicles from one city to another (e.g. from Zalău to Turda) and it is the most touristic part of the city, being an attraction for international festivals and sport competitions.

Table 2. *Concentration of tested PAHs in selected zone areas*

Compound	Abbrev	Concentration (ng/g dry moss)										
		S1.	S2.	S3.	S4.	S5.	S6.	S7.	S8.	S9.	S10.	S11.
Naphtalene	NP	0.78	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acenaphtylene	ACY	3.12	3.42	ND	ND	4.65	1.70	2.66	1.23	3.82	3.44	2.79
Acenaphtene	ACE	3.74	2.65	3.01	ND	6.34	1.44	2.16	1.45	2.12	2.78	2.35
Fluorene	FL	ND	3.81	3.30	6.53	2.77	2.32	8.97	3.77	3.64	4.56	2.68
Phenathrene	PHE	15.19	10.34	4.15	8.46	3.95	5.33	24.84	9.18	7.67	19.32	10.14
Anthracene	ANT	16.45	27.72	13.44	22.52	24.88	12.83	24.41	21.53	21.68	37.07	50.46
Fluoranthene	FLA	10.15	9.46	2.69	9.72	ND	1.45	28.68	7.98	ND	12.95	3.15
Pyrene	PYR	11.19	15.83	3.22	8.45	5.38	1.09	33.87	7.84	2.90	11.38	5.78
Benz[a]anthracene	BaA	4.70	1.19	0.62	0.77	1.23	ND	16.64	1.04	ND	3.52	0.98
Crysene	CHR	4.10	40.21	0.61	2.96	ND	ND	13.85	1.66	ND	2.92	ND
Benzo[b]fluoranthene	BbF	ND	ND	ND	ND	3.28	ND	27.10	ND	ND	ND	ND
Benzo[k]fluoranthene	BkF	108.6	ND	ND	7.80	24.23	ND	26.95	86.29	24.68	47.07	88.01
Benzo[a]pyrene	BaP	8.54	61.58	18.56	5.07	13.67	34.66	42.01	26.26	15.86	37.55	2.53
Indenol(1,2,3-cd)pyrene	IcdP	353.6	273.8	107.6	116.6	271.2	128.5	122.6	92.6	199.8	176.4	206.3
Dibenz[a,h]anthracene	DahA	ND	ND	ND	ND	ND	ND	ND	ND	ND	13.90	16.00
Benzo[ghi]perylene	BghiP	ND	ND	6.59	10.31	11.88	ND	9.02	ND	11.94	ND	2.81
	ΣPAHs	***540.2***	***450.0***	***163.8***	***199.2***	***373.4***	***189.3***	***383.8***	***260.8***	***294.1***	***372.9***	***394.0***
	min	0.78	1.19	0.61	0.77	1.23	1.09	2.16	1.04	2.12	2.78	0.98
	max	353.6	273.8	107.6	116.6	271.2	128.5	122.6	92.6	199.8	176.4	206.3

ND – not detected

Table 3. *The diagnostic ration of PAHs sources in studied area*

Isomeric ratios	Value	Source	S1.	S2.	S3.	S4.	S5.	S6.	S7.	S8.	S9.	S10.	S11.
ΣLMW/ΣHMW	<1	Pyrogenic	0.01	0.02	0.04	0.03	0.04	0.03	0.04	0.03	0.03	0.03	0.02
	>1	Petrogenic											
ΣCOMB/ΣPAHs	~1	Combustion	0.93	0.89	0.85	0.81	0.89	0.88	0.84	0.86	0.87	0.78	0.79
FL/(FL + PYR)	<0.5	Petrol emission	NA	0.19		0.44	0.34		0.21	0.32		0.29	0.32
	>0.5	Diesel emission			0.51			0.68			0.56		
ANT/(ANT+PHE)	<0.1	Petrogenic											
	>0.1	Pyrogenic	0.52	0.73	0.76	0.73	0.86	0.71	0.50	0.70	0.74	0.66	0.83
FLA/(FLA + PYR)	<0.4	Petrogenic		0.37			NA				NA		0.35
	0.4 – 0.5	Fossil fuels combustion	0.48		0.46				0.46	0.50			
	>0.5	Wood, coal, combustion				0.54		0.57				0.53	
BaA/(BaA + CHR)	0.2 - 0.35	Coal combustion		0.03									
	>0.35	Vehicular emission/ Combustion	0.53		0.51	0.21			0.55	0.39		0.55	
	<0.2	Petrogenic											
IcdP/(IcdP + BghiP)	<0.2	Petrogenic											
	0.2 – 0.5	Petroleum combustion											
	>0.5	Grass, wood, coal, combustion	NA	NA	0.94	0.92	0.96	NA	0.93	NA	0.94	NA	0.99
BaP/BghiP	<0.6	Non-traffic emission											
	>0.6	Traffic emission	NA	NA	2.82	0.49	1.15	NA	4.66	NA	1.33	NA	0.90

PAH diagnostic ratio

In moss samples there is a low variability in PAHs identify, but more pronounced in each PAH quantification. The quantity of specific PAHs depends on the processes producing them. Low molecular weight PAHs are usually formed during low temperature processes (e.g. wood burning), and higher molecular weight PAH compound are formed during high temperature processes (e.g. the combustion of fuels in engines). To distinguish each source by using PAHs profile, PAH diagnostic ratios may be used. The ratios (table 3) can distinguish diesel and gasoline combustion emission, crude oil processing products and biomass burning processes (Tobiszewski and Namiejnik, 2012).

The most commonly used ratio, ΣLMW (sum of Low Molecular Weight PAHs) / ΣHMW (sum of High Molecular Weight PAHs) indicates that in all locations the main emission source is pyrogenic, so the PAHs are resulted from combustion rather than from spills. The mainly combustion source is also sustained by the results of the ΣCOMB (FLA, PYR, BaA, CHR, BkF, BbF, BaP, IcdP and BghiP) / ΣPAHs ratio, the ANT/ (ANT+PHE) ratio, BaA / (BaA+CHR), and IcdP/(IcdP + BghiP).

The BaP/BghiP ratio indicates that in all location PAHs mainly originate from traffic emissions, a statement strengthened by the FLA / (FLA+PYR) ratio, with the exception of S2, which seems to have a coal combustion source. These findings confirm the expected results, Cluj-Napoca being a developing city, densely populate, so with an intense traffic.

In nature there rarely is a single emission type, so the FL/ (FL+PYR) ratio indicates that in some cases there also is a petrogenic source (S3, S6 and S8). The FLA/ (FLA+ PYR) ratio indicates that for S2 and S11 the source seems to have a petrogenic origin too, but, in a cross examination of the FLA/ (FLA+PYR) and ANT/ (ANT+PHE) ratios (figure 4) it can easily be seen that the main apportion for all the location is from pyrogenic sources. The IcdP/(IcdP + BghiP) also indicates that the combustion may not only be from traffic emissions, but also from grass, wood or coal combustion.

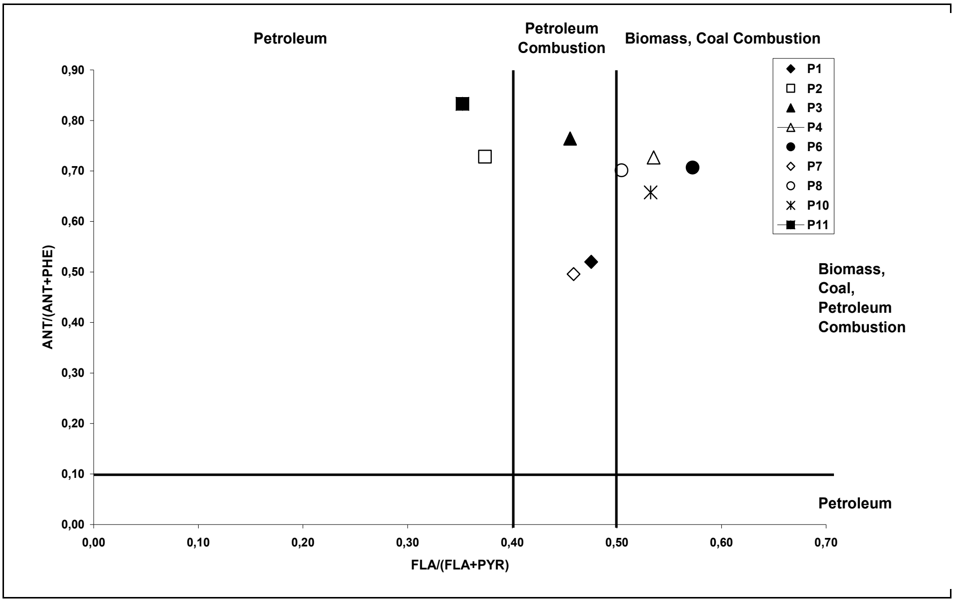

Fig. 4. *Cross examination of the FLA/ (FLA+PYR) and ANT/ (ANT+PHE) ratios in the study locations*

CONCLUSIONS

Residential areas characterized by both low population density and traffic intensity, like S3 – Gheorgheni, S4 – Gruia and S6 Zorilor neighborhoods, had the lowest concentration levels of ΣPAHs in moss samples, in all of these location the concentration level was below 200 µg kg^{-1}. Mărăști and Grigorescu, although quite similar residential areas, obtained levels of concentration between 200 and 300 µg kg^{-1}

due to the more intense traffic, and the locations that had PAHs concentration levels in moss exceeding 300 μg kg^{-1}, are either industrial areas or neighborhoods with intense traffic.

In all the study's locations the main emission source, according to PAHs diagnostic ratios, is pyrogenic, mainly originating from traffic emissions. But in nature there rarely is a single emission type, so the FL/ (FL+PYR) and FLA/ (FLA+ PYR) ratios indicate that in some cases there also is a petrogenic source (S2, S3, S6, S8 and S11), but in a cross examination of the FLA/ (FLA+PYR) and ANT/ (ANT+PHE) ratios it can easily be seen that the main apportion for all the location is from pyrogenic sources.

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