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

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THE CURRENT PROBLEMS OF URBAN DEVELOPMENT IN CLUJ METROPOLITAN AREA

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ABSTRACT. The Cluj Metropolitan Area is located in Cluj County, the north-western development region of Romania. The strategic option of polycentric territorial development was adopted on the basis of the principles outlined in the NDP (National Development Plan)- on spatial development at regional level. This involves supporting development processes within urban growth pole. The associative structure at the Cluj Metropolitan Area (CMA) was formed at the end of 2008, continuing the efforts to establish a metropolitan area with economic specificity, initiated by Cluj County Council in 2006. Communes included in Cluj Metropolitan Area are also part of different micro-regional associations with relatively homogeneous characteristics. These associations were formed at the initiative of city halls and they have legal personality.

Key words: *Cluj Metropolitan Area, peri-urban refuge, urban space, rural space, development strategy.*

INTRODUCTION

The city of the future must be an intelligent one, mostly named smart city, whose development is based on the exploitation of intellectual capital towards education/self-education, innovation and economic development among environment-friendly sectors of activity.

More specifically, municipal development should be based on high quality drinking water resources, appropriate waste management, improved air quality and appropriate hazard and risk management in order to maintain a clean and safe living environment. Thus, new challenges and associated problems emerged: the adaptation of transport infrastructure, sewerage and water supply, green spaces, sanitation.

The urban growth pole Cluj-Napoca cannot cope alone with these ambitions, because it needs vital geographic space. This space is taken from the surrounding rural areas. Thus, in the project Cluj Metropolitan Area (CMA), 17 municipalities joined; creating an area of over 1600 sq. Km in which the activities associated with the big city can take place.

The Cluj metropolitan area is thus ten times larger than the administrative structure of Cluj-Napoca, although the population is only 80,000 inhabitants (table 1). But the benefits of a surplus geographic space are more important because companies are easily finding investment location in the rural area (Baciu et al, 2010).

Urban-rural space - mutual benefits

The Cluj-Napoca urban growth pole includes the Cluj-Napoca municipality and the following administrative territorial units (within Cluj County): Aiton, Apahida, Baciu, Bonţida, Borşa, Căianu, Chinteni, Ciurila, Cojocna, Feleacu, Floresti, Petreştii de Jos, Tureni and Vultureni, with their localities included in their administrative territory. This is the core of Cluj Metropolitan Area – *Zona Metropolitană Cluj*. From the urban and economic development point of view, this area lays within a 30 km area around Cluj-Napoca, an optimal distance for the development of peri-urban space.

Regarding urban planning and economic development, this area is extremely heterogeneous. We have well-developed communes with urban aspect, such as Floresti, Baciu or Apahida, but also communes with a deep rural aspect, remaining at a deep rural level, such as Borșa, Vultureni, Petreștii de Jos (Baciu, 2013). For instance, nowadays Floreşti looks like an atypical village, characterized by visible urban footprints copied from the city in close proximity. A first visual aspect describes a peripheral urban landscape, or rather urbanized (Baciu et al., 2012, 2015). We are talking about a dynamic periphery, which gained the nickname of the most populous commune in

Romania. Between the 1992 census and the 2011 census it had a population growth of over 350% - from 6,088 to 21,832 inhabitants, instead of the urban service of Floreşti stresses that these figures are outdated statistics from censuses and population reached over 30,000 inhabitants (table 1).

Table 1. *The distribution of population and administrative areas in CMA*

	2011 (inh.)	2015 (inh.)	Administrative area (sq.km)	Density (inh./sq.km)
Cluj-Napoca	309,136	322,108	179,56	1,793
Florești	21,832	24,941	61	358
CMA	392,000	410,000	1,625	255

Regional decision-makers have defined so-called *functional clusters* of communes in the desire to select the most important economic features of rural areas. These clusters highlight the role and contribution of these communes in the Metropolitan Area of Cluj (figure 1) and they are distributed in two circular concentric metropolitan rings.

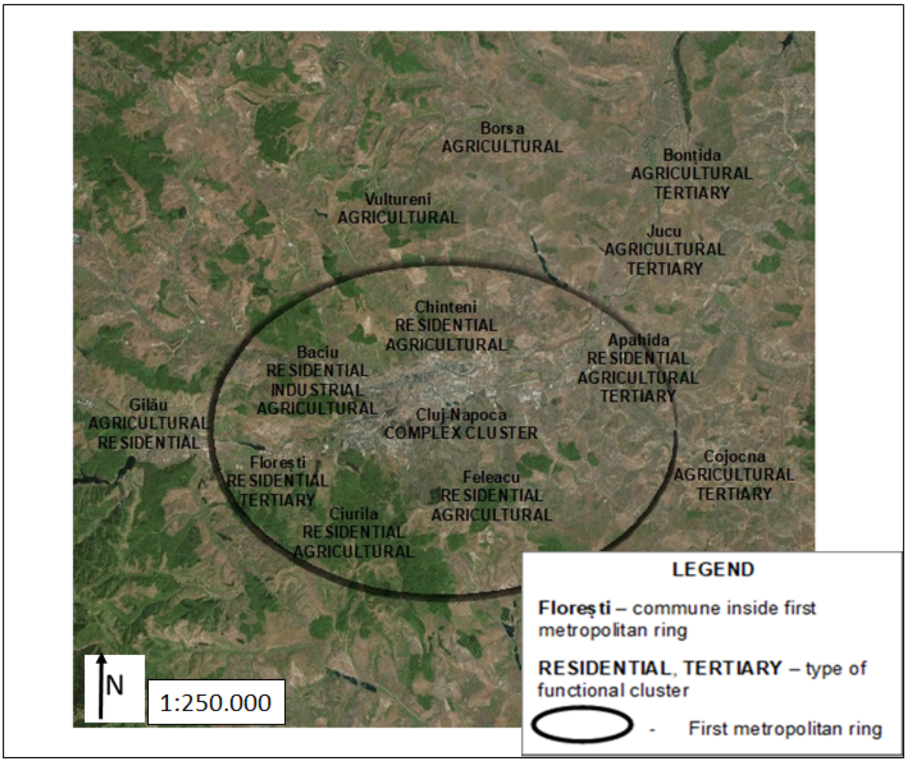


Fig. 1. *Functional clusters inside the first metropolitan ring*

The closest metropolitan ring is predominantly residential; that is so-called peri-urban refuge or urban bedroom, and the second ring is predominantly agricultural, with attractive investment spaces. The rural areas of the first metropolitan ring are evolving as peri-urban refuges, where real estate investments flourish. The agricultural lands have been abandoned and have gradually passed to the state of built-up areas. This process took place in two phases: 1996-2008 and 2014 to the present. Urban periphery has become dynamic and has begun to attract the population with medium and upper class income from great city in proximity or new employers from other regions of country.

The city of Cluj-Napoca and the analyzed peri-urban space have the following characteristics:

- Capability to support differentiated population growth among localities through taking surpluses from the big city and directing it to the localities;
- The city of Cluj-Napoca has the capability to take over a number of functions of the capital for a national decentralization. That could be done in the management of education (conceptually discussed at European level, we can apply for other metropolitan areas, e.g. Brașov to take the role of touristic center);
- A wide range of extremities supports the viability of an extensive development of the CMA: Transylvanian Plain, Someşan Plateau and the Apuseni Mountains, having a high capacity of material resources providers;
- Convergence of roads, railways, utility bridges and roads communication;
- The tradition of Cluj, along its history, to function as a center processing the resources in the area;
- Tradition of important administrative, cultural, and educational center;
- The important commercial function of the city; the importance of the regional business center function, the banking center, the IT industry center, which has led to the development of smart-city and green-city concepts;
- Also important, the function of the major center of the cultural and spiritual life of Transylvania.

Dysfunctions inside the CMA

The decades of unplanned and uncontrolled evolution of a socio-economic important phenomenon of urban development, inevitably leads to two types of dysfunctionalities:

a. The dysfunctions of the spatial planning during the communist period created industrial areas in the middle of city and residential areas with a density too high, space too little between blocks and too many levels, etc. These errors of planning - based on ideology on that time - creates today major road traffic problems, related to public transport, travel time to work, the availability of services and, in general, the quality of life. An example is the Mănăștur district, with nearly 100,000 inhabitants, insufficient big shopping stores, inadequate parking spaces, overall crowding, residential stress.

b. Another type of dysfunctions was created by the lack of urban development planning that began after 1990. This development caused some imbalances and urbanistic errors, as follows:

- degradation of places and peripheral natural spaces;
- an increased motorized drive;
- overstress of local community's budget;
- an overconsumption of natural and rural areas;
- landscape degradation;
- depletion of natural resources (e.g. the removal of soil into new residential areas, ballasts, quarries, which are not later exploited);

Both dysfunctions make their presence within CMA. The lack of basic infrastructure in the peri-urban space, poor connectivity and the permanent threat of a traffic jam in the city occurred in absence in the near future of an auto belt or highway belt.

Correcting dysfunctions

The removing of these errors requires good urban planning supported by political will at decision maker level. In the competition for external funding that will become more and more fierce among the major development areas in the country, the correct development and good use of the urban planning tool could mean the difference between those who attract and those who lose from the population groups (relatively young, educated, dynamic, high income) that are the engine of development.

Thus, in order to remedy the dysfunctions in the urban development, it is aimed at:

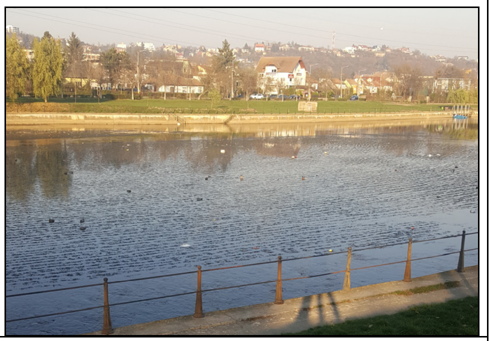
- a balance between urban upgrading and controlled urban development through the development of rural space on the one hand and the preservation of natural spaces, on the other hand;
- a diversity of urban functions and social diversity in urban and rural areas;
- an economical and balanced use of natural, urban, peri-urban and natural spaces in rural areas, controlling the need for movement and car traffic;
- conserving the quality of air, water, soil, subsoil, ecosystems, natural and urban landscapes, noise reduction;
- the protection of special urban heritage such as patrimonial buildings, prevention of natural and technological risks.

The attractiveness of an urban area is measured by the number and quality of what is called *poles of excellence*, consisting of the following objectives: presence of great universities; medical centers; research structures; high-tech enterprises; the major cultural, sports, leisure, exhibition facilities; financial markets; the headquarters of large European and international firms; a large volume of economic and financial exchanges; connection to large European and international networks through highways, airport, high-speed rail train.

CONCLUSIONS (as environmental strengths and weaknesses)

CMA covers a quarter of entire area of the Cluj County, which means that the environmental problems are vast and complicated.

Strengths	**Weaknesses**
Natural landscape	
The presence of various landforms (meadows, depressions, hills, mountains) in balanced proportions that ensure geo-ecological diversity and landscape mosaic; The existence of a climate without excesses and special risks; The presence of water resources with good quality that ensure the long-term consumption needs; Varied land use with important agricultural and forestry suitability;	Areas with geomorphological risks (landslides, slope erosion) (Rosian, 2011); Flood risk in eastern part of CMA; Sewage effect of the air masses in the west-east direction and the occurrence of thermal inversions in the depressions; Deterioration of natural heritage features (protected areas).

Strengths	Weaknesses
Natural landscape	
Tourist, natural and anthropic heritage (scenic landscapes, historical sites).	
Environmental state	
The presence of urban and metropolitan waste collection system; Large-scale implementation of selective waste collection; Strong awareness and environmental education among young people in the city.	Lack of landfills for waste resulted from construction; Existence of urban pollution sources (due to the increasing of motorized traffic); Maintaining poor traditional practices in rural areas in the management of living space and waste; Lack of ecological education in rural areas; Affecting the trophic chain of some biotic phenomena; Increasing the anthropic pressure on the protected areas; Reducing green spaces in favor of setting economic or public objectives (green space density: under 30 m²/inh.); Somes river eutrophication process, as seen it below: 
Technical infrastructure	
High density of the road network (over 0.40 km/km²); Access to natural gas supply; Access to centralized water supply; Full coverage of the mobile telephony network;	Car traffic with slow connections between peri-urban and Cluj-Napoca; Delays in the modernization of national roads connecting with other counties; The high degree of degradation of some county roads;
Increasing of modern and ecological public transport; The presence of various shopping centers; Top universities; medical centers; research structures; high-tech firms; the major cultural, sports, leisure, exhibition facilities, as part of the regional *poles of excellence;* Increasing the airport's role in passenger transport, which has already reached 2 million passengers per year.	The lack of a viable urban auto-belt, especially for heavy traffic in transit; Delays in the construction of highways.

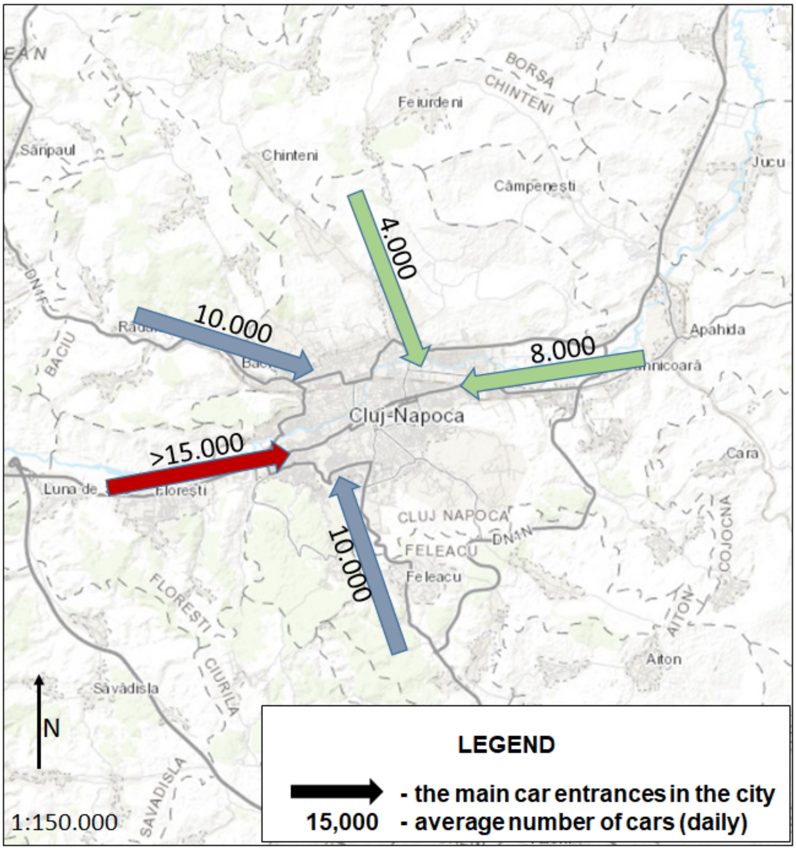


Fig. 2. *The daily road traffic value from CMA to Cluj-Napoca city*

The CMA and Cluj-Napoca city fit to the modern pattern of this new urbanism and they are connected to major modern issues (Dincă and Dumitrică, 2010). The development of the city can only be achieved through the absorption of vital rural space for residential buildings; these newly created spaces attract new inhabitants, who see in the big city an opportunity for personal and professional development. Relative isolation from the city creates the illusion of a quiet residence, but brings daily stress due to difficult mobility to the workplace. Every day, 15,000 cars enter the great city through west, 20,000 from the north, south (figure 2), from promised residential havens to well-paid jobs. This duality is based on a systemic balance called demand and supply.

REFERENCES

Baciu N., Stănescu C., Muntean O.L., Bodea C., 2010, Geo-systems and types of geo-facets in the Transylvanian Plain – tools for defining Cultural Landscapes, *Present Environment and Sustainable Development*, **4**, pp. 255-264.

Baciu N., Stănescu C., Schuster E., Mureșianu M., 2012, *Schimbări ale peisajului urban în vestul municipiului Cluj-Napoca*, Ed. MIRTON, Timişoara, pp. 311-317.

Baciu N., 2013, *Gestionarea durabilă a mediului urban și rural*, Ed. Bioflux, Cluj-Napoca, 97 p.

Baciu N., Stănescu C., Muntean O.L., Roșian, G., Mihăiescu, R., Schuster, E., 2015, A few malfunction related to the urban sprawl in the western part of Cluj-Napoca City. *Studii și cercetări. Geography-Geology*; Bistrița.

Dincă D., Dumitrică C., 2010, *Dezvoltare şi planificare urbană,* Editura Pro Universitaria, Bucureşti.

Roșian G., 2011, *Geomorfologia mediului*, Presa Universitară Clujeană, Cluj-Napoca, 266 p.

https://files.primariaclujnapoca.ro/dezbatere_publica/Strategia-integrata-de-dezvoltare-a-Zonei-Metropolitane-Cluj-N.pdf accessed 2 Nov. 2018

http://cmpg.ro/wp-content/uploads/2015/05/strategie-cluj-napoca-2014-2020.pdf accessed 30 Oct. 2018

https://natura2000cluj.wordpress.com/ accessed 1 Nov. 2018

https://www.researchgate.net/publication/287613842_Defining_the_peri-urban accessed 31 Oct. 2018

https://www.researchgate.net/figure/Implications-of-Periurban-Types, accessed 30 Oct. 2018

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THERMAL WATER AND RADON EXPOSURE THROUGH THE SKIN

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ABSTRACT. Low doses - non cancer effect involve also, exposure to RADON alpha particle, through the skin, during radioactive thermal baths. Alpha radiation is considered to have a high impact on the immune-suppressive cytokine and to a certain degree it can influence the temporary regeneration of impaired health function in autoimmune patients, due to their analgesic and anti-inflammatory properties. Considering the benefits of thermal water with 30 Bq/l Radon, from Felix-Oradea, Spa Resort, Bihor county, Romania, we analysed the variation of skin biophysical parameters like hydratation (HYDR), trans epidermal water loss (TEWL), sebum quantity (S), and skin surface temperature (T), for different water 'temperatures, looking comparatively between the left hand submerged in radioactive water and the right hand, submerged in normal water.

Key words: *skin anti-inflamatory exposure; radioactive thermal water.*

INTRODUCTION

Thermal waters have a certain degree of radioactivity attributed to elements of the uranium and thorium natural decay series. One of the isotopes contained in elevated concentrations is ^{226}Ra. It decays into Radon, noted ^{222}Rn. After that, through ^{222}Rn decays alpha-particles are emitted. These alpha-particles can enter into our body by inhalation, ingestion or through the skin, during dermal contact with thermal water. Radon arrived in our body are delivered via blood to other tissues, respectively other human' cells. Retention' time into the body is short, 50% disappearing within 15–30 min, mainly through exhalation and also through excretion and diffusion through the skin after the bath. Although the effect of Radon, other than causing lung cancer, has received little attention, epidemiological studies and the results of treatment of patients in radioactive spa waters suggest that the gas has an effect on the immune system, (Bituh et al., 2009; Hofmann et al., 1999). This study belongs to the field of radioprotection which considers the health effects of low-dose radiation, ^{222}Rn being a natural radionuclide. Not all dosimetry issues regarding Radon entrance into the skin are yet solved. The quantitative nuclide-specific information about the deposition, adsorption, absorption and penetration of radon progeny from the skin surfaces in our body is still missing. In this context, for a good dosimetric quantification, the mechanism of its transport from the surface to basal skin layer and its' arrival into the blood ought to be very well understood. Thus, the uncertainty of dose effect relationship can be significantly decreased. The therapeutic use of Radon involves the intake of Radon gas either through inhalation or by transcutaneous absorption of Radon dissolved in the bath water. The importance of entrance routes of Radon into the body should be changed according with environmental conditions: concentrations, humidity and temperature. Although inhalation is a very important route, particularly in conditions such as thermal spas, the absorption route should be more important. It has been observed, in 2002, that speleo therapeutic Radon exposure causes a considerable increase in Radon progeny activity on skin, due to high adhesive properties of Radon. Later, in 2010, it was pointed out that among Radon's progeny, ^{218}Po has the biggest contribution to the cellular doses measured on the skin due to its highest deposited activity and the emission of two alpha particles (Soto, 1997; HLEG, 2009; Falkenbach et al., 2002; Tempfer et al., 2010).

Considering the importance of skin structure for the modelling of dermal exposure, our purpose was to follow the biophysical properties of skin in contact with thermal water having a Radon activity of 30 Bq/l. We analysed the variation of the following biophysical parameters: HYDR, TEWL, S and T for the same thermal water at two different temperatures, looking comparative to the left hand submerged in radioactive water against the right hand, submerged into the Radon-free tap water.

MATERIALS AND METHODS

The study took place during May-July 2014, and thermal water was taken from a natural spring Felix-Oradea, Bihor county Romania where is a very well known Spa resort.

Non-invasive instruments were used to analyse: dermal hydration - (HYDR), trans epidermal water loss - (TEWL), sebum quantity - (S), and the increase of temperature at the skin surface (T). The measurements were initially performed without water contact (22±2^{0}C and 30-45% relative humidity, in the room) and were later compared with the ones performed after the skin contact with water at 36.5°C and 40°C respectively. Both hands were submerged simultaneously in water: left hand in thermal water and right hand in normal water; the exposure lasted - 6 minute. Before the analysis the water surplus was removed with a towel. The exposures were successively performed and detection was made on hand surface, in the same site.

HYDR was measured with Corneometer CM 825. The method involves the measuring of skin dielectric capacitance at surface. The method is very sensitive and the hydration can be assessed on the skin surface at depth of 10-20 µm in the stratum corneum. The results are expressed in arbitrary units from 0 to 100.

Tewameter TM 300 was used for the assessment of TEWL at the skin surface and the results are expressed in g/m^2/h.

Sebumeter SM 815 (Courage-Khazaka Electronics, Germany) was used for quantification of sebum secretion at the skin surface and the results were expressed in mg sebum/cm^2 skin. The software was also, from Courage-Khazaka Electronics, Germany. These methods are used frequently in skin research studies (Moldovan and Nanu, 2010).

The dermal infrared radiation was appreciated with Thermometer IR 900-30S, K-Type (Voltcraft Instruments, Germany), suitable for contactless temperature measurement when the surface emissivity is unknown. The radiation measurements were performed at 30 cm distance from the hand surface, in the same point, an area of 20 mm in diameter and were converted in ^{o}C. The analysis was performed in accordance with Lahiri et al. (2012).

Exposure group

Nine healthy volunteers aged between 18 and 75 years (seven females and two male), without dermatological diseases, history of allergies or other skin disease have been monitored, before and after the contact with normal and thermal water. They were asked not to use any cosmetic products before and during the study and not to wash the studied skin areas for about 24 h before the measurements. They were informed about the nature of the test and about the possible adverse reactions. All participants gave their written consent before starting the study.
All data were evaluated for normal distribution prior to statistical analysis. Data were expressed as Mean ± SEM. *P*-values <0.05 were considered significant. Statistical analysis was performed using one way Anova. All tests were interpreted using OriginPro 7.5.

RESULTS

Figure 1 presents a dermal hydration increase in thermal water at 40 ^{0}C with 47.79%, compared with background. This would suggest a changing of skin capacitance at depth of 10-20 μm as a consequence of water entering through dermal pores. A slight difference between left and right hand was observed at beginning, which is preserved at 36.5 ^{0}C (the left being less than the right). After the submerged in radioactive water at 40 ^{0}C, HYDR of the left hand became higher than the right hand (submerged in Radon-free tap water) with 19.56%. The results are statistically significant for both water temperatures, even if the trend reversed.

Figure 2 presents a greater skin barrier disruption, as the TEWL is increases. The increase of TEWL was observed for all volunteers, in both water types, being significant in comparison with the start value. The growth of TEWL was 266.9% higher in thermal water and 271.7% higher in Radon-free tap water, compared with the start. Although HYDR was 19.56% higher in thermal water at 40 ^{0}C, TEWL was 12.56% lower, most likely due to activation of homeostatic mechanisms, increase of local vasodilatation and blood flow.

Figure 3 shows that how the Sebum amount (S) from the skin surface decreases significantly with the increase of water temperature. At the beginning, S was higher for the right hand, due to local pattern of sebaceous gland (Figure 4). After 6 minute in thermal water at 36.5 ^{o}C the S value decreased with approximately 47% while in Radon-free water 85.9%. However, in water at 40^{0}C, the sebum amount dropped close to zero, with no differences observed between left and right hand.

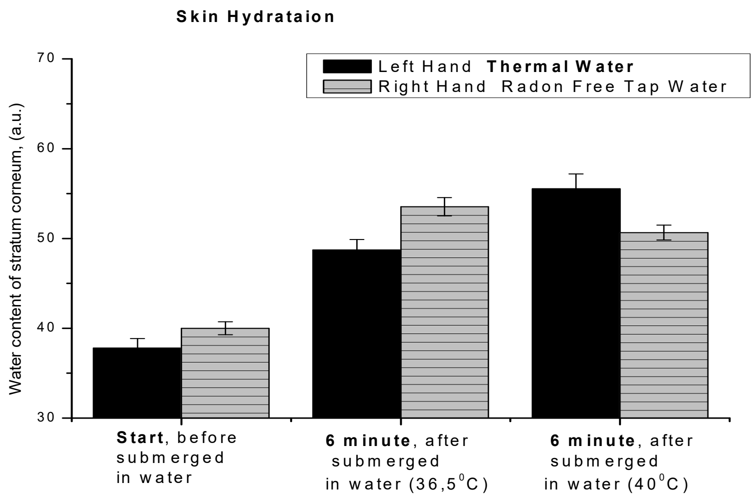

Fig.1. *Skin hydratation (HYDR) after the submersion of left hand in thermal water and right hand in the Radon-free tap water, (Mean ± SEM, are indicated)*

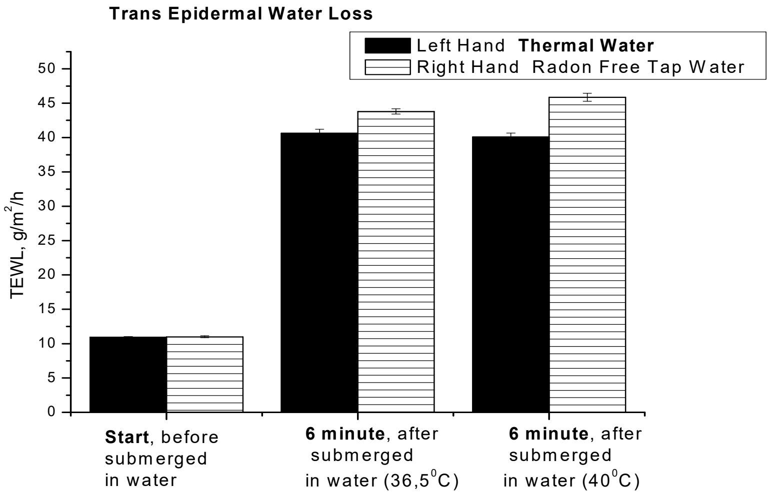

Fig. 2. *Trans Epidermal Water Loss (TEWL) after the submersion of left hand in thermal water and right hand in the Radon-free tap water, (Mean ± SEM, are indicated)*

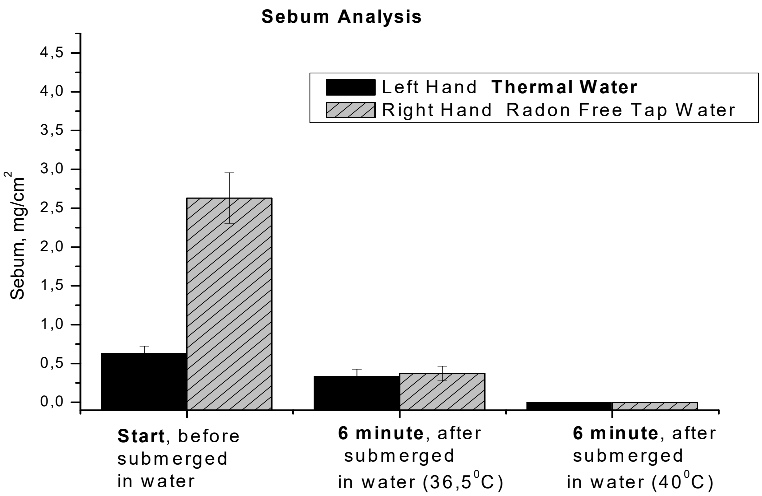

Fig. 3. *Sebum quantity (S) after the submersion of left hand in thermal water and right hand in the Radon-free tap water, (Mean ± SEM, are indicated)*

Figure 4 presents the surface temperature (T), measured at 30 cm from the skin to where were emitted expression of infrared dermal radiation. Due to the difference in blood flow, significantly higher average temperature was observed for the right hand.

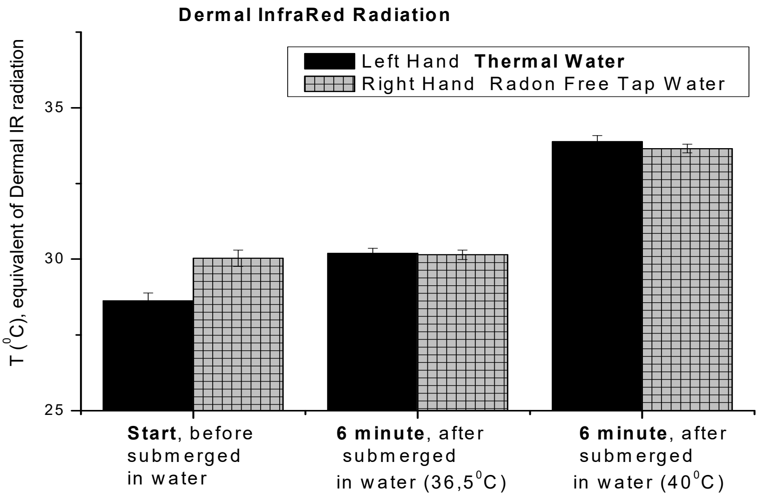

Fig. 4. *Dermal Infrared Radiation converted in ^{0}C after the submersion of left hand in thermal water and right hand in the Radon-free tap water, (Mean ± SEM, are indicated)*

The average temperature of the left hand increased with 5.4% following the submersion into thermal water, at 36.5 ^{0}C.

Similar reaction was observed for the right hand. In thermal water of 40^{0}C the increase was around 18.37% for the left hand, while in Radon - free tap water was only 12.04% compared to the start values. A local vasodilatation explains this local heat of temperature, in accordance with our observation regarding the activation of homeostatic mechanisms with imbalance between inflow and outflow of water from dermis.

DISCUSSIONS

The skin is a highly organized structure consisting of three main layers. The layer thickness of human forearm skin assessed by various imaging methods is stratum corneum 0.010−0.020 mm, living epidermis 0.030−0.130 mm, dermis 1.1 mm and subcutaneous fat 1.2 mm. The sebaceous gland can be found at 1-4 mm (Falke, 2005).

According to our results, the contact with thermal water during the bath had a significant influence. With measurements of TEWL and S we assess the skin surface changes and with HYDR, the changes on depth of 10-20 µm, corneum stratum which is the superficial layer of epidermis. Increased in skin hydration observed in thermal water means the alteration of electrical properties in stratum corneum layer, which is constituted by several plans of dead cells intimately linked by an extracellular array composed of lipid bilayer, formed by ceramides, cholesterol and fat acids. An increase of water content at this level changes the ions content and distribution (particularly calcium), which may cause perturbation of signalling pathways, the balance of epidermal cell proliferation / differentiation by influencing the calcium homeostasis and cytokine expression (Pinnagoda et al., 1990; Proksch et al., 1993).

The barrier to water permeation is not absolute and the normal movement of water through the stratum corneum into the atmosphere is known as TEWL and constitutes part of insensible water loss. An increase in TEWL, often results in significant changes of hydration at epidermis level. Generally, increasing of TELW means disruption of dermal barrier and increasing of skin vulnerability, due to disorganization in bilipid layer of the stratum corneum. This correlation cannot be made during the submersion in thermal water due to activation of homeostatic mechanism with increasing of blood flow and emitted infrared radiation from the skin surface. Loss of sebum quantity at skin surface was observed after both submersions in thermal water and in the Radon-free tap water. A lot of functions attributed to sebum in humans may be thus affected, such as photo protection, antimicrobial activity and delivery of fat-soluble anti-oxidants to the skin surface and pro- and anti-inflammatory activity exerted by specific lipids, (Zouboulis et al., 2008; WHO, 2009). Radon is lipophilic;

therefore, its absorption is enhanced in fat-containing tissues. The entrance through disrupted skin barrier will be higher, according to the increase of hydratation. Once entered and attached to the lipid bilayer, it cannot get any easier. This observation is in accordance with the results of Tempfer et al., (2010), who calculate a decreasing of Radon progeny activity at the depth of 20 μm, using a skin thickness model of 55 μm.

During measurement of dermal emitted infrared radiation, the influence of thermal water was observed at a depth of milimeters, greater than the thickness of corneum stratum. Increasing of dermal temperature, after exposure in thermal water, based on our results could have many more consequences on physiological processes via the micro-dermal circulatory beds, which justify its application in therapeutic treatment in radioactive spas, (Falkenbach et al.,2005; Shehata et al., 2006; Moder et al., 2011).

CONCLUSIONS

Radon exposure through the skin is possible due to contact with thermal water. A radioactivity of 30 Bq/l in the thermal water can induce several changes at skin surface and deeper into the dermal layer, meaning a barrier disruption. At the same time activation of homeostatic process can be possible.

REFERENCES

Bituh T., Marovic G., Petrinec B., Sencar J. and Franulovic I., 2009, Natural Radioactivity of ^{226}Ra and ^{228}Ra in Thermal and Mineral Waters In Croatia. *Radiat. Prot. Dosim*. **133** (2), pp. 119–123.

Falke M. H.,2005, *Mechanical behaviour of human epidermal and dermal layers in vivo*. Eindhoven: Technische Universiteit Eindhoven, ISBN 90-386-2896-X.

Falkenbach A., Kleinschmid J., Soto J., Just G.,2002, Radon progeny activity on skin and hair after speleotherapeutic radon exposure. *Journal of Environmental Radioactivity*, **62**, pp. 217-223.

Falkenbach A., Kovacs J., Franke A., Jorgens K., Ammer K., 2005, Radon therapy for the treatment of rheumatic diseases—review and meta-analysis of controlled clinical trials. *Rheum Int*, **25**, pp. 205–210.

Hofmann W., Lettner H., Winkler R., Foisner W., 1999, Perkutaner Radon-Transfer und Strahlenexposition durch Radonzerfallsprodukte beim Radon-Thermalwasserbad. In: Deetjen, P., Falkenbach, A., (eds) *Radon und Gesundheit*. Lang, Frankfurt, pp. 83–91.

Lahiri B.B., Bagavathiappan S., Jayakumar T., Philip J., 2012, Medical applications of infrared thermography: A review*, Infrared Physics & Technology*. **55**, pp. 221–235.

Moder A., Hufnagl C., Jakab M., Hitzl W., Ritter M., 2011, Radon- therapy in ankylosing spondylitis reduces auto-antibody titers, *Open Journal of Molecular and Integrative Physiology*, **1**, pp. 52-54.

Moldovan M., Nanu A., 2010, Influence of cleansing product type on several skin parameter after single use. *Farmacia*, **58** (1), pp. 29 – 37.

Pinnagoda J., Tupker R. A., Agner T., Serup J., 1990, *Guidelines for transepidermal water loss (TEWL) measurement,* A Report from the Standardization Group of the European Society of Contact Dermatitis. Contact Dermatitis, **22**, 164– 178.

Proksch E., Holleran W.M., Menon G., Elias P.M., Feingold K.R., 1993, *Barrier function regulates epidermal lipid and DNA synthesis. Br. J. Dermatol*. **128**, pp. 473–482.

Report of High Level and Expert Group on European Low *Dose Risk Research. Low Dose Risk Research: The MELODI European Platform Project*, 2009, www.hleg.de/melodi.html

Shehata M., Schwarzmeier J.D., Hilgarth M., Demirtas D., Richter D., Hubmann R., Boeck P., Leiner G., Falkenbach A., 2006, Effect of combined spa-exercise therapy on circulating TGF-β1 levels in patients with ankylosing spondylitis. *Wien Klin Wochenschr,* **118** (9–10), pp. 266–272.

Soto J., 1997, Effects of radon on the immune system. In: Pratzel, H.G., Deetjen, P., eds. *Radon in der Kurortmedizin*. Geretsried: ISMH:103–13.

Tempfer H., Hofmann W., Schober A., Lettner H., Dinu A.L., 2010, Deposition of radon progeny on skin surfaces and resulting radiation doses in radon therapy. *Radiat Environ Biophys,* **49**, pp. 249–259.

WHO, 2009, *World Health Organization handbook on indoor radon: A public health perspective.* Geneva.

Zouboulis C.C., Baron J.M., Bohm M., Kippenberger S., Kurzen H., Reichrath J., Thielitz A., 2008, Frontiers in sebaceous gland biology and pathology. *Exp Dermatol.,* **17**, pp. 542-551.

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(RECOMMENDED CITATION)
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COMPARATIVE STUDY REGARDING THE RISK PERCEPTION OF TSUNAMIS FROM EFORIE NORD (ROMANIA) AND NICE (FRANCE) COMMUNITIES

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ABSTRACT. The goal of this paper is to present a comparative study of the people perception from two different sites from Romania and France, regarding the tsunami risk in the Black and Mediterranean Seas communities. These two surveys over residents' and tourists' perception and preparedness of tsunami hazard were carried out for both towns, Eforie Nord(Romania) and Nice (France), in the frame of the ASTARTE project – „Assessment, Strategy And Risk reduction for Tsunamis in Europe" (EC Programme FP7).Data were collected by tsunami questionnaire developed in the project and translated in Romanian and French languages, and the questions are referring to: interviewee's relation to Eforie Nord and Nice sites, information about interviewed people, tsunami hazard knowledge/risk perception, evacuation issue, awareness of the existing warning system, information, and communication. A total of 256 subjects participated at surveys from both sites situated along coasts of Black and Mediterranean seas.The results of the survey showed a moderate level of tsunami preparedness and perception of people living in, working in, or visiting Eforie Nord and Nice sites, our respondents mentioned the tsunami as third rank in both sites, coming after earthquakes and storms/pollution.Whatever the respondent's status (i.e. local population, or tourists), earthquakes and sea withdrawal are cited as tsunami warning signs by 62% and 60% of the respondents from Eforie Nord and by 30% and 31% of the respondents from Nice, respectively.When considering a future tsunami being generated in Eforie Nord, 36,3% of the respondents think that the place could be affected by a tsunami and the waves could reach more than 2-5 meters (heights cited by approx. 14% of respondents) or even more than 5-10 meters (values cited by 15% of interviewed people). Regarding the Nice site, 78% of the respondents think that the place could be affected by a tsunami in the future. With such a negative perception of tsunamis, it is not surprising that more than 29% of the respondents from Nice site expect waves of more than 10 m high. This study provided evidence that tsunamis recently occurred in the world have a significant impact on people’s preparedness and perception.

Key words: *earthquake, tsunami hazard, tsunami warning system, resilience*

INTRODUCTION

The continuous development of the worldwide coastal areas have lead to the increase of the risk due to different types of hazards, natural or anthropic, permanent or episodic, which might endanger the health and stability of ecosystems and communities from these areas. Thus, even if tsunami is a relatively rare phenomenon comparing to other natural events, it represents a major natural danger involving a significant flooding risk in lower areas near the shorelines. The recent worldwide earthquakes from 26th of December 2004 in Sumatra and 11th of March 2011 in Japan, which triggered tsunami waves up to few tens of meters, have shown how devastating the consequences of such events can be. These events reveal the necessity of developing different actions used in the future for the reduction of damages and destructions caused by tsunamis in coastal area, became quite obvious. Therefore, increasing the tsunami resilience within the communities in areas exposed to risk is of critical importance in order to minimize the damages and to prevent human losses. According to the ADPC guide (2007), the resilience of the coastal communities represents the capacity of a community to adapt to and to influence the course of environmental, social and economic change. Coastal community resilience assessment studies can be useful to characterize the resilience status and trends at the community level and can identify strengths, weakness, and gaps in resilience capacity (ADPC, 2007). These points raise awareness and broadly assess community capacity and vulnerability to coastal hazards and develop mitigation measures (ADPC, 2007).

The main purpose of this study is to present in a comparative way the perception and preparedness of people from two sites from two different countries, Romania and France to natural hazards, with particular attention to tsunami in the Black and Mediterranean Seas. The investigations were carried out in the Eforie Nord and Nice sites (figure 1). In the days dedicated to the surveys, the investigators from both institutions (National Institute for Earth Physics - NIEP and Le Centre National de la Recherche Scientifique - CNRS) have conducted their activity with interviews with shop owners, employees, local population, people representing authorities and tourists from both sites. The questionnaire used for survey contains 51 questions (Constantin et al., 2017). Also by using this questionnaire we collected useful data on awareness of the warning system by the interviewed people, on information and communication regarding this topic (17 questions). At the end of 2015, both institutions finished the field work (questionnaires), processed and interpreted the data for each test site. The total number of questionnaires at the end of the surveys has reached 256 for both test sites (table 1).

Table 1. *Number of questionnaires per site*

Test site	No. of questionnaires	No. of field trips	Investigating institution	No. of investigators
Eforie N	84	2	NIEP	3 researchers
Nice	172	1	CNRS	4 researchers

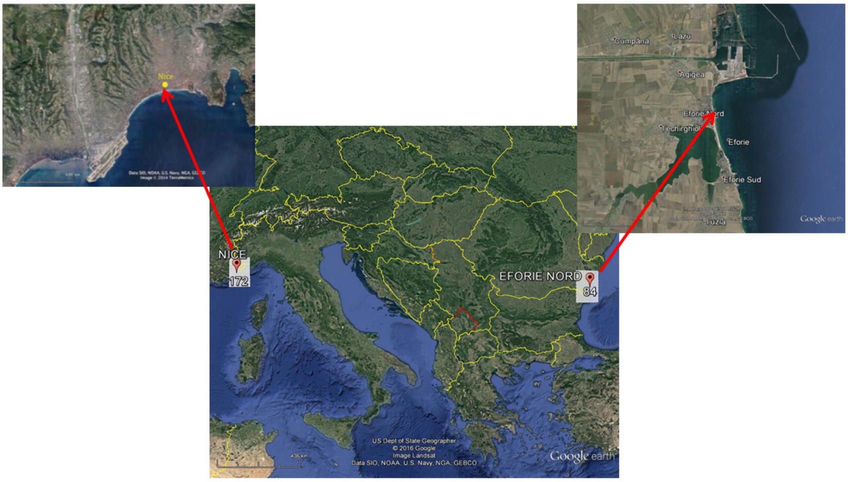

Fig. 1. *The studied areas and number of questionnaires for each site*

Background information

Eforie Nord is considered the second touristic city from the Romanian shoreline. In 2011, the population of the city was accounted as 5188 people, but during the summer time, between June and September of each year, an increase of 4 times the population was recorded (figure 2). Also, the existence in the area of many touristic and important infrastructures (Agigea port near) is very important in this respect. The Eforie Nord city is highly exposed to many possible sources of natural hazard such as earthquakes, land instability, flooding, extreme meteorological phenomena, gas hydrates activity,seashore erosion, submarine landslides and tsunami waves.

Tsunamis affecting Romanian Black Sea shore have all been rather small, causing no damage. Geological research since the late 1990's suggests that the Western coast of Black Sea has been impacted by palaeo tsunami (Ranguelov and Gospodinov, 1995; Dotsenko, 1995; Panin, 1996, 1997). In fact, this part of the Black Sea shore was hit in the past by three tsunami triggered by strong earthquakes generated in Shabla area, North-Eastern Bulgaria. First occurred on 1st Century BC, which damaged the city of Bizone, nowadays Kavarna (Nikonov, 1997). In 544/545 AC, another earthquake triggered 6 km of flooded land in south Dobrogea (today Bulgarian shore) (Ranguelov, 1998). The last strong earthquake (M 7.2) occurred on 31st of March 1901, in the same seismic zone, inducing few km landslides and a subsidence of approximately 3 m(Partheniu et al., 2014; Partheniu et al., 2015). The recent event occurred in 2007 was reported as being associated to a submarine landslide generated in the Bulgarian area of the Black Sea (Papadopoulos et al., 2011).

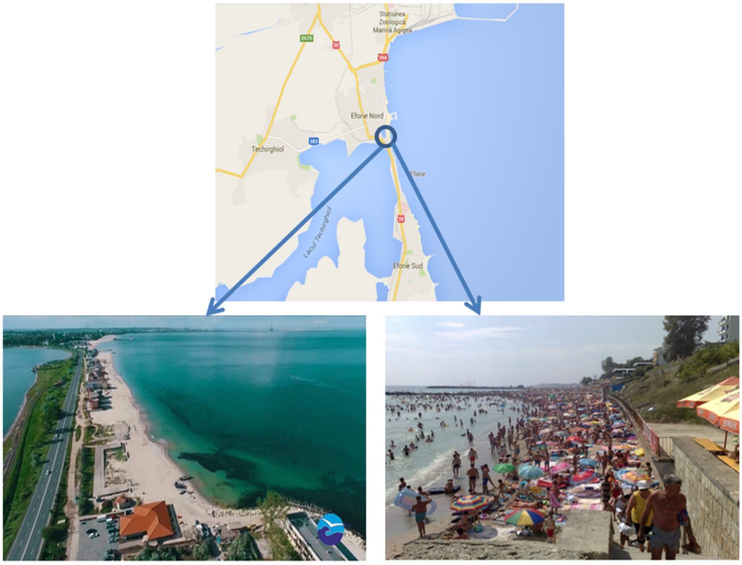

Fig. 2. *Aerial photo of the Eforie Nord site and super crowded beach in the summer*

The coastal city of *Nice* is characterized by high population density, with more than 340,000 inhabitants in 2009 and one third of the 4 millions of tourists frequenting the Riviera and other touristic and industrial infrastructures (airport and cruise port). The beach of Nice is highly frequented and characterized by an important vulnerability to tsunamis (figure 3).In the area, sources of tsunami hazard can originate by earthquakes from the North-African faults and by submarine landslides or local coastal landslides (Lavigne et al., 2014). Also, The Nice area is directly exposed to the Ligure fault, expecting a tsunami wave striking about 10 minutes after the earthquake. Seismic and tsunami catalogues account in the past three tsunamis concerned Nice in 1564, 1887 and 2003. In 1887, waves reached 2 m at Cannes and Antibes, submerging most of the beaches. The last one impacted in the night eight French harbors. Other tsunami struck the coast near Nice, on October 16, 1979 being triggered by a submarine landslide. Now, the city itself is not directly exposed to the tsunami hazard, since it is protected by a 5 meters dike. Then, no tsunami wave striking buildings and streets is expected, but the beach, is directly exposed (Fressard et al., 2017).Despite a low extent phenomenon compared to the events of Indonesia in 2004 and in Japan in 2011, the risk in Nice is actual.

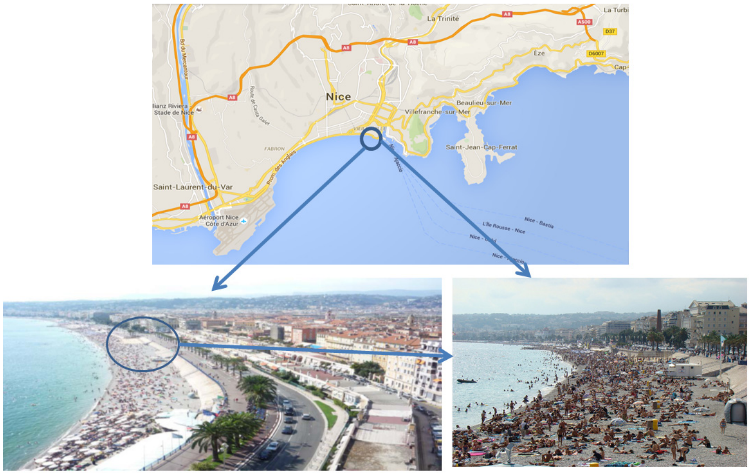

Fig. 3. *The Nice seafront, viewed from the Bellanda Tower (photo by J. Lopes, 19/08/2009) and crowded beach (photo by Plamen Dragozov)*

For such reasons and similarities of costal shapes of both sites, in the areas of Eforie Nord and Nice and their surroundings, many aspects of tsunami hazard, vulnerability and risk were investigated along the coasts of Western part of Black Sea and Mediterranean Sea.

PROFILE OF RESPONDENTS FROM EFORIE NORD AND NICE

In terms of the respondents, we questioned in the survey a large proportion of women 51.17% compared to 48.83% male (table 2), majority of them are adults aged 20-65 (82.8%) and few people aged over 65 (14.5%)

(figure 4). A total of 256 subjects participated at surveys from both sites situated along coasts of Black and Mediterranean seas.

Table 2. *Profile of interviewed people from Eforie Nord and Nice*

Gender balanced	Mean age	Education level	Status	Nationality
51,17% female 48,83% male	46	85% University degree	48% residents/ workers, 52% tourists	91,8 % nationals, 8,2% foreigners 10 nationalities

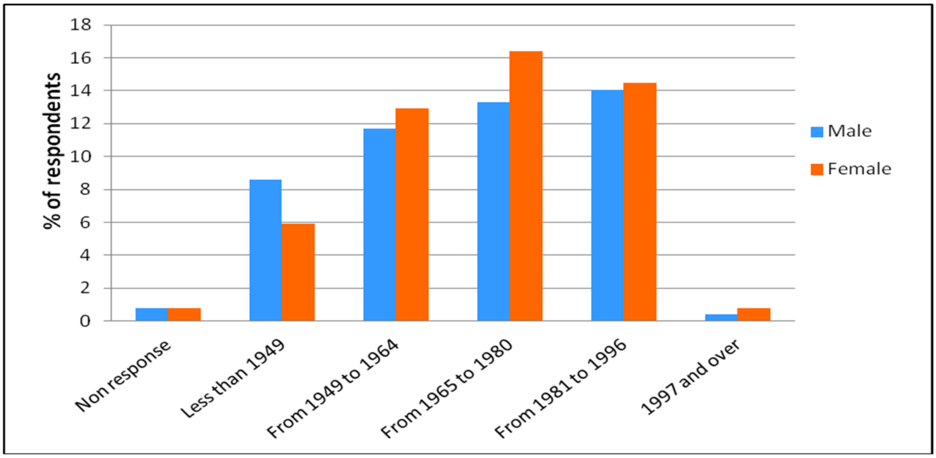

Fig. 4. *Proportion (%) of individuals from Eforie Nord and Nice by year of birth and sex*

Tsunami hazard knowledge and risk perception in Eforie Nord and Nice

The data was collected by tsunami questionnaire developed in the ASTARTE project and translated in Romanian and French languages, and the questions are referring to: interviewee's relation to Eforie Nord and Nice sites, information about interviewed people, tsunami hazard knowledge/risk perception, evacuation issue, awareness of the existing warning system, information and communication.

Respondents from both test sites (Eforie Nord and Nice) have mentioned from natural and anthropic types of hazards, the tsunami as third rank, coming after earthquakes and storms/pollution (table 3 and figure 5).

Table 3. *Natural and anthropic hazards in Eforie Nord and Nice*

	Natural and anthropic hazard							
Ranking	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Eforie Nord	Earth quake 39%	Storm 37%	***Tsunami 22%***	Flood 16%	Land-slide 11%	Tornado 6%	Erosion 3%	Fires 2.5%
Nice	Earthquake 34%	Pollu-tion 19%	***Tsunami 13%***	Storm 12%	Flood 10%	Incivility 5%	None 3%	

"In your opinion what are the main hazards that could affect this area?"

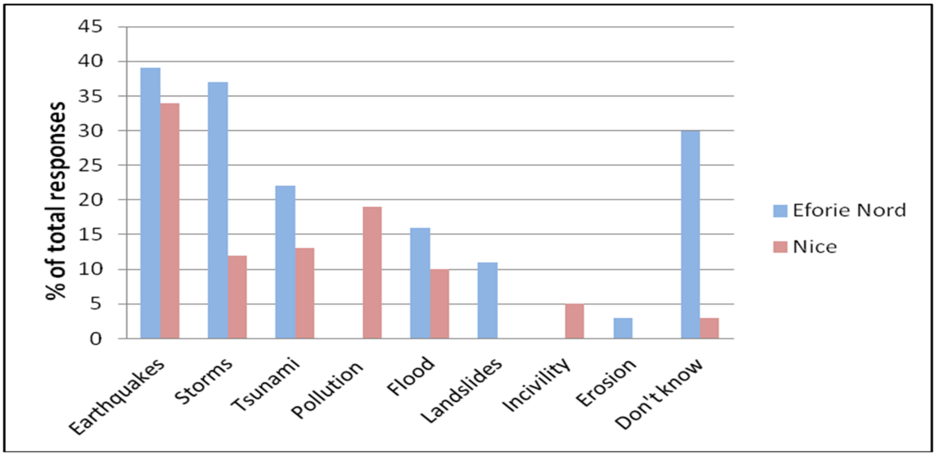

Fig. 5. *Possible natural and anthropic hazards that could affect Eforie Nord and Nice (in %)*

Regarding the above question, TV and media coverage of big and recent events (tsunami from 2004 in Sumatra and the one from Japan 2011) have been the main opportunity to learn the word tsunami for the respondents from both sites. Also, the internet and education are more efficient in Eforie Nord than Nice (figure 6).

"Where did you hear or learn the word Tsunami?"

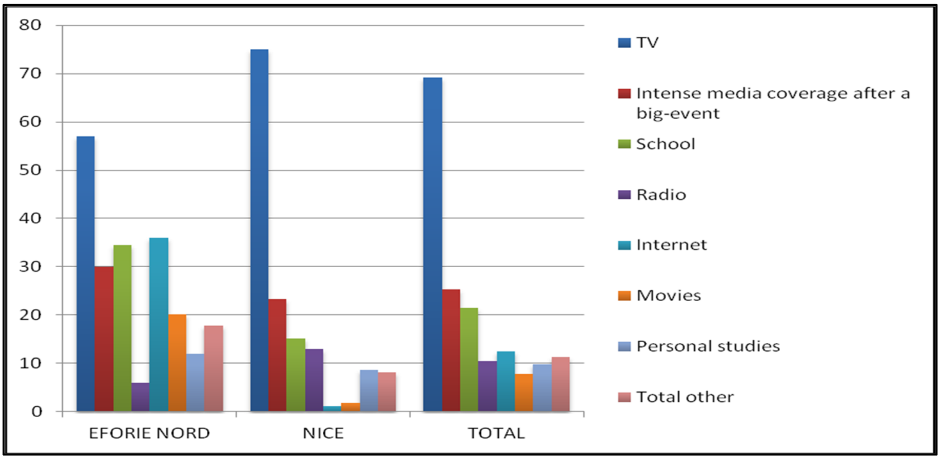

Fig. 6. *Knowledge about the word „tsunami" (in %)*

"In your opinion this area could be affected by a tsunami?"

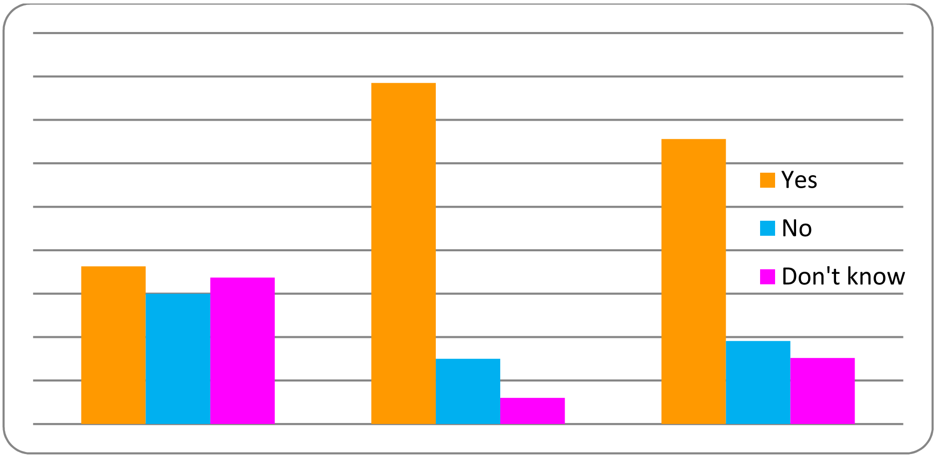

Fig. 7. *Possibility of a tsunami event in the future (%)*

When considering a future tsunami being generated in Eforie Nord, 36,3% of the respondents think that the place could be affected by a tsunami (figure7) and the waves could reach more than 2-5 m (heights cited by approx. 14% of respondents) or even more than 5-10 m (values cited by 15% of interviewed people) (figure 8). Regarding the Nice site, 78% of the respondents think that the place could be affected by a tsunami in the future. With such a negative perception of tsunamis, it is not surprising that more than 29% of the respondents from Nice site expect waves of more than 10 m high (figure 8).

“In your opinion what could the maximum tsunami wave height be in this area?"

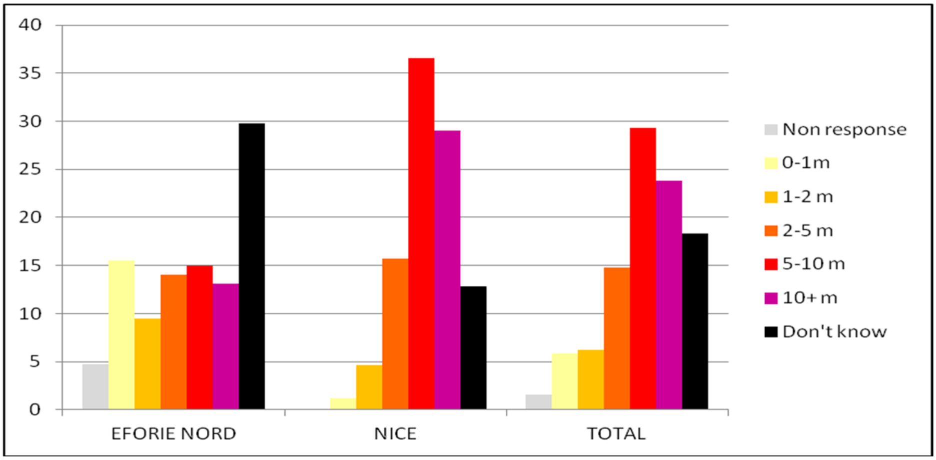

Fig. 8. *Supposed wave heights in case of a tsunami (%)*

Very light difference regarding the answers given by respondents from both sites with respect the predicted maximum tsunami waves height of 2-5 m. But, a high procentage of population from Nice consider that tsunami waves could reach up to 5-10m and even more than 10 m. We can conclude that in Nice is an overestimation of tsunami hazard. It's seems that media coverage of big and recent events had a major role in this overestimation. Nevertheless, only in Eforie Nord a significant procentage of respondents have estimated maximum tsunami wave height between 0 - 1 m, this value being much closer to the (tsunami) model results obtained for this site. It's seems that romanian people are more realistic (figure 8).

After the survey, earthquake, sea withdrawal, animal behavior, and big waves were mentioned in both countries as the 4 pre-signs of a tsunami. Whatever the respondent's status (i.e. local population, or tourists), earthquakes and sea withdrawal are cited as tsunami warning signs by 62% and 60% of the respondents from Eforie Nord and by 30% and 31% of the respondents from Nice, respectively (figure 9).

“What are the indicators that a tsunami could happen soon? (precursor signs)”

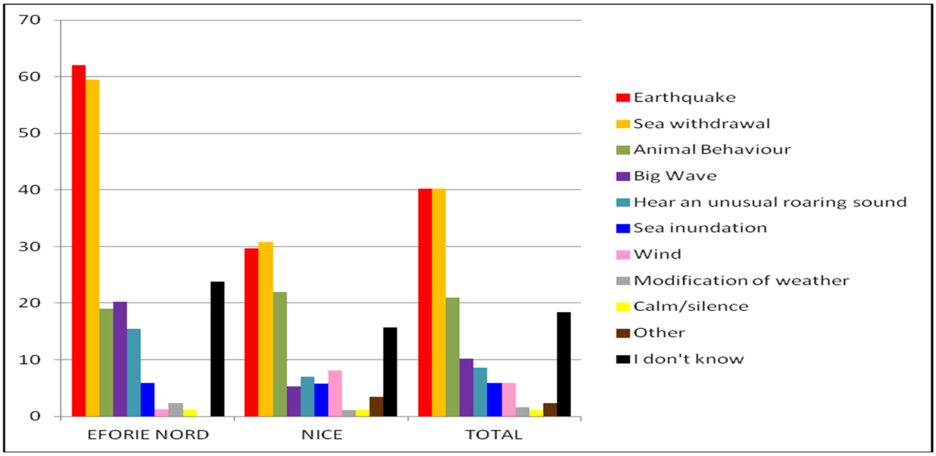

Fig. 9. *Precursor signs of a tsunami cited by the interviewees in both countries (in %)*

Behavior after an earthquake

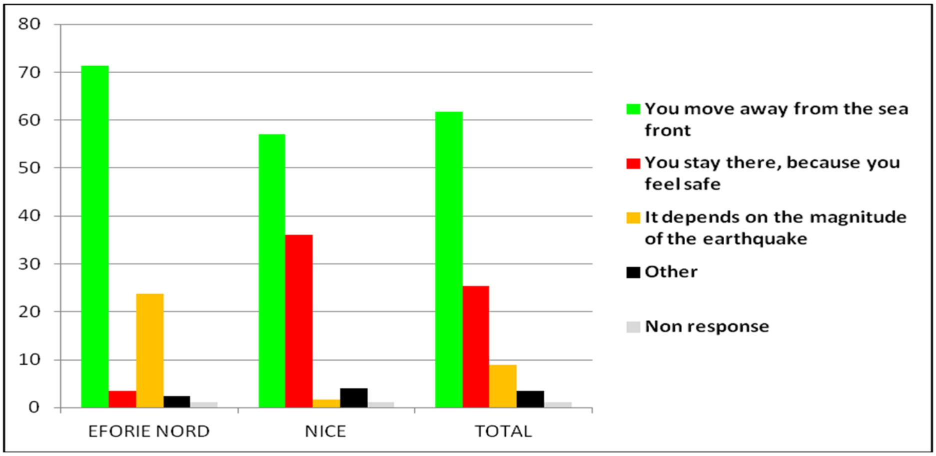

Fig. 10. *Perceived reaction in relation with people's behavior after an earthquake that might trigger a tsunami (in %)*

Very big difference between the answers given by respondents from the two sites regarding the behavior after an earthquake: in Nice a high percentage of the interviewed people (36%) answered that they would not leave the beach, because they feel safe.In Eforie Nord people are more cautious about their safety, 71% from the respondents would move away from the sea front in the case of a tsunami (figure 10).

At this question the respondents from both test sites have an accurate behaviour, but a high percentage of respondents (70%) from Eforie Nord answered that they will look first for a higher site. Also, 61% of the respondents from Nice, answered that they will move away from the beach (figure 11).

Behavior after a sea withdrawal

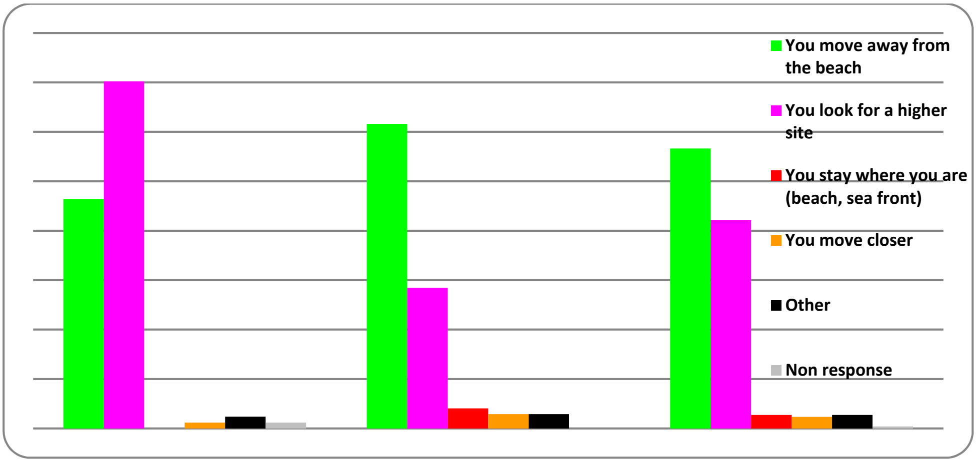

Fig. 11. *Perceived reaction in relation with people's behavior after a sea withdrawal (in %)*

CONCLUSIONS

From all the data collected through these two surveys performed in order to find out the level of knowledge, resources, and attitude of the Romanian and French population regarding the tsunami phenomenon on the Black and Mediterranean Seas, it appears that the preparedness level is average, and in general, in Europe a low attention is paid to tsunami risk, maybe due to their relative infrequency and, also their smaller scale.Our respondents from both sites mentioned the tsunami as third rank in both sites, coming after earthquakes and storms/pollution. Following this study, one may conclude that part of the interviewed people from Romania are well documented (through school and internet) and are aware of the phenomenon, meanwhile others,french people especialy, know about tsunami only from TV. Important to emphasize is the fact that people are aware (65%) that a tsunami might happen in the future (reported in both test sites), they have a fairly good knowledge of precursor signs (more than 40% cited earthquakes and sea withdrawal), and in a case of tsunami over 60% of the respondents will evacuate the beach. One of the weak point in Nice is the overestimation of the tsunami height compared with the tsunami model results developed for that area: 37% of the people expect a wave height in excess of 5 m and 29% up to 10 m, whereas the modeled heights are less than 4 m for the worst cases (Lavigne et al., 2017). This overestimation is mainly due to extensive media coverage of the disasters caused by the major tsunamis trigerred by the earthquakes from December 26, 2004 in Sumatra and March 11, 2011 in Japan.

When you associate low to moderate levels of risk perception and hazard knowledge with innapropriate expected attitudes of the people (locals and/or tourists), a disaster is imminent althought only small tsunami waves (with heights less than 2 m) might occur during the day in full summer season (in July and August).

The main conclusion that we can underline is the need of education which is considered a key instrument for the increase of the resilience for any type of hazard, natural or anthropic. For that purpose, the results of this study illustrate the necessity of education and training of the coastal communities about the tsunami hazard.

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REFERENCES

ADPC, 2007, *How Resilient is your Coastal Community? A guide for evaluating coastal community resilience to tsunamis and other hazards*; U.S. Indian Ocean Tsunami Warning System Programme, Printed in Bangkok, Thailand, pp. 10–164.

Constantin A. P., Moldovan I. A., Lavigne F., Grancher D., Partheniu R., 2017, Perception And Preparedness Of The Tsunami Risk Within The Black Sea (Romania) Communities, *Proc. of the 17th International Multidisciplinary*

Scientific GeoConference, STEF92 Technology Ltd., ISBN 978-619-7408-00-3, pp. 311-318,

Dotsenko S. F., 1995, The Black Sea tsunami. *Atmospheric and ocean physics*, **30** (4), pp. 483 – 489.

Fressard M., Grancher D., Taillandier P., Brunstein D., Lavigne F., 2017, *EU report – D 9.36 - Large scale accessibility mapping and evacuation simulations using GIS tools and Multi-Agent Systems*, FP7 ASTARTE project -FP7-ENV2013 6.4-3- Project number: 603839/2013.

Lavigne F., Goeldner-Gianella L., Grancher D., Anselme B., Liotard A., Lopes J., Charpentier C., Lenouvel J., et al., 2014*, ASTARTE Report: D.9.7- Report on preparedness skills, resources and attitudes within the communities*. FP7 Project (FP7-ENV2013 6.4-3) - Project number: 603839/2013.

Lavigne F., Quernez R., Fressard M., Brunstein D., Grancher D., Goeldner-Gianella L., Burnel M., Liotard A., Plattard O., Leone F., Gherardi M., Péroche M., Aguirre Ayerbe I., Zaniboni F., El Mouraoua A., Benchekroun S., Dogulu N., Kalaycioglu S., Duzgun S., Yalciner A. C., Kanoglu U., Papadopoulos G.A., Baptista M.-A., Omira R., 2017, *ASTARTE Report: D.9.36- Large scale accessibility mapping and evacuation simulations using GIS tools and Multi-Agent Systems*. FP7 Project (FP7-ENV2013 6.4-3)- Project number: 603839/2013.

Nikonov A., 1997, Izvestiya, *Physics of the Solid Earth*, **33**, pp. 77-78.

Panin N., 1996, *Impact of global changes on geo-environmental and coastal zone state of the Black Sea, GEO – ECO – MARINA*, Bucharest, **1**, pp. 7-23.

Panin N., 1997, On the geomorphologic and the geologic evolution of the River Danube – Black Sea interaction zone, GEO – ECO – MARINA, Bucharest, **2**, pp. 31-40.

Papadopoulos G. A., Diakogianni G., Fokaefs A., and Ranguelov B., 2011, Tsunami hazard in the Black Sea and the Azov Sea: a new tsunami catalogue. *Nat. Hazards Earth Syst. Sci.*, **11**, 945–963.

Partheniu R., Diaconescu M., Grecu B., Ionescu C., Neagoe C., Marmureanu A., Verdes I., 2014, Earthquakes and tsunamis monitoring in the western Black Sea area, Proc. of the *5th National Conference on Earthquake Engineering* and the *1st National Conference on Earthquake Engineering and Seismology – 5CNIS & 1CNISS,* June 2014, ISBN 978-973-100-342-9, Editura Conspress, pp. 157-164.

Partheniu R., Diaconescu M., Ioane D., Marmureanu A., 2015, Tsunami modeling scenarios for some of the seismic sources in the black sea area, using tsunami analysis tool software, Extended abstract of the *8th Congress of the Balkan Geophysical Society*, Chania, Creta, Grecia.

Ranguelov B. K., Gospodinov D., 1995, Tsunami vulnerability modeling for the Bulgarian Black Sea coast. *Wat. Sci. Tech.*, **32** (7), pp. 47 – 53.

Ranguelov B., 1998, Abst. Intl. Symp HAZARDS'98, Chania, Crete, may 17 - 22, pp.125.

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(RECOMMENDED CITATION)
DOI:10.24193/subbambientum.2018.2.04

ECO-FRIENDLY RECYCLING POTENTIAL OF MICROWAVE MELTING FOR THE RECOVERY OF USEFUL AND PRECIOUS METALS FROM E-WASTE

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ABSTRACT. The processing of waste electrical and electronic equipment (WEEE) has become an issue of significant importance due to the large volumes being generated and to the content of rare and valuable metals as well as environmentally toxic materials (organic compounds). Presently, WEEE is regarded as an important secondary resource of useful metals.

The aim of this study is to evaluate the content of base and precious non-ferrous metals in such wastes collected in Romania and to assess the potential of their recycling through processing in microwave field.

Electric and electronic wastes are complex mixtures of materials and components, with chemical compositions which depend on their sources (printed circuit boards - PCBs, mobile phones, television and radio sets, home appliances and industrial equipment). In PCBs the metallic fraction is of approximately 30-50 wt.% (with 45-65 wt.% Cu, 0.5-20% Pb, 15-25% Sn, 5-8% Zn, 0.4-0.8% Ag, 0.08-0.2% Au and 2-5% other metals such as Fe, Ni, Al, Sb, Cr, Mn etc.). The non-metallic fractions, which account for 50-70 wt.%, contain substances such as brominated flame retardant,

thermosetting resin, reinforced materials and other toxic and hazardous organic compounds. The combustion of these materials during the pyrometallurgical processes may cause serious environmental problems, due to the generation of toxic gases.
The microwave melting of WEEE represents a promising state-of-the-art, ecological and energy efficient alternative for the conventional methods with a remarkable applicative potential. The advantages of this method are: ***i.*** reduced melting time with energy savings of 30-40%, compared to traditional processes (a microwave furnace can easily attain temperatures up to 1600°C in less than 30 minutes); ***ii.*** low content of organic substances. ***iii.*** facile extraction of the enclosed metal fractions; ***iv.*** improved process control; ***v.*** absence of direct contact with the melting materials and ***vi.*** environmental-friendly approach through the possibility of treating the toxic gas emissions in a microwave field at high temperatures (1300 ÷ 1400^0C).

Key words: *recycling, non-ferrous metals, microwaves, e-wastes*

INTRODUCTION

In the economy of today the production of metals has heavily increased in order to meet the need of metals for a wider range of applications. The development of the industry in general and particularly of the metallurgical industry is conditioned by the solution of major issues, which ensue the relation between the industry and nature, strictly oriented towards the protection of natural and energy resources and pollution control. Currently, the source of metals has shifted from highly concentrated ores to ores with low concentrations and various industrial wastes (Grundas, 2011). Although the practice of recovering valuable metals has been applied for a long time, today the protection of natural resources and of the environment is a significant incentive for the recovery of metals after use.

The concerns about the conformation to the legislation regarding environment protection and the necessity to harmonize the processes and the technological progress and the sound management of raw materials and energy resources must lead to the exploitation of wastes by technologies which offer the optimum solution, both economically and environmentally. The collection, recycling and processing of wastes represent a priority which is found in the commitments assumed by Romania towards the European Union. In Romania, waste deposits are amongst the sources which generate impact and risk for human health and for the environment, as a result of a lack of facilities and insufficient exploitation.

Apart from the primary obtaining of non-ferrous metals from ores, a process which requires high energy consumption, recycling is gaining an increasing importance. Recycling constitutes a major component in the replacing of the ores for several metals. The demand for metallic wastes depends on the structure of the industry and on the availability of waste processing technologies for obtaining products with high added value. The goals of the development strategies for various industrial domains are encompassed in two directions:

- the development of state-of-the-art technologies which significantly reduce emissions;
- the increase of recycling and recovery efficiencies to values close to 100% for byproducts.

The metallic wastes can be recovered from a wide range of products which are at the end of their lifecycle, rejects or metallic scraps resulting from machining. Beside the base metal, some metallic wastes also contain other metals such as: zirconium, tungsten or precious metals. Thus, copper, aluminum, lead, zinc, precious and refractory metals, as well as other metals, can be recovered from products or their residues and can be reintroduced in the economic cycle by recycling. Through processing wastes are transformed in secondary raw materials. The introduction of a higher proportion of secondary raw materials in the production processes leads to the substantial reduction of ore and energy consumptions (IPPC, 2001), thus contributing to the increase of the industrial profitability (www.cee-environmental.com, Resource Recycling Fund Management Committee, Govt moves to stem tide of 'e-waste').

The energy saving is so high that it is possible to also re-melt economically the wastes with a low metal content, as well as impure and coated wastes (plated or coated parts, burnt or etched wires). The production of secondary nonferrous metals consumes a much lower quantity of energy, compared to the winning of primary metal from the ore (table 1).

Table 1. *Energy and materials savings in non-ferrous metals recycling*

Recycled metal	Percent of recycled metal used in obtaining new metal	Energy savings
Aluminum	39 %	95 %
Copper	32 %	85 %
Lead	74 %	60 %
Zinc	20 %	60 %

The value of the recycled non-ferrous metals is very high, for copper representing approximately 95% of the value of the primary metal extracted from the ore. The recycling rates of nonferrous metals are significant, with values starting from 67% and up to 92% in the automotive industry, constructions, electronics and packaging.

Another major advantage of recycling non-ferrous metals from wastes is the reduction of the CO_2 emissions produced during the processes of obtaining primary metals. Recent EU data state that the use of recycled raw materials, including metals, leads to the reduction of CO_2 emissions with approximately 200 de million tons/year. In the case of copper recycling, the CO_2 emissions are reduced with almost 65%, and in the case of lead the reduction is of approx. 99%.

The electronic products waste also contains valuable secondary materials - metals and plastics – which can be used in the manufacturing of new products. Approximately 25% of the annual Ag and Au production and 65% of the Pd and Pt production come from recycled materials (WEEE[1] and catalyzers), (*Sustainable Innovation and Technology Transfer Industrial Sector Studies, Recycling – from E-Waste to Resources*, 2009*)*. The necessity of WEEE processing results from the large quantities generated and the content of valuable metals (0.1 % Au, 0.2 % Ag, 20 % Cu, 4 % Sn-figure 1) (*Recycling technology advances and new material development key to successful e-waste recovery, Integrated Approach to Electronic Waste (WEEE) Recycling, 2007*). It is estimated that approximately 20 ÷ 25 Mtons/year of electronic wastes are generated globally, the largest

[1] WEEE – electric and electronic equipment waste

quantities being produced in Europe, USA and Australia (Havlik et al., 2009; Robinson, 2009). In the EU, approx. 6.5 ÷ 7.5 Mtons WEEE/year are generated, representing 16 Kg/inhabitant. The WEEE[2] composition is presented in figure 1.

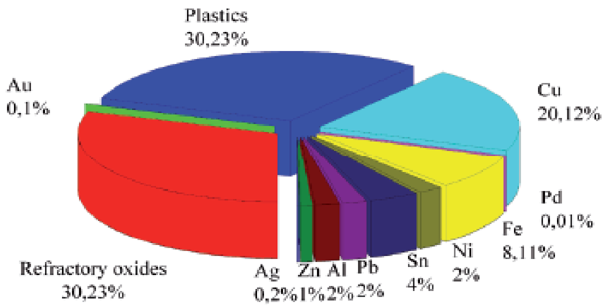

Fig. 1. *WEEE composition*

Generally, the process of recycling non-ferrous metals implies several steps, such as: sorting, shredding, pressing and melting the wastes in various types of furnaces. The resulting alloys are cast in the shape of slabs or ingots and are used directly in the metallurgical industry or they can be transformed in metal sheet or other products.

Depending on materials, various types of equipments are used for melting the secondary non-ferrous metals. For this purpose, the selection of the optimum melting method is determined by the metallic component of the waste, the waste geometry, the waste composition and by the manner of operating the furnace. For the oxide-poor wastes or with organic impurities, the adequate melting equipment is the hearth furnace, with no salts addition. The large sized wastes are melted in crucible or double chamber furnaces. Even scrapings can be melted with high extraction efficiency in hearth furnaces. The metal extraction efficiency is the main productivity criterion of waste melting.

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[2] *An Integrated Approach to Electronic Waste (WEEE) Recycling*, Project funded by DEFRA Waste and Resources Research Programme Reference WRT208, Final Project Report, Deliverable M12 SID5 Form – Section 8, 2007

USING MICROWAVE ENERGY FOR MELTING NONFERROUS METAL WASTES

The pyrometallurgical process represents a common solution for recovering valuable elements from various industrial wastes. However, these conventional pyrometallurgical recycling processes (e.g. the Waelz process) present some inherent drawbacks.

The use of microwaves (MW) for heating originated in 1946 and has been applied in various fields (Grundas, 2011). Recently, researchers investigated the microwave heating process as a promising recycling method, since it presents characteristics such as a fast heating rate and direct internal heating. Microwave heating can also provide significant time and energy savings.

Until recently, metal heating was not a major application field of microwave energy. It is well known that while a bulk metal reflects microwaves, metal particles and thin films can be easily heated. Another well-known fact is that ferro-magnetic metals can be heated more, which indicates that magnetism is tightly connected to the heating mechanism. Walkievics (1988), while testing the heating of various metallic powders, reported an interesting experimental result which demonstrated that there are differences in their heating rates. Some reports related to heating of metals (cermets, composites) were presented in the 1991 and 1992 MRS symposia, (Lorenson et al., 1991; Bescher et al., 1992). Mingos and his co-workers researched the synthesis of a metal sulfide by microwave heating of metals (Whittaker and Mingos, 1995). Roy and collaborators (1999) reported the successful microwave sintering of metals. Later on, they investigated the heating of metals in the separated Electric (E-) and magnetic (H-) microwave fields (Cheng et al., 2002; Roy et al., 2002). Research on microwave metal heating was carried on also in Europe (Rodiger et al., 1998; Leonelli et al., 2008). This research motivated the MW investigators to a more intense pursue of the study of metal heating.

A special symposium on metal heating was held in the annual meeting of the Japan Institute of Metals in 2005. Yoshikawa published a major review article (Yoshikawa, 2009) in which the recent results were presented and the application areas were classified.

The separated electric and magnetic microwave heating is directly related with the basic principles of the microwave heating mechanisms and of the microwave interaction with materials.

The various types of industrial wastes (mill scale, slag, dust, sludge etc.) contain useful elements such as Fe, Zn, etc., and consequently many researchers have suggested various methods for recycling the valuable metals. The most recent technology under investigation is microwave processing.

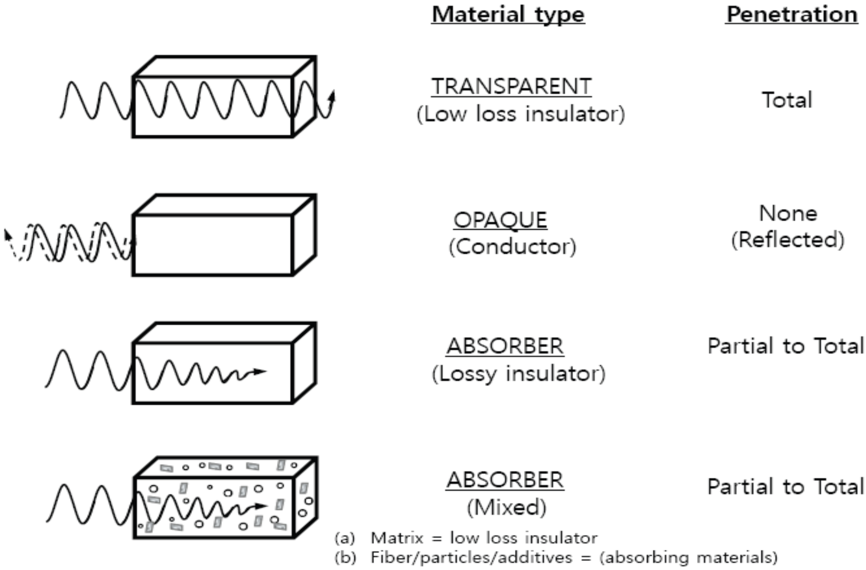

Fig. 2. *Material behavior in a microwave field*

Microwaves are electromagnetic waves with frequencies ranging from 300 MHz to 300 GHz and with wavelengths of microwaves ranging from 1 mm to 1 m, which is much larger than the molecular (nm) or crystalline (μm) grain size. Therefore, microwaves can provide energy to the valence electrons, leading to electron fluctuations. Microwaves can be absorbed, transmitted, or reflected, depending on the material type (figure 2). When microwaves are absorbed in a material, the electron fluctuation is finally transferred to the lattice ions and they create vibrations in the atomic lattice, resulting in heating energy. The heating rate varies with the electromagnetic properties of the material (complex permittivity and permeability), and the average power which can be absorbed by a material is the sum of the electric and the magnetic losses.

When microwaves are concentrated in a certain location on the material, the local temperature becomes higher than in the neighboring areas. As the local temperature surpasses a critical value, the heating rate becomes much higher, leading to the acceleration of the heating rate of the surrounding areas. This sudden thermal behavior can be very useful to significantly accelerate high temperature reactions and to diminish energy consumptions. Standish and Huang successfully recovered the metallic component from magnetite and hematite using microwave heating and reported that the microwave heating was five times faster than the conventional heating (Standish and Huang, 1991).

The microwave furnace is composed of three major elements: the microwave source, the transmission lines and the applicator (Das et al., 2009). The process is performed in a metallic applicator, which can be a traveling wave applicator, a single mode applicator or a multimode applicator, depending on the material to be processed. The single mode applicator and the traveling wave applicator are designed for processing materials with a simple geometry. The multimode applicator is used to produce large components with complex features and thus it is used for industrial applications. The material contained in the applicator absorbs or reflects the electromagnetic radiation generated by the source and delivered by the transmission lines (Thostenson and Chou 1999).

EXPERIMENTAL RESEARCH FOR MELTING E-WASTES IN A MICROWAVE FIELD

Hereafter are presented the results of experiments carried on for melting electrical and electronic equipment wastes (WEEE). The design of the experimental installation for the recovery of non-ferrous metals by using microwave energy for melting metallic wastes is given in figure 3.

The installations mainly consist of the steel casing of the furnace (1), on which three microwave generators are mounted on the exterior. The microwave susceptor graphite crucible (4), in which the metallic waste is contained, is placed inside the furnace. For eliminating the heat losses through the chamber walls, between the exterior wall of the crucible and the furnace chamber a thermal isolation layer (2) is placed, manufactured from super aluminous ceramic fiber and resisting temperatures of up to 1600^{0}C. The heating of the material is carried on using three microwave generators (6) of 800 W each, mounted on the furnace walls. In order to diminish the risk of metals oxidation during melting, a melting flux is added (a mix of NaCl + KCl in a 1:1 ratio) in quantities representing 5-10 wt.% of the total waste quantity, and the furnace is designed with a system for obtaining an inert nitrogen atmosphere, at a pressure of approximately 0.5 bar. Inside the crucible, the temperature is measured using a wire Pt/Pt-Rh thermocouple (8).

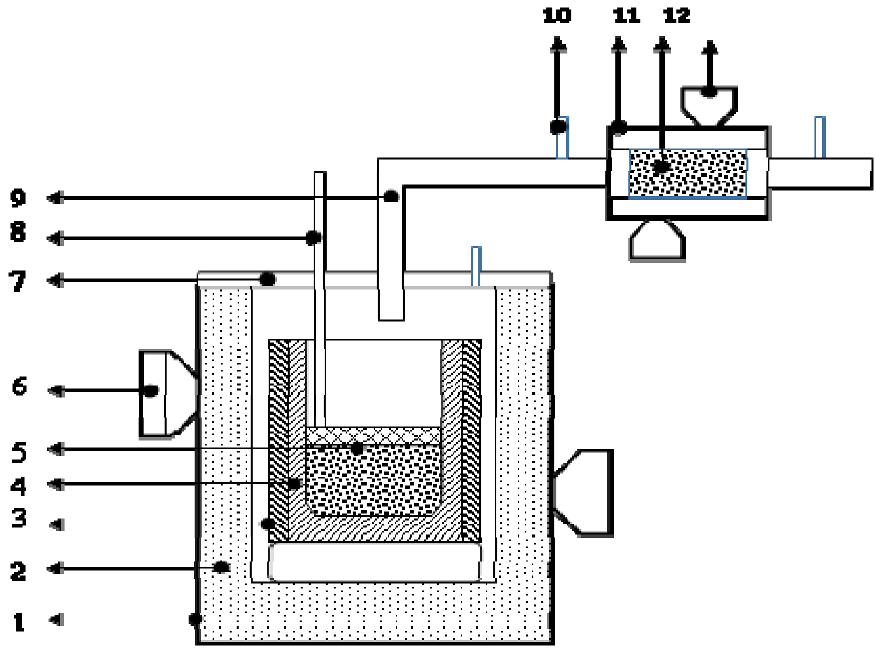

Fig. 3. *Design of the experimental installation for the recovery of nonferrous metals from metallic wastes by melting in a microwave field: 1. Furnace body (steel); 2. Thermo-insulating material; 3. Microwave susceptor material (SiC); 4. Graphite crucible; 5. Crushed PCBs+Fluxes charge ; 6. Microwave generators; 7. Furnace cover (steel); 8. Thermocouple (Pt/Pt-Rh); 9. Gas exhaust tube (steel) ; 10. Gas sampling tube; 11. Microwave field gas treating filter; 12. Microwave susceptor material (SiC pellets); 13. Microwave generators.*

The PCB wastes used in the experiments require a melting temperature of approximately 1000 ÷1200^{0}C. The flowchart of the melting process in a microwave field is given in figure 4.

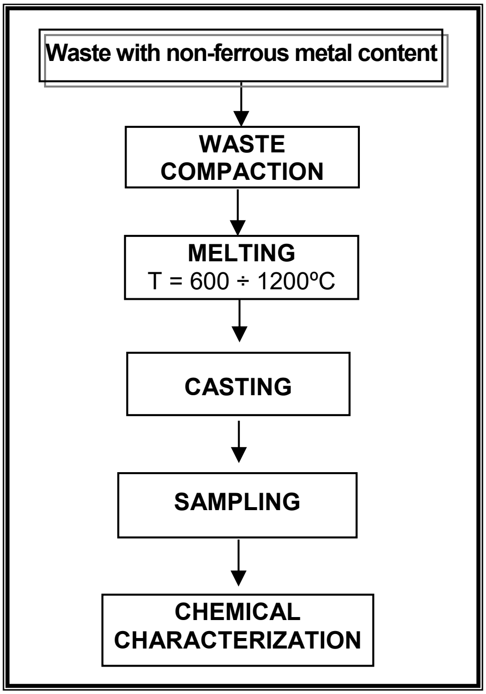

Fig. 4. *Flowchart of the melting process for wastes with non-ferrous metals content*

WEEE which result from the dismantling of electric and electronic equipment come in the form of powders with particle sizes of approximately 0.5-2 cm (figure 5). The powder contains approx. 50% organic fraction and ceramic components.

Fig. 5. *Grinded electric and electronic equipment wastes*

The wastes are mixed with the flux (NaCl + KCl in a 1:1 ratio), which represents 5% of the total waste quantity (calculated at an approximately 50% non-ferrous metal content in the waste). The mixture is introduced in the graphite crucible and is heated in the furnace using microwave energy, in a first step from 300 to 500^{0}C, when the pyrolysis of the organic materials present in the grinded printed circuit boards takes place. Subsequently, the temperature is risen to approx.1100^{0}C for melting the non-ferrous metals which have higher melting points, respectively: Cu (preponderant), Au, Ag.

The resulting multi-component alloy is casted as ingots (figure 6). The analysis of the chemical composition is presented in table 2. The metal recovery efficiencies were of approx. 44 ÷ 46%, the organic and ceramic fractions representing almost 50% of the initial wastes.

Fig. 6. *Multi-component alloy ingots resulting from the melting of WEEE in a microwave field*

Table 2. *Chemical analysis of the multi-component alloy resulting from the WEEE melting, %*

Cu	Al	Sn	Zn	Pb	Fe	Ni	Sb	Si	Mg	Mn	Au	Ag	Pd
rest	0.056	31.5	7.8	6.2	0.26	0.78	0.17	<0.1	<0.005	<0.002	0.016	0.075	0.0082

The experimental conditions of the gas treatment process are given in the table 3 and the results are presented in table 4. The emissions were measured at the exhaust outlet located behind the thermal filter that is positioned at the top of the melting furnace. The sampling was performed using the non-extractive method that did not require sample absorption and was limited to the gas flow existing in the pipe. The sampling plane was located in a section of the waste gas pipeline where homogeneous flow conditions and concentrations are expected, away from any fluctuation which could result in a change in effluent direction (a pipe section with a right line length of at least 5 hydraulic diameters upstream and 2 hydraulic diameters downstream of the sampling plane).

Table 3. *Experimental conditions for the treatment of gaseous emissions in microwave field*

Temperature [°C]	Gases flow [m^3/min]	Material filter	No. of magnetrons
1300 ÷1400	**0.1 ÷ 0.2**	**SiC (pellets)**	**3 @ 850 W**

Table 4. *Chemical composition of the effluent gases before and after the microwave thermal treatment*

Components	Concentration, [mg/m³]		
	Out furnace		Out filter
	$T_{furnace}$ 300ºC	$T_{furnace}$ 500-800ºC	T_{filter} 1300-1400ºC
Ethyl chloride	6.42	1.37	-
Methyl chloride	1.95	0.76	0.08
Ethylic alcohol	1.25	0.42	0.028
Butanol	6.06	0.92	0.05
Benzene	5.43	14.70	0.035
Ethylbenzene	-	1.31	0.072
Styrene	-	0.37	0.098
Toluene	1.07	2.88	0.06
m/pXilen	-	1.56	0.004
Acetone	105.70	1.80	-
Bromomethane	82.57	-	-
Trimethylbenzene	1.35	5.30	0.015

A TESTO 435 analyzer was used for the determination of the exhaust gas physical parameters (rate, temperature, pressure).

It can be observed that the treatment of the resulting exhaust gases in a microwave environment at a temperature of 1300 ÷ 1400°C lead to a reduction of up to 98% of the toxic compounds by thermal neutralization.

CONCLUSIONS

Compared to the classical pyro metallurgical technologies for the processing of non-ferrous metal wastes, microwave melting represents a modern, ecological and efficient alternative, with high applicability. The process presents as main advantages: low melting time with energy savings of approximately 35% in comparison to conventional methods; an improved process control; lack of direct contact with the melting materials; Environmental friendly process, due to the possibility of treating the toxic gases resulting from melting wastes in a special microwave installation.

A complete separation of the organic components and metallic fraction was achieved by melting PCBs in a microwave furnace. The efficiency of metal recovery was higher than 96%.

The treatment of the resulting exhaust gases in a microwave environment at a temperature of 1300 ÷ 1400°C lead to a reduction of up to 98% of the toxic compounds by thermal neutralization.

The preliminary experiments demonstrated that the melting of crushed PCBs in a microwave field furnace is an efficient and environmentally friendly route for the recovery of metals, with low energy and time consumptions.

Acknowledgements

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REFERENCES

Bescher E.P., Sakkar U., Mackenzie J., 1992, Microwave Processing of Aluminum Silicon Carbide Cermets. *Mat.Res.Symp, Proc.*, **269**, pp. 371-378.

Cheng J., Roy R., Agrawal D., 2002, Radically different effects on materials by separated microwave electric and magnetic fields. *Mater. Res. Innovat.*, **5**, pp. 170-177.

Das S., Mukhopadhyay A. K., Datta S., Basu D., 2009, Prospects of microwave processing: An overview. *Bull. Mater. Sci.,* **32** (1), pp. 1–13.

Grundas S., 2011, Advances in Induction and Microwave Heating of Mineral and Organic Materials*, InTech,* India, pp. 3-5 and 303-312.

Havlik T., Petranikova M., Orac D., Miskufova A., 2009, Hydrometallurgical treatment of used printed circuit boards after thermal treatment*, 3rd AMIREG International Conference*: Assessing the Footprint of Resource Utilization and Hazardous Waste Management, Athens, Greece, pp. 164-169.

Leonelli C., Veronesi P., Denti L., Gato A., Iuliano L., 2008, Microwave assisted sintering of green metal parts. *J. Mater. Process. Technol*., **205**, pp. 489-496.

Lorenson C., Ball M.D., Herzig R., Shaw H., 1991, The Microwave Heating Behavior of Metallic-Insulator Composite Systems. *Mat. Res. Symp. Proc.,* **189**, pp. 279-282.

Robinson B. H., 2009, E-Waste: An assessment of global production and environmental impacts. *Science of the Total Environment*, **408**, pp.183-191.

Rodiger K., Dreyer K., Gerdes T., Willert-Porada M., 1998, Microwave Sintering of Hardmetals. *Int. J .Refractoy Met and hard Mater.,* **16**, pp. 4-6, and 409-416.

Roy R., Agrawal D., Cheng J., Gedevanishvili S., 1999, Full sintering of powdered-metal bodies in a microwave field. *Nature*, **399**, pp. 668-670.

Roy R., Peelamedu R., Hurtt L., Cheng J., Agrawal D., 2002, Definitive experimental evidence for Microwave Effects: radically new effects of separated E and H fields, such as decrystallization of oxides in seconds. *Mater. Res. Innovat.*, **6**, pp. 128-140.

Standish N., Huang W., 1991, Microwave Application in Carbothermic Reduction of Iron Ores. *ISIJ International*, **31**, pp. 241-245.

Thostenson E. T., Chou T.-W., 1999, *Composites: Part A 30* 1055.

Walkievicz J., Kazonich G., MacGill S.L., 1988, Microwave Heating Characteristics of Minerals and Compounds. *Min. Metall. Processing*, **5**, pp. 39-42.

Whittaker A.G., Mingos D.P., 1995, Microwave-assisted solid-state reactions involving metal powders. *J. Chem. Soc.,* pp. 2073-2079.

Yoshikawa N., 2009, Fundamentals and Application of Mcrowave heating of Metals. *Materia, Japan (Bulletin of Japan Inst. Metals)*, **48** (1), pp. 3-10.

*** An Integrated Approach to Electronic Waste (WEEE) Recycling, 2007, Project funded by DEFRA Waste and Resources Research Programme Reference WRT208, Final Project Report, Deliverable M12 SID5 Form – Section 8.

*** Govt moves to stem tide of 'e-waste' (http://www.nationmultimedia.com);

*** Prevention and integrated control of pollution (IPPC), 2001, Reference Document on the Best Techniques Available in the Non-ferrous Metals Industry, Romanian Ministry of Environment and Water Management, National Agency for Environment Protection, December 2001, page ii, www.anpm.ro (Romanian).

*** www.cee-environmental.com

*** Recycling technology advances and new material development key to successful e-waste recovery, http://www.emsnow.com/npps/story

*** Resource Recycling Fund Management Committee, Environment Protection Administration, Taiwan, ROC. http://cemnt.epa.gov.tw/eng/.

*** Sustainable Innovation and Technology Transfer Industrial Sector Studies, Recycling, 2009, – from E-Waste to Resources, United Nations Environment Programme.

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CRITICAL ANALYSIS OF MATERIAL AND ENERGY RECOVERY PROCESSES OF MUNICIPAL SOLID WASTE IN SATU MARE COUNTY

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ABSTRACT. This study suggests the description and the analysis on the ways of material and energy recovery of municipal solid waste, emphasizing on the stream that cannot be integrated into the classical recycling flux. We refer to the waste of this kind that includes, in a degraded state, plastic, paper and textiles that cannot be recycled or recovered through the existing procedures.

Among the principal's targets of this study, we enumerate: the analysis of stored waste composition in the regional DOBA store and its recovery potential; the material, energetical and environmental value determination of waste with recovery potential; Critical analysis on material and energetical recovery procedure of municipal solid waste.

The motivation of this study is determined by the increasing of the volume of wrapping waste, plastic, paper and wood and by the low level of recycling that leads to finding alternative solutions for depositing, especially for components that have no recycling solutions. For these components, we are looking for alternatives developing the concept of material value; energetical value and environmental value for public waste, witch in this structure are identified, with their history, as "unusefull components" of a specific management process of circular economy. In concrete manner, appreciations are made on the following procedures: the material recovery, after a quick processing, selection and chopping; waste can be integrated in different composite materials, that can be used later, in constructions or urban furniture manufacturing; the energetical recovery, by co incineration in technological processes or by transforming waste into refuse derived fuel. Waste composition and value realization is made for specific Satu Mare county area.

Key words: *municipal solid waste; material recovery, energetical recovery, environmental value, un-useful component*.

REASONS FOR WORK

The paper proposes to identify and solve two current problems: reducing the volume of landfilled waste and reducing fossil fuel consumption by exploiting the energy potential solutions thereof. There are different technologies to convert municipal waste into heat and electricity, such as incineration, incineration in co-generation plants, and incineration in the cement industry (Soporan et al., 2008). These technologies present two major inconvenient: the high investment in the combustion plant and waste transportation problem. Based on these considerations, it appears to be necessary to develop new methods and technologies for incorporation of municipal waste in different materials and perfecting recipes for solid fuel briquette type (Njenga, 2009). Therefore, work motivation is driven by developing technologies that help to solve the two problems arising from the current EU public policies: reducing the large volume of waste bound for storage and need their energy potentials. Given the prevailing conditions in Romania, the collection is not performed selectively and disposal is at 98%, we believe that the motivation shown is real, very current and pressing.

OBJECTIVE OF WORK

This paper aims to find a method of determining the potential material and energy of existing materials in the waste, given that it is not subject separately collected and its use is the disposal in landfills, as a prerequisite to establishing a recovery methods and technologies.

PROBLEM FORMULATION

The research expressed in this work, is to establish a methodology for determining the potential material and energy waste which have not undergone separately collected and pre-collection has made improper use of materials and / or energy methods become traditional. Extending the scope of the waste deposits reached the level becomes an important part of the problem.

RESEARCH METHOD

Solving the problem formulated is achieved in the present paper, by establishing factors that influence material and energy potential of waste and critical analysis of methods and technologies to optimize recovery and adoption of optimal variant for the state are waste. The working method as preliminary stage experiments, the study is based on information provided by the literature. Concretization accumulations informative develop a methodology that applies to waste generated in the county of Satu Mare, mainly on regional landfill DOBA.

RESEARCH ACHIEVEMENTS

Research conducted in a solution formulation of the problem posed is related to the following aspect: the waste structure analysis at regional landfill DOBA and capitalized on their potential; determining the value of materials, energy and environmental waste potentially valorification; critical analysis of material and energy recovery processes municipal waste.

Waste composition analysis

According to data from the Regional Waste Management Service of the Satu Mare County Council, waste deposited in 2012 have the following composition: 9.1% cardboard paper; wooden 1.26%; Textile 4.64%; 4% glass; 5% metal; 14% plastic; 45% biodegradable materials; others 17%;

Total 100% (E211-2013 feasibility study, the closing of cell nr.1 urban waste landfill DOBA, Satu Mare, 2013).

These data resulted in the composition of waste daily determinations over a period of a week. Sampling was done in both urban waste - Satu Mare and in rural areas. As methodology, it analyzed a daily amount of 0.25 m^3 approximately by manual separation. Data were processed and confronted with the literature.

Determining the value of material and energy

Presented at the level of waste composition shows that the potential for material and energy recovery is particularly high, with a condition that they have a pre-collection and collection process to preserve potential they have.

From the point of view of the problem to be solved we deal with waste altered by mixing some with a significant loss in that they have already reached storage. This position is confirmed by the judgment "Georgescu-Roegen" which makes a parallel between physical economic system and mainframe systems, introducing the notion of entropy, which describes the degree of degradation of inputs intervening in manufacturing goods. So, from this point of view we can appreciate the "energy value", "material value" and "environmental value". The loss of these values increases entropy, reducing resilience (Pop, 2015).

In light of circular economy, the goal should be keeping entropy initial conditions of factors of production, avoiding degradation to be reused in other words "the amount consumed in production of the category values renewable" (Pop, 2015), or a solution of compromised given the state of waste to value some material or energy value. From this perspective, the amount of waste is expressed by the following: the energy value; material value and environmental value.

Value of materials that can be recovered from waste

This indicator quantifies the value of materials which can be recovered from waste and can be expressed by the following relationship:

$$V_m = \sum \left(V_{mi} - C_{ri} \right) \times P_i$$

Where: V_m - value of waste material;

V_{mi}- The value of the material i;

C_{ri} - Costs and material recovery i;

P_i- Share the material I in goods become waste.

This value can be expressed in lei / ton waste.

According to data on the composition of waste deposited and the rate recovered to 70% can be recovered from each ton of waste deposited: Plastic 0098 t, paper 0.064 t, metal 0.035 t, glass 0.025 t of each ton of waste stored.

Resource material consumed in the recovery process is water, the amount of material recovered from waste deposited ton: 9.8 m^3. Energy consumption in the processing of materials is estimated: 10.19 GJ / t processed waste.

The energetic value

The two aspects of the energy value of waste, the total energy consumed in the production process of goods become waste.

To determine that value requires in depth analysis of manufacturing processes to take into account the total amount of energy consumed in the manufacturing process and transportation energy consumed by raw materials or finished products. According to this reasoning, the energy value of "un-usefull component" waste can be broken down into two components, one with a fixed value that expresses the amount of energy consumed in the manufacturing process and a variable value that expresses the energy consumed in transportation (Pop, 2015).

The calculation formula can be expressed as follows:

$$E_t = E_f + E_v$$

Where

E_f - The total energy consumed in the production process, including energy consumption for raw materials.

E_v - The total energy consumed in transporting raw materials and distribution of goods.

The total energy consumed in the production process of the waste materials: 27 GJ / t deposited waste and energy consumption in the process of recovery is 10.19 GJ / t processed waste (Prawisudha, 2012).

Energy recovered from "the unequipped" municipal waste, we can define as energy that is released by burning them and is expressed in calorific value.

To determine calorific value, literature indicates two ways: by measuring the energy released experiment with oxidative, in caloric bomb, and analytical of which the best known is the empirical formula of Mendeleyev. Calorific components are: paper 12.29 MJ / kg, wooden 15.68 MJ / kg, plastic 46.08 MJ / kg. Proposed empirical formula of the best known is that of Mendeleev:

$$Q_s = 81C + 300H - 26(O - S) \text{ [GJ / t]}$$

The recoverable energy through energy recovery: 53.34 GJ / t deposited waste, including biodegradable waste.

The environmental value of waste

This component quantifies all emissions generated by the production and transport of materials and finished products become waste. The indicator relative to climate change due to emissions of greenhouse gases is measured by Global Warning Potential (GWP) defined by the IPCC (Intergovernmental Panel of Climate Change) is an organization of UNED (United National Environment Programme) and WMO (World Meteorological Organization).

GWP expressed for a given gas, the ability to absorb infrared rays with respect to a reference gas which is carbon dioxide. Therefore, each component gas emission flow is converted into a stream of CO_2 equivalent, representing the contribution to the increase in the greenhouse effect.

This can be accompanied by equivalent expression, depending on the type of part of municipal waste, other elements that can be quantified in the value of the environment.

The total emissions calculated with 16 WARM calculation model developed by EPA, is as follows:

- For storage: 19 t CO_2 / year;
- In case of partial recovery by energy recovery, savings reach 20 t CO_2 emissions / year.

Analysis material and energy recovery

For the capitalization of waste materials stored, the options are reduced; practically, the only solution is energy recovery. This can be achieved by two methods, incineration in the cement production process, or briquetting of waste and use of them as solid fuel. Variant advantageous economically is briquetting, thus saving the costs of incineration.

Worldwide there are a variety of studies aimed at turning waste into useful fuel and transport. They are studying various aspects of the manufacturing process, such as humidity, particle size, composition of the feedstock, the temperature and pressure influence.

As the composition of the raw material, we meet a huge variety of raw materials used for example in crop residues (Chuen-Shii, 2009) and industrial residues of coal (coal dust) using binder waste plastics (Massaro et al., 2014). Mechanical, pyrolysis, and combustion characterization of briquetted coal fines with municipal solid waste plastic (MSW binders) pelletizing municipal solid waste composted (Pasek et al., 2013), study mixtures of waste from agriculture waste plastic degraded (Auprakul et al., 2014).

Recipes studied 80% coal dust, 20% binder HDPE (Massaro et al., 2014), or 75% paper 25% pills recycled (PET, PP and HDPE), coal 80%, DSM 17% (paper, plastic and wood) bonded 3% (Orsulik and Jachyra, 2013) presented the good results in terms of the physical properties of the briquettes (resistance to compression). Studied literature focuses on two directions regarding recipes: using mostly coal dust and waste from agriculture (straw) in combination with DSM, mostly paper, plastic and wood, using recycled plastic binder. Considering the composition of the waste described in the previous chapter, with a calorific value of 52 MJ / kg, there is a real chance that directs briquetting to lead to optimal results.

Grain feedstocks have a great influence on the physical properties and combustion properties of lighters. It found that grain feedstock should not exceed 8mm, the best being 2-6 mm (Massaro et al., 2014). This grain feedstock can blend in, so that burning briquettes to be optimal.

Another important aspect is the moisture content; the DSM has high moisture content (30-40%). Therefore, it is necessary to include in the manufacturing process, the drying step to a moisture content of max. 10 to 20%.

In terms of pressing technology, there are two technologies: extrusion (Zafar and Kianmehr, 2012; Marsh et al, 2007) for manufacturing pellets or briquettes manufacturing pressing (Orsulik and Jachyra, 2013), the concept of energy production on the basis of modern alternative fuel). If the binder is used in the composition of the waste plastics, the optimum temperature ranges pressing cycle through 110-150 °C. The pressure necessary to produce briquettes depends on particle size and temperature of the mixture and ranges from 1 to 10 MPa (Gug, et al., 2015).

The fuel thus obtained can be used in boilers with gasification, combustion furnace where the temperature reaches 1200 °C, at which temperature, all harmful components from waste plastics are burned completely.

MAJOR CONTRIBUTION OF RESEARCH

As a novelty, we propose converting waste into briquettes /pellet type fuel. Required combustion temperature is over 850 ºC, the condition that a majority of gasifying solid fuel boilers.

The mix of materials, paper, plastic, wood proportions of waste deposited, provides a calorific value of briquettes 21 MJ / kg, higher calorific related biomass briquettes.

The proposed technology consists of four phases: grinding, mixing, pressing and drying lighters.

CONCLUSIONS

To achieve a sustainable waste management, it requires a more realistic application of Directive 2008/98/EC, which defines solutions for waste management, namely prevention, preparation for reuse, recycling, energy recovery and storage.

Efforts are big on the implementation of this Directive, in order to reduce the amount of deposited waste. Although there have been great advances in recycling materials still remains a considerable amount of material that cannot be recycled because of degradation or lack of specific infrastructure. Analyzing the Eurostat data it can be seen, that in countries where technology for energy recovery exists (incinerators, co incinerators) recyclability rate is much higher. The costs of incineration with energy recovery installations are very high (Buica, 2012).

At DOBA Regional landfill, by making a briquetting line, volume of stored waste can be reduced by 27% and can achieve consistent income.

REFERENCES

Buica M., 2012, *Theoretical contributions and experiment with the use of biogas installations related to household waste dumps"* Thesis UTCN.

Chuen-Shii C., 2009, The optimum Preparing Conditions for solid fuel briquette of rice straw by the piston-mold process Using the Taguchi method. *Fuel Processing Technology*, **90** (7).

Gug J., Cacciola D., Sobkowicz M.J., 2015, Processing and properties of the solid fuel energy from municipal solid waste (MSW) and recycled plastics. *Waste Manag.*, **35**, pp. 283-392.

Kers J., Kulu P., Aruniit A., Laurmaa V., Križan P., Šooš L., Kask Ü., 2010, Determination of physical, mechanical and Burning Characteristics of waste polymeric material briquettes. *Estonian Journal of Engineering,* **16** (4), pp. 307-316

Marsh R., Griffiths A.J., Williams K.P., Wilcox J., 2007, Physical and thermal propreties of extruded refuse derived fuel. *Biofuels for Transportation,* **88** (7), pp. 701-706

Njenga M., Karanja N., Prain G., Malii J., Munyao P., Gathuru K., Mwasi B., 2009, *Community-based urban energy from organic waste Briquette production at Kahawa Soweto Informal Settlement, Nairobi, 26 p.*

Massaro M. M., Son S.F., Groven L.J., 2014, Mechanical, pyrolysis, and combustion characterization of municipal solid briquetted coal fines with plastic waste (MSW) binders. *Fuel*, **115**, pp. 62-69.

Orsulik E., Jachyra J., 2013, The concept of energy production on the basis of modern alternative fuel. *Archives of Thermodynamics*.

Prawisudha P., Namioka T., Yoshikawa K., 2012, Coal alternative fuel production from municipal solid wastes employing hydrothermal treatment. *Applied Energy*, **90** (1), pp. 298-304.

Pasek A. D., Gultom K. W., Suwono A., 2013, Feasibility of Recovering Energy from Municipal Solid Waste to Generate Electricity. *J. Eng. Technol. Sci.,* **45** (3), pp. 241-256.

Pop A., 2015, Raport Cercetare IV.
Soporan V., Rusu T., Nemes O., 2008, *Waste and recovery technologies*, Publisher UTPRESS, Cluj Napoca.
Auprakul U., Promwungkwa A., Tippayawong N., Chaiklangmuang S., 2014, Densified Fuels from Mixed Plastic Wastes and Corn Stover. *Advanced Materials Research.* **931-932**, pp 1117-1121.
Zafar A., Kianmehr M. H., 2012, Effect of raw material propierties and die geometry on the density of biomass pellets from composted municipal solid waste, *BioResources*, **7** (4), pp. 4704-4714.
*** Waste-to-Energy in Europe Third report on WTE plants in Italy CEWEP - April 2012
*** Directive 2000/73 / EC
*** Directive 2008/98 / EC
*** H.G no. 128/2002 on waste incineration (Official Gazette no. 160 of 6 March 2002) as amended by Government Decision no. 268/2005 (Official Gazette no. 332 of 20 April 2005);
*** Order no. 756/2004 for the approval of Technical Norms on the incineration of waste (Official Gazette no. 86 dated 26 January 2005, published in Official Gazette no. 86bis of 26 January 2005);
*** Order 1274/2005 regarding the issuance of the environmental closure of waste disposal or storage and incineration (Official Gazette no. 1180 of 28 December 2005), complemented by the MESD Order no. 636/2008 (Official Gazette no. 425 of 6 June 2008
*** SR EN 12390-6: 2002 / AC: 2006
*** SS 187 120 (pellets) and SS 187 121 (briquette)
*** STAS 3361 / 2-87
***http://agrobiobrichet.ro/presa-brichetat-masina-brichetat.html (accessed 06/12/2015)
***http://www.undp.md/projects/Biomass/Ghid%20pentru%20furnizorii%20de%20Bio-Combustibil.pdf (accessed 12/06/2015)
***http://appsso.eurostat.ec.europa.eu/nui/setupDownloads.do (accessed 12/06/2015)
***http://www.waste-management-world.com/articles/print/volume14/issue5/featu-res /time-out-for-waste-to-energy-in-europe.html -Last access 12/06/2015
***http: //www.martingmbh.de/index_en.php? Level = 2 & CatID = 6.73 & inhalt_id = 60 -Last http://centrale-buderus.com.ro/accesare 12.06. 2015
***Integrated Waste Management System in Satu Mare
***Studiu de Fezabilitate NR. E211-2013, Inchidere celula nr.1 Depozit Regional DOBA – Ecotec Invest Satu Mare

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ASSESSMENT OF CHINTENI RIVULET (ROMANIA) WATER QUALITY UNDER THE IMPACT OF THE ANTHROPOGENIC FACTOR

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ABSTRACT. In the environmental issue context, surface water quality has an important place. Implementing measures truly effective, sustainable in prevention and control of water pollution, is urgently needed, because degradation of their quality affects the quality of human life. This paper presents the study and research on the assessment of quality status of Chinteni Rivulet (Cluj County) under the pressure created by possible anthropogenic pollution sources. Water sampling was conducted in the period November 2015 - May 2016, in five representative points. We measured the physico-chemical parameters (pH, temperature, total dissolved solids, electrical conductivity, redox potential, chlorides, sulfates, nitrates, nitrites, ammonium, filterable residue dried at 105 °C, suspended matter and total chromium) and oxygen regime parameters (dissolved oxygen, chemical oxygen demand). Results show that there were registered high contents of nitrates, nitrites, sulfates, oxidisable organic substances, chlorides and total chromium, downstream from the anthropogenic sources of pollution. The anthropogenic sources of pollution put pressure on the water quality of Chinteni rivulet, and the trend is of the increase of pollutants and is directly proportional to the population density and intensification of economic activities

Key words: *Chinteni rivulet, contamination, water quality, pollutants, nitrates*

INTRODUCTION

The purpose of this study is to establish the surface water quality from Chinteni Rivulet and to identify the pressure created by possible sources of anthropogenic pollution in the area (economic agents and households not included in the sewerage network, which evacuates untreated waters into natural receptors). In the environmental issue context, surface water quality also has an important place. Implementing measures truly effective, sustainable in prevention and control of water pollution, is urgently needed, because degradation of their quality affects the quality of human life (Xin et al., 2015).

We chose the Chinteni rivulet as a study area, because the number of studies conducted on this watercourse is low, therefore the existing data on the physico-chemical composition of water is vaguely outlined and there is a possibility that the rivulet to transport the pollutants to the Someşul Mic river through the discharge of waste water or other wastes from domestic or economic activities, because the sewerage network does not exist across the entire area through which this Chinteni rivulet passes. After the discharge of the waste waters into the surface waters, there take place a series of physical, chemical and biological processes (Cojocaru, 2012).

Over the past 15 years, a number of substantial reforms have been developed, which correspond to the overall objective of efficient and sustainable water resource management. The European Union and other regions have recognized the issue of degradation of ecosystems and water quality and have established innovative reforms through regulatory frameworks to restructure the water management approach (Cross and Latorre, 2015).

For the evaluation of the Chinteni rivulet quality was calculated the Water Quality Index (WQI), the evaluation using integrated indices, can be a complex process, including a semnificative number of parameters wich contribute with diferent pressure on surface water quality (Teodorof et al., 2016; Bharti and Katyal, 2011).

The Water Quality Index (WQI) provides complex scientific information and embraces a series of data in a single number, with a simple logical connotation ie whether the water is in the grade of the proposed use (Tyagi et al., 2013).

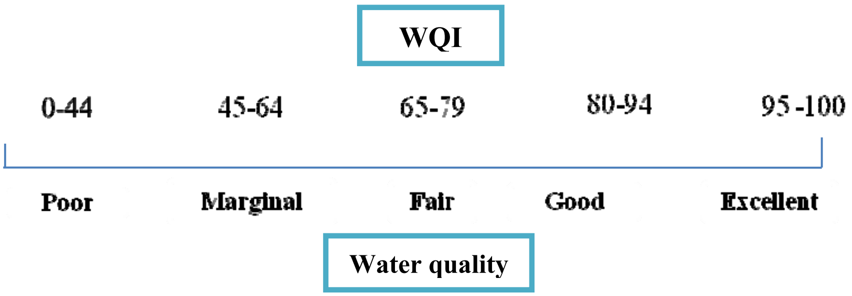
Several methods of determining WQI are known in the literature, such as the National Sanitation Foundation Water Quality Index (NSFWQI), Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI) , Oregon Water Quality Index (OWQI), Weighted Arithmetic Water Quality Index Method an others.

In this study we used the Canadian method for calculating the water quality index of the Chinteni rivulet, whose empirical equation is below (ecuation 1).

$$WQI = 100 - \frac{\sqrt{F1^2 + F2^2 + F3^2}}{1.732} \qquad (1)$$

where **WQI** = is a number between 0 and 100 (for significant pollution levels the value may exceed 100);
F1 (Scope) = number of variables, whose objectives are not met.
F1= [no. of failed variables /total no. of variables]*100
F2 (Frequency)= number of times by which the objectives are not met, in relation to
MCL (Class II, acording 161/2006 Order)
F2 = [no. of failed tests/total no. of tests]*100
F3 (Amplitude) = amount by which the objectives are not met (20/50/80) (CCME, 2001).

This Canadian method has been developed to evaluate surface water for protection of aquatic life in accordance to specific guidelines and can be used in various countries with slight modification (Khan et al., 2005; Kankal et al., 2012; Lumb et al., 2006). The obtained results will be in the standard values of the method which are presented as follows (CCME, 2001):



EXPERIMENTAL

The water samples were collected from the Chinteni rivulet monthly, between November 2015 and May 2016, to observe the spatial and time evolution of the main water quality parameters. The sampling points were chosen as representative for the area (upstream and downstream of possible sources of pollution) as shown in figure 1. PC0, PC1, PC2, PC3 – are the sampling points along the rivulet and G1 discharge canal of wastewater in Chinteni rivulet.

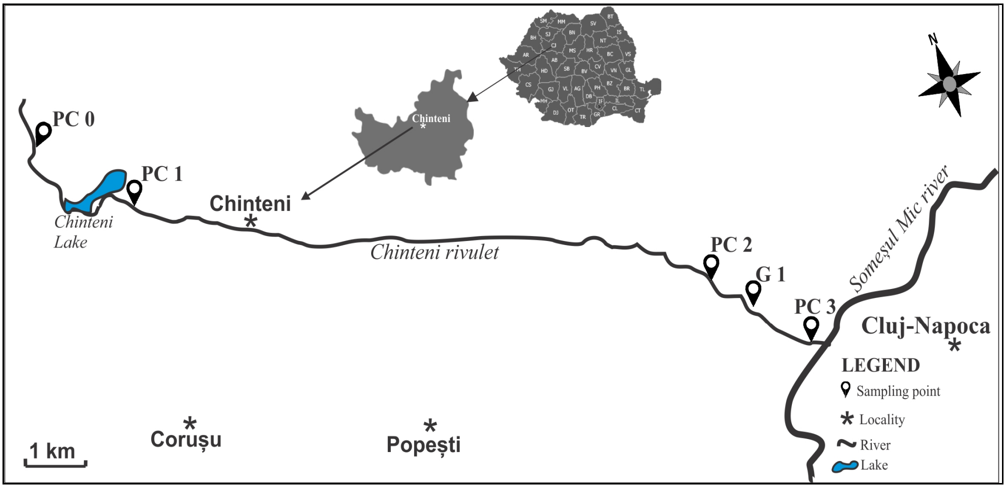


Fig. 1. *Map of the sampling points*

For the analysed parameters were used: *potentiometric methods*: pH, total dissolved solids, electrical conductivity, redox potential with the use of a WTW inoLab 720 series Multiparameter; *volumetric methods*: dissolved oxygen (DO), chemical oxygen demand (COD-Cr and COD-Mn), chlorides, ammonium; *spectrometry methods*: nitrates, nitrites, sulfates, total chromium with UV-VIS Aquamate Molecular Spectrophotometer (TermoSpectronic); *gravimetric methods*: filterable residue dried at 105 °C, suspended matter. The sampling, the sample preparation and analysis was made according to ISO standards.

RESULTS AND DISCUSSION

The variation of pH in surface water is the result of the hydrolysis of various salts and dissolved gases (Iticescu et al., 2014). The pH values in all the sampling points were in the limits given by the Order 161/2006 for surface water, with values from 6.83 to 8.28 (see figure 2).

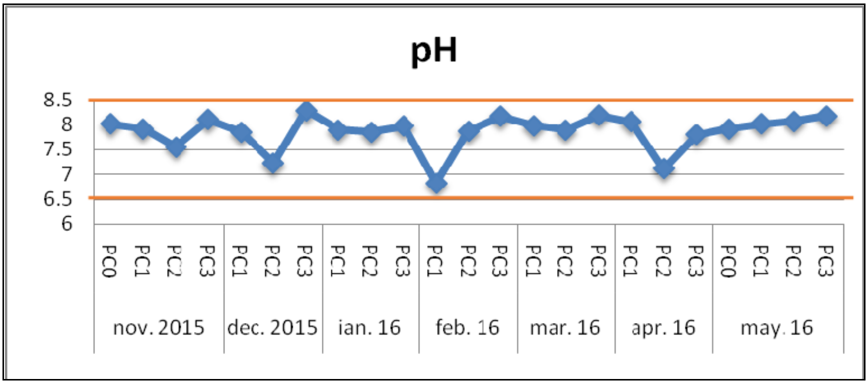


Fig. 2. *pH values from Chinteni rivulet*

The electrical conductivity of the water samples varied significantly and ranged from the maximum value of 1412 µS/cm recorded at the PC2 point to the minimum value 454 µS/cm, at the PC1 sampling point (see figure 3). At PC1 point, immediately after Lake Chinteni, is a lower conductivity due to the dilution with water leaking from the lake and springs from the area, and after the rivulet takes up wastewater, conductivity increases. The redox potential values are all negative, indicating an oxidizing environment consuming organic matter. The variation of the total dissolved solids is similar to conductivity.

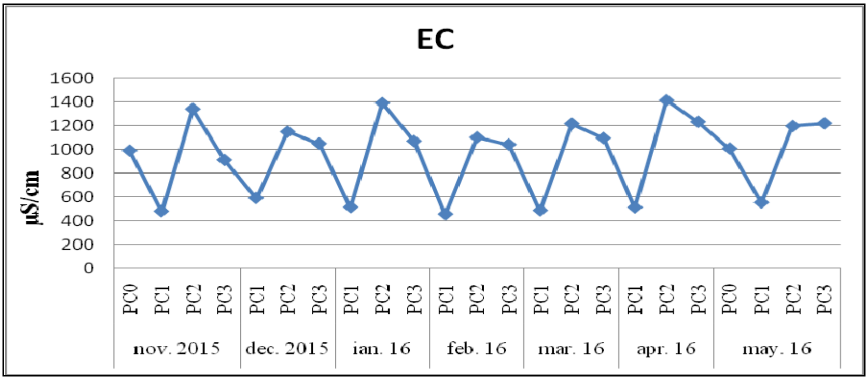
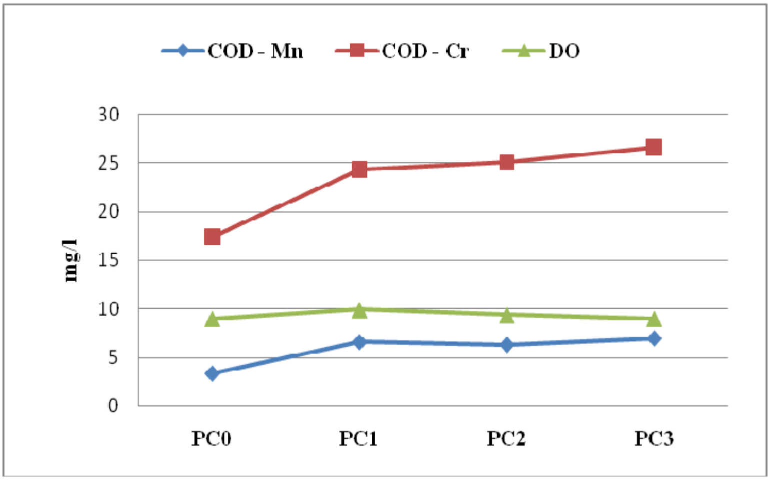


Fig. 3. *EC values from Chinteni rivulet*

For the oxygen regime parameters were observed fluctuations, especially in the case of COD-Cr. In the below figure (no. 4) are shown the average values from Chinteni rivulet.



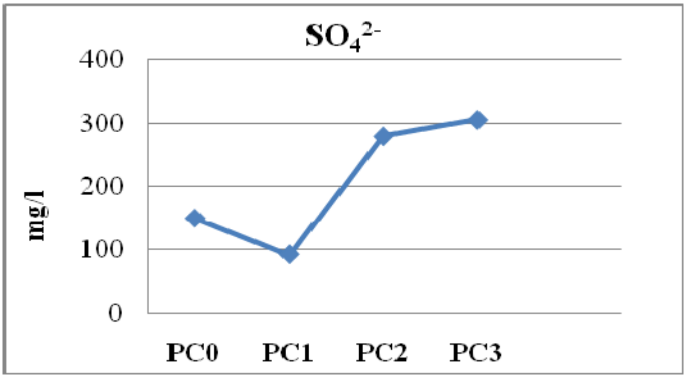
Parameter	Category				
	I	II	III	IV	V
DO (mg/l O_2)	9	7	5	4	<4
COD-Mn (mg/l O_2)	5	10	20	50	>50
COD-Cr (mg/l O_2)	10	25	50	125	>125

Fig. 4. *Average values for oxygen regime parameters from Chinteni rivulet and water categories*

The water quality of the Chinteni rivulet according to the measured values for DO is included in 1st category, and according to the values of COD-Cr and COD-Mn is in the 2nd category and in some periods in 3rd category (COD-Cr).

For chlorides the maximum recorded level was 58 mg/l in PC3 point (included in 3rd category), according to values from PC0 and PC1 sampling points the water quality is included in 1st category.

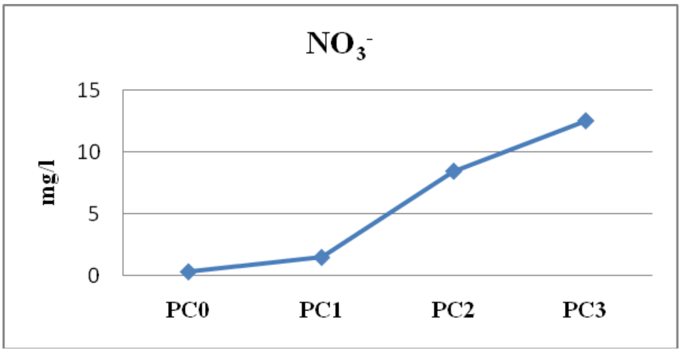
The values obtained for sulfates (see figure 5) have the tendency to increase from upstream to downstream, the 4th category is characteristic to PC2 and PC3 sampling points and 2nd category for PC0 and PC1 sampling points.



Parameter	Category				
	I	II	III	IV	V
Sulfates (mg/l)	60	120	250	300	>600

Fig. 5. *Average sulfates values from Chinteni rivulet and water categories*

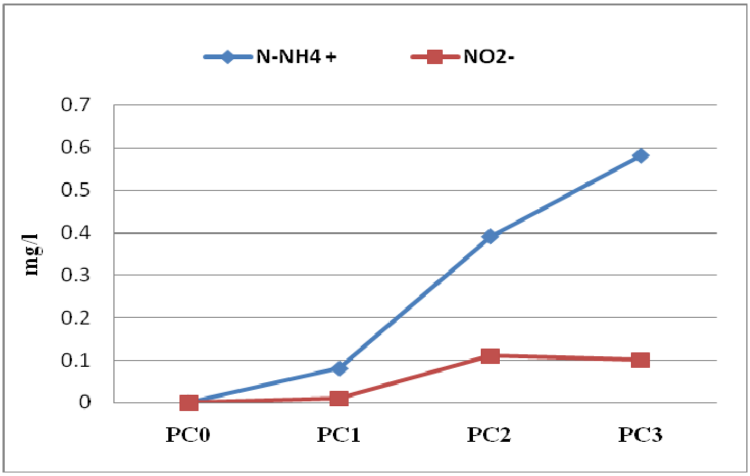
The maximum value for nitrate was recorded at PC3 point (19.2 mg/l in March 2016) and the minimum value (0.27 mg/l in May 2016) in PC0 sampling point (figure 6). According to the recorded values for nitrates, the water quality is on the 1st category at point PC0, 2nd category in PC1 point, 3rd category in PC2 point and 5th category in PC3 point.



Parameter	Category				
	I	II	III	IV	V
Nitrate (mgN/l)	1.3	5	5.6	11.2	>11.2

Fig. 6. *Average nitrate values from Chinteni rivulet and water categories*

For nitrite it was observed the same tendency of degradation of the water quality (figure 7), from upstream to downstream, the first two points (PC0 and PC1) are included in the 1st category and the last two (PC2 and PC3) in the 4th quality category.



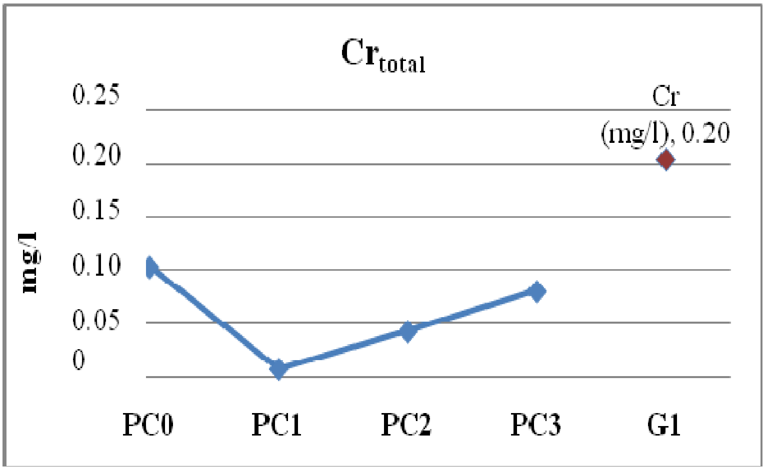
Parameter	Category				
	I	II	III	IV	V
Ammonium (mgN/l)	0.4	0.8	1.2	3.2	>3.2
Nitrite (mgN/l)	0.01	0.03	0.06	0.3	>0.3

Fig. 7. *Average values for N-$NH_4^+$and NO_2^- from Chinteni rivulet and water categories*

For point G1 (discharge) the mean value for ammonium is 5.26 mg/l, with a maximum of 10.64 mg/l and a minimum of 1.68 mg/l, the concentration of ammonium in this point is much higher than in other sampling point, influencing in a great manner the quality of rivulet downstream.

For fixed residue and suspended matter the smallest values were obtained in point PC1 due to aport of fresh water from springs and lake, which modifies the initial characteristics of the water (point PC0). In the rest of the points, the water quality of the Chinteni rivulet is included in the 2nd category. No limitation in surface water is prescribed by law (in Romania) for the suspended material content, the maximum recorded value for this parameter was 46 mg/l in PC3 sampling point and a minimum of 8 mg/l in PC0 sampling point.

Cromium and his compounds can be found in waters only in trace amounts and can be discharged in surface water through various industries. The occurrence of dissolved Cr(III) and Cr(VI) in untreated source water is affected, partialy by aqueous pH. Cr(III) generally is insoluble between pH=6–10 and Cr(VI) is increasingly soluble above pH 6 to virtually 100 percent soluble above pH 8 (Mills and Cobb, 2015).



Parameter	Category				
	I	II	III	IV	V
Cr_{total} (mg/l)	0.025	0.050	0.100	0.250	>0.250

Fig. 8. *Average values for Cr_{total} from Chinteni rivulet and water categories*

The highest values recorded for this indicator were found in G1 (discarge) sampling point, with a maximum of 0.24 mg/l in May 2016. The total cromium content in Chinteni rivulet was found in range of 0.005 – 0.116 mg/l (see figure 8). Acording to this values, the water quality is in the 1st category at PC1 sampling point , 2nd category in PC2 point and 3rd category for PC0 and PC3 sampling points.

To calculate the WQI for Chinteni rivulet were chosen two data sets: the mean values for al sampling dates and the values obtained in May 2016. The values of WQI were calculated using the formula writen above (ecuation 1) and the MCL values for 2nd category for surface water from 161/2006 Order.

The WQI value obtained for the mean values (november 2015 – may 2016) is 69.50 and for the values recorded in may 2016 is 69.31. These values indicate fair water quality for Chinteni rivulet.

CONCLUSIONS

From the analyses of the 15 physico-chemical parameters we drew the conclusion that the water of Chinteni rivulet is occasionally deteriorated and the conditions somtimes deviate from the natural or desirable levels.

The research hypothesis is confirmed: the sources of anthropogenic pollution put pressure on the water quality (from upstream to downstream) and the tendency of increasing pollution is directly proportional to the population density and the intensification of the economic activities.

From the perspective of the Normative 161/2006 on surface water quality, the results obtained divide the water of the rivulet in two distinct sections:

1. Upstream (PC0 and PC1) where the water quality for most of the investigated parameters is in the 1st and 2nd category;

2. Downstream (PC2 and PC3) with inferior water quality - 7 of 11 parameters, wich are normated, are in 3rd, 4th and even in 5th category.

The highest concentrations recorded throughout the course of the Chinteni rivulet are for nitrate, nitrite, sulphates, chemical oxigen demand, chlorides and total chromium chemical parameters.

The investigated wastewater discarged in the rivulet (point G1) brings a large supply of chromium, ammonium, nitrite and organic mater.

The chemical risk assessment indicated a moderate degree of pollution of the Chinteni rivulet with WQI of 69.5.

REFERENCES

Bharti N., Katyal D., 2011, Water Quality Indices Used for Surface Water Vulnerability Assessment. *J Environ Protection and Ecology*, **2** (1), pp. 154-173.

CCME, 2001, Canadian water quality guidelines for the protection of aquatic life: CCMEWater Quality Index 1.0, User's Manual. In: Canadian environmental quality guidelines, Canadian Council of Ministers of the Environment, Winnipeg.

Cojocaru I., 2012, Modulul 1- Biotehnologii de decolorare a apelor uzate COPMED – Competențe pentru protecția mediului, Surse, procese și produse de poluare. Iaşi.

Cross K., Latorre C., 2015, Which water for which use? Exploring water quality instruments in the context of a changing climate. *Aquatic Procedia*, **5**, pp. 104-110.

Iticescu C., Georgescu P., Topa C., Murariu G., 2014, Monitoring the Danube water quality near the Galati City. *J. of Environmental Protection and Ecology*, **15** (1), pp. 30-38.

Kankal N. C., Indurkar M. M., Gudadhe S. K, Wate S.R., 2012, Water quality index of surface water bodies of Gujarat, India. *Asian J. Exp. Sci.*, **26** (1), pp. 39-48.

Khan A. A., Tobin A., Paterson R., Khan H., Warren R., 2005, Application of CCME procedures for deriving site-specific water quality guidelines for the CCME water quality index. *Wat. Qual. Res. J. Canada*, **40** (4), pp. 448-456.

Lumb A., Halliwell D., Sharma T., 2006, Application of CCME water quality index to monitor water quality: a case of the Mackenzie river basin, Canada. *Environ. Monit. Assess.*, **113**, pp. 411- 429.

Mills P. C., Cobb R. P., 2015, Hexavalent and total chromium at low reporting concentrations in source-water aquifers and surface waters used for public supply in Illinois, 2013. *U.S. Geological Survey Scientific Investigations Report 2015–5020*, 58 p.

Order 161/2006 approving the Norms on surface water quality classification to determine the ecological status of water bodies, published in Official Gazette 511 of 13.06.2006.

Teodorof L., Burada A., Despina C., Seceleanu-Odor D., Tudor A. I.-M., Ibram O., Navodaru I., Tudor M., 2016, Integrated indices for surface water and sediment quality, according to water framework directive. *J. of Environmental Protection and Ecology*, **17** (1), pp 42-52.

Tyagi S., Sharma B., Singh P., Dobhal R., 2013, Water Quality Assessment in Terms of Water Quality Index. *Am J. Water Resources*, **1** (3), pp. 34-38.

Xin X. K., Li K., Finlayson B., Yin W., 2015, Evaluation, prediction, and protection of water quality in Danjiangkou Reservoir, China. *Water Science and Engineering*, **8** (1), pp. 30-39.

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COMPARISON BETWEEN TSUNAMI MODELING SCENARIOS FOR SHABLA AREA (BLACK SEA) USING TWO DIFFERENT SOFTWARE

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ABSTRACT. There are evidences of 22 past tsunamis generated in the Black Sea area. Shabla area is the most dangerous for the Romanian shoreline and triggered past high magnitude earthquakes and tsunamis. According to National Oceanic and Atmospheric Administration (NOAA) data base, 3 important events occurred in Shabla: the most recent, on 31st of March 1901, an earthquake of magnitude 7.2 triggered waves of 5 m, other sources estimating 2.5 - 3 m; the oldest documented event, in the1st Century BC, in Bisone area, and the third one, year 543 AC, when a 7.5 magnitude earthquake generated tsunami waves of 2 - 4 m.
Tsunami modeling was accomplished for Shabla area using two software, Tsunami Analysis Tool (TAT) and TRIDEC Cloud, and past earthquake parameters (location, depth, focal mechanism). A comparison between the results of the two software was accomplished, for the same input parameters: magnitudes of 7, 7.2, 7.5 and 8, depths of 5, 10 and 30 km and 5 fault plane solutions. The worst case scenario with TRIDEC software displays waves of maximum 2.62 m in Varna, for a magnitude 8 and a depth of 5 km,

with 0.32 m in Constanta; the worst case using TAT software shows maximum waves of 4.3 m in Kamen Bryag, with 4Romanian locations affected (2 m waves in Costinesti). Moderate waves are given by scenarios using magnitude 7.5, with 0.6 - 0.8 m heights. For lower magnitudes (7 - 7.2), the modeling estimates very low waves, 0.2 - 0.4 m.

Key words: *tsunami modeling, Shabla area, Black Sea, earthquakes.*

INTRODUCTION

Documents show the evidence of 22 tsunamis generated in the past, in the Black Sea area (Altinok, 1999). All the countries surrounding the area have faced tsunamis in the past, but the most dangerous seismogenic/tsunamigenic zone for the Romanian shore is Shabla. There are scientific papers describing 3 past events in the area, triggered by earthquakes (according to National Oceanic and Atmospheric Administration - NOAA data base), as follows: 31st of March 1901, an 7.2 M earthquake generated waves of 5 m (Papadopoulos et al., 2011), other sources estimating 2.5 - 3 m height (Ranguelov and Gospodinov, 1995); the oldest documented event, in the 1st Century BC, in Bisone area (Nikonov, 1997); year 543 AC, an earthquake of 7.5 M generated tsunami waves of 2 - 4 m (Ranguelov, 1998), displayed in table 1 and figure 1.

Table 1. *Tsunami past events generated in Shabla area (NOAA database)*

Number	Date	Magnitude	Lat.	Long.	Max. wave (m)
1	1st Century BC	-	43.01	28.2	-
2	Year 544	7.5	43.2	28.3	2 - 4
3	31st of March 1901	7.2	43.3	28.7	5

Fig. 1. *Map with the locations of past tsunamis from Shabla area, extracted from the total number of 22 events. Numbers 1, 2 and 3 correspond to seismic tsunamis (table 1). Number 4 represents a submarine landslide source*

Tsunami modeling was performed based on past earthquakes parameters and the bathymetry of the Black Sea, using two different software, Tsunami Analysis Tool (TAT) and TRIDEC Cloud. The modeling results display maximum wave heights, affected locations, tsunami arrival times and propagation, etc. In order to better estimate the effects of a future tsunami in the area, the results were compared and some conclusions are drawn regarding maximum waves that might be generated.

METHOD AND RESULTS

Two software were used for modeling: Tsunami Analysis Tool (figure 2), provided and developed by the Joint Research Center (JRC), Ispra, Italy (Annunziato, 2007) and TRIDEC Cloud (figure 3), provided by German Research

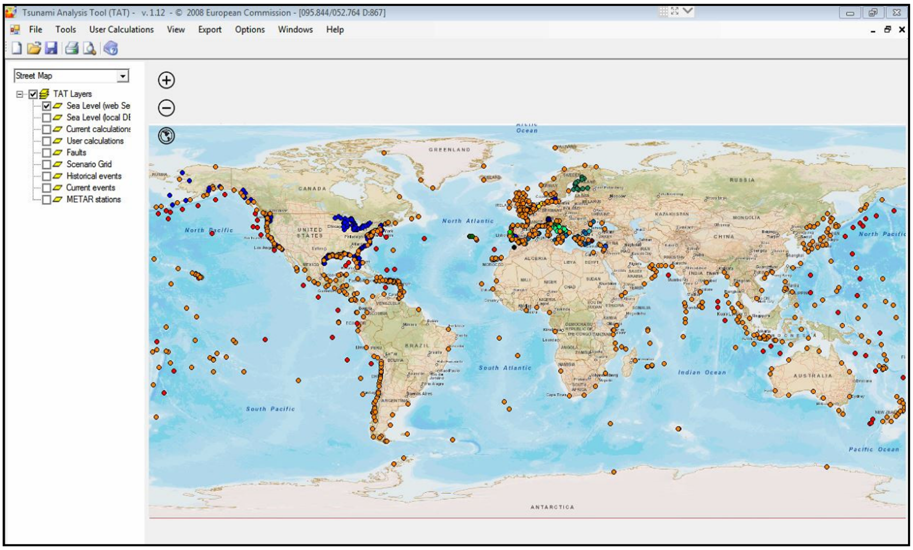

Fig. 2. *Display of the TAT software interface (http://webcritech.jrc.ec.europa.eu/TATNew_web/)*

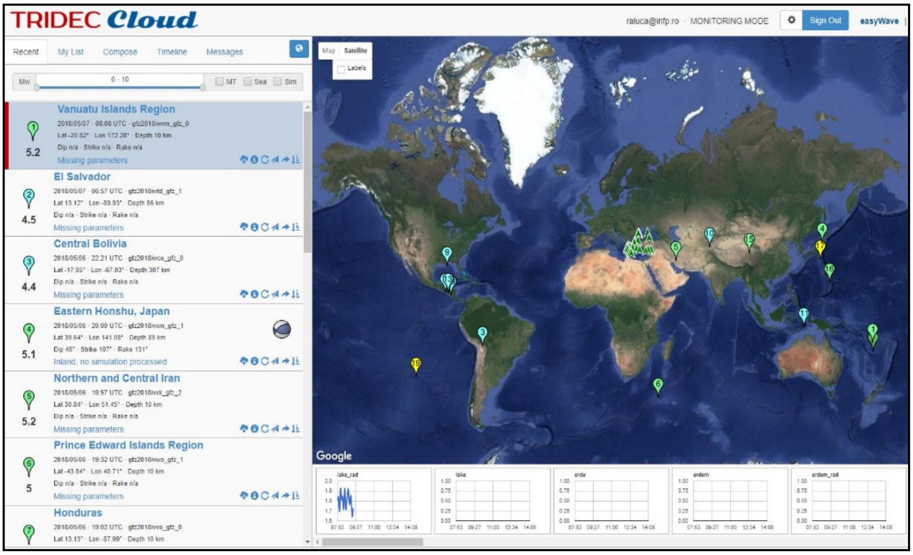

Fig. 3. *Display of the TRIDEC Cloud software interface (https://trideccloud.gfz-potsdam.de/)*

Center for Geosciences (GFZ), Potsdam, Germany (Hammitzsch et al., 2016). A comparison between some of the results accomplished with the two software is presented in table 2, for the same input earthquake parameters, varying magnitudes between 7, 7.2, 7.5 and 8, maximum possible for Shabla area (Solakov et al., 2014), also depths of 5, 10 and 30 km and 5 different fault plane solutions. The worst case scenarios are presented for each software, for a magnitude 8 potential earthquake and a depth of 5 km. Decreasing the magnitude leads to lower waves generation.

Table 2. *Comparison between the modeling results with TAT software vs. those with TRIDEC, for the same earthquake parameters*

SOFTWARE	LAT.	LONG.	MAG.	DEPTH (km)	MAX WAVE (m)
TAT	43.45	28.69	7	5	Varna 0.1, Techirghiol / Costinesti 0.1
TRIDEC					Varna 0.25
TAT	43.45	28.69	7.2	10	Varna 0.2, Constanta / Techirghiol 0.1
TRIDEC					Varna 0.41
TAT	43.45	28.69	7.5	10	Varna 0.6, Costinesti / Mangalia / Constanta 0.3
TRIDEC					Varna 0.8, Constanta 0.11
TAT	43.45	28.69	7.5	30	Bliznak 0.2, Varna 0.2, Mangalia 0.1
TRIDEC					Varna 0.87, Constanta 0.13
TAT	43.45	28.69	8	10	Kraveno 0.8, Varna 0.5, Costinesti / Mangalia / Techirghiol 0.6
TRIDEC					Burgas 1.07, Varna 0.55, Constanta 0.65
TAT	43.45	28.69	8	5	Kamen Bryag 4.3, Varna 2.1, Costinesti 2.0
TRIDEC					Varna 2.62, Burgas 0.7, Constanta 0.32

Parts of the results are displayed in table 2, with the input earthquake's parameters and the maximum resulted waves for different locations from Romania and Bulgaria.

The worst-case scenario for TRIDEC Cloud shows waves of maximum 2.62 m in Varna (Bulgaria), for a possible earthquake of M 8, located at a depth of 5 km, with 0.32 m waves in Constanta. The worst case scenario for TAT displays maximum waves of 4.3 m in Kamen Bryag (Bulgaria), with more than 1 m wave heights on 3 locations from the

Romanian shore, at Costinesti (2 m), Constanta (1.5 m), and Mangalia (1.4 m). Moderate tsunami waves are given by scenarios using magnitude 7.5, with 0.6 - 0.8 m maximum heights. For lower magnitudes (7 - 7.2), the modeling estimates very low waves, of 0.2 - 0.4 m (Varna).

The results using TRIDEC Cloud show the following: maximum waves of 2.62 m in Varna, for a possible earthquake of M 8, located at a depth of 5 km, with 0.32 m waves in Constanta, 0.7 m in Burgas (Bulgaria), and 0.34 in Kirklareli Igneada (Turkey) and 0.25 m at Kocaeli Kefken (Turkey) - see figures 4, 5 and table 3; waves of 1.07 m at Burgas (Bulgaria) for a M 8, depth 10 km, with 0.55 m at Varna and 0.65 at Constanta (Romania); values of maximum 0.87 m at Varna for an earthquake of M 7.5 generated at 30 km depth, with 0.13 m at Constanta; moderate heights of 0.8 m at Varna for a magnitude 7.5 and a depth of 10 km, with 0.11 m at Constanta; low waves of 0.41 m in Varna for a M 7.2 and a depth of 10 km; and the lowest waves of 0.25 m (Varna) are generated by an M 7 earthquake at a depth of 5 km.

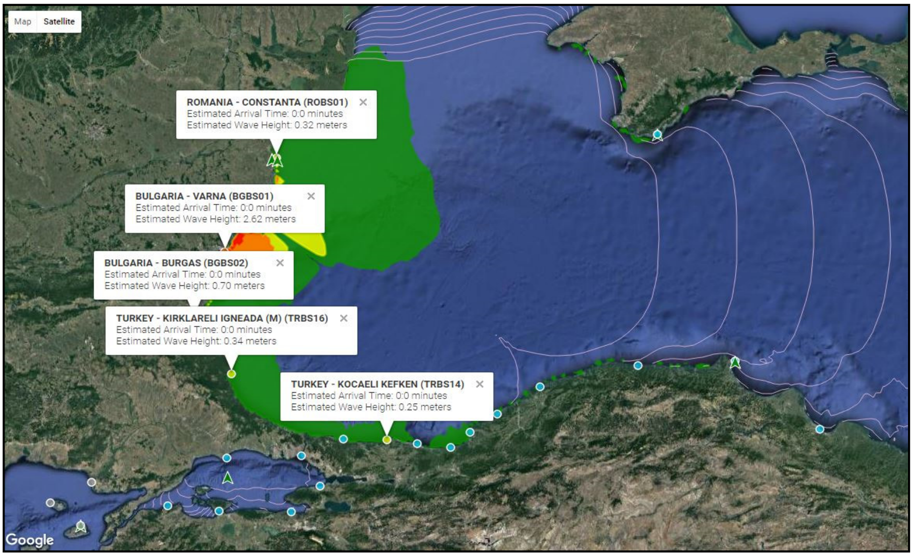

Fig. 4. *Map with the estimated wave heights for certain locations for the worst case scenario (M 8, depth 5 km) using TRIDEC software*

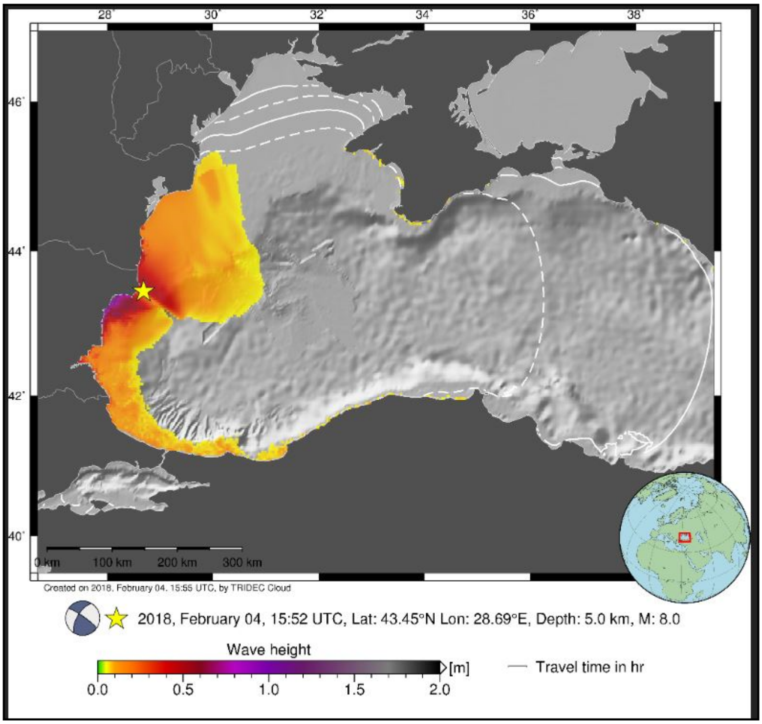

Fig. 5. *Maximum wave heights and travel times for the worst case scenario (M 8, depth 5 km) using TRIDEC software*

Table 3. *Table with the estimated wave heights for certain locations, for the worst case scenario (M 8, depth 5 km) using TRIDEC software*

Location	**Max wave height (m)**
Varna	2.62
Burgas	0.7
Kirklareli Igneada	0.34
Constanta	**0.32**
Kocaeli Kefken	0.25

The results using the TAT software displays maximum waves of 4.3 m in Kamen Bryag (Bulgaria), 2.9 m at Bulgarevo (Bulgaria), 2.1 m in Varna, 1.8 m in Bliznak (Bulgaria), 1.7 m at Kranevo and Balchik (Bulgaria), 1.6 m in Krapets (Bulgaria), with 4 locations from the Romanian shore affected, Costinesti (2 m), Constanta (1.5 m), Mangalia (1.4 m) and Techirghiol (0.9 m) - see figure 6 and table 4; waves of 0.8 m at Kraveno (Bulgaria) for a M 8, depth 10 km, with 0.5 m at Varna and 0.6 m at Mangalia, Costinesti and Techirghiol; values of maximum 0.2 m at Bliznak (Bulgaria) for an earthquake of M 7.5 generated at 30 km depth, with 0.2 m at Varna and 0.1 m at Mangalia; moderate wave heights of 0.6 m at Varna for a magnitude 7.5 and a depth of 10 km, with 0.3 m at Constanta, Costinesti and Mangalia; low waves of 0.2 m in Varna for a M 7.2 and a depth of 10 km, with 0.1 m at Techirghiol and Constanta; and the lowest waves of 0.1 m (Varna) are generated by an M 7 earthquake at a depth of 5 km, with 0.1 m at Costinesti and Techirghiol.

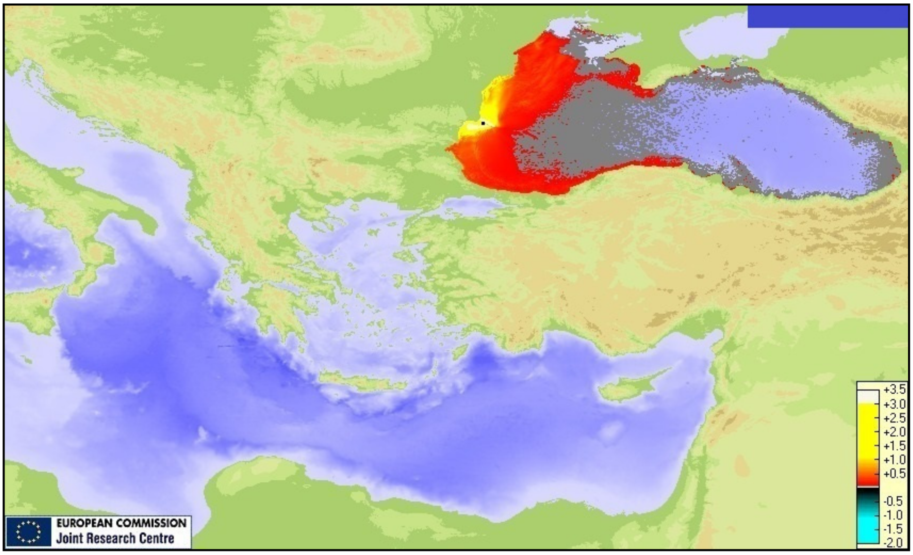

Fig. 6. *Maximum wave heights for the worst case scenario (M 8, depth 5 km) using TAT software*

Table 4. *Affected locations for the worst case scenario (M 8, depth 5 km) using TAT software*

Date of maximum Tsunami wave	Name	Wave height (m)	Delay of tsunami arrival (hours)	Delay of maximum tsunami (hours)	Latitude	Longitude
20 Oct 2014 12:10	Kamen Bryag	4.3	00:02	00:02	43.45	28.55
20 Oct 2014 12:21	Bulgarevo	2.9	00:02	00:12	43.38	28.43
20 Oct 2014 13:07	Varna	2.1	00:10	00:58	43.20	27.93
20 Oct 2014 13:27	Costinesti	**2.0**	**00:12**	**01:18**	**43.95**	**28.64**
20 Oct 2014 13:09	Bliznak	1.8	00:10	01:00	43.05	27.90
20 Oct 2014 12:55	Kranevo	1.7	00:04	00:46	43.35	28.07
20 Oct 2014 12:55	Balchik	1.7	00:04	00:46	43.40	28.16
20 Oct 2014 12:19	Krapets	1.6	00:04	00:10	43.64	28.58
20 Oct 2014 13:57	Constanta	**1.5**	**00:16**	**01:48**	**44.19**	**28.66**
20 Oct 2014 13:16	Mangalia	**1.4**	**00:10**	**01:08**	**43.81**	**28.59**
20 Oct 2014 13:09	Shkorpilovtsi	1.3	00:14	01:00	42.98	27.90
20 Oct 2014 13:09	Byala	1.3	00:16	01:00	42.88	27.90
20 Oct 2014 13:09	Durankulak	1.3	00:06	01:00	43.70	28.57
20 Oct 2014 13:09	Obzor	1.2	00:16	01:00	42.83	27.89
20 Oct 2014 13:58	Techirghiol	**0.9**	**00:14**	**01:50**	**44.07**	**28.65**
20 Oct 2014 13:03	Akhtopol	0.7	00:28	00:54	42.10	27.94

Besides the worst cases presented above, for both software, a moderate scenario is displayed bellow, for an earthquake of magnitude 7.5, generated at a depth of 10 km, with the following results: TRIDEC Cloud - maximum waves of 0.8 m in Varna, 0.14 m in Burgas, 0.11 m in Constanta and 0.07 m in 2 locations from Turkey (Kirklareli Igneada, Kocaeli Kefken) - see figures 7 and 8; TAT - maximum 0.6 m in Varna and Kamen Bryag (Bulgaria), 0.4 m and Bliznak, Bulgarevo (Bulgaria), 0.3 m in Kranevo and Shkorpilovtsi (Bulgaria), 0.3 m in Constanta, Mangalia and Costinesti, and 0.2 m at Techirghiol (figure 9, table 5).

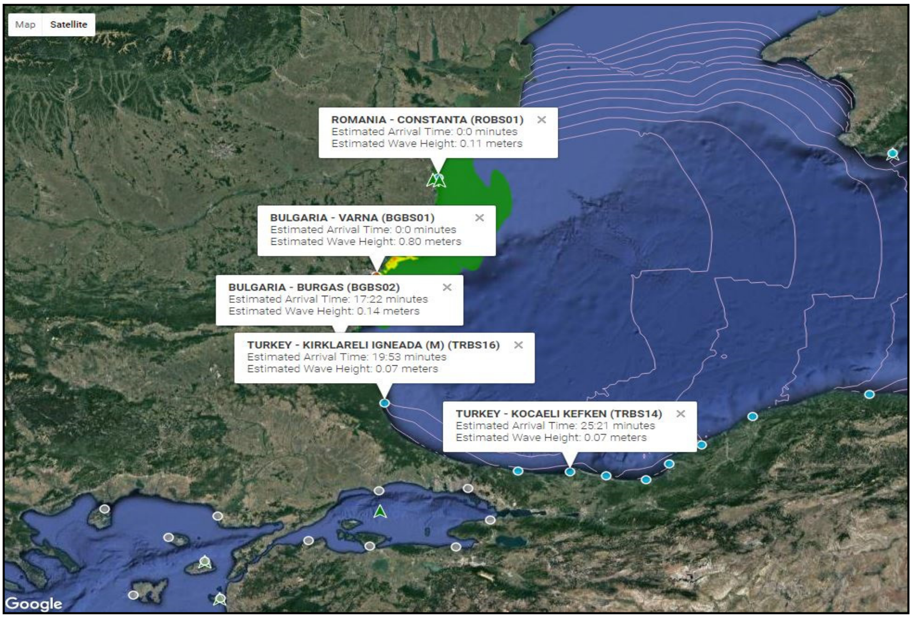

Fig. 7. *Map with the estimated wave heights for certain locations for a moderate scenario (M 7.5, depth 10 km) using TRIDEC software*

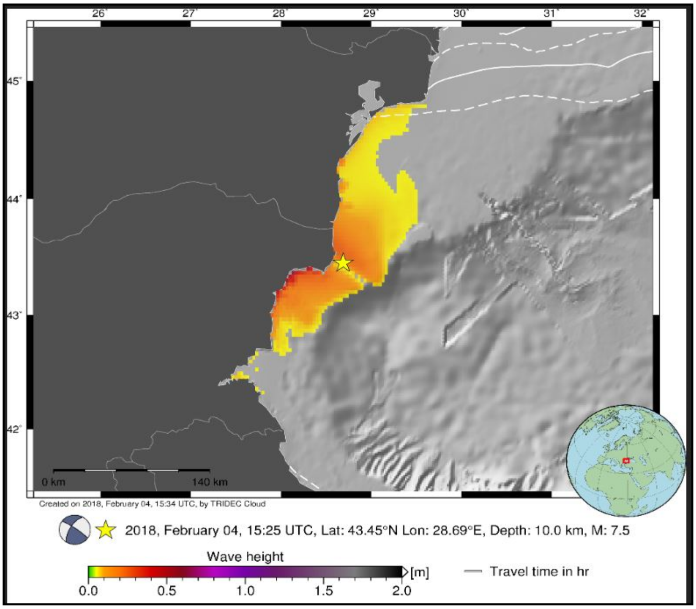

Fig. 8.*Maximum wave heights and travel times for amoderate scenario (M 7.5, depth 10 km) using TRIDEC software*

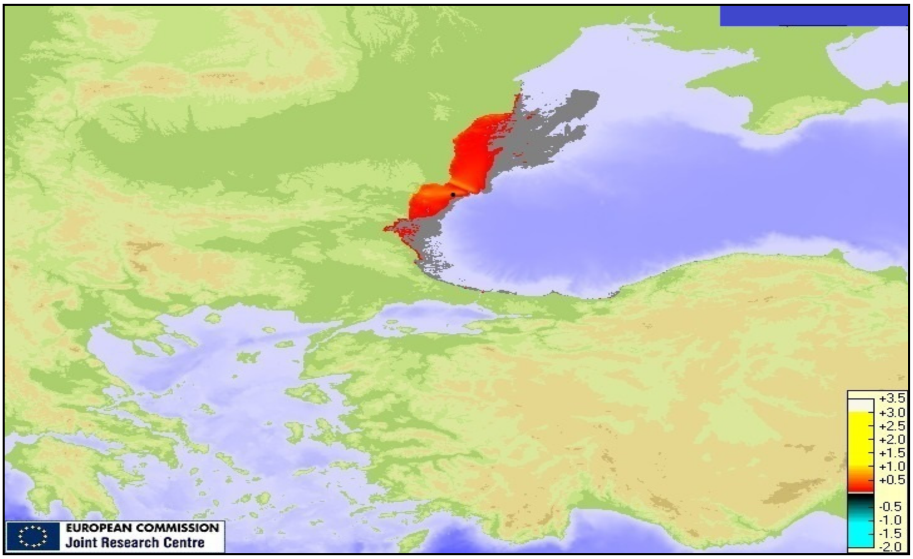

Fig. 9. *Maximum wave heights for the moderate scenario (M 7.5, depth 10 km) using TAT software*

Table 5. *Affected locations for the moderate scenario (M 7.5, depth 10 km) using TAT*software

Date of maximum Tsunami wave	Name	Wave height (m)	Delay of tsunami arrival (hours)	Delay of maximu m tsunami (hours)	Latitude	Longitude
05 Aug 2009 08:53	Varna	0.6	00:24	01:04	43.20	27.93
05 Aug 2009 07:50	Kamen_Bryag	0.6	00:02	00:02	43.45	28.55
05 Aug 2009 08:49	Bliznak	0.4	00:30	01:00	43.05	27.90
05 Aug 2009 08:13	Bulgarevo	0.4	00:06	00:24	43.38	28.43
05 Aug 2009 08:38	Kranevo	0.3	00:14	00:50	43.35	28.07
05 Aug 2009 08:50	Shkorpilovtsi	0.3	00:32	01:02	42.98	27.90
05 Aug 2009 09:07	Costinesti	0.3	**00:30**	**01:18**	**43.95**	**28.64**
05 Aug 2009 08:50	Mangalia	0.3	**00:22**	**01:02**	**43.81**	**28.59**
05 Aug 2009 09:32	Constanta	0.3	**00:54**	**01:44**	**44.19**	**28.66**
05 Aug 2009 09:49	Byala	0.2	00:34	02:00	42.88	27.90
05 Aug 2009 08:55	Krapets	0.2	00:08	01:06	43.64	28.58
05 Aug 2009 09:17	Techirghiol	0.2	**00:42**	**01:28**	**44.07**	**28.65**
05 Aug 2009 09:07	Durankulak	0.2	00:18	01:18	43.70	28.57
05 Aug 2009 09:43	Obzor	0.2	00:36	01:54	42.83	27.89
05 Aug 2009 11:32	Rumelifeneri	0.1	00:52	03:44	41.25	29.10
05 Aug 2009 11:32	Iriva	0.1	00:54	03:44	41.22	29.15

The two software display different results, those with TRIDEC are more complex and interactive. On the other hand, the table with the affected locations given by TAT shows more cities, their exact location (Latitude, Longitude) and arrival times. For most of the cases, TRIDEC's results are higher than those given by TAT software, except for M 8, depth 5 km, where the situation is reversed.

CONCLUSIONS

In order to help estimating the effects of a tsunami triggered in Shabla coastal area, series of numerical simulations of the tsunami wave's height in different locations were accomplished. Using past earthquakes parameters and information about the bathymetry of the Black Sea, different tsunami modeling simulations were obtained for possible strong earthquakes generated in this area.

Past studies have shown that the tsunami hazard is a real threat for the Romanian and Bulgarian shores, with evidences of maximum 5 m tsunami waves generated by a 7.2 magnitude earthquake (event number 3). However, the simulation results give lower estimates for waves heights for 7.2 magnitude, with both software. This may be due to the fact that in the historical times there were no dedicated equipment for water level measurements, and all information was provided by local witnesses.

Tsunami modeling was accomplished using also the following two software, Tsunami Analysis Tool and TRIDEC Cloud, by varying magnitudes between 7, 7.2, 7.5 and 8, also depths of 5, 10 and 30 km and 5 different fault plane solutions

Only four examples are given in this paper, for a possible earthquake of magnitude 8 and depth of 5 km, and for a magnitude of 7.5 and a depth of 10 km.

The results show worst case scenarios with TRIDEC Cloud of maximum 2.62 m waves in Varna, for an earthquake of M 8, depth 5 km, with 0.32 m waves in Constanta. For the same earthquake's parameters, TAT displays maximum waves of 4.3 m in Kamen Bryag, with 2 m in Costinesti, 1.5 m in Constanta and 1.4 m at Mangalia. Moderate tsunami waves are given by magnitude 7.5 (0.6 - 0.8 m), and for low magnitudes (7 - 7.2) the modeling estimates waves of only 0.2-0.4 m in Varna.

Furthermore, the tsunami modelling data could be useful for a comparison with real sea level measuring data, in case of a tsunami triggered in the future by a high magnitude earthquake. Although these are only modelling scenarios, at some point they could be improved and used by the local authorities in order to evacuate possible affected areas and also for warning and prevention measures.

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REFERENCES

Altinok Y., 1999, Tsunamis along the coasts of the Black Sea, Second Balkan Geophysical Congress and Exhibition. *Proceedings of the Conference*, Istanbul, pp. 46 - 47.

Annunziato A., 2007, The Tsunami Assessment Modelling System by the Joint Research Centre. *Science of Tsunami Hazards*, **26** (2), pp. 70 - 92.

Hammitzsch M., Spazier J., Reißland S., 2016, Advances in the TRIDEC Cloud, *Geophysical Research Abstracts*, General Assembly European Geosciences Union, Vienna, EGU2016-12426, **18**.

Nikonov A. A., 1997, Tsunamis occurrence on the coasts of the Black Sea and the Sea of Azov, Izvestiya. *Physics of the Solid Earth*, **33**, pp. 77–87.

Papadopoulos G.A., Diakogianni G., Fokaefs A., Ranguelov B., 2011, Tsunami hazard in the Black Sea and the Azov Sea: a new tsunami catalogue. *Nat. Hazards Earth Syst. Sci.*, **11**, pp. 945–963.

Ranguelov B., Gospodinov D., 1995, Tsunami Vulnerability Modelling for the Bulgarian Black Sea Coast. *War. Sci. Tech.*, **32** (7), pp. 47-53.

Ranguelov B., 1998, Tsunami investigations in the Black Sea - new data from discovered tsunami deposits. *Abst. Intl. Symp HAZARDS'98*, Chania, Crete, May 17 - 22, 125 p.

Solakov D. E., Simeonova S., Ardeleanu L., Alexandrova I., Trifonova P., Cioflan C.O., 2014, Compte rendus de l'Academie bulgare des Sciences: sciences mathenatique et naturelles, Tome, *Geophysique, Sismologie*, **67** (6), pp. 835-842.

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CHEMICAL CHARACTERISATION OF ACID MINE DRAINAGE AND ITS IMPACT ON SURFACE WATER QUALITY IN THE FORMER MINING AREA OF VALEA VINULUI (BISTRIȚA COUNTY – ROMANIA)

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ABSTRACT. Acid mine drainage (AMD) represents a major source of environment pollution in both active and former mining areas. AMD have a high acidity and high levels of sulphate and toxic metals. The present study was focused on assessing the chemical caracterisation of AMD generated Gheorghiu gallery - Valea Vinului minining area and to evaluate the impact of AMD disposal onto surface water by calculating relevant water index. The AMD samples proved to be highly acidic (pH between 2.6 and 4.0) and contaminated with Zn, Cu, Al and Mn. The discharge of untreated acidic waters has a negative impact on Valea Băilor creek by increasing the content of Zn and Mn. The values of both HPI and MI confirm the negative impact of AMD discharge on the quality of surface water.

Key words: *acid mine drainage, mining area, Valea Vinului mine, heavy metal pollution index, metal index.*

INTRODUCTION

Once exposed to water and oxygen, most sulphide minerals are oxidised and form sulphuric acid, metals ions or sulphate, generating acid mine drainage (AMD) (Akcil and Koldas, 2006; Skousen et al., 2018; Skousen et al., 1999). The AMD are characterised by low pH, high conductivity and high levels of alkaline-earth metals, iron, aluminium, manganese, sulphate, bicarbonate and various toxic metals (Pb, Ni, Cd, As, etc.) (Equeenuddin et al., 2010). AMD is one of the severe environmental problems, which once generated is difficult to control and treat (Kefeni et al., 2017). When acidic waters reach surface or underground waters, they can contaminate the water body with toxic metals and making it unsuitable for domestic, agricultural or industrial usage (Skousen et al., 2018; Evans et al., 2015; Hogsden and Harding, 2012). The AMD can also degrade the soil quality by contaminating the soil with sulphate or heavy metals. The abandoned mines represent the main contributor of AMD.

In recent years, much attention has been paid to the assessing of water heavy metal contamination through specific indexes like heavy metal pollution index (HPI) and metal index (MI) (Pal et al., 2017; Mohan et al., 1996; Reddy, 1995; Balakrishnan and Ramu, 2016). HPI is reflecting the composite influence of different heavy metals present in water samples and it is calculated considering the suitability of water for human consumption. The critical HPI value for drinking water should be less than 100. Metal index (MI) is useful in evaluating the overall quality of drinking water, by taking into account the possible additive effect of heavy metals on human health (Balakrishnan and Ramu, 2016).

The present study was focused on assessing the chemical caracterisation of AMD generated in Valea Vinului minining area and to evaluate the impact of AMD disposal onto surface water by calculating relevant water index. The results of the preliminary study conducted in the area were published last year by the authors (Roba et al., 2017). In order to improve the investigation, the study continued during 2017 and 2018 by analizing new chemical parameteres. Few recent studies were conducted in the area (Maicaneanu et al., 2013; Nimirciag, 2012).

Valea Vinului village is located in Rodna commune (Bistrița Năsăud County, Romania) close to Rodnei Mountains National Park. Valea Vinului mining area is situated at about 13 km from Rodna. The mineral exploitations dates back to the Roman times and it was focused on iron and lead extraction, while during the medieval times, the gold and silver were mainly extracted (Maghiar and Olteanu, 1970; Nimirciag, 2012).The complex ore contains high amounts of Zn (5–15%), Pb (up to 4%) and Ag (30–40 g/t) (Mârza, 1977; Maicaneanu et al, 2013), the minerals being extracted from adits located between 665 and 1225 m in depth. In 1996 Valea Vinului mine was declared as being in conservation and in 1998 the mine was closed by a Government decision.

MATERIALS AND METHODS

Sampling

A total of 24 samples were collected from the acidic mine drainage generated by the Gheorghiu Gallery (Valea Vinului mine), from six sampling points (P1 – P6), over a distance of 100 m (figure 1). The AMD are discharged in Valea Băilor creek and then later in Someșul Mic River. In order to evaluate the impact of AMD discharge onto surface water quality, 12 samples were collected from Valea Băilor creek, from one sampling point (P7) located 100 m upstream of the acidic mine discharging site and two sampling points (P8 and P9) located 100 m and 200 m respectively, downstream of the acidic mine discharging site (figure 1). The waters were sampled during summer (June 2017, July 2017) and spring season (April 2018, May 2018).

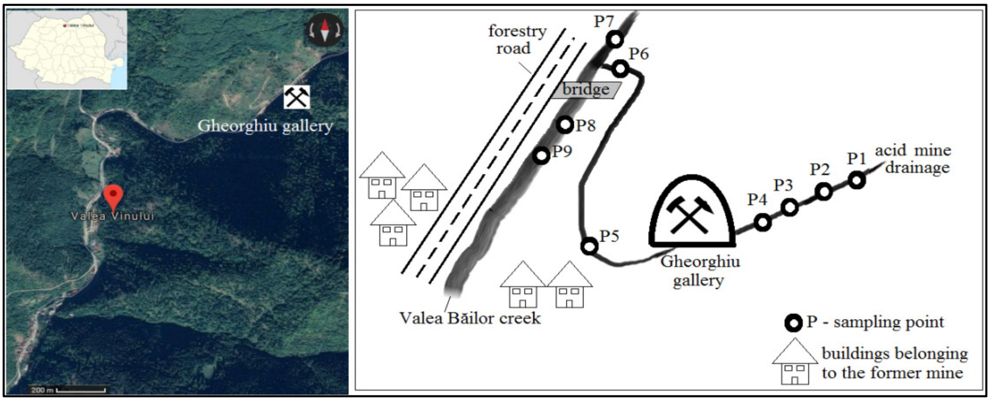

Fig.1. *Location of the investigated area (left) (modified after Google Earth) and sketch with the position of the sampling points (right).*

Analysis of the quality parameters

In order to assess the water quality, a total of 17 physicochemical and chemical parameters were analysed for each sample.

The investigated physico-chemical parameters were: pH, redox potential (ORP), electrical conductivity (EC), total dissolved solids (TDS), and salinity. These parameters were measured *in situ* using a portable multiparameter (WTW multi350i, Germany). Chemical parameters included twelve metals (Na, Al, Mn, Zn, Mg, Ca, Ni, Pb, Cu, Cd, Ti and Sr), which were analysed by inductively coupled plasma mass spectrometry (ICP-MS) by using an Perkin Elmer ELAN DRC-e instrument, equipped with a Meinhard nebulizer and a glass cyclonic spray chamber for pneumatic nebulization. The operating conditions were: nebulizer gas flow rates, 0.92 /min; auxiliary gas flow, 1.2 l/min; plasma gas flow, 15 l/min; lens voltage, 7.25 V; radiofrequency power, 1100 W; CeO/Ce ratio = 0.030; and Ba++/Ba ratio =0.026.

Before ICP-MS analysis, the water samples were filtrated (0.45 µm) and acidified to pH≈2 (with HNO_3 65%). The samples were stored in the laboratory at dark and 4ºC, and analysed within three days from sampling.

Heavy metal pollution index (HPI) and metal index (MI)

HPI was calculated based on the equation given by Mohan et al. (1996):

$$HPI = \frac{\sum_{i=1}^{n} W_i \cdot Q_i}{\sum_{i=1}^{n} W_i}$$

where: W_i is the unit weightage of the i^{th} parameter defined as reciprocal value of S_i (Pal et al., 2017) (S_i is the maximum permissible limit for drinking water given by national legislation – Law 458/2002 regarding the quality of drinking water) and Qi is the sub quality index and is calculated using the formulae (Mohan et al. 1996; Pal et al., 2017):

$$Q_i = \sum_{i=1}^{n} \frac{M_i}{S_i} \cdot 100$$

where: M_i is the monitored value of heavy metal, S_i is the standard value (maximum permissible limit for drinking water given by national legislation)

MI was preliminarily defined by Tamasi and Cini (2004) as follows:

$$MI = \sum_{i=1}^{n} \frac{C_i}{MAC_i}$$

where: C_i is the concentration of each metal in the sample, MAC_i is the maximum allowed concentration for each element (maximum permissible limit for drinking water given by national legislation).

RESULTS AND DISCUSSIONS

Chemical characterisation of acid mine drainage and Valea Băilor creek

The AMD samples (samples P1 – P6) were highly acidic having the pH between 2.6 and 4.0 (Fig. 2), being considerably lower than the permissible limit (6.5 – 8.5) imposed by national legislation for wastewaters discharged into natural surface waters (Government Decision no. 352/21 April 2005). The most acidic values were registered during April 2018, fact that can be correlated with the snow melting process and the high amount of precipitation which has increased the acidic mine drainage. Based on the previous study (Roba et al., 2017), the waters proved to be more acidic in April 2018 (pH between 2.6 and 3.2) than in April 2017 (pH between 3.1 and 3.4). These acidic waters are discharged into Valea Băilor creek without any prior chemical treatment. As a consequence, in some sampling intervals, the creek water had a pH lower than 6.5 – 8.5, which is the permissible limit impose by national legislation (Order no. 161/16 February 2006) (Fig. 2). It is necessary to treat these AMD waters in order to reduce their impact on Valea Băilor creek, Someșul Mic River, or onto underground water and the soil from the area.

Because of the low pH, the AMD waters had a positive ORP, between +169.2 and +228.8 mV, comparing to Valea Băilor creek, where the ORP was lower (-14.6 and +43.6 mV) (Fig.2). The AMD samples had high levels of EC (1426 – 2490 μS/cm), TDS (892 – 1556 mg/l) and salinity (0.7 – 1.3 ‰), reflecting the high amount of dissolved salts (figure 2). Generally, these parameters were higher during April 2018 (Fig. 2), fact that can be correlated with the snow melting and the high amount of precipitation registered during that period, which increased the acidic mine drainage and the dissolution of ions especially sulphates. After the discharge of AMD, there was a slightly increasing of EC, TDS and Salinity levels between the upstream (P7) and downstream (P8 - P9) sampling points (figure 2).

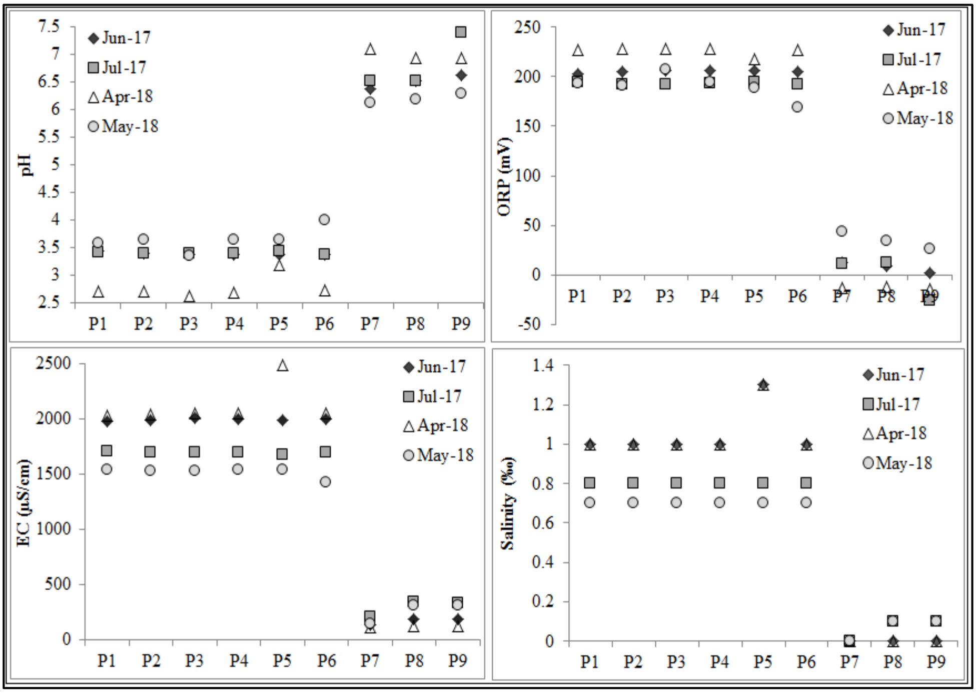

Fig. 2. *Seasonal fluctuation of physico-chemical parameters in acid mine drainage (P1 - P6) and surface waters (P7 - P9).*

All the parameters showed a relatively homogenous distribution for both AMD and surface water samples (figure 2).

The AMD samples proved to have high levels of metals, the total content of metals ranged between 210.6 and 217.2 mg/l, comparing to Valea Baii creek (26.7 and 34.1 mg/l) (figure 3). By comparing the total content of metals registered upstream and downstream of AMD discharging point, the results confirm the impact of AMD on the quality of Valea Băii creek.

The metals distributions fallowed the sequence: Ca>Mg>Zn>Mn>Al>Na>Sr>Ti>Cd>Cu>Pb>Ni (figure 4), the values being considerably lower in surface water than in AMD samples.

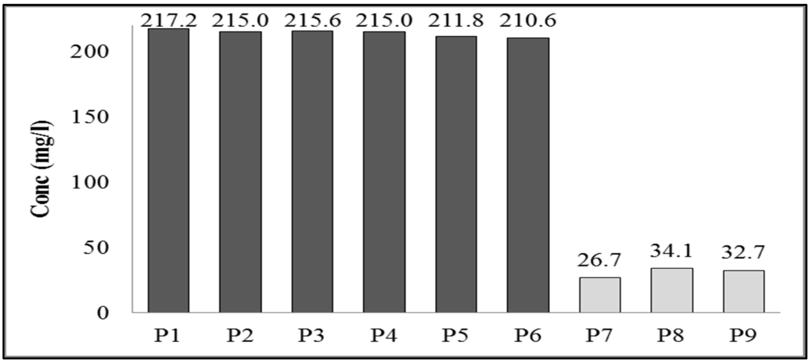

Fig. 3. *Total content of metals in acid mine drainage (P1 - P6) and surface waters (P7 - P9).*

The content of Ca (77.6 – 90.2 mg/l), Mg (61.1 – 79.6 mg/l), Cd (0.14 – 0.18 mg/l), Ni (0.042 – 0.047 mg/l), Pb (0.023 – 0.029 mg/l) from AMD samples was within the permissible limits (300 mg/l for Ca, 100 mg/l for Mg, 0.5 mg/l for Ni, 0.2 mg/l for Pb and Cd) imposed by national legislation for wastewaters discharge into natural surface waters (Government Decision no. 352/21 April 2005). The concentrations of Zn (39.66 – 45.57 mg/l), Cu (0.09 – 0.18 mg/l), Al (5.07 – 6.24) and Mn (7.57 – 8.04) in all acidic mine waters exceeded the national standards (0.5 mg/l for Zn and 0.1 mg/l for Cu, 5 mg/l for Al, 1 mg/l for Mn) imposed for wastewaters discharge into natural surface waters. The AMD samples had a relatively low content of Na (1.9 – 4.6 mg/l), Ti (0.38 – 0.39 mg/l) and Sr (0.35 – 0.45 mg/l).

Considering the low content of Ca (16.6 – 25.5 mg/l), Mg (6.1 – 7.1 mg/l), Na (0.7 – 3.7 mg/l), Cu (1.3 - 9.9 µg/l), Pb (0.1 – 2.1 µg/l) and Ni (1.7 – 2.7 µg/l), the Valea Băilor creek can be classified as 1st water quality class – very good ecological status) (Order no. 161/2006 for the approval of the Normative regarding the classification of surface water quality in order to establish the ecological status of the water bodies, elaborated by the Ministry of Environment and Water Management from Romania). The results obtained in the present study indicated the impact of AMD discharge onto the zinc and manganese level from Valea Băilor creek, which correspond to 5th water quality class (very poor ecological status) and 4th water quality class (poor ecological status).

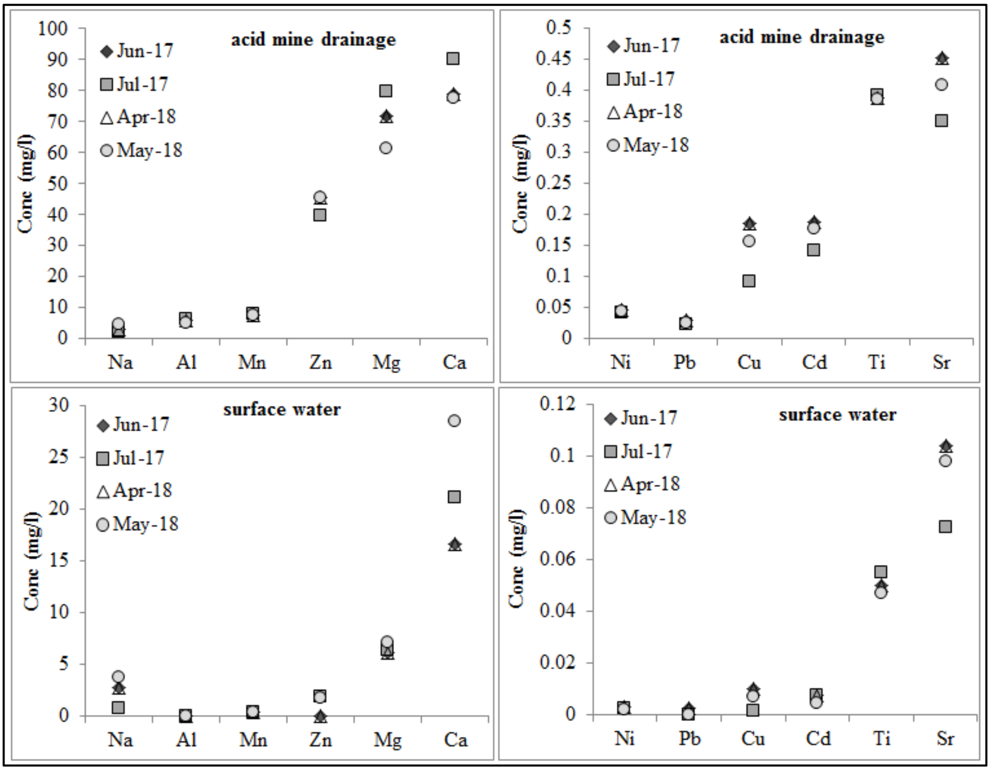

Fig. 4. *Seasonal fluctuation of metals in acid mine drainage (P1 - P6) and surface waters (P7 - P9).*

No significant fluctuation of metals content was observed during the four months.

The Heavy Pollution Index (HPI) and Metal Index (MI) of surface water

The HPI value for the waters sampled upstream of the AMD discarge point (P7) was below the critical index value of 100 (figure5), while the waters sampled downstream (P8 and P9) had the HPI above critical leveel, coresponding to a very poor quality.

Based on MI value, the water samples collected upstream of the AMD discarge (sampling point P7), correspond to class V – strongly affected with respect to metal pollution, having the MI level between 4 and 6 (Lyulko et al., 2001), while the samples collected downstream from AMD discharging point (P8 and P9) are classified as seriously affected, having the MI > 6 (Lyulko et al., 2001) (figure 5).

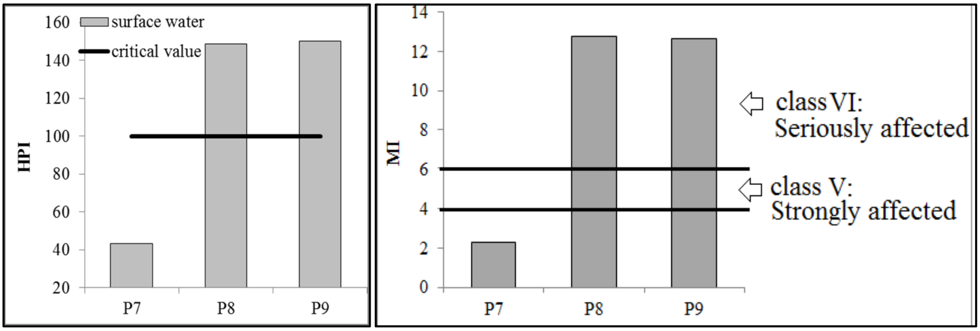

Fig. 5. *The average values for Heavy Pollution Index (**HPI**) and Metal Index (**MI**) for the analysed surface waters.*

The values of both HPI and MI confirm the negative impact of AMD discharge on the quality of Valea Băilor creek. In the proximity of AMD discharging point, the surface water dilution is not high enough to dominate the metal content from AMD. Future investigations should be performed in order to evaluate the quality of Valea Băilor creek on longer distances.

CONCLUSIONS

It can be concluded that the AMD from the Gheorghiu gallery are highly contaminated with Zn, Cu, Al and Mn. The discharge of untreated acidic waters has a negative impact on Valea Băilor creek by increasing the content of Zn and Mn, which correspond to 5th water quality class (very poor ecological status) and 4th water quality class (poor ecological status).

The values of both HPI and MI confirm the negative impact of AMD discharge on the quality of surface water. It is necessary to treat these AMD waters in order to reduce their impact on Valea Băilor creek, Someșul Mic River, or onto underground water and the soil from the area.

REFERENCES

Akcil A., Koldas K., 2006, Acid mine drainage (AMD): causes, treatment and case studies. *J. Clean. Prod.*, **14**, pp. 1139–1146.

Balakrishnan A., Ramu A., 2016, Evaluation of heavy metal pollution index (HPI) of ground water in and around the coastal area of Gulf of Mannar Biosphere and Palk Strait. *Journal of Advanced Chemical Sciences*, **2** (3), pp. 331–333.

Equeenuddin S.M., Tripathy S., Sahoo P.K., Panigrahi M.K., 2010, Hydrogeochemical characteristics of acid mine drainage and water pollution at Makum Coalfield, India, *Journal of Geochemical Exploration*, **105**, pp. 75–82.

Evans D., Zipper C., Hester E., Schoenholtz S., 2015, Hydrologic effects of surface coal mining in Appalachia (US). *J. Am. Water Res. Assoc.*, **51**, pp. 1436–1452.

Government Decision no. 352 of 21 April 2005 on the modification and completion of the Government Decision no. 188/2002 approving some norms regarding the discharge conditions in the aquatic environment of the waste waters, Published in Official Monitor no. 398 of May 11, 2005, in Romanian: http://legislatie.just.ro/Public/DetaliiDocument/61585

Hogsden K., Harding J., 2012, Consequences of acid mine drainage for the structure and function of benthic stream communities: a review. *Freshw. Sci.*, **31**, pp. 108–120.

Kefeni K.K., Msagati T.A.M., Mamba .BB., 2017, Acid mine drainage: Prevention, treatment options, and resource recovery: A review. *Journal of Cleaner Production*, **151**, pp. 475-493.

Law 458/2002 regarding the quality of drinking water, modified and completed by the Government Ordinance no. 22 from 30 August 2017, published in the Official Monitor no. 705 from 31 August 2017, in Romanian: http://www.monitoruljuridic.ro/act/ordonan-nr-22-din-30-august-2017-pentru-modificarea-i-completarea-legii-nr-458-2002-nbsp-privind-calitatea-apei-potabile-emitent-192779.html

Lyulko I., Ambalova T., Vasiljeva T., 2001, To integrated water quality assessment in Latvia. In: MTM (Monitoring Tailor-Made) III, Proceedings of International Workshop on Information for Sustainable Water Management, Netherlands, pp. 449–452.

Maghiar N., Olteanu S., 1970, *From the mining history of Romania (in Romanian)*, Scientific Press, Bucharest, Romania.

Maicaneanu A., Bedelean H., Ardelean M., Burca S., Stanca M., 2013, Hanes and Valea Vinului (Romania) closed mines Acid Mine Drainages (AMDs) – Actual condition and passive treatment remediation proposal. *Chemosphere*, **93**, pp. 1400–1405.

Mârza I., 1977, *Geology of ore deposits. Romania*., Babes-Bolyai University, Cluj-Napoca.

Mohan S.V., Nithila P., Reddy S.J., 1996, Estimation of heavy metal in drinking water and development of heavy metal pollution index. *J. Environ. Sci. Health A,* **31** (2), pp.283-289.

Nimirciag R., 2012, Heavy metals in the soils of Rodna mining area, Romania and zeolite efficiency for remediation. *Environmental Engineering and Management Journal*, **11** (2), pp. 421-426.

Order no. 161/2006 for the approval of the Normative regarding the classification of surface water quality in order to establish the ecological status of the water bodies, elaborated by the Ministry of Environment and Water Management from Romania, published in Official Monitor no. 511 from 13 June 2006, in Romanian: http://legislatie.just.ro/Public/DetaliiDocument/72574

Pal R., Dubey R.K., Dubey S.K., Singh A.K., 2017, Assessment of Heavy Metal Pollution through Index Analysis for Yamuna Water in Agra Region, India. *Int.J.Curr.Microbiol.App.Sci*, **6** (12), pp. 1491-1498.

Reddy S.J., 1995, *Encyclopedia of environmental pollution and control*, Enviro. media, Karada, Apple Academic Press, Inc., India, **1**,342 p.

Roba C., Pistea I., Bindiu S., Rosu C., 2017, Effects of former mining activities on surface water. Case study: Valea Vinului mine – Romania. *SGEM2017 Conference Proceedings*, ISBN 978-619-7105-98-8 / ISSN 1314-2704, 29 June - 5 July, 2017, **17** (11), pp. 833-840.

Skousen J., Rose A., Geidel G., Foreman J., Evans R., Hellier W., 1999, *Handbook of technologies for avoidance and remediation of acid mine drainage*. National Mine Land Reclamation Center, West Virginia University, Morgantown, WV.

Skousen J.G, Ziemkiewicz P.F., McDonald L.M., 2018, *Acid mine drainage formation, control and treatment: Approaches and strategies*, The Extractive Industries and Society, https://doi.org/10.1016/j.exis.2018.09.008

Tamasi G., Cini R., 2004, Heavy metals in drinking waters from Mount Amiata (Tuscany, Italy) Possible risks from arsenic for public health in the province of Siena. *Sci. Total Environ*., **327**, pp. 41-51.