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Cover 1: *Taxodium distichium* with *Tillandsia usneoides* (moss).
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THE EVOLUTION OF RURAL CLUSTERS WITHIN THE CLUJ METROPOLITAN AREA

Nicolae BACIU[1]*, Gheorghe ROŞIAN[1], Octavian-Liviu MUNTEAN[1], Vlad MĂCICĂŞAN[1], Viorel ARGHIUŞ[1], Carmen STĂNESCU[2]

[1] *Babeş-Bolyai University, Faculty of Environmental Science and Engineering, 400294 Cluj-Napoca, Romania*
[2] *I. Haţieganu School, 400000 Cluj-Napoca, Romania*
* Corresponding author: nicubaciu2 @yahoo.com

ABSTRACT. The identification of the metropolitan area was limited to the surrounding localities in a radius of about 30 km around Cluj-Napoca. This distance is considered in EU the best practice for the development of the peri-urban space. The Cluj Metropolitan Area (CMA) is located in Cluj County, the north-western development region of Romania. The Cluj Metropolitan Area is composed from voluntary association of communes plus the city of Cluj-Napoca, forming an urban network composed of two metropolitan rings. The first metropolitan ring is the purpose of our study. The transformation of communes into residential and complex clusters is also analyzed. The seven localities inside the first ring had significant changes in population and land use between 2002 and 2020. The increase of the population and decrease of the agricultural land area are premises in achieving urban homogeneity in the metropolitan area.

Key words: *Cluj Metropolitan Area, metropolitan rings, urban space, rural clusters.*

INTRODUCTION

The conceptual framework for spatial planning, especially from the point of view of decision-makers at local level, which plans its strategy for absorbing European funds, is territorial cohesion, economic cohesion and social cohesion at EU level. They determine European development policies, which lead to EU-funded development programs.

In the project Cluj Metropolitan Area (CMA), 19 municipalities joined at the beginning of 2000, creating an area of over 1600 sq. km, separated into two metropolitan rings. *The first metropolitan ring* includes seven communes: Apahida, Baciu, Chinteni, Ciurila, Feleacu, Florești and Gilău, which are best integrated in residential development and urban transport policies, and where activities associated with the city take place. Thus, the Cluj Metropolitan Area became ten times larger than the administrative structure of Cluj-Napoca city (Baciu et al., 2018).

From the beginning, CMA had three major targets (according to the Cluj County Council):

1. Accelerated infrastructure development to European standards: - access infrastructure, as express roads and highway, airport development, railway modernization, introduction of high-speed trains; - essential utilities in rural clusters (water, sewerage / purification, sanitation, natural gas); - energetic efficiency.

2. Increasing economic competitiveness by attracting strategic investors, increasing entrepreneurial capacity, stimulating the concentration of brand and tradition enterprises, superior capitalization of the tourist potential, stimulating the innovative and competitive potential of the economic sector.

3. Human resource development and education, such training programs, continuing education and research.

Initially, the big city contributes with human resources, know-how and educational experience, and communes offered the rural-agricultural land for investments. Thus, a big and *complex administrative cluster* (Cluj-Napoca) and 19 communes as *rural and agricultural clusters* were crystallized (figure 1).

The core of Cluj Metropolitan Area represents the first metropolitan ring, including Cluj-Napoca city and seven communes: Apahida, Baciu, Chinteni, Ciurila, Feleacu, Florești and Gilău.

Starting with the year 2000, the idea of the metropolitan area developed, but the profile of the communes around Cluj-Napoca was an agricultural one, with an obvious tendency to decrease the population. This situation did not encourage investment and partnerships in large-scale projects between administrative entities (Baciu, 2013). The big city gradually imposed economic and social policies and created a favorable framework for large real estate investments in the surrounding communes, attracting young people from all counties of the country.
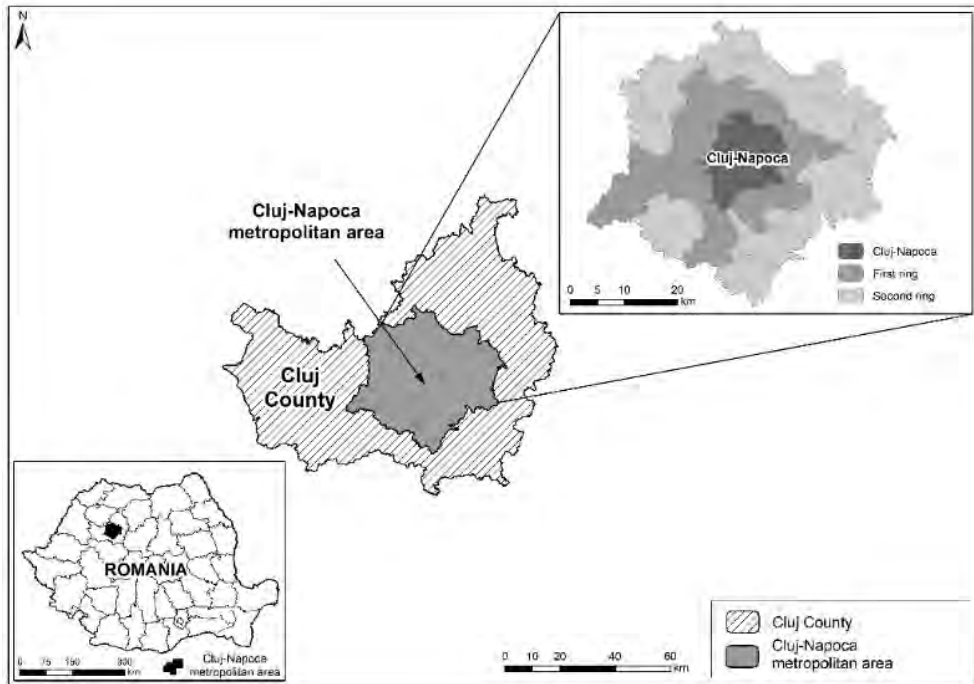
Fig. 1. *Cluj Metropolitan Area (CMA) and the two metropolitan rings*

Initial typology of rural clusters

The area of first metropolitan ring looked extremely heterogeneous. We had well-developed communes with incipient urban profile, such as Florești, Baciu, Gilău or Apahida, but also communes with a deep rural aspect – Chinteni, Ciurila, Feleacu. This strong agricultural profile was highlighted by the structure and occupation of the population or the structure of land use (Baciu et al., 2012, 2015; Roșian, 2017). The first 4 communes registered over 7-8000 inhabitants in 2002, having 40-50% of the active population employed in the industry and services of the big city. However, the frequency of agricultural land is important in those administrative units. In Apahida the arable lands represent almost 40% of the commune's surface, in Baciu and Florești 20-30%, in Gilău – due to the mountain morphology – less than 20%.

Frequency of meadows from the total surface of communes represents almost 30% in Apahida, Florești and Baciu, and just fewer than 20% in Gilău. The surfaces covered of hay fields was 10 to 20% of the total area (Pop, 2007).

Anticipating the inevitable peri-urban development, local decision-makers have allocated more and more space to the built-up area, creating the premises for real estate development. This approach was facilitated by the inhabitants of the communes, who saw in the change of land use from *outside of built-up area* to *built-up area*, the possibility of selling agricultural properties at a higher price.

The three communes with a deep rural profile during 2002 – Chinteni, Ciurila, Feleacu – have maintained this status for the most part even today, but the trends of peri-urbanization are becoming more and more evident, especially in Chinteni (Chinteni City Hall intends to allocate in the new General Urban Plan over 3600 ha for built-up area - compared to 582 ha in 1990). The agricultural profile was highlighted by the structure of land use. The frequency of arable lands represents almost 40% of the commune's surface in Chinteni and Ciurila, and over 20% in Feleacu commune. Frequency of meadows from the total surface of communes represents between 20-30% in Chinteni, Ciurila and Feleacu. The surfaces covered by hay fields were 10 to 20% of these three communes. The population of communes with agricultural profile was in 2002 between 1500 inhabitants (Ciurila) and 3810 inhabitants (Feleacu), as shown in table 1.

Changes in the typology of clusters in the first metropolitan ring

After 2002, there were dramatic changes in the territory superimposed over the first metropolitan ring. The changes in the demographics of the communes, the architecture of the new residential complexes, the level of investments, have definitively changed the profile of the *rural clusters*. They have undergone an adaptation to the requirements of the Cluj-Napoca attraction pole, so that the agricultural clusters have been transformed by 2020 into *residential and service clusters* (*tertiary clusters*). A type of organic connection was installed between the big city and the surrounding communes, based on the idea of a center-periphery mutual benefit policy. The need for investment

space in the metropolis has slightly exceeded administrative boundaries and agricultural land (especially arable land and pastures – table 2) have been targets of real estate, logistics, industrial or commercial facilities projects.

The need to modernize the rural space, to adhere to urban projects: transport infrastructure, water and sewerage network, environment and waste management; have acquired immediate and mandatory value for local decision makers. City halls also took advantage of this business opportunity to attract the labor force required by the big city to their administrative territory, creating an unexpected increase in the volume of taxes and duties to the local budget.

The explosive population growth of the first metropolitan ring is the first and most important feature of the definitive change of agricultural clusters (Baciu et al., 2018). The population growth is allogeneic, external, attributed to immigration from all counties of the country. The best example is provided by Florești, which in the period 2002-2021 evolved from 7470 inhabitants to 46535 inhabitants, resulting in an increase of over 523% (table 1, figure 2.a, 2.b).

Table 1. *The evolution of population between 2002 and 2021*

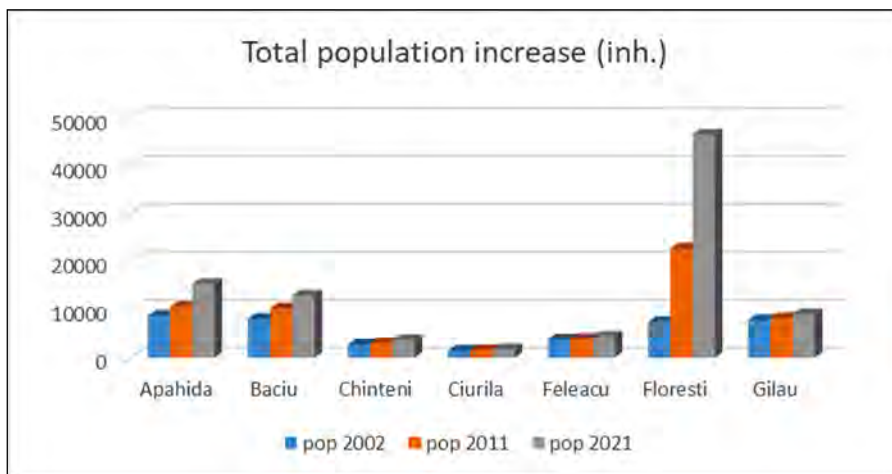| Nr. Crt.	Communes	Inh. 2002	Inh. 2011	Inh. 2021
1	**Apahida**	8785	10685	15391
2	**Baciu**	8139	10317	12983
3	**Chinteni**	2786	3065	3717
4	**Ciurila**	1509	1594	1794
5	**Feleacu**	3810	3923	4409
6	**Florești**	7470	22813	46535
7	**Gilau**	7861	8300	9112

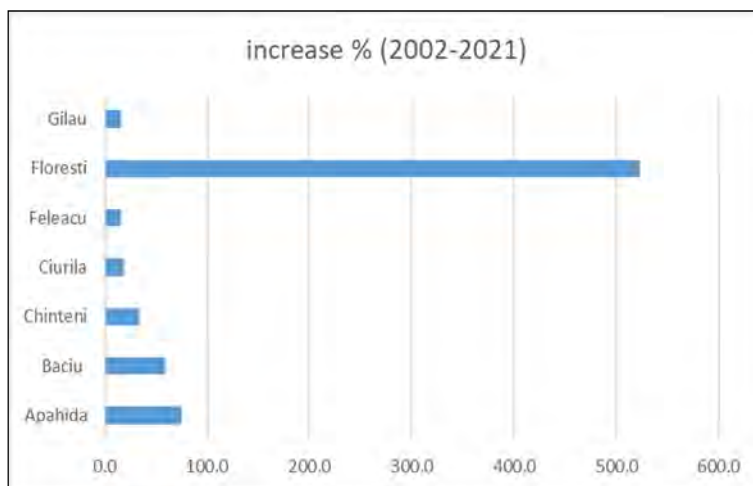**Fig. 2.a.** *The evolution of population between 2002 and 2021*

Fig. 2.b. *Population growth (%) inside the first metropolitan ring*

Another spectacular change in the area of the first metropolitan ring was the change of land use between 2002 and 2020. Here we refer in particular to the increase of *non-agricultural land* in most administrative units.

This is the result of continued pressure on local decision-makers by investors to make built-up area land available. The most affected were the communes: *Florești* – increase of 70% between 2002 and 2020, which had a constant strong urbanization trend; *Feleacu* – increase of 20% due to new infrastructural projects and real estate trend in the vicinity of commune's center; *Chinteni* is experiencing an investment boom in terms of residential areas, starting with the years 2011-2012. Local decision makers have an extremely favorable and friendly policy towards real estate investors. The new General Urban Plan of the commune, still unapproved, proposes a very generous surface of 3685 ha for the built-up area. This would be the most spectacular urban growth in the metropolitan communes since 1990 (from 582 ha to 3685 ha). For the time being, between 2002 and 2020, non-agricultural growth is 16.7% (figure 4 and 5).

The decrease of the non-agricultural land from *Apahida* (-3.5%) is explained by the loss of some forest areas and the transformation of some floodable lands from the Someș corridor into agricultural lands. Also, the new General Urban Plan did not allocate new places to the built-up area, because the last one - seven years ago - had allocated sufficient areas, which are still being in built (figure 3 and figure 4).

Baciu commune continues the growth trend of the built-up area, but at a slower pace than in Florești (3.8%). This commune has two distinct categories of investment destinations: one is for real estate projects in the central and northern part, and the other for investments in industry and trade, in the southern part.

The small commune of Ciurila, located in the southern part of the first metropolitan ring is the newest attraction for individual real estate investments and group residential areas, in the so-called oasis of peace in Făget Forest and Feleacului Hill. With a slight increase in population from 1509 inhabitants (2002) to 1794 inhabitants (2021), in the coming years the General Urban Plan will generate new areas for built-up area (table 2, figure 3, figure 5).

Table 2. *The evolution of land use between 2002 and 2020*

Nr. Crt.	Communes	S. total (Ha)	Agric. 2002 (Ha)	Agric. 2020 (Ha)	Non Agric. 2002 (Ha)	Non Agric. 2020 (Ha)	difference 2002-2020 Nonagr (Ha)	difference 2002-2020 Nonagr (%)
1	**Apahida**	**10602**	9102	**9396**	1250	**1206**	**-44**	**-3.5**
2	**Baciu**	**8751**	5890	**5559**	2724	**2827**	**103**	**3.8**
3	**Chinteni**	**9651**	7455	**7242**	2064	**2409**	**345**	**16.7**
4	**Ciurila**	**7222**	5655	**5689**	1536	**1533**	**-3**	**-0.2**
5	**Feleacu**	**6196**	4094	**3724**	2059	**2472**	**413**	**20.1**
6	**Floreşti**	**6074**	4397	**4129**	1141	**1945**	**804**	**70.5**
7	**Gilău**	**11682**	3898	**3740**	7756	**7840**	**84**	**1.1**
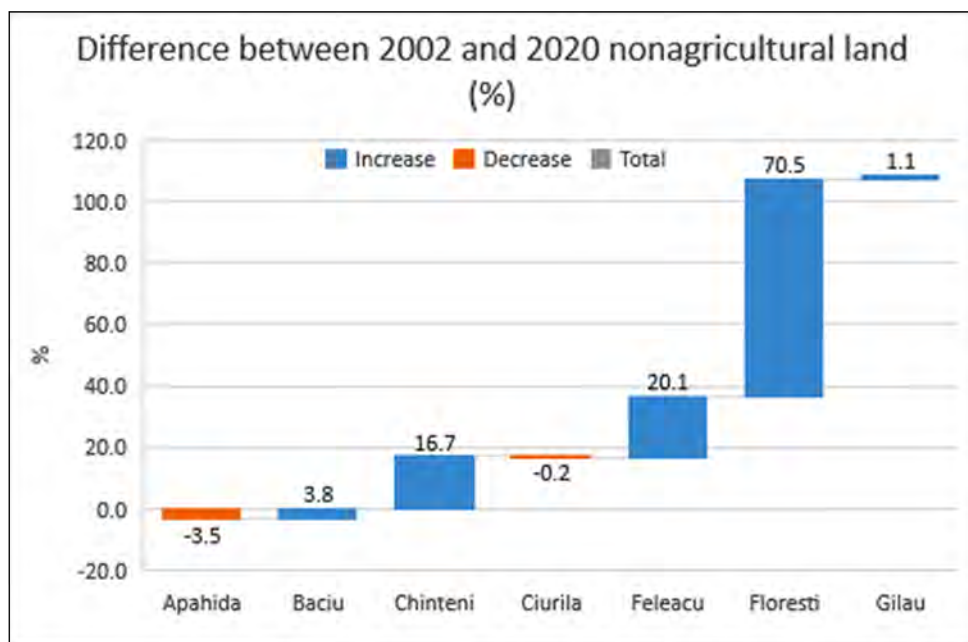
Fig. 3. *Nonagricultural land use change (%) between 2002 and 2020*

CONCLUSIONS
(related to tertiary clusters in the first metropolitan ring)

The evolution of communes in the first metropolitan ring of the CMA from deep agricultural clusters to dynamic tertiary clusters, so well anchored in urban complexity, is a development model for regional and national planning programs.
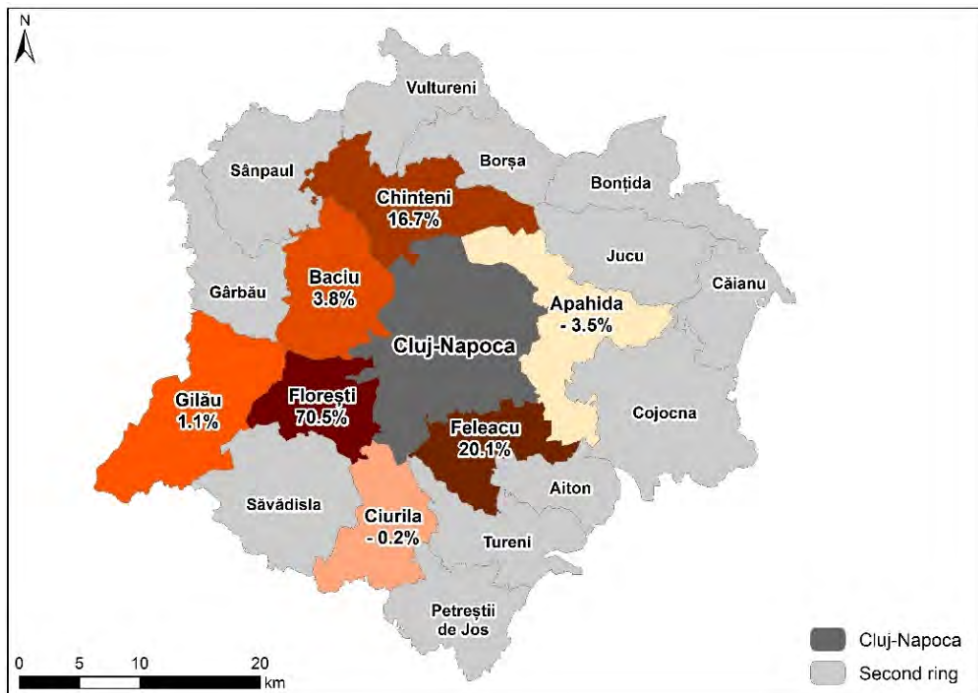
Fig. 4. *Tertiary clusters inside the first metropolitan ring –*
change in nonagricultural land use (2002-2020)

We must emphasize the fact that the favorable evolution in a short time of the communes around the city of Cluj-Napoca is influenced by positive structural, historical and economic-social characteristics of the big city. The role of regional polarization center was crystallized 500 years ago, and then gradually this function was amplified. The regional leadership role of Cluj can no longer be questioned since the 18th century. The cultural

function completed the function of university center and completed the complex profile of this regional urban attractor. Therefore, the development of the communes around Cluj is not accidental. The rural and agricultural space provided exactly the type of land the city needed. The mutual benefits were visible immediately after the establishment of the metropolitan area, the nearby communes taking advantage of the development projects.
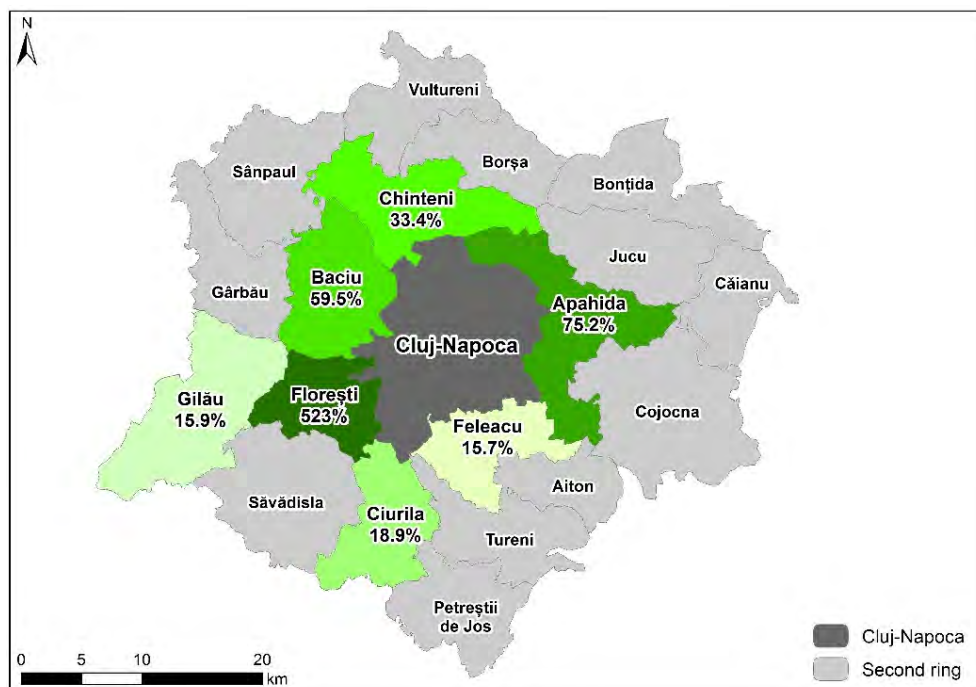
Fig. 5. *Tertiary clusters inside the first metropolitan ring – population increase (2002-2021, in %)*

As in any functional group, there are dysfunctions. Among the weaknesses of the metropolitan area we mention: large differences in budget allocations and projects between the center and the periphery; the majority of the stable population in communes represents labor for the big city only; connectivity and fluidization problems in transport; biodiversity loss and urban pollution sources (due to the increasing of motorized traffic); poor traditional practices in rural areas in the management of living space and

waste; increasing the anthropic pressure on the protected areas; reducing green spaces in favor of built-up areas (green space density: under 30 m²/inh.); delays in construction of metropolitan express road.

But strengths will always be the most important arguments for regional development: top universities, medical centers, research structures, high-tech facilities, the major cultural, sports, leisure, exhibition facilities. All these represent part of so-called *regional poles of excellence*. The presence of the big city that has adopted the modern phrases as *smart city* and *green city* are a guarantee of balanced development of the metropolitan area. Its development is based on the exploitation of intellectual capital towards education, innovation and economic development, including eco-friendly concepts.

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ASSESSMENT OF HEAVY METALS CONTENT IN THE PROXIMITY OF A CONTAMINATED SITE FROM CLUJ-NAPOCA (ROMANIA)

Georgiana GROSU[1], Carmen Andreea ROBA[2], Ramona BĂLC[1], Maria Lucia BIZĂU-CÂRSTEA[1]*

[1]*Babeş-Bolyai University, Faculty of Environmental Science and Engineering, Fântânele 30, 400294 Cluj-Napoca, Romania*
[2]*Babeş-Bolyai University, Research Institute for Sustainability and Disaster Management based on High Performance Computing (ISUMADECIP), Faculty of Environmental Science and Engineering, Fântânele 30, 400294, Cluj-Napoca, Romania*
*Corresponding author: marialucia.bizau@ubbcluj.ro

ABSTRACT. The present study was conducted in the proximity of a contaminated site from Cluj-Napoca city (Cluj County, Romania), where metal processing activities have been carried out for decades. Metal content and physico-chemical parameters were analyzed in soil, water and sediment samples, while organic matter (OM) and total organic carbon (TOC) was additionally analyzed for the soil samples. The sources of heavy metals were evaluated based on multivariate statistical analysis, while the soil and sediment contamination degree was assessed based on specific pollution indices. The calculated indices indicated a significant pollution with Cd and Pb, which may represent a risk if the area would become a residential area.

Key words: *heavy metals, contaminated site, soil pollution indices, multivariate statistical analysis, Cluj-Napoca*

INTRODUCTION

Large areas with variable metal concentrations are distributed in different regions in Romania. In most cases, these metal accumulations in soil represent the negative consequences of anthropic activity, such as

mining activities, operating metallurgical plants, fuel stations and depots, waste disposal etc. (Li et al., 2013; Comm (2006) 231). According to the Romanian legislation (Law 74/2019), when the metal concentrations exceed the intervention thresholds, these areas are classified as contaminated sites. Metal polluted sites are difficult to remediate because these contaminants cannot be biologically degraded, but can become bioavailable for the microorganisms and plants developing in those soils (Jézéquel and Lebeau, 2008). The bioavailability of metals is directly linked to solubility of the solid-phase form into a solution phase. Soil microorganisms and root exudates can increase the solubility rate and act as metal sorbents (Traina and Laperche, 1999; Majewska et al., 2007). Some organisms can develop metal tolerance, while others cannot cope with the ecotoxicological effects. Thus, heavy metals (HMs) can pose a risk to human health by passing into the food chain and generate imbalances in the natural ecosystems.

Following the previous European demarches for creating a Soil Directive, each member state of the EU had to identify the contaminated sites present at national level. In 2015, nine potentially contaminated sites and 19 contaminated sites were reported for Cluj County (Romania) based on the national environmental legislation (HG 683/2015). According to the public information provided by the Environmental Protection Agency of Cluj, eight contaminated sites are found in the administrative territory of Cluj-Napoca (Annex no 8). The contamination of these areas was mainly generated by landfill activities, fuel supply and depots, metal processing and galvanizing activities, where heavy metals (HMs) and petroleum hydrocarbon (PHC) were identified as the main pollutants found in soil.

In Romania, various studies were conducted in different areas identified as contaminated sites, in order to assess HMs effects on soil quality, vegetation development, microbiota diversity or human health (Damian et al., 2019; Mihăileanu et al., 2018; Rogozan et al., 2016). Dispersion into the environmental factors needs to be evaluated in order to link the negative effects with the real sources of HMs. Pollutants tend to exceed the initial surface, considered to be polluted, due to their propagation from an environmental factor to another, thus generating a spread environmental impact (Bizo et al., 2015; Muntean et al., 2015).

The present study was conducted in the industrial area of Cluj-Napoca city (Cluj County, Romania), in the proximity of a contaminated site where, for decades, metal processing activities took place. Since the municipality plans

to redevelop this industrial part of the city in terms of a residential area with neighborhoods and playgrounds for the inhabitants, it is necessary to perform a study focused on the possibility of HMs spreading in the surrounding environment. Metal content and physico-chemical parameters were analyzed in soil, water and sediment samples, while organic matter (OM) and total organic carbon (TOC) was additionally analyzed for the soil samples. The sources of heavy metals were evaluated based on multivariate statistical analysis. Additionally, the contamination degree was assessed based on specific pollution indices.

MATERIALS AND METHODS

Study area, samples collection, processing and analyzing

The study area is located in Cluj-Napoca city (Romania), near a contaminated site situated on the eastern side of Someșul Mic River (figure 1). In the proximity of the site are Feroviarilor Park, Central Railway station of Cluj-Napoca and Nadăș River. The activity that generated the contaminated site was based on metal processing and has been in operation for decades (Annex no 8).

A total of nine water (A), sediment (B) and soil (C) samples were collected downstream (sampling point 1), in the proximity (point 2) and upstream (point 3) from the contaminated site, along the Nadăş River. Supplementary, a soil sample was collected from a park (point 4) located in the proximity of the contaminated site (figure 1).

The water was sampled in 250 ml sterile bottles, by immersion under the surface water, according to ISO 5667-3:2018 and ISO 5667-1:2006. Approximately 500 g of sediment samples were collected in sterile polyethylene bags, with a clean stainless steel hand auger. In the case of soil sampling, the surface vegetation was first removed and then 500 g of soil were collected from the surface (0 – 10 cm in depth) by a stainless steel hand auger and transferred to polyethylene bags, according to Order 184/1997. All the samples were transported to laboratory in cold (4ºC) and dark conditions.

The pH, redox potential (E_h), electrical conductivity (EC), total dissolved solids (TDS) and salinity of water samples were measured *in situ* by using a portable multiparameter (WTW Multi 350i, Germany). In the case of soil and sediment samples, these parameters were measured in the aqueous extract of soil/sediment (5:1 ratio), using the national protocol SR 7184-13/2001 (Ispas et al., 2020).

Fig. 1. *Study area with the sampling points*

In order to perform the heavy metals analyses on soil and sediments samples, the samples were previously air dried, grounded, sieved through a 250 μm sieve, mineralised with *aqua regia*, filtered and diluted with HNO_3 (0.5 M) to a final volume of 100 ml, according to ISO 11466:1995 protocol (Roba et al., 2015). The water samples were previously filtered and acidified to a pH of 2 with HNO_3 (63%). The analyses were performed by using an atomic absorption spectrometer (AAS, Analytik Jena ZEEnit 700, Germany) equipied with an air-acetylene flame and a graphite furnace.

The total organic carbon and organic matter was determined through Walkley and Black's (1934) method.

The grain-size analysis (sedimentation and sift method) was done according to national and international protocols (SR EN 14688-2: 2005; SR ISO 11465:1998).

Determination of pollution indices and multivariate data analysis

A variety of evaluation indices such as Geo-accumulation index (I_{geo}) (Muller, 1969), Contamination factor (CF) (Loska et al., 1997), Pollution load index (PLI) (Tomlinson et al., 1980) and Enrichment factor (EF) (Islam et al., 2018) were used to quantify the degree of metal contamination in both soil and sediment samples (table 1).

Table 1. *Pollution indices*

Indices formulae	Quality class
$$I_{geo} = log_2 \frac{C_n}{1.5 \cdot B_n}$$ C_n – concentration of metal n in soil or sediment; B_n – geochemical background; 1.5 – correction factor for background values	unpolluted ($I_{geo} \leq 0$); unpolluted to moderately polluted ($0 < I_{geo} < 1$); moderately polluted ($1 < I_{geo} < 2$); moderately to strongly polluted ($2 < I_{geo} < 3$); strongly polluted ($3 < I_{geo} < 4$); strongly to extremely polluted ($4 < I_{geo} < 5$); extremely polluted ($I_{geo} \geq 5$) (Muller, 1969)
$$CF = \frac{C_n}{B_n}$$ C_n – concentration of metal n in soil or sediment; B_n – geochemical background	low contamination factor (CF<1); moderate contamination factor ($1 \leq CF < 3$); considerable contamination factor ($3 \leq CF < 6$); very high contamination factor ($CF \geq 6$) (Loska et al., 1997)
$$PLI = (CF_1 \cdot CF_2 \cdot \ldots \cdot CF_n)^{1/n}$$ CF – contamination factor for metal n	unpolluted (PLI<1) and polluted (PLI>1) (Tomlinson et al., 1980)

Indices formulae	Quality class
$$EF = \frac{C_n/C_{Fe}}{B_n/B_{Fe}}$$ C – concentration of metal n and reference metal (Fe) in soil or sediment; B_n – geochemical background *for metal n* and reference metal (Fe)	deficiency to minimal enrichment (EF<2); moderate enrichment (2<EF<5); significant enrichment (5<EF<20); very high enrichment (20<EF<40); extremely high enrichment (EF>40) (Islam et al., 2018)

Multivariate data analysis – hierarchical clustering and principal component analysis (PCA) – was performed on all three types of samples to determine groups and the main elements of groups in order to identify the sources of provenance for the analyzed metals. The data analyses were performed using Past version 3.26b.

RESULTS AND DISCUSSION

Physico-chemical parameters

The soil and sediment samples proved to have a predominantly sandy texture (table 2), the highest value of sand being registered in sample B2 (75.18%) and the lowest in sample C2 (45.01%). Regarding the clay content, the highest value was identified in sample C2 (21.36%) and the lowest in sample B2 (7.61%). The presence of coarse particles may influence the heavy metals accumulation through sedimentation rather than their accumulation by adsorption processes.

Table 2. *Grain-size composition of sediment (B) and soil (C) samples*

Sample	Texture	Clay (%)	Silt (%)	Sand (%)	Gravel (%)
B1	Clayey sand	8.25	17.59	74.16	0
B2	Sand	7.61	3.75	75.18	13.47
B3	Clayey sand	15.99	11.35	72.66	0
C1	Clayey sand	11.77	13.53	58.99	15.72
C2	Sandy clay	21.36	20.05	45.01	13.58
C3	Clayey sand	15.60	18.95	65.23	0.20

The values of physico-chemical parameters for the investigated samples can be seen in table 3. All the samples exhibit a neutral to slightly alkaline pH. All the water samples had the pH within the limits (6.5 – 8.5) imposed by national legislation (Order 161/2006). Furthermore, a correlation can be observed between pH and Eh. The negative values indicate a reducing environment. The analyzed soils and sediments have a neutral to slightly alkaline pH, which does not favor the mobilization of heavy metals like in the case of a strong acidic pH (Frențiu et al., 2009).

Table 3. *The physico-chemical parameters of water (A), sediment (B) and soil (C) samples*

Parameters	A1	A2	A3	B1	B2	B3	C1	C2	C3	C4
pH	7.7	7.7	7.7	7.6	7.4	7.5	7.5	7.5	7.7	7.7
Eh (mV)	-61.0	-58.0	-61.7	-52.7	-44.9	-49.5	-51.3	-53.1	-63.0	-60.9
TDS (mg/l)	522	528	532	568	681	581	110	209	113	109
EC (µS/cm)	822	824	832	885	1210	903	171	328	176	169.8
Sal (‰)	0.3	0.3	0.3	0.4	0.4	0.4	0.0	0.0	0.0	0.0

The lowest values of TDS were identified in aqueous soil solution and the highest one in the aqueous sediment solution (table 3). It is important to mention that the soil and sediment samples collected near the contaminated site (B2 and C2) recorded higher values for TDS and EC, which may be correlated with the anthropogenic activities from the area. Salinity registered constant values for each investigated component (table 3).

Heavy metal content in water samples

The metal content in Nadăş River was correlated with the environmental regulations for surface water quality (Order 161/2006), in order to establish the ecological status of the water bodies (table 4). Based on Zn, Cu, Fe, Mn and Cd level, the analyzed samples belong to 1st water quality class (very good ecological status) (Order 161/2006). It was observed that the Zn and Cd concentrations decrease from upstream to downstream, while Cu concentrations increase from downstream to upstream. Since these differences are not significant, the presence of these heavy metals in water cannot be correlated with the proximity of the contaminated site.

Table 4. *Heavy metals concentration in water samples*

Heavy metal	Water sample (µg/l)			Quality class (Order 161/2006) (µg/l)				
	A1	**A2**	**A3**	**I**	**II**	**III**	**IV**	**V**
Zn	23	24	24	**100**	**200**	**500**	**1000**	**>1000**
Cu	19	18	15	**20**	**30**	**50**	**100**	**>100**
Pb	32	21	21	**5**	**10**	**25**	**50**	**>50**
Ni	28	28	30	**10**	**25**	**50**	**100**	**>100**
Fe	43	54	20	**300**	**500**	**1000**	**2000**	**>2000**
Mn	ND*	ND	ND	**50**	**100**	**300**	**1000**	**>1000**
Cd	ND	0.31	0.38	**0.5**	**1**	**2**	**5**	**>5**
Cr	45	9	18	**25**	**50**	**100**	**250**	**>250**

ND – not detected

The Pb concentrations from samples A2 and A3 correspond to 3rd water quality class (moderate ecological status), while the Pb level from A1 belongs to 4rd water quality class (low ecological status). The content of lead increases from upstream to downstream, so the contaminated site may have an impact on the river water quality. Considering the content of Ni and Cr, the sample A1 belongs to 2nd quality class (good ecological status). Since there is no upward trend for metal concentration, either downstream or upstream, the presence of Cr cannot be correlated with the anthropic activities from the contaminated site, but rather with different sources.

For better understanding of possible metal sources, multivariate hierrarchical clustering and principal component analysis was used. Based on statistical analysis, two clusters and two sub-clusters were differentiated (figure 2A). Cluster 1 grouped five elements (Pb, Cu, Ni, Zn, Fe), where Pb, Cu, Ni and Zn formed sub-cluster 1a, and Fe formed sub-cluster 1b. The arrangement from sub-cluster 1a indicates that Pb and Cu have a different source than Ni and Zn. The position of Fe in PCA, clearly separated by other elements may indicate a different source of provenance, probably a natural

one (figure 2). Cluster 2 grouped two elements (Cd and Mn), clearly separated from other metals. Considering that the presence of Cd is often associated with industrial activities, this may suggest another anthropogenic source for these two elements.
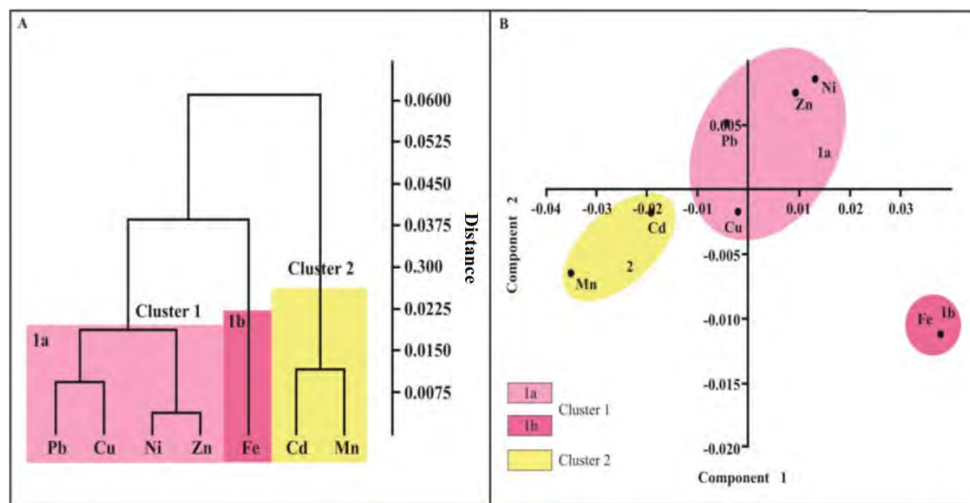
Fig. 2. *Distribution of the chemical elements on clusters (A) and principal component analysis (B) in water samples*

Principal Component Analysis revealed two main principal components (figure 2B). Principal component 1 (PC1) retains 89.24% of the variance and groups only the samples with positive values (> 0.70 correlation) for all the investigated elements. Principal component 2 (PC2) retains 8.87% of the variance and groups the elements with positive values (Ni) (>0.60 correlation), which was negatively correlated with all the other elements. In conclusion, based on statistical analysis a certain increase of concentration for Ni, Zn and Pb can be outlined, probably due to the anthropogenic activities in the investigated area.

Heavy metal contamination in sediment

The content of metals in the sediment from Nadăș River was evaluated according to national legislation (Order 161/2006) (table 5). Zn and Cr have

been identified in the accepted limits by the environmental legislation. Even though Fe and Mn indicate elevated concentrations, they cannot be assessed in terms of ecological status because there are no listed national limits for these metals in sediments (Order 161/2006). Their occurrence might be correlated with the natural background of the area, but other studies should be performed or confronted.

Table 5. *Heavy metals concentration in sediment samples*

Heavy metal	Sediment sample (mg/kg)			*Regulation limit (*Ord. 161/2006*) (mg/kg)*
	B1	B2	B3	
Zn	88	49	93	150
Cu	39	28	47	40
Pb	28	102	31	85
Ni	38	9	30	35
Fe	20452	10121	10554	-
Mn	334	212	494	-
Cd	2	1.47	1.88	0.8
Cr	48	17	37	100

Cadmium exceeds the maximum allowed limits in all the samples (table 5), recording the highest concentration downstream, while near the contaminated site was identified the lowest concentration. A downstream Cd accumulation can be supposed, but the source of contamination can be disputed because a descending trend from upstream is not observed in the analyzed samples. Lead was found with the highest concentration near the contaminated site (B2). Considering the sand texture of this sample (table 2), sedimentation followed by accumulation in the sediment layer is expected to be favored for heavy metals (Salomons and Stigliani, 1995). Thus, the contaminated site might represent the source of pollution with Pb in the area, this element being present in high concentration in the water sample too. Copper exceeded the limits in the upstream sample (B3), while the lowest concentration was identified near the contaminated site (B2). These results indicate that Cu might have another contamination source than the evaluated

site, considering that a lower content was registered downstream. Nickel exceeded the limit in the downstream sample (B1), but the lowest concentration was again near the contaminated site (B2). Comparing the sediment texture (table 2) with the heavy metals content it was observed that upstream and downstream samples are both containing a higher percentage of clay, thus might have led to higher metal adsorption rates.

Because it is hard to predict the source of contaminations, multivariate hierarchical clustering and PCA were used for a better understanding. The multivariate clustering analysis generated two main clusters and two sub-clusters (figure 3A). Cluster 1 comprises six elements (Pb, Zn, Ni, Cu, Cd, Mn) which are divided in sub-cluster 1a with five elements (Pb, Zn, Ni, Cu, Cd) and sub-cluster 1b with one element (Mn). Given this grouping, is considered that there exist two different sources for the analyzed metals, corresponding to each sub-cluster. Cluster 2 is also formed by a single element (Fe), located far from other metals, so it is believed to correspond to a third source of provenance, a natural one as in the case of water samples. Being known the close connection between water and sediment as environmental components is assumed that the presence of Pb, Zn, Ni, Cu, Cd and Mn can be correlated with anthropogenic sources.
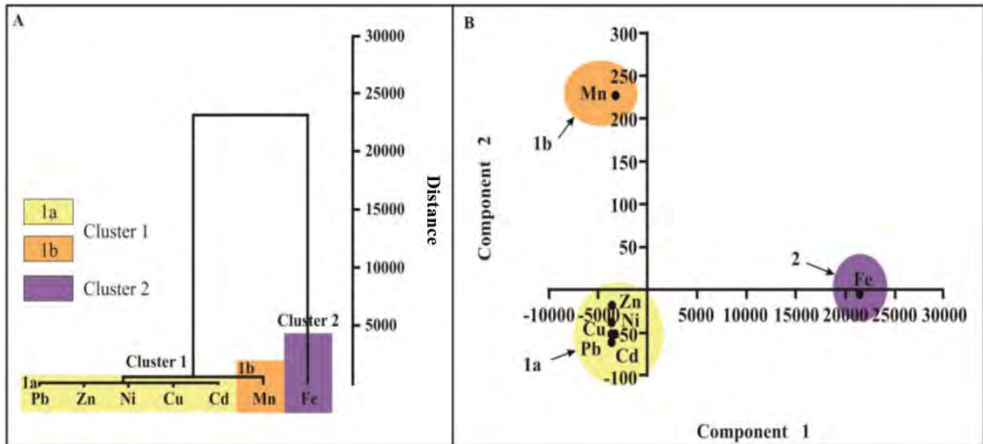

Fig. 3. *Distribution of the chemical elements on clusters (A) and principal component analysis (B) in sediment samples*

Principal component analysis (figure 3B) confirms the cluster division, with a clear differentiation of chemical elements. PC1 retains 99.98% of the variance and groups all the elements with positive values (>0.9 correlation), and PC2 retains only 0.01% of the variance, including only one element (Mn) with positive values (>0.020 correlation) which negatively correlates with all other elements. Thus, a certain increase in Mn content in sediments can be assigned to anthropogenic activities.

Heavy metal contamination in soil

The metal concentration in soil was correlated with the environmental thresholds set for less sensitive use of soil (table 6) because the investigated area is found in the proximity of a contaminated site. Mn and Cr concentrations were found under the normal threshold, so the surface of the investigated area was not contaminated with these metals. Fe indicated elevated concentrations, but compared with the control sample (C4), located approximately 1 km further, is noted that the highest concentration of Fe was in the control area.

Table 6. *Heavy metal concentration in soil samples*

Heavy metal	Soil samples (mg/kg)				*Pollution thresholds (mg/kg)		
	C1	**C2**	**C3**	**C4**	**Normal**	**Alert**	**Intervention**
Zn	131	127	59	118	100	700	1500
Cu	107	59	25	47	20	250	500
Pb	63	87	24	98	20	250	1000
Ni	29	23	25	19	20	200	500
Fe	20452	20230	10554	20844	-	-	-
Mn	537	444	340	503	900	2000	4000
Cd	1.96	1.97	1.63	1.59	1	5	10
Cr	29	28	23	22	30	300	600

According to Ord. 756/1997 approving the Regulation regarding the assessment of environmental pollution, for less sensitive uses of soil

Based on these results, is clear that Fe has a natural occurrence in the environment, as it was assumed for Fe content in sediments. The Fe contents in soil and sediment are comparable, so it can be assumed that Fe is present in the natural background. The low Fe concentrations in water samples strengthen this assumption, because the Fe fraction found in the background is not water soluble (Zimmerman and Weindorf, 2010).

The other analyzed metals, Zn, Cu, Pb, Ni and Cd, exceed only the normal thresholds for less sensitive use of soil in all samples, but this is already an indicator for contamination. Comparing with the thresholds for sensitive use, Pb would exceed the alert threshold (50 mg/kg) and would be very close to exceed even the intervention threshold (100 mg/kg). Is known that an area can be framed as potentially contaminated site when the alert thresholds are exceeded and becomes a contaminated site when the intervention thresholds are overpassed (HG 683/2015). Considering that in the surroundings of the contaminated site are living or working buildings of Cluj inhabitants, is difficult to establish a clear demarcation between less sensitive and sensitive use of soil. Therefore, special measurements should be considered regarding remediation of the area, starting with the decontamination of the investigated site, which can be considered the main source of metal dispersion. Another argument for this recommendation is given by the increased content of Zn, Cu, Pb, Ni and Cd also in the control sample (C4), exceeding the normal thresholds. The control sample was collected from Feroviarilor Park, an area considered to be unpolluted, and where redevelopment plans are being considered. Especially Pb is critically close to reach the intervention threshold (100 mg/kg) for sensitive type of soil. This might be an indicator that the contamination is more expanded than initially thought.

Statistical analysis differentiated two main clusters and two sub-clusters (figure 4A). Cluster 1 includes five elements (Pb, Cu, Zn, Cd, Ni) grouped as following: Pb+Cu+Zn and Cd+Ni. This distribution suggests distinct source for each group. Since Zn is mentioned as a pollutant in the contaminated site (Annex no. 8, PUG 2014), is assumed that Pb and Cu are generated from the same anthropogenic source. The elements order in soil was the same with the one in sediment samples. Cluster 2 clearly separated Fe and Mn in two sub-clusters, thus indicating different source of provenance. Sub-cluster 2a comprises Fe and was considered to have a natural source as previously discussed, while sub-cluster 2b is formed by Mn, its source being pointed out by the further discussed PCA.
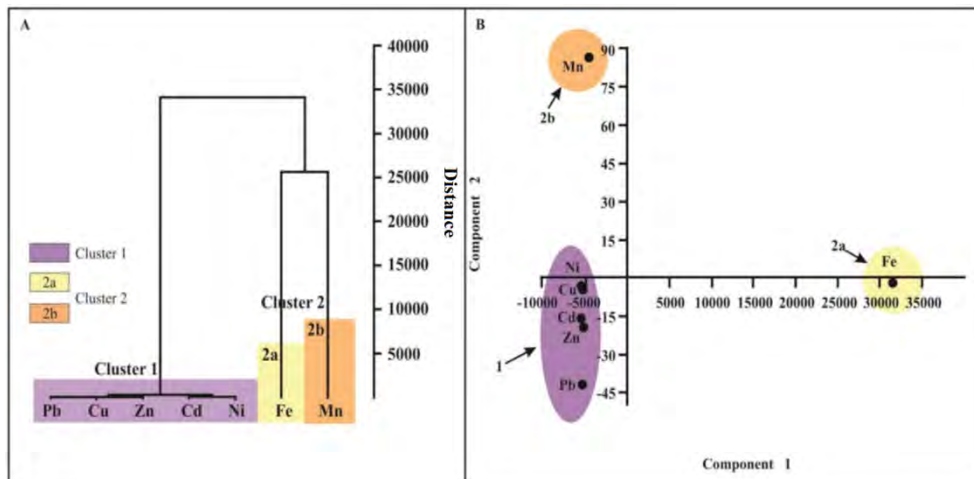
Fig. 4. *Distribution of the chemical elements on clusters (A) and principal component analysis (B) in soil samples*

Cluster separation is outlined by principal component analysis too (figure 4B). PC1 retained 99.99% of the variance and groups the elements with positive values (> 0.9 correlation). PC2 retained only 0.0009% of the variance and groups the positive values of Mn which negatively correlates with Pb. Thus, a certain increase in Mn can be assigned to anthropogenic activities.

Total organic carbon (TOC) and organic matter (OM) in soil

Heavy metals mobility in soil can be influenced by different factors, like the pH and total organic carbon (Walker et al., 2004; Zeng et al., 2011; Bian et al., 2014; Khan et al., 2014; Khadar et al., 2020; Zhong et al., 2020). Organic matter contains several active groups influencing the adsorption of heavy metals and preventing their desorption (Zhang et al., 2020). In the investigated area, TOC ranged from 0.18% (C3) to 0.95% (C1), recording lower concentrations than the soil from the park (C4) (1.73%) (figure 5). Similar variation was observed for OM, ranging between 0.5% (C3) and 2.8% (C1)

in the study area, compared to 5.1% in control sample (C4) (figure 5). The lower levels of TOC and OM, registered in the proximity of the contaminated site, comparing to the sample collected from the park, can indicate that the identified metal contamination generated a degradation of soil quality in the proximity of the contaminated site. The affinity of heavy metals to organic matter was lower for Zn, Ni, Cu and Cd, these metals being negatively correlated with soil organic carbon, and higher for Pb which is positively correlated with soil organic carbon. Other studies have reported that Cu and Pb were strongly retained in the soils with higher concentrations of organic matter or Fe/Mn oxides than Zn and Cd (Martínez and McBride, 1999).
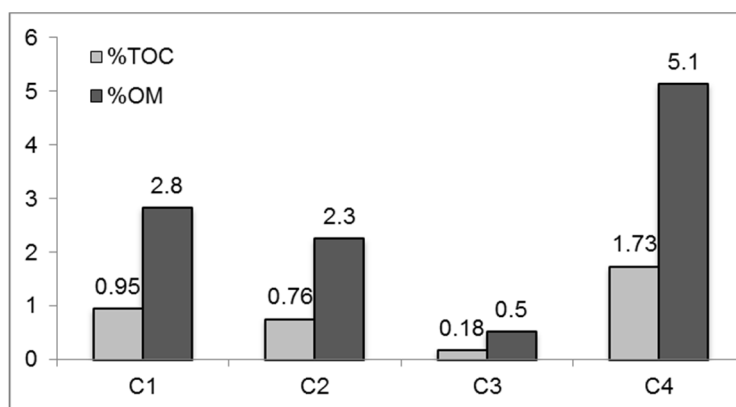
Fig. 5. *Total organic carbon (TOC) and organic matter (OM) content in soil samples*

Soil quality indicators

Based on the previous analyses, various levels of metal contamination with different sources of propagation were identified. For a better understanding upon the involved processes in metal occurrence in soil and sediment samples, several soil quality indicators were calculated.

Considering the values obtained for the geo-accumulation index (I_{geo}), Cd indicated an intense process of accumulation in soil (C1, C2) and sediment (B1) samples (figure 6), corresponding to an extremely high level of contamination (quality class 6). The sediment located near the contaminated site (B2) can be considered heavily contaminated with Cd (quality class 4).

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It is important to mention that the soil sampled from the park (C4) corresponds to a heavily to extremely contaminated soil with Cd (quality class 5). Except for Fe, which confirmed the assumption of natural occurrence related to background because no contamination can be assumed in this case (quality class 0), the content of Zn, Cu, Pb, Ni and Mn corresponds to unpolluted to moderately polluted soil and sediments (quality class 1).
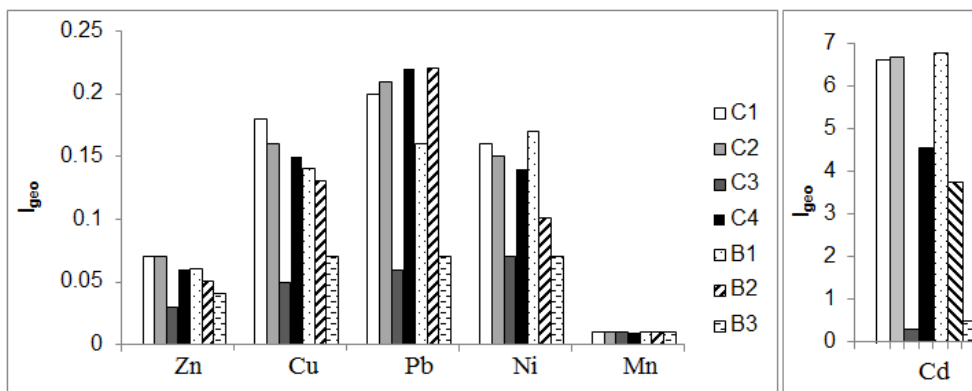
Fig. 6. *Geo-accumulation index for soil (C1 – C4) and sediments (B1 – B3)*

Another indicator used in the assessment was the contamination factor (CF). Based on the Cf values for Zn, Cu (excepting sample C1), Ni, Fe, Mn and Cr, the soil and sediments samples correspond to low and moderately contamination factor (figure 7). Samples C1, C2, C4 and B2, registered a considerable contamination factor for Pb. There is only one metal (Cd), which exhibits a very high contamination factor for all the investigated soil and sediments samples.

Pollution load index assesses the overall soil quality in regard to accumulation of several metals, not just one individual metal (Tomlinson et al., 1980). PLI ranged between 1.03 (B2) and 2.05 (C1), indicating the fact that the analyzed soil and sediments can be considerate polluted with heavy metals (especially with Cd). This is a consequence of the high values obtained for CF_Cd, this metal exceeding the normal threshold in soil and the maximum limit in sediments (Ord. 756/1997; Ord. 161/2006).
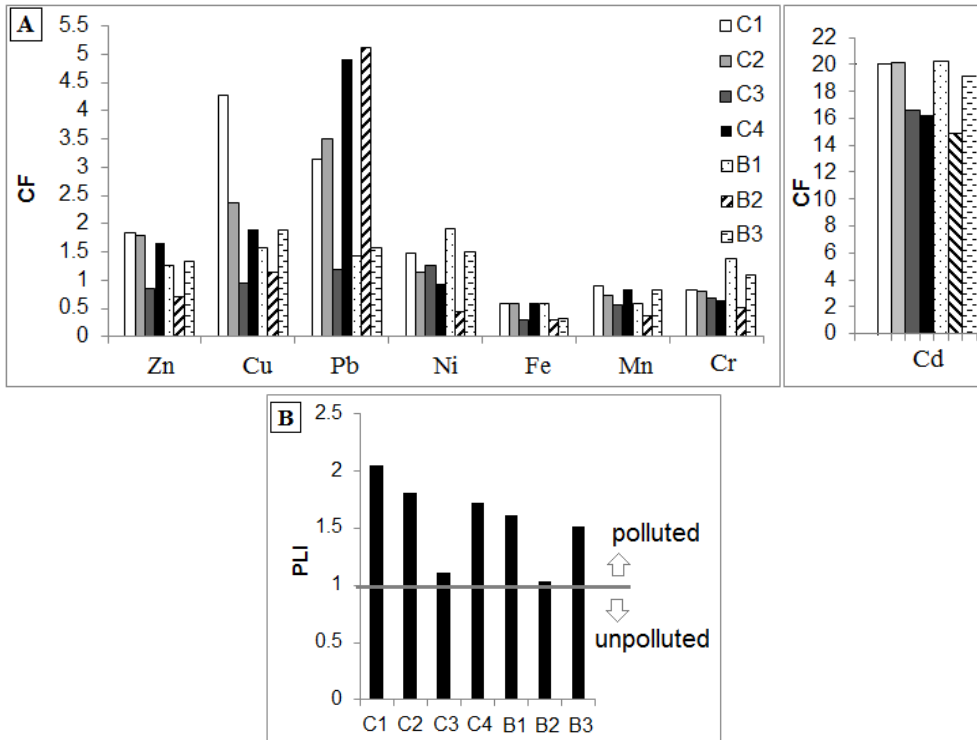
Fig. 7. *Contamination factor (A) and pollution load index (B) in soil (C1 – C4) and sediments (B1 – B3)*

The last indicator used in the assessment was the enrichment factor (EF), whose results are presented in figure 8. Cadmium indicated a very high (C1, C2, C4 and B1) and extremely high (C3, B2 and B3) enrichment, followed by Cu and Pb with a moderate to significant enrichment (figure 8). For Ni, Zn, Mn and Cr, the value of EF corresponded to deficiency to moderate enrichment. If the EF values are higher than 10, it is considered that those metals do not have a crustal sources, but they have an anthropogenic origin (Daskalakis and O'Connor 1995). In the present study the EF_Pb exceeded 10 value only in on sample, while EF_Cd exceeded this level in all the samples. Based on multivariate statistical analyses, not only Cd and Pb can have an anthropogenic source, but some other metals too.
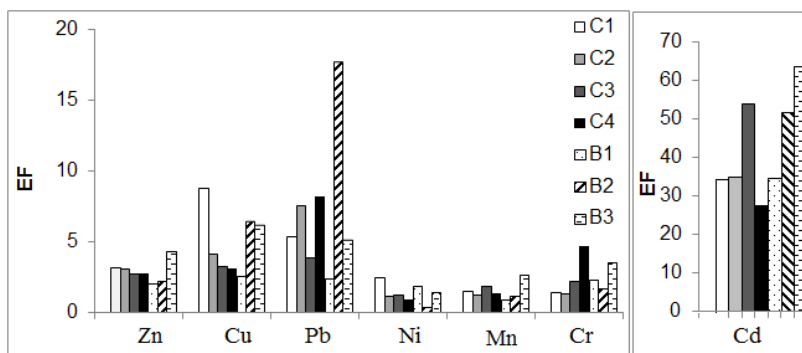
Fig. 8. *Enrichment factor in soil (C1 – C4) and sediments (B1 – B3)*

Cadmium content in sediments exceeded the limit imposed by national legislation, while in soil samples exceeded the normal value, being within the alert threshold. However, the values of the pollution indices indicated a significant contamination with cadmium in the investigated area. In literature, the reference values used for calculating the specific pollution indices may vary greatly. The indices are calculated based on the pre-industrial reference level, the average crust level, background level, or the average content of shale heavy metals (Yahaya et al., 2021). This may lead to a discrepancy in pollution assessment of highly toxic metals, like cadmium.

CONCLUSION

The principal component analysis confirmed the natural source for Fe, related to the abundance in parent material, while the other metals originated from anthropogenic sources. The data may suggest that the presence of Cd and Pb can be associated with the anthropic activities from the contaminated site, while the other metals may have other distinct sources.

Based on the calculated pollution indices, the present study could bring more arguments regarding the impact of the anthropogenic activities on the soil and sediment quality in the proximity of the contaminated site. The indices indicated a significant pollution with Cd and Pb, which may represent a risk if the area would become a residential one. In order to have more comprehensive understanding upon the studied contamination, a much more complex study should be performed in the area.

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RECOVERY OF WASTE LEATHER FROM TANNERIES AS AGGREGATE IN COMPOSITE MATERIALS

Gabriela-Emilia POPIȚA[1], Cristina ROȘU[1]*, Dorin MANCIULA[1], Ofelia CORBU[2], Antoanela POPOVICI[3]

[1] *Faculty of Environmental Science and Engineering, Babeș-Bolyai University, 30 Fântânele Street, 400294, Cluj-Napoca, Romania*
[2] *Central Laboratory of the Faculty of Civil Engineering, Technical University of Cluj-Napoca, 28 Memorandumului Street, 400114, Cluj-Napoca, Romania*
[3] *National Environmental Protection Agency, 294 Splaiul Independenţei Street, 060031, Bucharest, Romania*
* Corresponding author: cristina.rosu@ubbcluj.ro

ABSTRACT. This study proposes a recovery method for waste leather from tanneries, with high chromium content, by incorporating it into a composite material with cement matrix. The natural aggregates were substituted with CRT (cathode ray tubes) glass waste, with high lead content, originated from televisions and monitors dismantling. The material technological production flow was as follows: grinding skin (two types of skin: black and brown were used), mixing the ingredients after own recipes, pouring the mixture into molds, maturation, demoulding.

The new material obtained was submitted to leachability tests to determine, using AAS (Atomic Absorption Spectrometry), the total chromium and lead concentration released from the material. The results showed that Cr and Pb were well retained in the cement matrix. The low levels of total Cr and Pb concentration were recorded at pH = 9-10 and pH = 12, for the composite containing black leather waste and and at pH = 2-3 and pH = 12 for the composite containing brown leather waste. Mechanical tests were also provided to evidence the mechanical properties of the composite. The new composite material obtained may be considered as construction material and can be classified in mortars class because of the size of the used aggregate (CRT glass waste).

The objective of this study was to obtain a composite material that can be used as material for construction, in compliance with current standards in construction and environmental legislation.

The proposed method for leather waste recovery is viable and environmentally friendly and could bring economic benefits.

Key words*: leather, waste, CRT, composite, material.*

INTRODUCTION

The leather industry production and processing sector generates high quantities of tanned leather waste, whereby, an important amount reaches the municipal landfills.

The leather is an intermediate industrial product with numerous applications in various sectors. Globally are processed annually approximately 5.5 million tonnes of wet salted hides, of which are produced about 460,000 tons raw leather and 940 million square meters of finished leather.

It is worth to mentioning that in EU, in 2006 leather processing sector reached about 3,700 enterprises (Eurostat, 2009). These are small and medium-sized family tanneries. European tanners are dependent on raw material from outside the European continent. In recent years, this sector has a downward trend since the Asian and American market experienced a significant development.

Europe annually produces about 74,000 tons of raw leather and approximately 240 million square feet of finished leather. Leather processing generates large amounts of waste. Thus, after processing 1,000 kg of wet salted skin were obtained only about 200 kg of usable leather, remaining 800 kg of waste, such as: waste tanned leather (about 250 kg), waste leather untanned (350 kg) and wastewater (about 200 kg). The amount of required water is about 45-50 m^3 to 1,000 kg of processed leather. Also, the consumption of chemical reagents used for the tanning of 1,000 kg of wet salted skin is very high, an amount of about 400 kg of chemicals, such as: sodium chloride, lime, sodium sulfide, sulfuric acid, chromium sulfate, etc (BAT, 2013).

Because the factories produce various leather items, they produce significant amounts of wastewater and used chemicals (Famielec et al., 2011), and these mostly arrive at municipal landfills and are considered as hazardous waste (Regulation 301, 2014; Roşu et al., 2015). The quantity of such waste should be reduced because biodegradation is very slow and the emissions of chemicals into the environment are important.

Recovery of waste leather can be made by replacing the toxic chemical auxiliaries; find alternatives to chrome tanning; by recovery and recycling of solid waste (Kurian et al., 2009), but also is a goal of "clean technologies" because only 25% of raw skin is found in finished products (Ollé et al., 2013). Worldwide, about 70% of proteic waste are recovered, the rest being undertaken research to find solutions for use (Yilmaz et al., 2007). Waste from buffalo leather, 70% chromed is used mixed with soft leather and hard leather waste shredded to obtain artificial sole (Petrescu, 2011).

For fully and effective recovery of the solid waste from processing and manufacturing of leather, actions must be directed to: find new areas of recovery by processing; by physical-mechanical processing to obtain building materials or synthetic polymers mixtures for various uses; by physico-chemical processing in order to obtain chemical auxiliaries; incineration with heat recovery, which is a more efficient method in terms of environmental protection than landfilling them on the ground (Jing et al., 2011).

In leather industry, European Union practices the following waste recovery methods:

▪ Obtaining biofuel from waste from fleshing skins (pre-tanned). These wastes are mostly animal fats and meat pieces remaining on the skin. This process provides a washing stage, to remove dirt and blood, then a heating one to a temperature of 110°C, afterwards a filtration to remove the remaining pieces of meat. After these steps, the waste fat obtained is mixed with an acid and a catalyst to give the methyl ester (Alptekin et al., 2012; Onga et al., 2013).

▪ Biofuel production by pyrolysis in a fluidized bed reactor at a temperature between 450- 600°C, use the leather waste in post-tanning stage (finishing leather shavings, chips) (Yilmaz et al., 2007).

The purpose of this study was to obtain a composite material containing a mixture of leather waste with chromium content and CRT (catode ray tubes) glass waste (cone) with a high content of lead, as agregate, to replace the natural agregate and to provide an alternative for the disposal of this waste, which can be used as a construction material.

Also, one of the objectives was to study the metal (Cr and Pb) concentration from the leachate resulted by immersing the composite material in various solutions, simulating the behavior of this material in different environmental conditions.

About CRT (catode ray tubes) glass waste, various studies (Popovici et al, 2013[a]; Popovici et al, 2013[b]; Corbu et al., 2014; Corbu et al., 2015; Popovici et al., 2015[a]; Popovici et al., 2015[b]; Pop et al., 2016, Popița et al., 2016) have shown that this waste can be successfully used to replace natural aggregate in mortars used in construction.

MATERIAL AND METHOD

To achieve the study objective was used a recipe for the composit material based on clasical mortar recipe (cement matrix, water, aggregates) replacing natural aggregates (sand) with waste leather (two types: black and brown) and CRT glass waste.

For the preparation of the composite material was used white cement CEM_II_A-L_52.5N (used to obtain high-performance concretes) Portland Cement Composition (80 to 94%), additions - limestone (6 ÷ 20%), minor component (0 to 5%); initial setting time (≤ 5 min) (Lafarge, 2013).

In the beginning the leather was grinded. The grinding device IKA A11 basic can be used for different procedures: grinding of hard, brittle soft fibrous or non-elastic materials; with Mohs hardness of up to 6 (IKA).

The composite material was prepared by mixing: cement matrix, water, waste leather (14%) and CRT glass waste (14%). For this study were used to types of leather waste: black and brown.

For the chemical analysis were needed small samples and the homogenized material was poured into a mold 2 cm^3, allowed to cure three days and then peeled.

Chemical analysis

In a first stage the samples were immersed in different pH solution and ultrasonicated to activate the metal leaching; in the second stage the leachate was analyzed to detect chromium and lead that could migrate of the composite material structure.

The different pH solution was made with distilated water by adding HNO$_3$ and NaOH. The obtained solutions had pH=2-3, pH=5-6, pH=9-10 and pH=12. The ratio liquid/solid was chosen according to OM 95 (2005).

Afterwards, the samples were immersed and were ultrasonicated for 30 minutes at room temperature (20°C).

In figure 1 is presented the preparation for the ultrasonication and the ultrasonic bath (S 10 H Elmasonic) used.

Fig. 1. *Preparation for the ultrasonication and the ultrasonic bath S 10 H Elmasonic*

The ultrasonic bath (S 10 H Elmasonic) has dimensions of 190x85x60 mm and the capacity is 0.8 L. Operating frequency is 37 kHz and uses a propagation system of waves type sandwich. This model has more features: the heating function, the self-degassing and sonication autostart when the desired temperature is reached (Elmasonic).

After ultrasonication, the leachate was filtered and the pH was adjusted to a pH=2 to can analyze the leachate samples by absorption atomic spectrometry (ZEEnit 700 by Analytik Jena), used for metal analyses (flame method for concentration of mg/L, error ± 5%).

The obtain results were demonstrated that metals (Cr and Pb) concentrations in leachate was within acceptable limits or even lower.

Physical and mechanical tests

Designing and manufacturing the mortar mixtures were conducted to demonstrate the ability of the construction material, namely mortars, to integrate / embed successful hazardous waste type (leather with Cr content and CRT glass with Pb content) retaining its mechanical properties up to standard limits.

The used materials for manufacturing the samples for the mechanical tests were: cement, leather waste type: black, CRT waste glass (cone) and water of the drinking water source of the city.

It was performed the first blank recipe (M) / benchmark for mortar with gray cement CEM I 42.5 R Potland, according to SR EN 196-1 standard profile: 2006 Methods of testing cement. Part 1: Determination of mechanical resistance.

In the second blank recipe, (M_A) has replaced the Potland cement CEM I 42.5 R (gray) with a white cement type CEM II A-L 52.5N to highlight used waste in mixtures to their installation and subsequent finishing.

The third recipe (M_{AST}) was carried out by the complete replacement of river sand used in conventional / ordinary mixtures with glass with maximum diameter of 4 mm.

In the fourth recipe (M_{ASTPG}) the natural aggregate (sand) was replaced with CRT waste glass (94%) and grinding leather waste type black (6%).

It is worth to mention that compared with ultrasonic procedure where a higher percentage of waste leather was embedded to observe the metal migration from the composite material structure, for the mechanical tests was respected the aggregate proportion established by standards for building materials.

Technical characteristics of gray cement CEM I 42.5R are: Portland clinker (95 ÷ 100%) minor component (0 ÷ 5%) initial setting time (60 min), flexure strength at 2 days (minimum 20 N/mm^2); flexure strength at 28 days (42.5 < x ≥ 62.5 N/mm^2) (Holcim, 2013).

In figure 2 are presented the four recipes prepared for foundry casting.
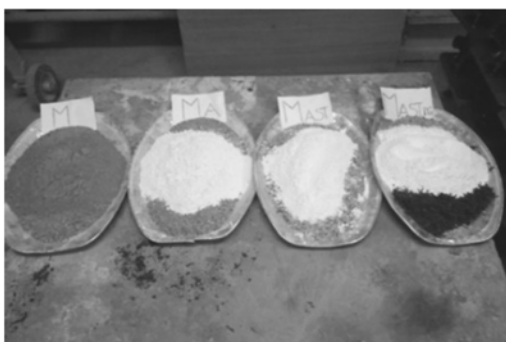

Fig. 2. *The four recipes prepared for foundry casting*

After completing the milling stages, weighing, and placing the material in tray, was passed to molding the composite. It was molded in standard moulds with the cross-section of 40 mm × 40 mm and a length of 160 mm, with stable walls by approximately 10 mm thick, were previously smeared with oil avoid joining fresh mass of the composite.

After mixing and pouring every composite and casting in moulds a vibrating table was used to push up to the surface of the material the air bubbles and water. The mixtures of the four composite molded into standardized moulds (40x40x160 mm) are presented in the figure 3.

Fig. 3. *Mixtures of the four composite molded into standardized moulds (40x40x160 mm)*

The samples were peeled after curing 24 hours, then weighed, labeled and immersed in water at room temperature until the age test (2, 7, 28 days). At dipping into the water basin the samples were placed on a rubber mat nicked so samples are separated and water can get free on the six faces.

The mechanical tests used for this study were: flexural strength test and compressive strength test. The equipments used for the mechanical tests, are hereunder described:

Flexural strenght test was made with a Technotest device. Before the flexural strength test the samples were weighed. The flexural load was applied vertically, with a 50 N/s until the material failed. Normally rupture should occur within a period of 30-90 seconds. Attempts were compliant to SR EN 196-1: 2006.

Compressive strength test was made also with a Technotest device. In the test device was placed in turn half an angle prism obtained from the flexural strength test. Following compression applied prism halves were broken into 2-3 pieces.

RESULTS AND DISCUSSION

Interpretation of the chemical analysis results

In Table 1 is shows the obtained results for total chromium and lead concentrations from leachate analysis (black waste leather) using AAS ZEEnit 700 Spectrometer by Analytik Jena, flame method (without atomic speciation).

Table 1. *The influence of pH on total Pb and Cr concentration for the composite with black and brown leather waste content*

Composite with leather	pH	Cr total (mg/kg) determinated	Cr * total (mg/kg) legislation	Pb total (mg/kg) determinated	Pb * total (mg/kg) legislation
Black	2 - 3	**0.53**		**2.12**	
	5 – 6	**0.31**	0.20	**1.89**	0.20
	9 - 10	**0.31**		*BDL*	
	12	**0.42**		0.06	
Brown	2 - 3	**0.39**		*BDL*	
	5 - 6	**0.92**	0.20	**4.83**	0.20
	9 - 10	**0.71**		**7.48**	
	12	**2.35**		*BDL*	

*MO 95/2005 – MAC – Maximum Allowed Concentration
*BDL - Below Detection Limit

From Table 1 the leachate of the black leather composite at a pH=2-3 and pH=5-6, the total Cr and Pb concentrations exceeded the MAC (maximum allowable concentration). At a pH=9-10, the total Cr concentration has an identical value to that obtained for a pH=5-6, so very close to MAC, however, the total Pb has concentration values below the detection limit. At pH=12, the total Cr concentration of 0.42 (mg/kg) exceeds two times the MAC, and the total Pb concentration value of 0.06 (mg/kg) is well below MAC.

The obtained results for the leachate of the composite material with brown leather waste content at pH=2-3, the total Cr concentration exceeds two times the MAC and total Pb is BDL. At pH=5-6 and pH=9-10 the total Cr and Pb concentrations values were significantly above MAC. At pH=12, the total Cr concentration exceeds 12 times the MAC, but total Pb concentration is BDL.

Interpretation of the physical-mechanical tests results

For all determination were made three samples (the moulds are designed for three samples), were weighted and the density and average density were calculated (table 2). Mechanical determinations: determination of flexural strength and determination of compressive strength.

Table 2. *Weight and density of samples after stripping*

Sample name 40x40x160mm	Sample number	Weight (g)	Density D=W/V (kg•m^{-3})	Average density (kg•m^{-3})
M-blank	1	577.9	2,257.42	
	2	581	2,269.53	**2,261.46**
	3	577.9	2,257.42	
M$_A$-blank with white cement	1	568.1	2,219.14	
	2	572.5	2,236.33	**2,223.18**
	3	566.8	2,214.06	
M$_{AST}$-CRT glass waste	1	628.4	2,454.69	
	2	624.5	2,439.45	**2,439.97**
	3	621	2,425.78	
M$_{ASTPG}$-Leather (type black) and CRT glass waste	1	560.9	2,191.02	
	2	574.6	2,244.53	**2,226.17**
	3	574.2	2,242.97	

Once samples have been peeled, each one was weighed separately. It was observed that higher weight had the M_{AST}-glass samples and the lowest the samples M_{ASTPG} + glass-leather.

After the test age (2, 7 and 28 days) the samples were weighted again (table 3), and it can be observed that again the higher weight had the M_{AS}-glass samples and the lowest the samples M_{ASP} + glass-leather.

The density (average) is higher than 1,300 kg•m^{-3} which mean that the samples overdraw the light mortars.

Table 3. *Weight and density of samples after age tests*

Sample name 40x40x160mm	Sample number	Age test (days)	Weight (g)
M-blank	1	2	**581.2**
	2	7	**598.2**
	3	28	**600**
M_A-blank with white cement	1	2	**575.2**
	2	7	**590.1**
	3	28	**598**
M_{AST}-CRT glass waste	1	2	**632.4**
	2	7	**640.5**
	3	28	**650**
M_{ASTPG}-Leather (type black) and CRT glass waste	1	2	**568.7**
	2	7	**592.7**
	3	28	**600**

Flexural strength interpretation results

Flexural strength tests were performed according to SR EN 196-1:2006, as follows: the prism is placed in the flexural strength device with the lateral side of the sample on the roll support and with the longitudinal axis perpendicular to the support. Vertical load applied by load roll on the opposite side of the prism and constantly increase the load with (50 + 10) [N/s] to failure. Half prism is maintained until their compressive strenght test.

Flexural strength, Rf, was calculated by the following formula (according to SR EN 1015-11 /2002):

$$Rf = \frac{1.5 \times Ff \times l}{d \times b^2}$$ [1]

where: Rf = flexural strength [MPa] or [N•mm^{-2}]; d = square section prism side [mm]; b = length of the sample [mm]; Ff = applied load in the middle prism at breaking [N]; l = distance between supporting rolls [mm].

Taking the samples M and M_A as blank and comparing them with standard limits, it can be said that samples containing CRT glass waste (M_{AST}) and glass + leather waste (M_{ASTPG}) have values close to the blank values. The sample M_{ASTPG} has the flexural strength values under the blank values, but closer.

According to SR EN 1996-3 Eurocode 6, the characteristic flexural strength values range between 0.2-2 [MPa, N·mm^{-2}].
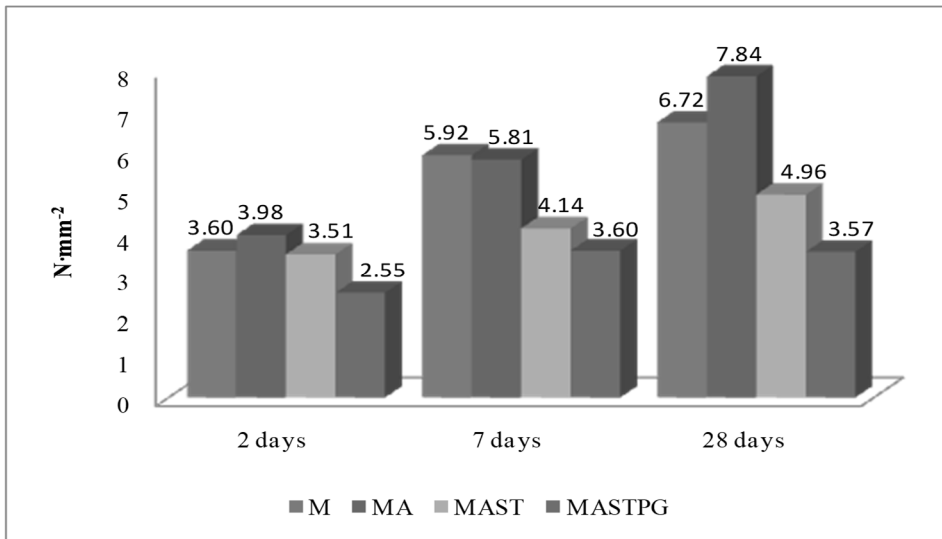

Fig. 4. *Flexural strength of the composite samples*

From figure 4 can observe that the obtained composite material had good mechanical properties above the flexural strength standard values.

Compressive strength interpretation results

Compressive strength tests were conducted according to SR EN 196-1: 2006. It was attempting prism halves from flexural strength to the lateral sides of the sample. It crosses every half prism side relative to the platters/ plates of the machine with accuracy $\pm$0.5 mm.

The compressive strength Rc was calculated with the formula 2 (according to SR EN 1015-11 /2002) as follows:

$$Rc = \frac{Fc}{1600} \qquad [2]$$

where: Rc = compressive strength [N•mm^{-2}]; Fc = maximum load when prism is breaking [N]; 1600 = platters area [mm^2].

As was observed and demonstrated by various researchers (Ling et al., 2011; Moncea et al., 2012), the compressive strength decreases with increasing the amount of waste CRT glass, the results were confirmed for samples (M_{AST}) containing CRT glass waste and for the samples (M_{ASTPG}) with glass + leather waste the compressive strength decreases two times comparative with M_{AST} results (figure 5).
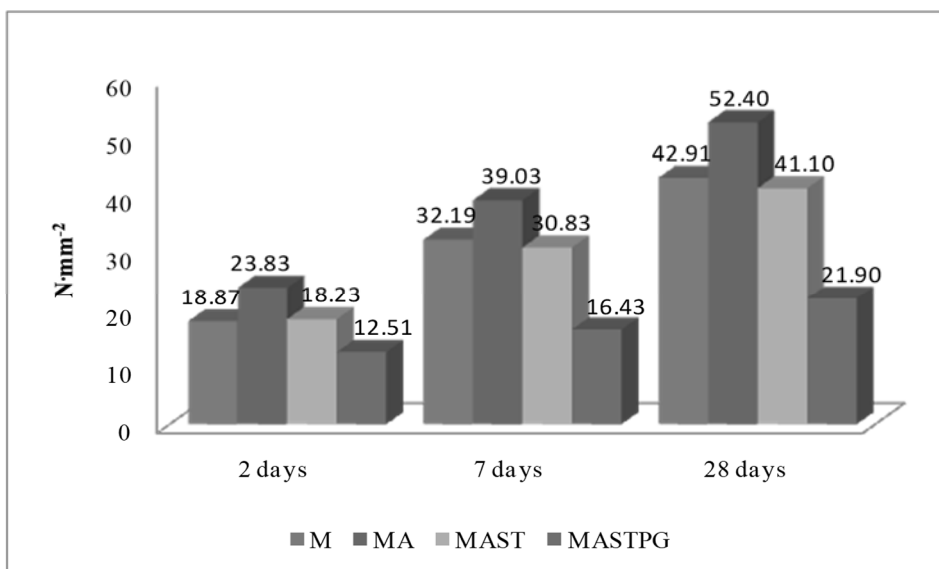

Fig. 5. *Compressive strength of the composite samples*

The obtained results for compressive strength were compared with the values from SR EN 998-1: 2011 for plastering mortars and shown in Table 4.

Table 4. *Comparison of the obtained results compressive strength with standard values for plastering mortars*

Mortar class	Compressive strength (28 days)	
	Standard values [N·mm^{-2}]	Experimental obtained values [N·mm^{-2}]
CS I	0.4-2.5	
CS II	1.5-5	21.9 - 52.04
CS III	3.5-7.5	
CS IV	≥ 6	

All obtained values exceed the compressive strength for plaster mortars, and the composite material may be classified in mortar class CS IV.

Also, the obtained results for compressive strength were compared with the values from SR EN 998-2:2011 for masonry mortars and presented in table 5.

Table 5. *Comparison of the obtained results compressive strength with standard values for masonry mortars*

Mortar class	Compressive strength (28 days)	
	Standard values [N·mm^{-2}]	Experimental obtained values [N·mm^{-2}]
M1	1	
M2,5	2.5	
M5	5	
M10	10	21.9 - 52.04
M15	15	
M20	20	
Md	d; d≥25	

The experimental obtained values offered the possibility of framing the composite obtained in class M20 and Md. The mortar containing waste glass and leather can fit in M20 class.

From the above tables we had obtained a material with good mechanical properties which can be proposed for use in building construction and can be used to produce of decorative elements, joints.

CONCLUSIONS

To propose practical applications for a composite material containing waste (CRT glass and leather) by replacing natural aggregate (sand) was studied the leachability mechanisms of total chromium and lead from material immersed solutions with different pH. From the obtained results can conclude that:

- low levels of total Cr concentration were recorded at pH = 9-10 and pH = 12 for the composite containing black leather waste and at pH = 2-3 for the composite containing brown leather waste.
- low levels of total Pb concentration were recorded at pH = 9-10 and pH = 12 for the composite containing black leather waste and at pH = 2-3 and pH = 12 for the composite containing brown leather waste.

The obtained values for the other pH concentrations exceed the MAC from legislation, but the values are not very high, further studies are needed to improve the recipe with other material to chelating the two metals.

After studying the mechanical behavior of the composite material can be made the following statements:

- new composite material obtained may be considered as construction material and can be classified in mortars class because of the size of the used aggregate (glass).
- the embedding of the leather waste together with CRT glass waste, was successful with good results for the flexural and compressive strength.

The composite may be used to produce of lightweight building elements, decorative objects, such as: embroidered decorative elements for facades, decorative elements for interior, decorative elements for parks and gardens.

Manufacture of a composite containing CRT glass and leather waste, can reduce the waste CRT glass and leather quantities, leading to solve an important environmental protection objective, namely reducing/eliminating landfilling of these types of waste.

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DETERMINATION OF PETROLEUM HYDROCARBONS CONTENT IN SOILS FROM SUPLACU DE BARCĂU, ROMANIA

**Loredana Mihaela ŞEUTE, Dan Florin COSTIN,
Carmen Andreea ROBA, Maria Lucia BIZĂU-CÂRSTEA***

*Babeş-Bolyai University, Faculty of Environmental Science and Engineering,
Fântânele 30, 400294 Cluj-Napoca, Romania
* Corresponding author: marialucia.bizau@ubbcluj.ro*

ABSTRACT. The level of pollution with petroleum compounds was evaluated in Suplacu de Barcău area based on the assessment of total petroleum hydrocarbons (TPH) concentrations in soil. As source of contamination, one active and another inactive petroleum extraction wells were chosen, and the concentrations were determined by fluorescence spectrometry. The results indicated alarming exceedances of the intervention thresholds, especially in the area where the activity is stopped, thus indicating long-term accumulation of pollutant and persistence in soil.

Key words: *petroleum hydrocarbons, soil pollution, TPH, fluorescence spectrometry*

INTRODUCTION

Soils polluted with petroleum hydrocarbons (PHCs) represent a serious concern for the environment due to various and multiple sources of contamination, such as extraction, refining, storage, transport, and petroleum marketing (Kaimi et al., 2007; Micle et al., 2018). PHCs represent a complex mixture of linear or branched alkanes, cycloalkanes, aromatic compounds, and other complex chemical compounds (e.g., asphaltenes), reason for which pollution with PHCs generates important imbalances in soil quality,

fertility, and biodiversity, therefore affecting the physico-chemical and biological components of the terrestrial ecosystems (Zhou et al., 2011). The main cause of pollution is represented by leaking and spilling of PHCs on the surface or in the underground soil, followed by long-term accumulation that, at the end of anthropogenic activity, exceeds the environmental regulations.

PHCs are characterized by a relatively high hydrophobicity, reason for which these pollutants have an increased ability to accumulate in soil compared to aquatic environments, where they bind to soil particles (Shirdam et al., 2008). In addition to low water solubility, PHCs feature high recalcitrant properties which lead to their persistence in soil (Khatibi and Hosseini, 2018). Therefore, the removal of PHC to perform soil decontamination might be difficult and expensive. Conventional soil remediation involves physical or chemical techniques (e.g., soil washing, solidification, stabilization, gaseous extraction, etc.) that have proven their efficiency, but involve high costs and high energy consumption (Kaimi et al., 2007; Jing et al., 2008). Another disadvantage of these conventional techniques is represented by the degradation of soil natural functions such as fertility, texture, and structure (Megharaj et al., 2011). Thus, phytoremediation is considered an alternative because the use of higher plants implies the use of energy from sunlight, maintains, and in some situations even improves, the natural functions of the soil, enhances the landscape of the contaminated area during the remediation process, and was indicated as a cost-effective technique (Banks et al., 2003; Glick, 2003; Shirdam et al., 2008).

Even though petroleum is not a renewable resource, it remains the main energy source in the world (Bastida et al., 2016), a reason for which soil contamination continues to spread, either at the surface, either in depth, thus becoming a critical environmental issue. This situation is present also in Romania, where petroleum is being exploited in different parts of the country. Suplacu de Barcău is one petroleum exploitation area, where active and inactive wells represent the source of contamination. Until today, a number of 2626 wells were drilled in the exploitation area (Ionescu et al., 2019). Geological data indicates that Suplacu de Barcău is the largest oil field in the Romanian sector of Pannonian Basin, with approximately 144 million barrels of recoverable oil (Dolton, 2006). The oil exploitation in Suplacu de Barcău area has started in 1961 with dissolved gas drive mechanism applied to monocline geological structure, starting from the uppermost part of reservoir (Asghari, 2009). Due to the very low recovery value, enhanced

oil recovery methods were applied since 1964. To increase the production rate, a thermal method (*in situ* combustion) was considered appropriate to extract the high viscosity oil from Suplacu de Bracău heavy oil reservoir (Carcoana, 1990). The oil extraction operations carried out over 60 years have led to a significant environmental impact. The main cause of soil pollution around the exploitation wells is represented by the oil spilling due to the improper maintenance, especially at the old wells, currently closed and decommissioned.

The aim of this investigation is to contribute to the environmental evaluation of the Suplacu de Barcău area considering contamination with PHCs. Soil samples were collected from the proximity of active and inactive wells used for petroleum extraction. Total petroleum hydrocarbons (TPHs) concentrations were determined to appreciate the level of pollution and how the soil quality was affected by their presence.

MATERIALS AND METHODS

Suplacu de Barcău is located in the north-western part of Romania, in Bihor (BH) County (figure 1). The study area was chosen in the petroleum exploitation area, found in the western part of the Suplacu de Barcău village. Agricultural fields are present in the proximity of the study area.

The environmental evaluation was based on 4 soil samples collected nearby the exploitation wells (figure. 1), from a depth between 10 and 15 cm, after the surface vegetation was removed. To compare the possible sources of contamination, two soil samples (P1 and P2) were taken nearby two active exploitation wells, and other two samples (P3 and P4) were taken from the proximity of two inactive exploitation wells. As reference, another soil sample (R) was collected from the shore of the accumulation lake from the area, located in the southern part of the village and considered to be unpolluted. Approximately 500 g of soil were collected from each sampling point with the use of a stainless steel hand auger, transferred to polyethylene bags, and transported at a constant temperature of 4 °C and in the absence of light.

The collected soil samples were dried at room temperature (approx. 20 °C, open air), homogenized, grounded and sieved to collect the fraction below 2 mm. A mass of 5 g of processed soil was transferred to glass tube, followed by the addition of 2 g of anhydrous sodium sulphate and 20 ml of

n-hexane. The mixture was vigorously shaken for 5 minutes, then the solvent was allowed to separate for 5 minutes and the vials were depressurized.
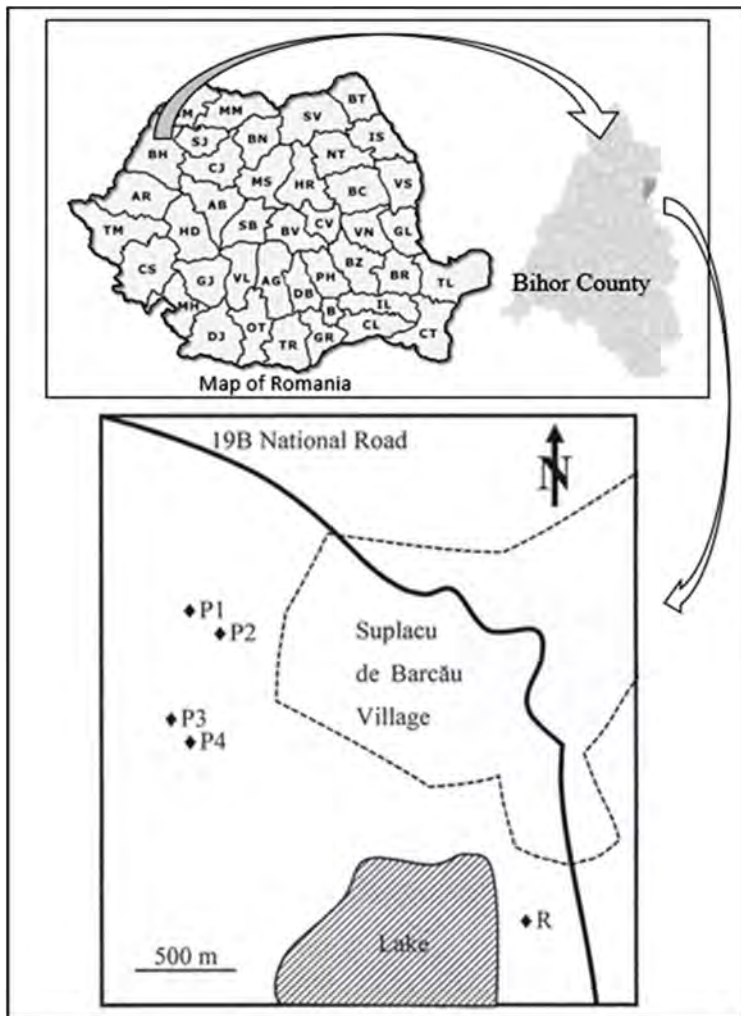

Fig. 1. *Localization of Suplacu de Barcău and field sampling points in the study area*

The organic fraction was separately collected and filtered through 0.20 μm pore size membrane filters before analysis (Brost et al., 2011), (www.oilinwatermonitors.com).

The TPHs concentration from the extracts was determined by fluorescence spectrometry using a Turner TD-500 fluorometer.

RESULTS AND DISCUSSION

The TPHs concentrations are presented in figure 2. The results indicated a high pollution with PHCs in the study area considering the environmental limits set for both sensitive and less sensitive uses of the soil.
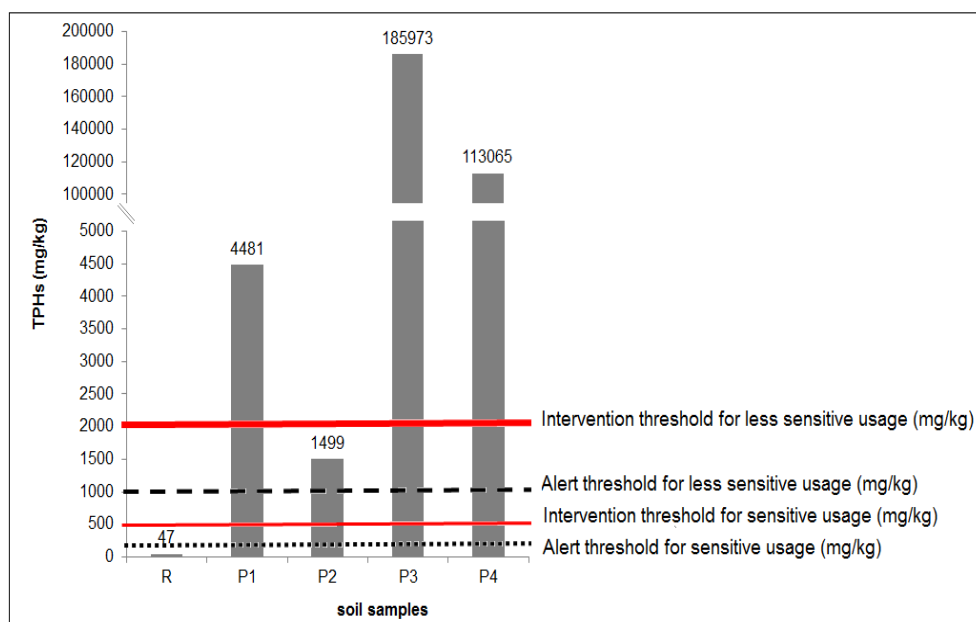

Fig. 2. *TPHs concentration in soil samples from the study and reference area, and the legislative threshold (Order 756/1997)*

Samples P1 and P2 were collected nearby two active wells. To assess the possible influence of PHCs in soil, the two sampling points were chosen considering the presence or absence of vegetation close to the extraction wells. P1 was characterized by a lack of vegetation within a radius of 1-2 meters from the extraction well, while P2 featured dried vegetation.

Correlating with the TPHs concentration (figure 2), where P1 is 3 times higher than P2, it can be assumed that the increased level of pollution is severely affecting the vegetation in the proximity of the well. While P1 was collected near the extraction well and directly under the petroleum transport pipe, P2 was established at a distance of 5 meters from the well. Based on the TPHs results, it can be assumed that the level of pollution at the surface of the soil decreases with the increase of distance from the source, but still exceeds the intervention threshold for sensitive usage (500 mg/kg), and exceeds the alert threshold for less sensitive usage (1000 mg/kg). For both situations, the environmental impact is significant and remediation processes should be implemented in the area.

To compare the sources of pollution, samples P3 and P4 were collected from the proximity of two inactive wells. Even though vegetation was present and appeared more abundant compared to the areas with active wells, most parts of it presented features of dried vegetation. It is important to highlight that the level of TPHs is 90 times higher than the intervention threshold for less sensitive soils (2000 mg/kg) in sample P3 and 56 times higher in sample P4, a reason for which remediation strategies are urgently demanded in the area. This high pollution might be a consequence of continuous and long-term contamination with PHCs caused by uncontrolled spills of petroleum. In some areas, the soil presented black spots at the surface, a feature that might be considered as evidence for the assumed spills. Even though the soil is covered by a layer of vegetation that might indicate the ability of native flora to develop, it is important to specify that only spontaneous vegetation, represented mainly by grass species, is present. Considering the long-term pollution, is known that resistant plants can develop adaptation strategies to specific pollutants, thus the present grass species might imply detoxification or tolerance mechanisms to PHCs.

Contamination problems with PHCs in the Suplacu de Barcău area have been indicated only in few studies, even though the assumptions upon environmental problems are well known at least at national level. Puia et al. (2016) assessed the level of TPHs in 4 sampling points within the oil exploitation area and revealed concentrations between 8850 – 46600 mg/kg. These concentrations also exceed the national thresholds (2000 mg/kg) and indicate different levels of contamination that can be influenced by typical sources of pollutant propagation found in a petroleum activity. These variations have been observed also by Costin et al. (2017) on soil samples

collected nearby other two exploitation wells (one active and another inactive). Close to the active well the TPHs concentration ranged between 347 – 5092 mg/kg, while in the proximity of the inactive well the TPH concentration increased, ranging between 24105 – 610801 mg/kg. Costin et al. (2017) identified exceedances of the legal thresholds also in the proximity of the air compression station located within the exploitation site, where TPHs concentrations ranged between 5135 – 12460 mg/kg.

Considering the observed variations of soil pollution, is assumed that the areas with inactive wells feature a higher pollution than the areas with an ongoing activity, as the case of active wells. Besides multiple factors that could be responsible for this variation, time and hydrophobicity of PHCs are the major ones. PHCs contamination has increase throughout the period of activity due to the availability of the source of pollution. During this time, PHCs will accumulate in soil because they cannot be dissolved by the atmospheric precipitations (Shirdam et al., 2008). Even though the source of propagation is stopped, the PHCs will remain present in soil due to recalcitrant properties which lead to their persistence in soil (Khatibi and Hosseini, 2018). Thus, the longer the period, the higher the contamination will be.

CONCLUSION

Contamination with TPHs has led to a high level of pollution in the Suplacu de Barcău exploitation area. Considering the alarming exceedances of the national thresholds for TPHs, the investigated area can be framed as contaminated site. Following the environmental protection regulations, the whole area should be subjected to remediation until the levels of pollution would decrease beneath the alert threshold. In order to apply a proper remediation technology, more studies should be performed to gain better knowledge on the spread of pollution at surface and in depth of the soil, and to characterize the reaction of PHCs with the soil matrix of the area.

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