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Cover 1: *Taxodium distichium* with *Tillandsia usneoides* (moss).
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DESCRIPTION AND COMPARISON OF AEROSOL PROPERTIES OVER CLUJ-NAPOCA - ROMANIA AND KOFORIDUA – GHANA, USING AERONET NETWORK DATA

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ABSTRACT. This article presents a description and a comparative study of the optical and microphysical properties of aerosols measured above Cluj-Napoca city in Romania and above Koforidua city in Ghana. Atmospheric aerosols have a major impact on climate and our health. We analyzed the Aerosol Optical Thickness at 440 nm (AOT), the Ångström parameter (α 440 – 870 nm), the fine and coarse volume concentrations and the single scattering albedo, in order to describe the aerosol properties at these 2 stations. We used daily averages which are calculated for every day when the available number of measurements is higher than 3. At CLUJ_UBB station, the Aerosol Optical Thickness at 440 nm wavelength has values between 0.031 and 0.699, with an average of 0.229 ± 0.11. At Koforidua_ANUC station, the AOT440 has values between 0.106 and 2.580, with an average of 0.742 ± 0.50, much higher than the values measured at CLUJ_UBB. The aerosol at the two locations has different properties, at Cluj-Napoca the urban industrial type is predominant while at Koforidua the predominant type is mineral dust.

Key words: *aerosol, sun-photometer, AERONET network*.

INTRODUCTION

An aerosol is defined as a set of liquid or solid particles suspended in a gaseous medium. In the atmosphere, these particles are mainly located in the troposphere. Desert dust carried by wind or soot resulted from biomass fires are examples of atmospheric aerosols (Seinfeld et al., 2006). These aerosols can be of natural or anthropogenic origin (aerosols resulting from human activities) and have different sources depending on geographical location, weather and environmental conditions (Boucher et al., 2013). The aerosols are classified into several categories: terrigenous aerosols or dust from deserts or bare ground, oceanic or spray aerosols from maritime areas, soluble aerosols like sulphates and nitrates, very common in urban environments, biomass fires and house fires, industrial emissions, traffic and volcanic aerosols (Ramanathan et al, 2001; Ştefănie et al., 2015).

Aerosols have a major impact on climate and human health. Due to their small size, they have a negative effect on human health that can be associated with a significant mortality rate. Health effects are mostly associated with small particles in the fine or accumulation mode. The inhalation of these fine particles, results in different diseases such as different allergies, asthma and lung cancer (Pope et al., 2002). In the environmental field, aerosols affect the climate in a variety of ways: directly by diffusion or radiation absorption, and indirectly by acting as condensation nuclei for cloud formation or altering optical properties and clouds life (Boucher et al., 2013).

In this study, we analyze and compare the optical and microphysical properties of aerosols derived by means of passive remote sensing, using the Aerosol Robotic Network – AERONET column integrated data measured with sun photometers at two stations: Cluj-Napoca (Romania) in South-Eastern Europe and Koforidua (Ghana) along the Gulf of Guinea and Atlantic Ocean in Western Africa.

The AERONET global network provides information regarding the aerosol optical and microphysical properties and precipitable water content using solar-powered CIMEL Electronique 318 A (figure 1) spectral radiometers that measure Sun and sky radiances at a number of fixed wavelengths within the visible and near infrared spectrum (Holben et al., 1998). Data collected at the stations are automatically transferred to the AERONET processing

system through the internet. Afterwards, the data are processed with inversion algorithms and then made available to users in near real time: level 1 data – unscreened and level 1.5 – automatically cloud screened. The level 2 data – cloud screened and quality assured are available only after the calibration of the instrument at a calibration center. CLUJ_UBB AREONET station is located at the Faculty of Environmental Science and Engineering in Cluj-Napoca city (Lat.: 46.76833° Long: 23.55139° E.; elevation: 405 m), Romania (Ajtai et al., 2013) and Koforidua _ANUC AERONET station at the All Nations University College in Koforidua City (Lat :6.109° N, Lon :0.302° W, 205 m), Ghana.

Fig. 1. CLUJ_UBB site AERONET sun-photometer

Over Romania, the most common aerosol type is the urban industrial. Nevertheless, very often, long range transport of aerosol may occur. Mineral dust from Sahara is transported with the south western winds, especially during the spring (Ştefănie et al., 2015). Also, biomass burning aerosol from Balkan Peninsula and Eastern Europe occur frequently during the summer months. The biomass burning aerosol may have also a local origin. Volcanic ash may be present in the atmosphere after large volcanic eruptions in Sicily or Iceland (Ajtai et al., 2010).

In South Western Africa, in the Gulf of Guinea countries – Ghana, Togo, Benin there is an important presence of aerosol especially mineral dust from Sahara, marine aerosol, smoke from biomass fires and urban industrial aerosol generated in the big cities like Accra, Lomé and Porto-Novo. However, the natural sources of aerosol have an important contribution, as the two winds that blow across the entire region. First, the Harmattan wind, from December to March, which blows from the Saharan Desert to the South, brings large amounts of mineral dust. Also, it can transport aerosol resulting from biomass fires in the African savannah. Second, the monsoon system of periodic winds from the tropical regions that blows from South to the North from July to September. Regarding the precipitations, we have two rainy seasons: the big season from April to June, and a small rainy season between September and October, and two dry seasons: the big dry season due to the Harmattan and the small dry season due to the monsoon.

METHOD AND PARAMETERS

The two stations which provided data for our study are located in different regions: South Eastern Europe – Romania and in Western Africa - Ghana, the stations having different geographical and meteorological conditions.

We compared the available measurements – daily averages - from January 2016 to December 2018. For CLUJ_UBB station, level 2 data were available for the entire period except the month of December 2018, when we used level 1.5 data. For Koforidua_ANUC station, level 2 data were available until April 2018, for the remaining period level 1.5 data being used. We should underline that sky-radiance measurements in general introduce sampling bias, because cloudy days are underrepresented in the database.

The AERONET network provides two types of data: direct Sun spectral data based on the extinction of light through the atmosphere and inversion data derived from the angular distribution of the sky radiance. In this study we analyzed the main two parameters derived from direct Sun measurements: the AOT - Aerosol Optical Thickness and the Ångström parameter α.

The Aerosol Optical Thickness or optical depth is defined as the integrated extinction coefficient over a vertical column of unit cross section. The AOT is the degree to which aerosols prevent the transmission of light.

The Ångström parameter describes the dependency of the aerosol optical thickness on wavelength. The first derivative of AOT with wavelength in a logarithmic scale is known as the Ångström parameter (Holben et al., 1998).

Regarding the inversion products, the AERONET network provides aerosol properties such as size distribution, the real and imaginary part of refractive index, spectral single scattering albedo, phase function, asymmetry factor and others. These properties are retrieved from sky spectral radiance and polarization measurements by inverse procedures (Dubovik and King, 2000). In our study we analyzed the fine and coarse volume concentrations (Cvf and Cvc) and the single scattering albedo (Kaufman et al., 1994).

The fine and coarse volume concentrations ($\mu m^3/\mu m^2$) are retrieved within the size range of 0.05 μm ≤ r ≤ 15 μm. Fine and coarse mode separation is obtained using the inversion code which finds the minimum within the size interval from 0.439 to 0.992 μm. The single scattering albedo, SSA(λ), is represented by the ratio of scattering efficiency to total extinction efficiency at wavelengths corresponding to the sky radiance measurements (Holben et al., 2001).

RESULTS AND DISCUSSIONS

The measurements from the 2 stations included in our study are analyzed and compared. We used daily averages which are calculated for every day when the available number of measurements is higher than 3.

In table 1 we present the monthly available number of days with measurements at each station. There are more measurements performed in the months with clear sky conditions. At CLUJ_UBB station in Romania we have a high number of measurements from April to September, except the month of July. The lack of data for this month is due to calibration of the instrument performed in 2017, when no data where available. At Koforidua_ ANUC station the numbers of days with measurements are more frequent from January to April and from September to December.

Table 1. Available number of days for each month of the year

Station/Month	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Total
CLUJ_UBB	28	28	38	57	75	51	31	59	49	41	36	30	523
Koforidua_ANUC	76	55	70	52	39	37	38	23	51	43	48	51	583

Aerosol Optical Thickness – AOT_{440}

At CLUJ_UBB station, the Aerosol Optical Thickness at 440 nm wavelength has values between 0.031 and 0.699, with an average of 0.229 ± 0.11. The error of the mean value is the standard deviation used in order to highlight the spread of the values. The daily values are characterized by significant variation, but the yearly average is in good agreement with other urban industrial sites – Paris, France: 0.26, Greenbelt, USA – 0.24 (Dubovik et al., 2002).

At Koforidua_ANUC station, the AOT_{440} has values between 0.106 and 2.580, with an average of 0.742 ± 0.50, much higher than the values measured at CLUJ_UBB. The monthly minimum, maximum and average values for the two stations are presented in table 2 (CLUJ_UBB) and table 3 (Koforidua_ANUC).

As seen in Figure 2, at CLUJ_UBB station, the monthly AOT_{440} has the highest values during the summer months – July and August, mainly due to the low level of precipitation.

Table 2. Monthly AOT_{440} averages measured at CLUJ_UBB station

Station/ Month		I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
CLUJ_UBB	Min	0.06	0.03	0.07	0.05	0.07	0.06	0.11	0.06	0.06	0.05	0.04	0.04
	Avg	0.20	0.19	0.25	0.21	0.22	0.25	0.26	0.29	0.22	0.19	0.18	0.47
	Max	0.59	0.55	0.57	0.40	0.51	0.50	0.63	0.63	0.69	0.63	0.44	0.17

Table 3. Monthly AOT_{440} averages measured at Koforidua_ANUC station

Station/ Month		I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
Koforidua_ANUC	Min	0.85	0.34	0.10	0.24	0.11	0.10	0.21	0.29	0.10	0.16	0.24	0.48
	Avg	1.4	1.33	0.61	0.54	0.35	0.36	0.51	0.68	0.34	0.44	0.55	1.08
	Max	2.58	2.46	1.45	1.40	0.6	0.79	1.29	1.64	0.66	0.93	0.82	2.59

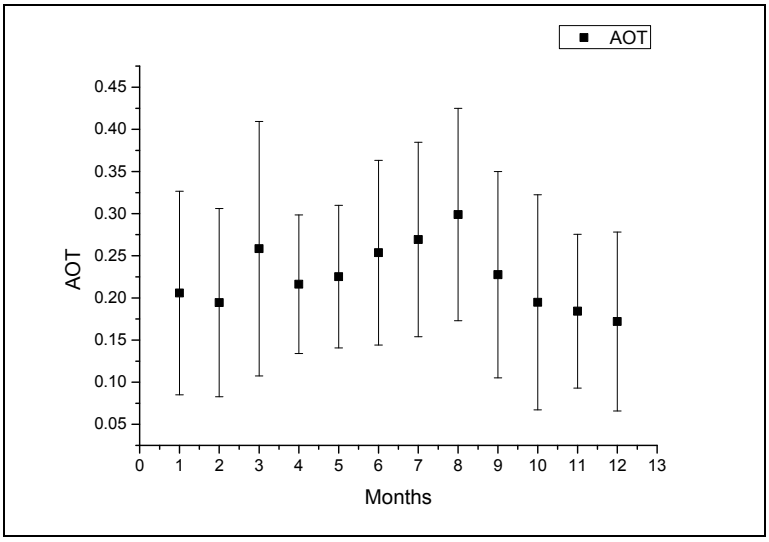

Fig. 2. Monthly AOT_{440} at CLUJ_UBB station

At Koforidua_ANUC (figure 3), the monthly AOT_{440} has the highest values from December to February during the Harmattan winds which bring high amounts of mineral dust from Sahara and also biomass burning aerosol from the savannah.

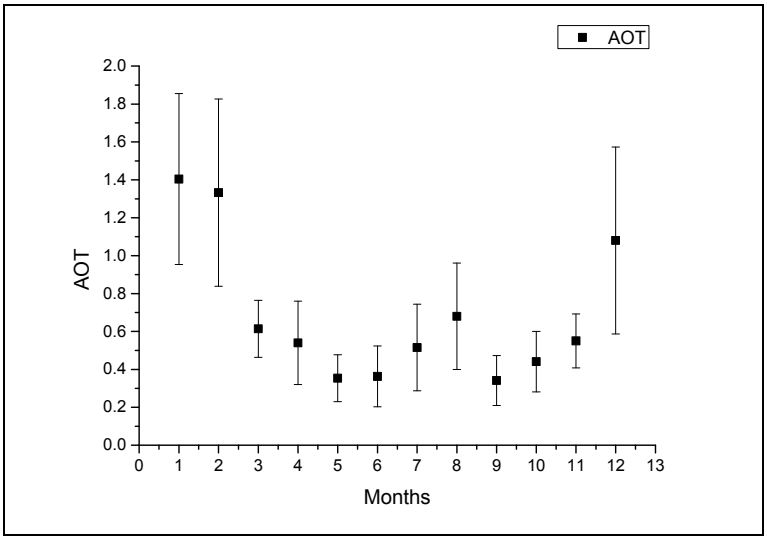

Fig. 3. Monthly AOT_{440} at Koforidua_ANUC station

Ångström parameter – α 440 – 870

The Ångström parameter is a good indicator of aerosol particles size. The large values indicate the presence of fine mode particles like urban industrial and biomass burning aerosols, whereas small values are associated with coarse particles like desert dust and marine aerosols.

At CLUJ_UBB station, the Ångström parameter has values between 0.27 and 2.00, with an average value of 1.48 ± 0.32. The small values are usually due to Saharan dust intrusions, while the high values are due to the presence of fine mode particles like biomass burning and urban – industrial aerosol.

At Koforidua_ANUC station, the Ångström parameter has values between 0.12 and 1.93, with an average value of 0.77 ± 0.36. The values are smaller than those measured at CLUJ_UBB station, due to the continuous presence of coarse mode aerosol particles like mineral dust and marine aerosols.

The monthly minimum, maximum and average values of the Ångström parameter at the two stations are presented in table 4 and table 5.

Table 4. Monthly α 440 - 870 averages measured at CLUJ_UBB station

Station/ Month		**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**	**X**	**XI**	**XII**
CLUJ_UBB	Min	1.06	0.31	0.95	0.27	0.53	0.28	1.40	1.12	1.09	0.85	0.70	1.13
	Avg	1.55	1.31	1.46	1.22	1.41	1.38	1.69	1.75	1.63	1.51	1.38	1.52
	Max	1.88	1.91	1.85	1.86	1.83	1.96	1.97	2.00	1.90	1.80	1.79	1.89

Table 5. Monthly α 440 - 870 averages measured at Koforidua_ANUC station

Station/ Month		**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**	**X**	**XI**	**XII**
Koforidua_ANUC	Min	0.29	0.29	0.14	0.12	0.16	0.17	0.27	1.14	0.19	0.30	0.24	0.22
	Avg	0.86	0.61	0.64	0.41	0.48	0.82	1.15	1.33	0.97	0.74	0.55	0.96
	Max	1.56	0.96	1.14	0.86	1.03	1.41	1.51	1.71	1.62	1.28	0.82	1.93

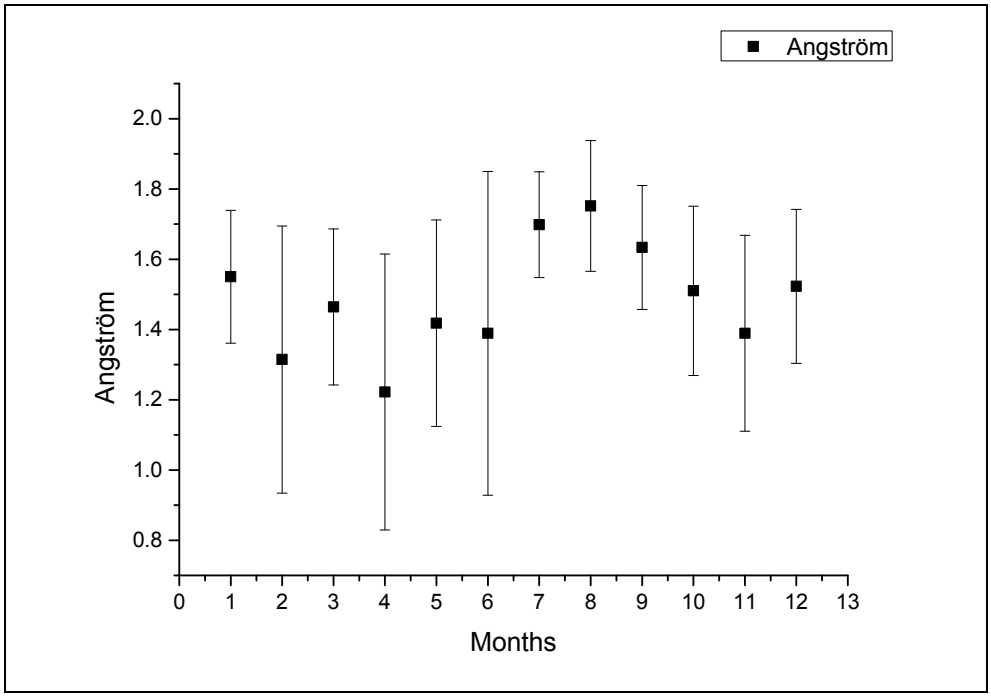

Fig. 4. Monthly Ångström parameter α 440 – 870 nm at CLUJ_UBB station

As seen in figure 4, at CLUJ_UBB station, the monthly α 440 - 870 nm has the high values during the dry months, with biomass burning aerosol intrusions and lower values during the spring months when the Saharan desert dust intrusions are more frequent. Also, the variability of values is higher from February to June.

As seen in figure 5, at Koforidua_ANUC, the monthly Ångström parameter has lower values than in Cluj, the mineral dust aerosol being present during the entire year. Also, the variability of the measured values is lower than at CLUJ_UBB station.

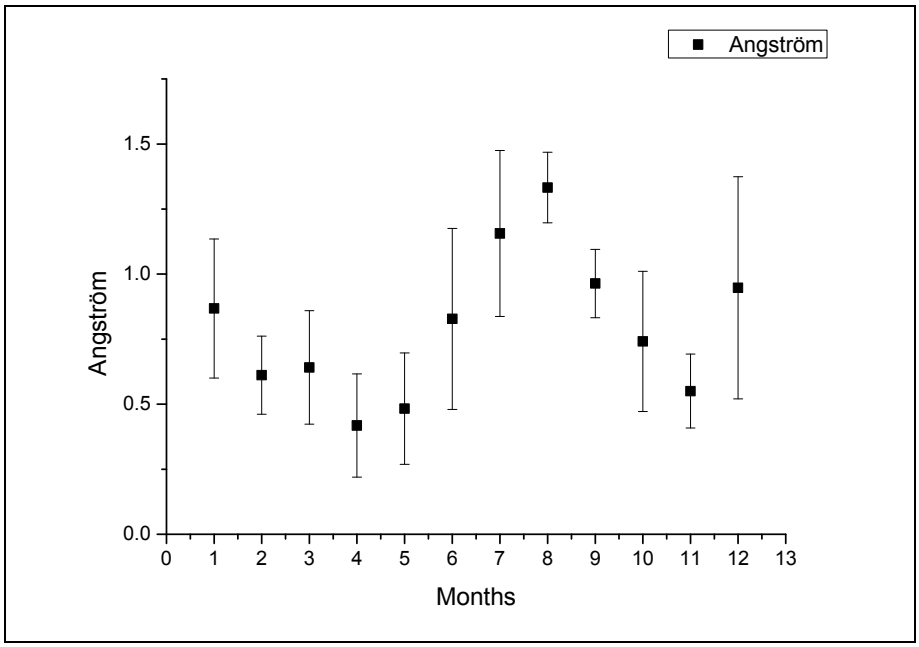

Fig. 5. Monthly Ångström parameter α 440 – 870 nm at Koforidua_ANUC station

Size distribution – the coarse and fine volume concentrations (Cvf and Cvc)

The numbers of days with indirect measurements are fewer. At CLUJ_UBB station we had 309 days with valid measurements, while at Koforidua_ANUC station we had 251 days with measurements.

At CLUJ_UBB station we observed a clear dominance of the fine mode Cvf over the coarse mode Cvc, specific to urban industrial aerosol. The exceptions are mainly represented by the desert dust intrusions. On the other hand, at Koforidua_ANUC station we observed a clear dominance of the coarse mode Cvc. This is typical for mineral dust originating from Sahara and also for marine salt.

Single Scattering Albedo - SSA(λ)

The single scattering albedo is a good indicator of the absorbing properties of the aerosols, high values of SSA(λ) indicate low absorption properties. At CLUJ_UBB station we observed an average value for SSA (440) of 0.92, similar with values measured in other European sites like Paris in France: SSA (440) of 0.94 (Dubovik et al., 2002). At Koforidua_ANUC station, we observed an average value for SSA (440) of 0.88.

CONCLUSIONS

In this paper we analyzed and compared the optical and microphysical parameters of aerosols at two AERONET stations with different geographical and climatic conditions: Cluj-Napoca (Romania) in South-Eastern Europe and Koforidua (Ghana) along the Gulf of Guinea in Western Africa. We analyzed 3 years of measurements made with CIMEL sun-photometers. The aerosol at the two locations has different properties. Over Cluj-Napoca in Eastern Europe, the urban industrial aerosol is present during the entire year. This type of aerosol is characterized by a high Ångström parameter and a pronounced fine mode fraction. Saharan desert dust intrusions are frequent during March and April and biomass burning aerosol intrusions in August and September. At Koforidua in Ghana and other neighboring countries like Togo and Benin the coarse mode aerosol like Saharan dust is dominant, with higher concentrations in April and May. This type of aerosol has a low Ångström parameter. In July and August, in the dry season with the monsoon winds from South, there are fewer days with Saharan dust. Also, other coarse aerosol like marine salt from the Atlantic Ocean is present in the region. The Aerosol Optical Thickness has also much higher values in Koforidua than in Cluj-Napoca, the aerosol pollution levels in the region being higher, especially during the Harmattan winds.

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ANALYSIS OF THE RELATIONSHIP BETWEEN THE CONTENT OF HEAVY METALS IN SOIL AND DUST IN COPŞA MICĂ

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ABSTRACT: The town of Copşa Mică is polluted with heavy metals due to the metallurgical plant that operated there. Even if the activities of the plant were drastically reduced and depollution equipment was installed, there were high levels of heavy metals in the soil, with long remanence. The major human exposure pathways of heavy metals in the soil are by ingestion of soil particles, by ingestion of home-produced vegetables and by inhalation of dust. This research investigated the levels of heavy metals in the soil, in outdoor and indoor dust, and the relationship between them. The statistical analysis through simple linear regression and correlation showed a statistically significant relationship between the level of heavy metals in the soil (independent variable) and the level of heavy metals in outdoor dust (dependent variable). For Pb and Zn, the linear regression model showed that in areas where high levels of heavy metals are recorded in the soil, high levels of heavy metals are expected in the outdoor dust. Distribution maps of heavy metals in soil and dust also highlight this relationship.

Key words: *soil, dust, heavy metals, Copșa Mică.*

INTRODUCTION

The town of Copșa Mică is polluted with heavy metals because of the metallurgical plant that operated there (Lăcătuşu, 2014, Szanto et al., 2012, A.P. Sibiu, 2010). Heavy metals have a long persistence in the soil, between tens and thousands of years (Kabata-Pendias, 2001), so the pollution and exposure problems of the population are present.

In Copșa Mică, the population health is affected by heavy metals in soil and dust, the main exposure pathways being by ingestion of soil particles, by inhalation of dust and by consumption of home-produced vegetables (Gurzău et al., 2010a, 2010b). The first cases of exposure to Pb were highlighted by Bardac (1999) and Comănescu et al. (2010), which showed that the occupational exposure of employees caused the occurrence of numerous cases of saturnism. Subsequently, research has been carried out to assess exposure to Pb of children (Gurzău et al., 2008). There were found high blod lead level (BLL) with values between 12.5-65 μg/dl in 2002, an average of 45 μg/dl in 2003 and an average of 39 μg/dL in 2008.

Even though the metallurgical plant (SOMETRA) has reduced its activity and the atmospheric emissions have decreased significantly since 2009 (A.P. Sibiu, 2010-2018), the high levels of heavy metals in the soil are a permanent source of population exposure.

There are researches showing that soil can become an important source of dust emissions containing heavy metals, under certain conditions of denuded soil, erosion, dryness and wind speed, surface particles being suspended and transported by air streams (Young et al., 2002, Hillel, 2008, Harris et al., 2009). Wind erosion can be an important source of airborne particulate loadings as well as of specific toxic constituents (Sullivan and Ajwa, 2011).

Other research evaluating the heavy metals in soil and dust on children's playgrounds has shown high levels of metals in the vicinity of industrial platforms. It has been concluded that some of the metals in the dust can be associated with the soil base material, while others are associated with atmospheric pollution, being transported by air and deposited on the surfaces.

Research results showed a strong spatial autocorrelation between the levels of heavy metals in dust and soil (Jin et. al, 2019).

In Copșa Mică, because the remanence of heavy metals in the soil is long-term, the soil is a permanent source of population exposure and a source of dust emissions containing heavy metals.

Because in industrial areas, the main human exposure pathways of heavy metals are by ingestion of soil particles and inhalation of dust (Gurzău et al., 2008), cumulated with the fact that under certain conditions the soil is an important source of heavy metals, through the phenomenon of suspension/ resuspension of the particles from its surface, the statistical analysis of the laboratory results was carried out. It has been tested if there is a statistically significant relationship between: 1) the content of heavy metals in the soil and also the content of heavy metals of outdoor dust; 2) the content of heavy metals content of the indoor and outdoor dust. It is important to understand the phenomenon to substantiate future measures in order to reduce the population exposure to heavy metals in soil and dust.

MATERIALS AND METHODS

Sampling methods

The study was conducted in Copșa Mică in 2014, where 20 individual households were investigated. Soil and dust samples were taken from certain functional areas within each household, as follows: 3 soil samples from each household, from the access area, yard and garden; 4 samples of dust from each household, from the access area, from the kitchen floor, bedrooms and from the investigated subjects right hands; one person from each household was investigated. 60 soil samples and 80 dust samples were obtained following the field stage.

Households were established to be evenly distributed in the town, on all directions, relative to the emission source (the flue-stack of the metallurgical unit), being localized as figure 1.

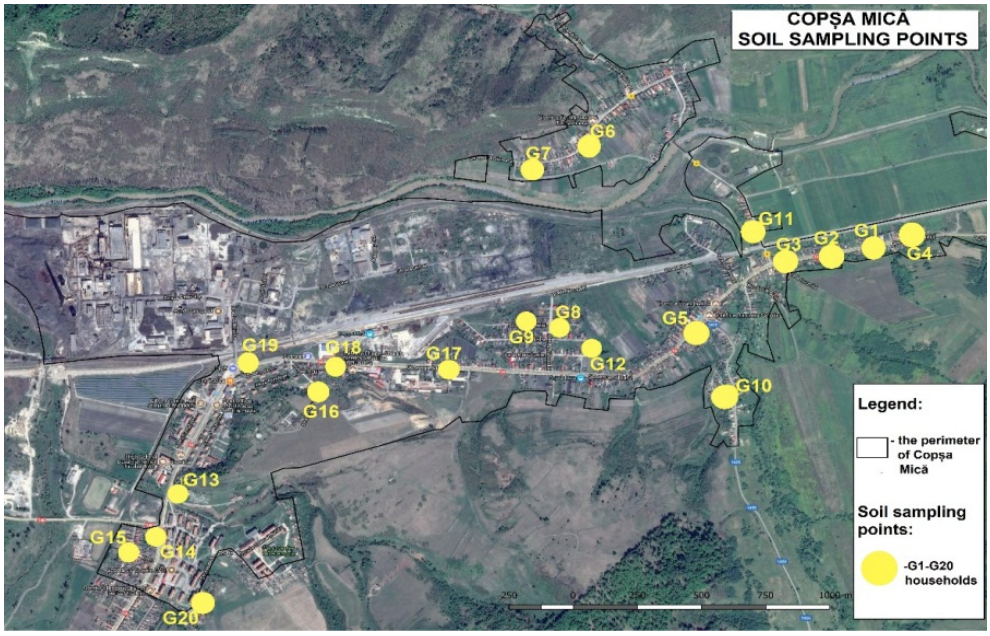

Fig. 1. Copșa Mică, location of investigated households

Because one of the objectives of the research is to establish a relationship between the content of heavy metals in the soil and the content of heavy metals in the dust, soil sampling was carried out from the horizon surface, from a depth of 0-5 cm. Furthermore, previous research has shown the highest concentrations of heavy metals being in the soil surface horizon (Damian et al., 2008).

Dust sampling was taken with dust sampling wipe (LeadWipe) pre-moistened with deionized water, polyorbate 20, methylparaben and propylparaben, used to collect samples of the following surface metals as specified in OSHA Method ID-125G, Addendum B: Pb, Zn, Cu, Cd, Cr, Ni etc. Sampling wipes have the dimensions of 5 x 7.75 inch, meaning 250 cmp, the sampled surface being the surface of the wipe used. Collection procedure complied with OSHA Technical Manual (OTM), Section II, Chapter 2, Apendix C – Procedure for Collecting Wipe Samples.

Soil and dust sample analysis

To determine concentrations of heavy metals in soil (Pb, Cd, Cu, Zn, As), the analyzes were performed in the Environmental Health Center laboratory, Cluj.

Analytical method for heavy metals in soil: X-Ray fluorescence spectrometry (XRF).

Analytical equipment used: Niton™ XL3t XRF Analyzer (Thermo Scientific™).

Method for laboratory analysis used: US EPA Method 6200 reference method.

To determine the level of heavy metals in dust (Pb, Cd, Cu, Zn, As), the samples were analyzed on the same equipment - Niton XL3t 600, by X-ray fluorescence spectrometry method.

Data analysis

Statistical analysis was conducted using Data Analysis tool in Excel. Pearson correlation analysis was conducted to estimate the linear dependence between variables (heavy metals in soil, in outdoor dust and in indoor dust). The correlation coefficient r (Pearson) takes values between -1 and +1, passing through 0, which indicates a null correlation. For the positive interpretation of the correlation coefficient (r) we use: $0 < r \leq 0.1$ - very weak correlation; $0.1 < r \leq 0.39$ - week correlation; $0.4 < r \leq 0.69$ - moderate correlation; $0.7 < r \leq 0.89$ - strong correlation; $0.9 < r \leq 1$ - very strong correlation (Schober et al., 2018).

Spatial distribution of heavy metal levels in soil and dust was performed using the Kriging interpolation method in the ArcGIS, a method which helps determine and assign values to missing points based on measured values in their vicinity.

After analyzing the spatial distribution maps, similarities were observed in the distribution of heavy metals in soil and dust, so advanced statistical methods were used to verify the relationships between them. Statistical data processing was performed using the simple linear regression model.

Linear regression represents a mathematical relationship between an independent variable and a dependent variable. In this research, the relationship between the heavy metal levels in the soil, as an independent

variable, and the levels of heavy metals in the outdoor dust, as a dependent variable, was tested and the results were interpreted in terms of statistical significance. It has been assumed that under certain conditions the soil becomes a source of heavy metals, by suspending the particles from its surface, possibly with a relationship between the level of heavy metals in the soil and the level of heavy metals in the dust.

Two other sets of data were tested, one representing the level of heavy metals in outdoor dust, as an independent variable and the level of heavy metals in indoor dust, as a dependent variable. It has been assumed that indoor dust comes partly from the outside of households, which is carried by air, footwear, clothing and other objects.

The ANOVA test was applied to verify the significance of regression and it shows that the model is relevant if the p (*Sig. F*) value <0.05, at a confidence level of 95%.

Before regression testing, the scatter-plot was used to bring information about the two data series and verify if there is a relationship between them.

RESULTS AND DISCUSSIONS

Analysis of heavy metal in soil

The results of the analyzes performed were centralized into a .xlsx document and were interpreted through summary statistical methods.

The results of the analyzes showed that average values of concentrations were recorded in decreasing order **Zn > Pb > Cu > As > Cd**, with the following values (mg/kgSU): Zn – 2350.23; Pb – 1307.85; Cu – 196.29; As – 54.94; Cd – 32.88.

Table 1. Values of minimum, mean and maximum concentrations for lead (Pb) and arsenic (As) in soil, in different function areas (mg/kgSU)

Sampling area	Pb			As		
	min	med	max	min	med	max
Access area (street)	157.73	1550.22	8141.12	16.85	63.06	302.51
Yard	214.98	1465.79	4496.61	12.97	62.84	152.29
Garden	270.54	**907.55**	2595.45	20.43	**36.93**	69.39

Table 2. Values of the minimum, mean and maximum concentrations for cadmium (Cd), copper (Cu) and zinc (Zn) in soil, in different function areas (mg/kgSU)

Sampling area	Cd			Cu			Zn		
	min	med	max	min	med	max	min	med	max
Access area (street)	9.54	46.26	236.90	57.68	232.91	1123.46	543.75	2843.85	17661.06
Yard	11.33	32.81	84.84	56.19	224.59	1373.17	531.21	2566.05	8221.26
Garden	8.84	**21.82**	53.28	61.76	**131.37**	233.87	610.00	**1640.81**	3599.07

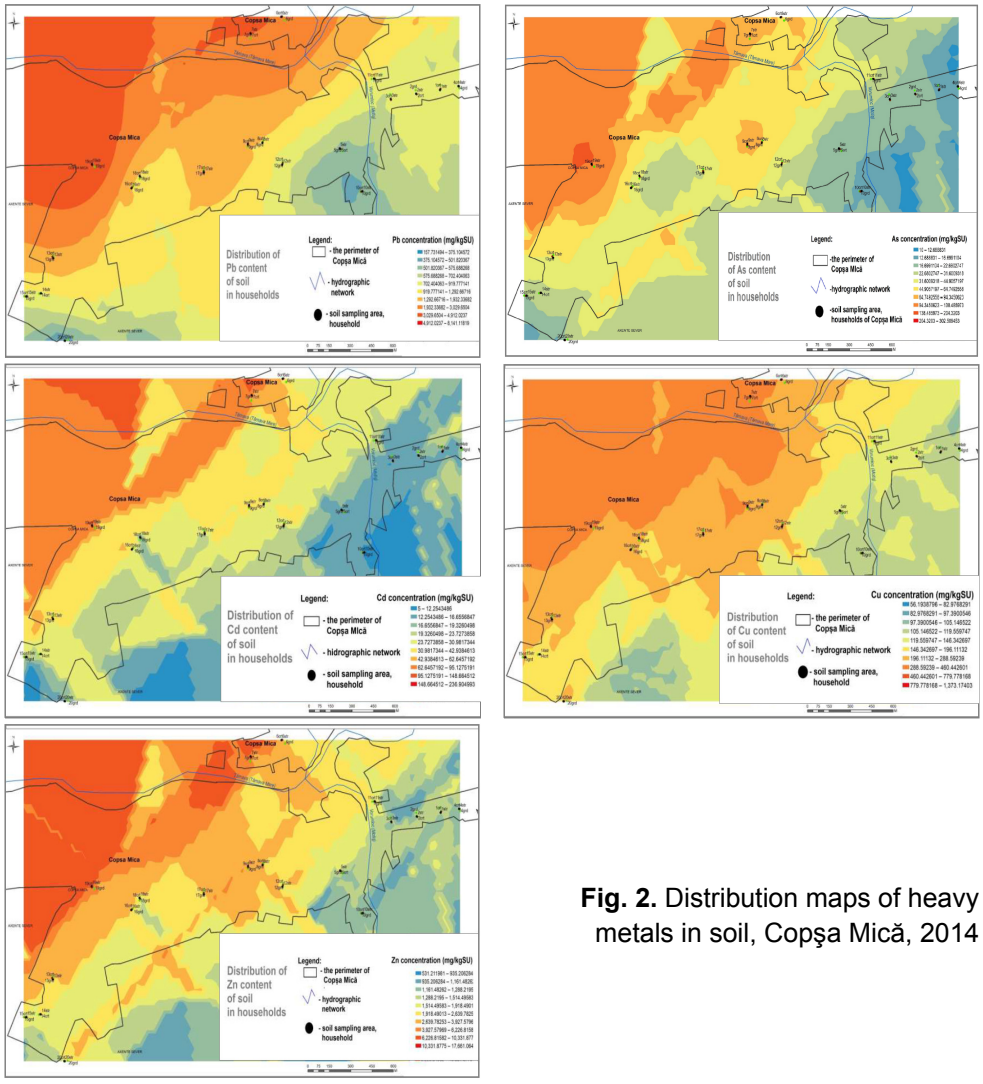

Fig. 2. Distribution maps of heavy metals in soil, Copşa Mică, 2014

Without exception, the average concentrations of heavy metals in the soil were recorded in descending order: **in the access area (street) > in the yard > in the garden**.

The spatial distribution of heavy metals concentrations in the soil of Copşa Mică highlights the areas most affected by pollution in relation to the emission source (the flue-stack of the metallurgical unit).

The distribution maps for heavy metals in the soil show a similarity between them in terms of peak concentrations, the highest values being recorded in 3 zones: at S of the industrial platform; in the Târnăvioara neighborhood, to NE of the industrial platform; in the E-SE neighborhood of the industrial platform. These are the areas most affected by pollution.

Correlation test for heavy metal in soil

Using the DataAnalysis tool in Excel, correlation matrix was accomplished.

Table 3. Correlation matrix for heavy metals in soil, Copşa Mică, 2014

	Pb	**As**	**Cd**	**Cu**	**Zn**
Pb	1				
As	0.856681	1			
Cd	0.962907	0.87753	1		
Cu	0.63614	0.770931	0.664759	1	
Zn	0.928036	0.940251	0.945554	0.835631	1

There is a very strong correlation between the concentrations of heavy metals for Pb-Cd, Pb-Zn, Zn-As, Zn-Cd, a strong correlation between As-Pb, As-Cd, As-Cu and a moderate correlation between Cu-Pb, Cu-Cd.

The correlation between these five metals is not by accident, and they are influenced by the same soil pollution phenomenon that has been present for decades in Copșa Mică.

Analysis of heavy metal in dust

Following the laboratory analysis, values below the method detection limit (< LOD) were recorded for As and Cd.

The results of the analyzes for Pb, Cu and Zn in dust, were centralized into a. xlsx document and were interpreted through summary statistical methods.

Table 4. Values of minimum, mean and maximum levels for lead (Pb), cooper (Cu) and zinc (Zn) in dust, in different function areas (μg/cm^2)

Sampling area	Pb			Zn			Cu		
	min	med	max	min	med	max	min	med	max
Acces area (yard)	0.0473	0.2160	0.5774	0.1319	0.2552	0.3857	0.0252	0.0395	0.0481
Chicken	0.0451	0.0780	0.1359	0.1069	0.1850	0.3163	0.0329	0.0400	0.0566
Bedroom	0.0397	0.1033	0.4576	0.1278	0.1943	0.3927	0.0313	0.0387	0.0527
Right hand	0.0607	0.1306	0.2672	0.1124	0.1692	0.3234	0.0340	0.0449	0.0878

The three metals analyzed from the dust have recorded average levels in decreasing order: **Zn> Pb> Cu**, as follows (μg/cm^2): Zn – 0.2009; Pb – 0.1598; Cu – 0.0408.

Comparing the average levels of heavy metals in dust, with the average concentrations of heavy metals in the soil, it can be observed that the highest average in soil was also recorded for Zn in descending order: **Zn> Pb> Cu**> As> Cd.

Unlike the concentrations of heavy metals in soil, where there is an order in functional areas, with the highest average of the access (street) and the lowest average in the gardens, there is no order for dust.

The highest average content of Pb and Zn in the dust were recorded outside the household area, while for Cu the highest average being recorded on the right hand of the investigated subjects.

The distribution maps for the 3 metals in the dust of Copșa Mică show a correlation regarding the highest levels in the SE of the town (figure 3). This area does not overlap areas with high concentrations of heavy metals in the soil.

For Pb and Zn, the highest values are in the NE – Târnăvioara neighborhood and in the vicinity of the industrial platform, in S of it, similar to the heavy metal distribution in the soil.

A relation to the spatial distribution of Pb and Zn from dust can be observed.

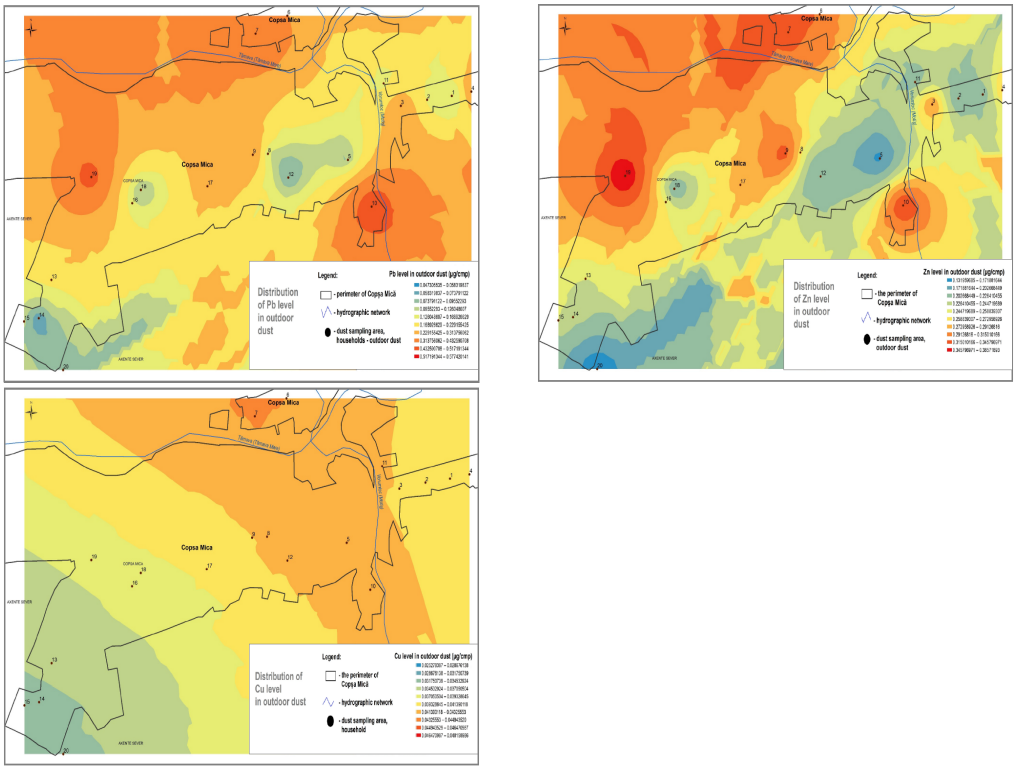

Fig. 3. Distribution maps of heavy metals in outdoor dust, Copşa Mică, 2014

Correlation test for heavy metal in dust

Using the DataAnalysis tool in Excel, correlation matrix was obtained.

Table 5. Correlation matrix for heavy metals in dust, Copşa Mică, 2014

	Pb	Cu	Zn
Pb	1		
Cu	0.298078	1	
Zn	0.822298	0.250295	1

As observed on the distribution maps, there is a strong correlation between the Pb-Zn levels in the dust and a poor correlation between Cu-Pb and Cu-Zn. The lowest values of the correlation coefficient are for Cu with the other metals, noticed also on the distribution maps. Similarly, in the correlation test for heavy metals concentrations in the soil, Cu recorded the lowest values of the correlation coefficient in relation to the other metals.

Statistical analysis of heavy metals in soil and in outdoor dust

Scattering diagrams for the data pairs have been developed: concentrations of heavy metals in soil – levels of heavy metals in dust. Because the As and Cd levels in the dust were below the method detection limit, the scattering and statistical regression analysis were performed only for Pb, Zn and Cu.

For each household, the average concentration of heavy metals in the soil was calculated in all three functional areas: from the access to the household, yard and garden. The obtained data series, represented by the average concentrations of Pb, Zn and Cu in the soil for each household, was considered as the independent variable, and the level of metals in dust from outdoor was considered the dependent variable.

Lead in soil and outdoor dust

According to the cloud of points form, a relationship between the level of Pb in the soil of households and the Pb level in outdoor dust is considered probable (figure 4).

The value of the correlation coefficient R^2 shows that the dependent variable (Pb in the dust) is explained in a proportion of 33.45% by the regression equation, i.e the independent variable (Pb in the soil). The linear regression model is defined by the equation given on the regression line.

The correlation test performed with the Data Analysis tool in Excel shows that there is a moderate correlation between the Pb level in the soil of households and the Pb level in outdoor dust ($r = 0.57$).

The statistics of correlation coefficient R^2 with the value of 0.334 shows that the model, as tested, justifies 33.4% of the variability of Pb levels in outdoor dust in relation to Pb level in the soil.

In the ANOVA test, p value (*Sig. F*) is less than 0.05, so the hypothesis of the lack of significance of the independent variable is rejected, in favor of the hypothesis that the regression model is statistically significant.

Coefficients in the regression equation are significant because p values are less than 0.05 ($p_{intercept}$ = 0.04 <0.05; $p_{Pb\text{-}soil}$ = 0.007 < 0.05), and the confidence intervals for the 2 coefficients do not contain the zero value, so the proposed model is statistically significant at a confidence level of 95%.

The regression equation that defines the model, resulted from the test and from the scattering diagram: y = 8E-05x + 0.1054; the coefficients of the equation are statistically significant.

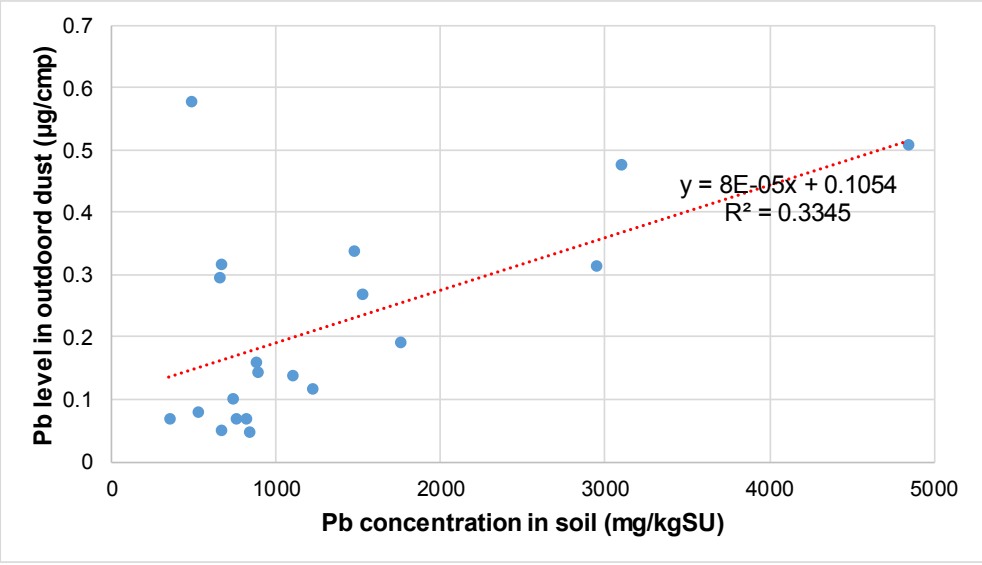

Fig. 4. Scattering diagram for Pb concentration in soil and Pb level in outdoor dust

Table 6. Correlation matrix for Pb in soil and in outdoor dust, Copşa Mică, 2014

	Pb-soil	Pb-dust yard
Pb-soil	1	
Pb-dust yard	**0.5783943**	1

The ANOVA test results and the linear regression coefficients obtained are presented.

SUMMARY OUTPUT	
Regression Statistics	
Multiple R	0.5783943
R Square	0.3345399
Adjusted R Square	0.2975699
Standard Error	0.1367547
Observations	20

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.1692322	0.169232232	9.048955139	0.00755
Residual	18	0.3366334	0.018701853		
Total	19	0.5058656			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.1054006	0.0478379	2.203285049	0.040840286	0.004897	0.205904
Pb-soil	8.462E-05	2.813E-05	3.008148124	0.007550401	2.55E-05	0.000144

Zinc in soil and in outdoor dust

According to the cloud of points form, a relationship between the level of Zn in the soil of households and the level of Zn in outdoor dust is considered probable (figure 5).

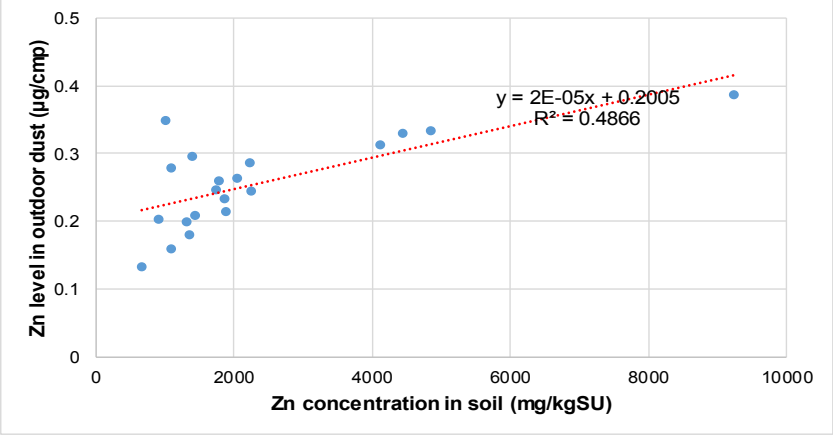

Fig. 5. Scattering diagram for the concentration of Zn in soil and Zn level in outdoor dust

The value of the correlation coefficient R^2 shows that the dependent variable (Zn in dust) is explained in a proportion of 48.66% by the regression equation, i.e the independent variable (Zn in soil). The linear regression model is defined by the equation given on the regression line.

The correlation test performed with the Data Analysis tool in Excel shows that there is a moderate to strong correlation between the Zn level in the soil of households and the level of Zn in outdoor dust (r = 0.697).

Table 7. Correlation matrix for Zn in soil and in outdoor dust, Copşa Mică, 2014

	Zn-soil	Zn-dust yard
Zn-soil	1	
Zn-dust yard	**0.697586**	1

The testing of the linear regression model, with ANOVA, is presented below.

Statistics of correlation coefficient R^2 with the value of 0.4866 shows that the model, as tested, justifies 48.66% of the variability of Zn levels in the outdoor dust in relation to the level of Zn in the soil.

In the ANOVA test, p value (*Sig. F*) is less than 0.05, so the hypothesis of the lack of significance of the independent variable is rejected, in favor of the hypothesis that the regression model is statistically significant.

Coefficients in the regression equation are significant because the p values are less than 0.05 ($p_{intercept}$ <0.05; $p_{Zn\text{-}soil}$ < 0.05), and the confidence intervals for the 2 coefficients do not contain the zero value, so the proposed model is statistically significant at a confidence level of 95%.

The regression equation that defines the model resulted from the test and from the scattering diagram (y = 2E-05x + 0.2005); the coefficients of the equation are statistically significant.

Statistical testing for the linear regression model showed that it is not significant for the relationship between Cu in soil and Cu in outdoor dust.

Statistical tests performed on heavy metals (Pb, Zn, Cu) in outdoor dust and indoor dust, or from the hands of the investigated subjects, did not show a statistically significant relationship. The influence of households cleaning activities and personal hygiene (hand washing) is an important one and significantly affects the level of heavy metals in indoor dust and on hands.

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.697586
R Square	0.486626
Adjusted R Square	0.458105
Standard Error	0.049087
Observations	20

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.041111	0.041111138	17.06217499	0.00062793
Residual	18	0.043371	0.00240949		
Total	19	0.084482			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.200549	0.017205	11.65661778	8.04173E-10	0.16440348	0.236695206
Zn-soil	2.33E-05	5.64E-06	4.130638569	0.000627934	1.1442E-05	3.51286E-05

CONCLUSIONS

For the analysis of heavy metals in the soil, the results showed that that average values of concentrations were recorded in decreasing order **Zn > Pb > Cu > As > Cd**, with the following values (mg/kgSU): Zn – 2350.23; Pb – 1307.85; Cu – 196.29; As – 54.94; Cd – 32.88.

Without exception, the average concentrations of heavy metals in the soil were recorded in descending order **in the access area (street) > in the yard > in the garden.**

The distribution maps for heavy metals in the soil show a similarity in their distribution, the highest values being recorded in three areas: at S of the industrial platform; in the Târnăvioara neighborhood, to NE of the industrial platform; in the E-SE neighborhood of the industrial platform.

The correlation test for heavy metals in soil shows that there is a very strong correlation between the concentrations of heavy metals for Pb-Cd, Pb-Zn, Zn-As, Zn-Cd, a strong correlation between As-Pb, As-Cd, As-Cu and a moderate correlation between Cu-Pb, Cu-Cd.

The correlation between these 5 metals is not a random, and they are influenced by the same soil pollution phenomenon that has been present for

decades in Copșa Mică. For Cu the lowest correlation indices have been recorded, besides the pollution phenomenon, probably coming from the natural background.

After analyzing the levels of heavy metals in outdoor and indoor dust, it was found that levels of Cd and As in the dust were below the method detection limit.

The three metals (Pb, Cu, Zn) in dust recorded average levels in a decreasing order **Zn > Pb > Cu**, with the following values (μg/cm^2): Zn – 0.2009; Pb – 0.1598; Cu – 0.0408. The decreasing level of average for heavy metals in the dust is similar to the decreasing order of the metals concentrations in the soil (**Zn > Pb > Cu** > As > Cd).

The highest averages for the content of Pb and Zn in dust were recorded outdoor; for Cu the highest average is recorded on the right hand of the investigated subjects.

Unlike heavy metal concentrations in the soil where a rule has been observed on functional areas, for heavy metals in the dust there is no rule. The cause may be that the level of heavy metals in the functional areas depends on the frequency and proper cleaning (dry/wet), and in the hands case depends on hands wash behavior.

According to the distribution maps for heavy metals in dust, the highest levels of Pb and Zn in outdoor dust were recorded in the vicinity of the industrial platform, at S; in NE, in the Târnăvioara neighborhood; in SE, at the exit towards Valea Viilor and the E-SE neighborhood of the industrial platform. The three areas with the highest levels of heavy metals in the dust overlap the areas with high levels of heavy metals in the soil.

The results of the correlation test for heavy metals in dust show a strong correlation between Pb-Zn and a poor correlation between Cu-Pb and Cu-Zn. The lowest values of the correlation coefficient are for Cu with the other metals in the dust, as well as for the soil.

Statistical analysis through regression and correlation did not reveal a statistically significant relationship between the levels of heavy metals in outdoor and indoor dust or on hands of investigated subjects. Proper households cleaning and hand washing behavior significantly influence the level of heavy metals in indoor dust and also dust on hands.

For Pb and Zn, the linear regression model highlights that in areas were high levels of heavy metals in soil are expected, linked to them, high

levels of heavy metals in dust are expected. This has also been highlighted on the distribution maps of heavy metals in soil and on the distribution maps of heavy metals in dust.

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STUDY OF SOIL POLLUTION WITH HEAVY METALS IN THE TOWN OF COPȘA MICĂ

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ABSTRACT. Copşa Mică is known to be one of the most polluted towns in Romania because of the historical pollution generated by non-ferrous metallurgy. The purpose of this study is to investigate soil quality in urban areas, where land is sensitive and where the population is most exposed. Heavy metals (Pb, As, Cd, Cu, Zn) from the horizon of the surface soil were analyzed using descriptive statistical analysis, geostatistical analysis and pollution indices. The results of the analysis showed that the most affected areas of Copșa Mică are in S of the industrial platform in N-E of the town – in the Târnăvioara neighborhood and also in E-SE of neighborhood of the industrial platform. In areas with different land uses, the average concentrations of heavy metals have been decreasing in the following way: in public areas > in access areas (streets) > in yards > in gardens. The level of heavy metals in soil is influenced by anthropogenic activities in each functional area. The pollution load index (PLI) shows a level of soil pollution between moderate and very high. The biggest contribution through the single pollution index (PI) is represented in descending order by the following: Pb, Zn and Cd. There is no correlation between the calculated values of the PLI and the distance from the emission source (the metallurgical unit basket). Because a large area of land is affected by pollution, it is not feasible to apply greening measures, so interventions should be focused on decreasing the exposure of the population to heavy metals.

Key words: *soil, heavy metals, Copșa Mică.*

INTRODUCTION

Copșa Mică is a heavily polluted industrial area where the retention of heavy metals in the soil is long-lasting and the effects on the health of the population are still present. This affirmation is supported by the results of population health studies (Gurzău et al., 2008, 2010b), but also the fact that the industrial platform of Copşa Mică is included in the preliminary inventory of potentially contaminated sites (A.P.M. Sibiu, 2017).

Over time, in Copșa Mică, soil quality was investigated through a series of studies. The first investigations carried out (Răuţă et al., 1987, Vădineanu et al., 1991, Toti et al., 1993, Comănescu et al., 2010, Lăcătuşu and Lăcătușu, 2010) have shown a polluted area of approximately 180,750 ha.

According to Damian et al. (2008) the highest concentrations of heavy metals are found in the horizons of soil surface where normal Pb values have been exceeded (5.61 to 27.68 times), for Zn (2.16 to 25 times) and for Cd (5.99 to 133.3 times).

According to Gurzău and Neamțiu (2010a), a research project carried out in Copşa Mică (and the area of Sălişte) has shown that here the level of pollution with Pb and Cd remained high.

Other investigations by Szanto et al. (2012), found that for Pb and Cd the intervention threshold for sensitive uses is exceeded. The highest concentration for Pb is in the surface horizon but is decreasing with depth and when the distance from the source is increasing. For Cu and Zn, the highest concentrations are recorded in the surface horizon where the alert thresholds for sensitive uses are exceeded.

According to Lăcătuşu (2014), the soil pollution level at Copşa Mică is assessed based on the values of the pollution index. The result showed that there is a moderate to high soil pollution of Cd and Pb, a moderate pollution of Zn and a low pollution of Cu.

Regarding soil pollution, effects are felt on land use. Thus, their economic value is diminished, there occur some conditions for use in case of future development of localities, and the perspective of territorial planning and urban development is not favorable. This means that the socio-economic environment has no optimistic prospects. Taking into consideration the land surface that has been affected by heavy metal pollution, methods for greening are unfeasible in such areas.

It is well known that historically polluted localities have low socio-economic development potential, which are *"hot spots"* at local and national level, not only from this point of view, but also as a theme in social, health and environmental policies.

MATERIALS AND METHODS

Sampling methods

The study was carried out in two research campaigns in 2014 and 2018, when samples were taken and analyzed from the urban area of Copșa Mică, from the superficial horizon of the soil (0-5 cm). Determination of soil sampling depth was made taking into account that most research in the area showed that the highest concentrations of heavy metals are recorded in the horizon of soil surface (Damian et al., 2008). The research area was established in the urban areas of Copșa Mică, on lands with sensitive uses, because they are currently used by the population and the population is exposed for the longest time.

In 2014, a number of 20 individual households from Copșa Mică were investigated. Samples were collected from the access area in households (at the front of the street), yards and gardens, resulting 60 soil samples analyzed.

In 2018, other 27 soil samples were collected from public areas, the most transited by the population, especially areas frequently used by children like schools, kindergartens, playgrounds, sports grounds, public administration, cult institutions, market and supermarket. Focus is on these areas because the group of population with the highest susceptibility to exposure to heavy metals in the soil is represented by children (Gurzău et al., 2008, 2010b), and the study about soil pollution was continued with a population exposure study to heavy metals in the soil.

The investigated points have been established to be uniformly distributed across all directions in the urban area of Copşa Mică. They were marked with G1-G20 (households), the investigated points in 2014, and P1-P27 (public areas), the investigated points in 2018. These points are located according to figure 1.

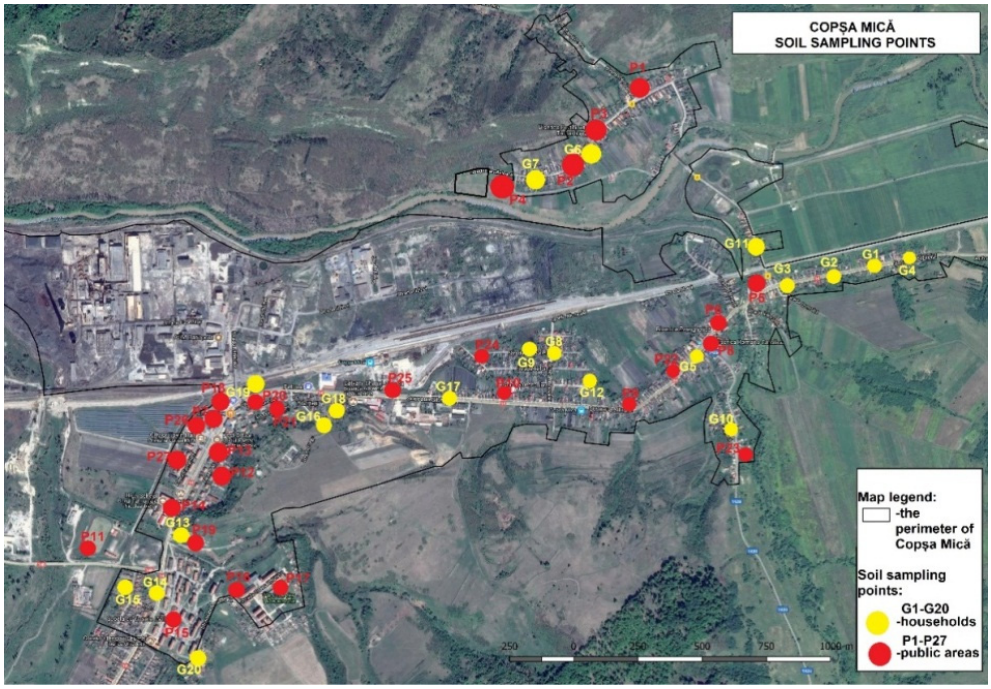

Fig. 1. Copşa Mică, soil sampling points

When soil samples were taken, the land was ment to be without filler materials, not affected by various material or waste and not being cemented or asphalted. Soil samples were collected after the vegetation was completely removed, the surface of the soil was cleared by removing dust, roots, leaves or other residues. The samples were handle carefully, not to be contaminated during sampling, storage, transport and during laboratory analysis.

To determine concentrations of heavy metals in soil (Pb, Cd, Cu, Zn and As), the analyzes were performed in the Environmental Health Center laboratory, Cluj.

Analytical method for heavy metals in soil is by X-Ray fluorescence (XRF) spectrometry.

Analytical equipment used: Niton™ XL3t XRF Analyzer (Thermo Scientific™).

Method for laboratory analysis used: US EPA Method 6200 reference method.

Descriptive statistical analysis

The results were centralized into a .xlsx document and were interpreted by descriptive statistics such as the measurement of the central trend (mean, median, frequency of occurrence of certain values / histogram) and by measuring the variability (data dispersion interval – value minimum and maximum, standard deviation). The statistical data analysis tool was used from Surfer 13 program.

Geostatistical Analysis

Spatial distribution of heavy metal concentrations in soil was performed using the Kriging Interpolation Method in the ArcGIS software, a method which helps determine and assign values to missing points based on measured values in their vicinity. Ordinary Kriging is a commonly used interpolation method to predict the overall trend of soil pollution.

Noticing similarities in the spatial distribution of heavy metals in urban areas, statistical testing was used through the correlation method. For the calculation of the correlation coefficient between heavy metals in the soil, the DataAnalysis tool in the Excel program was used and the matrix of the correlation coefficients was accomplished.

The correlation coefficient r (Pearson) takes values between -1 and +1, passing through 0, which indicates a null correlation. For the positive interpretation of the correlation coefficient (r) we use: $0 < r \leq 0.1$ – very week correlation; $0.1 < r \leq 0.39$ - week correlation; $0.4 < r \leq 0.69$ – moderate correlation; $0.7 < r \leq 0.89$ – strong correlation; $0.9 < r \leq 1$ – very strong correlation (Schober et al., 2018).

Soil contamination assessment methods

The assessment of the soil pollution degree was performed by calculating the pollution load index (PLI). This index shows the level of heavy soil contamination and was calculated based on the single pollution index (PI). These indices are calculated separately for each analyzed metal (Kovalska et al., 2018).

PLI is calculated as a geometric mean of PI according to the formula:

$$PLI = n\sqrt{(PI_1 \times PI_2 \times PI_3 \times ... PI_n)},$$

where: n – number of pollutant assesses; PI – single pollutant index of each metal assesses (Varol, 2011).

PLI values vary from 0 (unpolluted) to 10 or more (highly polluted) as follows: PLI = 0 – background concentration; 0 < PLI ≤ 1 – unpolluted; 1 < PLI ≤ 2 – moderately to unpolluted; 2 < PLI ≤ 3 – moderately polluted; 3 < PLI ≤ 4 – moderately to highly polluted; 4 < PLI ≤ 5 – highly polluted; PLI > 5 – very highly polluted (Zhang et al., 2011 and Kowalska et al., 2018).

The single pollution index (PI) is used to determine the metal that represents the greatest threat to soil (Zhang et al., 2011 and Kowalska et al., 2018). Calculate with the formula:

$$PI = Cn / GB,$$

where: Cn – concentration of metal in the soil sample; GB – geochemical background (mg/kg).

PI levels and significance: PI < 1 – non polluted; 1 ≤ PI < 2 – slightly polluted; 2 ≤ PI < 3 – moderately polluted; PI ≥ 3 – highly polluted (Jorfi et al., 2017).

When the individual pollution index (IP) was calculated, the level of geochemical background in Romania was taken into account (Utterman et al., 2006).

RESULTS AND DISCUSSIONS

The results of the analyzes performed were centralized into a .xlsx document and were interpreted through summary statistical methods.

Table 1. Values of minimum, mean and maximum concentrations for lead (Pb) and arsenic (As) in soil in different function areas (mg/kgSU)

Sampling area	Pb			As		
	min	med	max	min	med	max
Access area (street)	157.73	1550.22	8141.12	16.85	63.06	302.51
Yard	214.98	1465.79	4496.61	12.97	62.84	152.29
Garden	270.54	**907.55**	2595.45	20.43	**36.93**	69.39
Public area	36.27	2920.11	18514.66	18.62	199.02	803.57

Table 2. Values of the minimum, mean and maximum concentrations for cadmium (Cd), copper (Cu) and zinc (Zn) in soil, in different function areas (mg/kgSU)

Sampling area	Cd			Cu			Zn		
	min	med	max	min	med	max	min	med	max
Access are (street)	9.54	46.26	236.90	57.68	232.91	1123.46	543.75	2843.85	17661.06
Yard	11.33	32.81	84.84	56.19	224.59	1373.17	531.21	2566.05	8221.26
Garden	8.84	**21.82**	53.28	61.76	**131.37**	233.87	610.00	**1640.81**	3599.07
Public area	11.49	48.76	151.85	13.14	250.43	1272.93	34.76	2810.99	11346.43

The results of the analyzes showed that in 2014 average values of concentrations were recorded in all sampling areas in descending order Zn > Pb > Cu > As > Cd, with the following values (mg/kgSU): Zn – 2350.23; Pb – 1307.85; Cu – 196.29; As – 54.94; Cd – 32.88.

For the year 2018 heavy metals have recorded average concentrations in descending order Pb > Zn > Cu > As > Cd, with the following values (mg/kgSU): Pb – 2920.11; Zn – 2810.99; Cu – 250.43; As – 199.02; Cd – 48.76. Unlike in 2014, higher average concentrations were observed for all metals analyzed. One reason is that in 2014, more than 20% of soil samples were taken from heavily disturbed areas of gardens, where there are permanent interventions on the soil through usual farm work, manure fertilization and gardening etc.

It is known that soil intervention by mechanical work can lead to dilution of pollutant concentrations in the horizon of soil surface. Irrigation can also favor vertical transport. This fact is also highlighted in the tables, where it can be noticed that average concentration of heavy metals in the samples taken from the gardens are significantly lower than the other sampling areas.

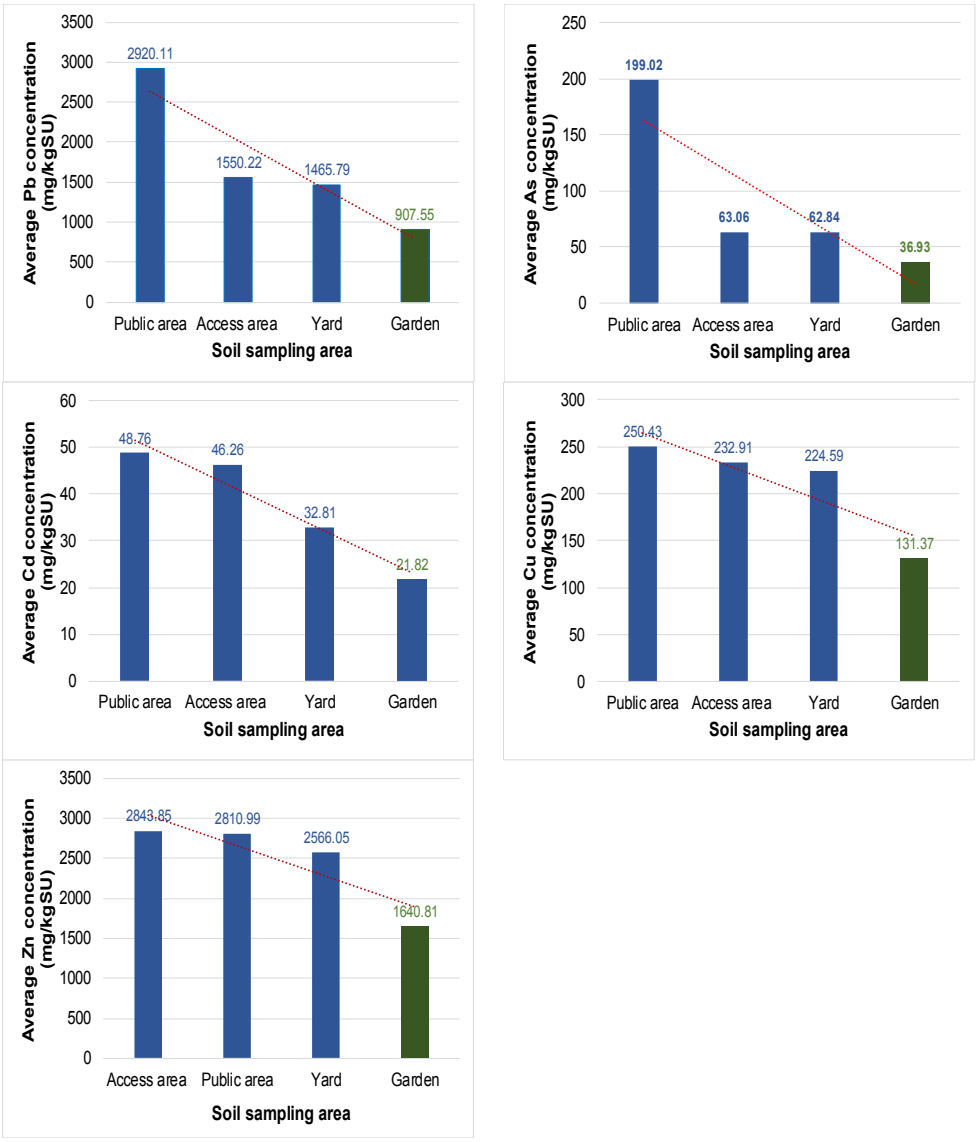

Fig. 2. Average concentration of heavy metals content of soil in different areas

According to graphics, the highest average concentrations were recorded in descending order in the public area > in the access area (street) > in the yard > in the garden. The exception is Zn, where the average concentration recorded on the access zones is slightly higher than the recorded average for the samples taken from public areas, but the difference is not significant (1.16%).

The highest average of heavy metals is recorded outside households. Theoretically, inside them there are frequently interventions, resulting in disturbing the superficial horizon of soil and dilution of pollutant concentrations. In gardens, interventions are most frequent, due to annual usual farm work. In public areas, interventions are lower compared to access areas in the household, where there are frequent interventions for the arrangement and maintenance to access households and only exceptional, with excavations for infrastructure works (water network construction between 2013-2014).

Spatial distribution of heavy metals content of soil in Copșa Mică

The spatial distribution of heavy metal content of soil registered in 2014 and 2018 in Copșa Mică, highlights the areas most affected by pollution compared to the emission source, which is the industrial platform SOMETRA, the flue-stack of the metallurgical unit.

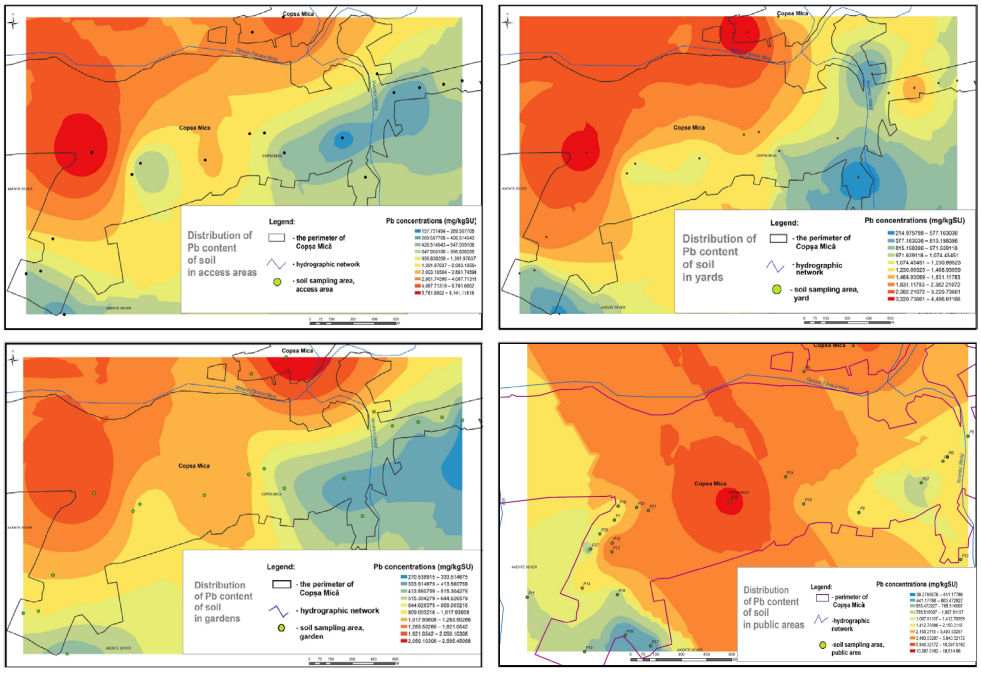

Fig. 3. The distribution map of Pb content of soil in different areas, Copşa Mică

We can see a rule on average concentrations of heavy metals depending on the field of land use. The highest concentrations being recorded in 2018 in public areas, with the lowest concentrations in 2014 in gardens (except Zn, insignificant difference). It was considered relevant to generate separate distribution maps for the four soil sampling areas: home access (street), yard, garden and public areas.

The distribution maps of Pb content of soil in different areas show similarity between them in terms of concentration peaks, the highest values being recorded in the vicinity of the industrial platform in S of it, in the Târnăvioara neighborhood – in the NE and in the E-SE of the industrial platform, indicating that these are the areas most affected by pollution.

Even if there are frequent soil interventions in the gardens, it is noted that the highest concentrations are maintained in the same areas of the town. It is explained by the fact that the interventions on the soil, the existing concentrations of pollutants, by dilution due to agricultural works, don't manage to go down to normal values.

As shown above, the average concentration recorded in the gardens is the lowest compared to the averages recorded in the other sampling areas, but the high concentrations of pollutants persist here as well.

The problem is that in the neighborhood located at the E-SE by the industrial platform and in Târnavioara, rural traditions are maintained meaning the population is cultivating vegetables for their own consumption, gardens drenched with water from fountains. The areas least affected by Pb pollution are those located in the E and SE parts of Copșa Mică, towards Mediaș and Valea Viilor.

To observe the distribution of other heavy metals in the soil (As, Cd, Cu, Zn), the distribution maps in the access area (street) are also presented, as an example.

The spatial distribution of the highest concentrations for As, Cd, Cu and Zn respects the model of Pb distribution.

For 2014, all heavy metals have recorded the highest concentration values in the vicinity of the industrial platform, in S of it, in the Târnăvioara neighborhood and in the E-SE neighborhood of the industrial platform. The exit from Copșa Mică to Mediaş and to Valea Viilor, the areas on the E and SE side of Copșa Mică are the least affected by pollution.

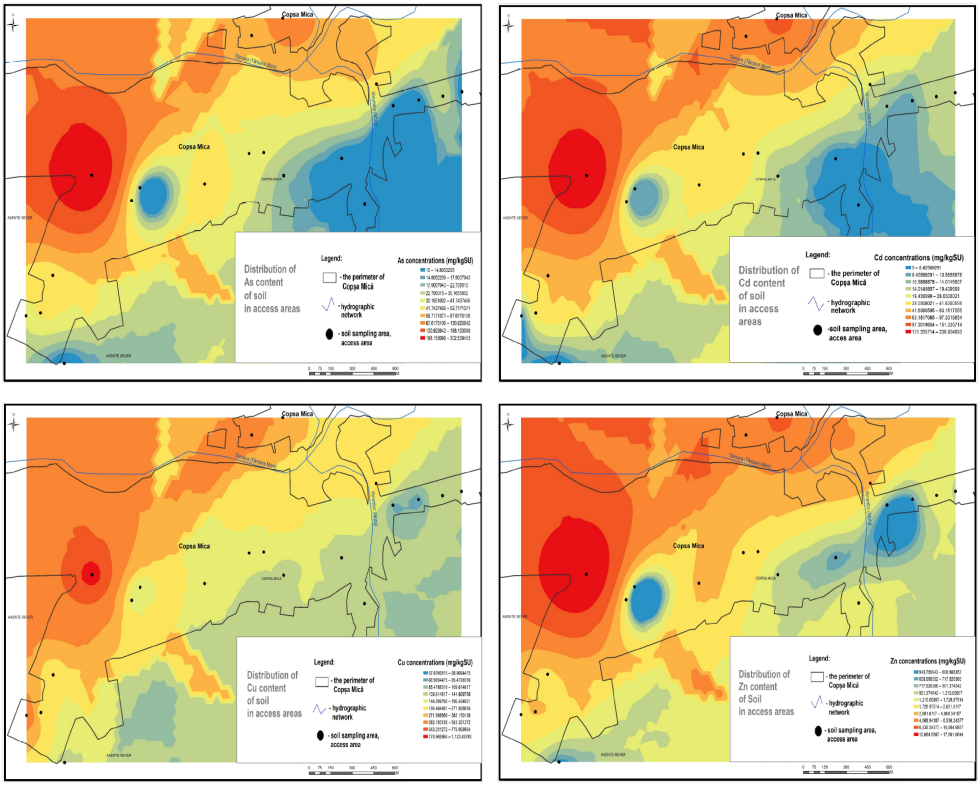

Fig. 4. The distribution map of As, Cd, Cu and Zn content of soil, in the access areas in households, Copșa Mică.

The spatial distribution maps of the heavy metal concentrations in the soil indicate that a correlation is possible between them in Copșa Mică.

Correlation test for heavy metal concentrations in soil

Using the DataAnalysis tool in Excel, the matrix of correlation coefficients was accomplished.

Table 3. Correlation coefficient matrix for heavy metals in soil, Copşa Mică, 2014 and 2018

	Pb	As	Cd	Cu	Zn
Pb	1				
As	0.873956	1			
Cd	0.708955	0.741514	1		
Cu	0.687042	0.791314	0.754622	1	
Zn	0.688901	0.718573	0.951336	0.877277	1

There is a very strong correlation between the concentrations of heavy metals for Zn-Cd, a strong correlation for Pb-As and Zn-Cu, a moderate correlation between Pb-Cd, Pb-Cu, Pb-Zn, As-Cd, As-Cu, As-Zn, Cu-Cd and Cu-Zn.

The lowest values of the correlation coefficients are for Pb and Cu in relations with the other metals.

The correlation between these five metals is not by accident, and they are influenced by the same soil pollution phenomenon that has been present for decades in Copșa Mică.

Calculation of pollution indices (PLI, PI)

The following graphs present the results of the calculations for PLI, for all samples taken in 2014 and 2018.

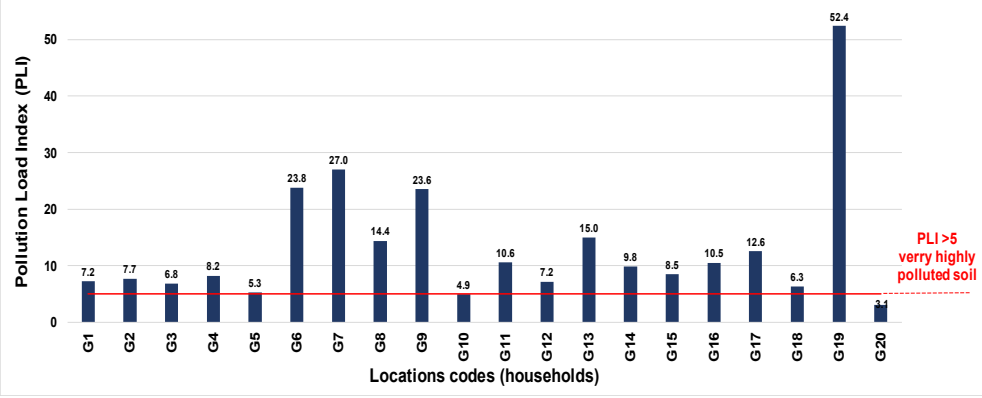

Fig. 5. Values of PLI for soil, Copșa Mică, 2014

PLI values indicate a moderately to highly polluted soil in one of the investigated households G20 (PLI = 3.1), a highly level of pollution in one household G10 (PLI = 4.9) and very highly polluted soil in the remaining of 18 households investigated.

The lowest levels of PLI are recorded in two households, one in SW of Copșa Mică to Axente Sever (G20), and one in SE of Copșa Mică to Valea Viilor.

The highest values of PLI were registered in the investigated households: G19 (PLI = 52.4), G7 (PLI = 27.0), G6 (PLI = 23.8) and G9 (PLI = 23.6). These households are located in the S of industrial platform, in the Târnăvioara neighborhood and in the E-SE neighborhood of the industrial platform.

To highlight the contribution of each metal to the total level of PLI in the soil (2014), graphical and percentage indices of individual pollution (PI) were represented in figure 6.

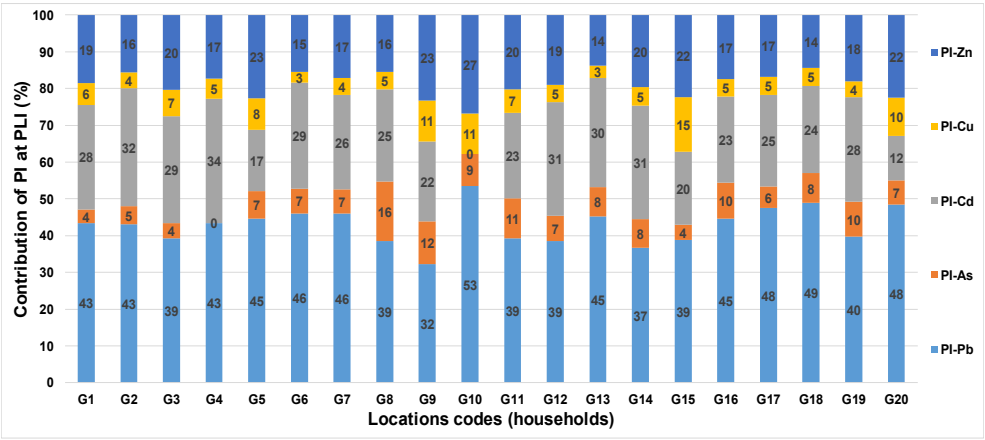

Fig. 6. Percentage contribution of PI at the level of PLI for soil, Copşa Mică, 2014

The highest contribution to the general level of PLI by individual pollution indices (PI) is in descending order Pb > Cd > Zn > As > Cu, with the following values: Pb – 42.9%; Cd – 24.5%; Zn – 18.8%; As – 7.4%; Cu – 6.4%.

For the year 2018, the calculated values of PLI (figure 7) indicate an unpolluted soil in two investigated points, P27 – playground Castanilor street (PLI=0.4) and P16 – playground no.1, 1st December neighborhood (PLI=0.9). The explanation could be that the soil was disturbed by recent arrangement of these areas, especially in P16.

For an investigated point P19, there was a low level of pollution (PLI=1.62), being the Copşa Mică Orthodox cemetery area. For two investigated points resulted a moderately polluted soil P1 (PLI=2.48) and P17 (PLI=2.34) – these were located in Tarnăvioara (playground) and playground no.2 in Copșa Mică, the explanation being that they were newly arranged and the soil being disturbed.

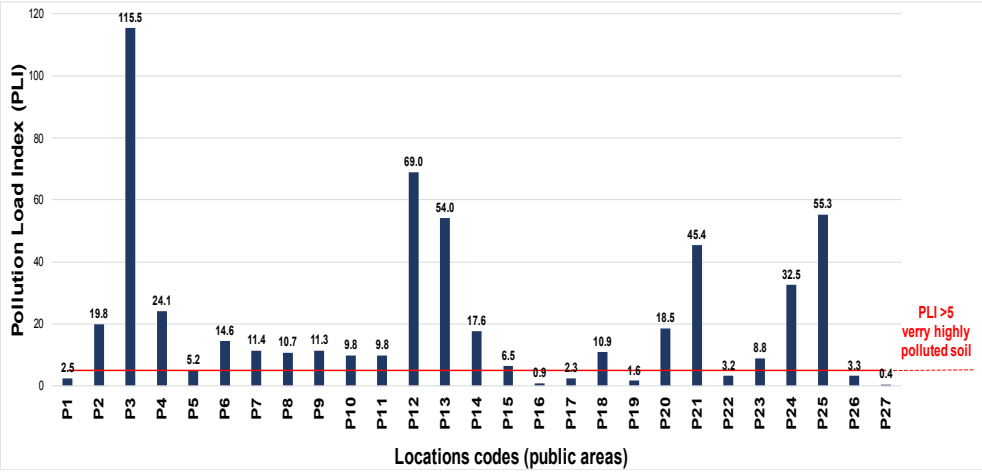

Fig. 7. Values of PLI for soil in Copșa Mică, 2018

There was a moderatey to highly polluted soil in points P22 (PLI=3.23), P26 (PLI=3.26), P22 (PLI=3.27) and P26 (PLI=3.3). A verry highly polluted soil (PLI > 5) resulted in the remaining 20 investigated points.

The highest levels of the PLI were recorded in the following points: P3-Orthodox Church Târnăvioara (PLI=115.47); P12-Kindergarten no.1 of Copşa Mică (PLI=69.0); P25-Copșa Mică Sport Hall (PLI=55.32); P13-playground Kindergarten no.1 (PLI=54.04) and P21-Copşa Mică playground (PLI=45.43). Most of these points are relatively close to the industrial platform and are frecvently used by children.

To highlight the contribution of each metal to the total level of PLI in the soil (2018), graphical and percentage indices of individual pollution (PI) were represented in figure 8.

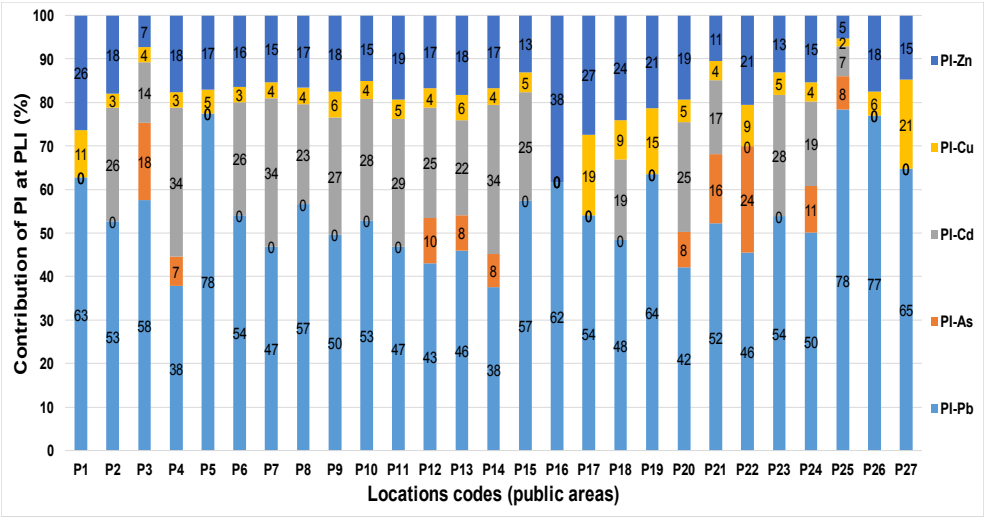

Fig. 8. Percentage contribution of PI at the level of PLI for soil, Copşa Mică, 2018

The highest contribution to the general level of PLI by individual pollution indices (PI) is in decreasing order Pb > Zn > Cd > As > Cu, with the following values: Pb – 54.5%; Zn – 17.8%; Cd – 17.1%; Cu – 6.3%; As – 4.3%.

Both in 2014 and 2018, the highest contribution to PLI is represented by PI calculated for Pb, Zn and Cd.

To verify if there is a correlation between the value of the general pollution index (PLI) and the distance from the industrial platform SOMETRA, especially the flue-stack of the metallurgical unit, a correlation test was performed using the DataAnalysis tool in Excel.

Table 4. Correlation test between PLI level and distance from emission source

	Distance	PLI
Distance	1	
PLI	-0.16907	1

There is a very weak, inversely negative correlation between the PLI level and the distance to the flue-stack of the metallurgical unit.

CONCLUSIONS

The highest concentration averages for the analyzed heavy metals were recorded for Pb, Zn, Cu, and then for As and Cd, the latter being recognized as having toxic potential even at low concentrations in the environment.

In 2018, higher concentration averages for heavy metals were found in the soil due to the fact that in the 2014 campaign at least 20% of soil samples were taken from areas disturbed by agricultural and infrastructure works (construction of water supply network, 2013-2014).

For the heavy metals analyzed, depending on the use of lands, highest concentration averages occur in a descending order: in the public area > in the access area (street) > in the yard > in the garden, this correlating with the anthropic intervention on these areas. The exception is Zn, where the concentration average recorded on access areas in households is slightly higher than the average recorded for public areas, but is insignificant (1.16%).

From the distribution maps of heavy metals content of soil it can be observed that the most affected areas are: in the vicinity of the industrial platform, in S of it; in Târnăvioara neighborhood, in the NE towards the industrial platform; and in E-SE of the industrial platform neighborhood.

The calculated pollution indices show mostly a level between moderate to very high soil pollution. The highest contribution to PLIs, by individual pollution indices (PIs), is in decreasing order: Pb, Zn and Cd.

Following the statistical correlation test between the PLI levels and the distance to the emission source (the flue-stack of the metallurgical unit), there was no statistically significant correlation between the PLI level and the distance from the emission source.

Like previous studies, in 2014 and 2018 results of the analyses obtained further indicate soil pollution with heavy metals at a level between moderate and very high, according to the pollution indices. Because the area affected by pollution is large, measures for greening the area are not feasible but there can be implemented measures to decrease the exposure of population in the most affected areas and within certain functional areas.

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THE ASSESSMENT OF CONTAMINATION AND SOURCE OF POLYCYCLIC AROMATIC HYDROCARBONS FROM THE SEDIMENTS OF THE SOMEȘ RIVER

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ABSTRACT. Polycyclic aromatic hydrocarbons (PAHs) represent an important class of environmental pollutants that are derived from both natural and anthropogenic sources. Due to their toxic, mutagenic, carcinogenic and bioaccumulation potential there are continuous concerns over the PAHs contents in the aquatic media. The aim of this work was to evaluate the distribution of PAHs in the sediments of Someș River, to assess their occurrence and to establish the origin (pyrogenic/petrogenic) of pollution sources. 13 sampling points were selected covering the distance from Cluj-Napoca to Satu Mare in order to assess the contribution of urban agglomeration over the concentration of PAHs in sediments. For the determination of the compounds GC-MS analyses were performed. PAH diagnostic ratios have been used as a tool for identifying and assessing the pollution emission sources. The obtained results showed that, the concentration of PAHs measured varied between 33.3 and 251.6 μg kg^{-1}. Benzo[a]pyrene was found in most of the samples. A general tendency of higher concentration values on the exit point of the river from cities than from the entering point was found. The isomeric ratios indicated that most of the sources were of pyrogenic origin, rather than petrogenic. As expected, the concentrations of ΣPAHs were below the maximum accepted limit of 1 mg kg^{-1} regulated in Romania.

Key words: *Someș River, PAHs, GC-MS, sediments.*

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds containing two or more condensed aromatic rings (Souza et al., 2018).

PAHs are ubiquitous organic pollutants all over the world, semi-volatile, lipophilic, photosensitive, persistent, having a high capacity of transport in the environment and have low solubility in water. With a wide environmental presence and multitude, only 16 congeners were classified as Prior Pollutants by the United States Environmental Protection Agency (USEPA) (Riaz et al., 2019; He et al., 2014; Zeng et al., 2018), some of them being considered carcinogens, mutagens and tend to bioaccumulate in the organisms (Tu et al., 2018; Zeng et al., 2018).

Rivers are the main way of transporting pollutants from the terrestrial environment into the aquatic environment. Polluted river beds and suspended particles can have a significant impact on riverine ecosystems (Schwientek et al., 2017).

The advantage of using sediments is that the fraction of organic matter influences the PAHs content, so once adsorbed, PAHs are no longer released into the water (Belles et al., 2016). For this reason, unlike other chemical compounds, such as trace elements, dioxins, chlorinated pesticides etc. the concentration of PAHs in sediments does not decrease with the passage of time (Sanctorum et al., 2011). Thus, analysing the content of PAHs in water or in suspended particles gives a picture of the degree of contamination of PAHs at that moment. In the meantime, the sediment provides a historical picture.

From this reason, in the last time, the use of sediments for the evaluation of the PAHs level rivers contamination is a topical subject for many researches (He et al., 2014; Grung et al., 2016; Beldean-Galea et al., 2016; Liu et al., 2017; Dubovina et al., 2018; dos Santos Rodrigues et al., 2018; Zeng et al., 2018; Davis et al., 2018).

Moreover, the normative regarding the classification of surface water quality in order to establish the ecological state of the water bodies stipulate that, the maximum allowable amount of PAHs (benzo[a]pyrene, naphthalene, anthracene, phenanthrene, fluoranthene, benzo[a]anthracene, crysene, indeno(1,2,3-cd)pyrene and benz[k]fluoranthene) in sediments is 1 mg kg^{-1} (Rowater).

PAHs appear in the environment from different sources and can be characterized as natural (resulting from chemical and biological transformations of organic matter, volcanic eruption, forest fires, oil seeps) (Rocha and Palma, 2019; Riaz et al., 2019) and anthropogenic which can be classified in pyrogenic (incomplete combustion of organic matter, fossil fuels and biomass such coal and wood, or industrial waste) and petrogenic originating from crude and refined petroleum like kerosene, gasoline, lubricating oils, diesel, asphalt etc. (Davis et al., 2018; He et al., 2014).

Identification of PAH sources in sediments is necessary, not only because of their persistence and effects on organisms, but also because sediments behave as a secondary source of PAH pollution, being a reservoir of these compounds. Locating the origins of PAHs in ecosystems allows reducing pollution from the sources of emissions. A challenge in identifying sources of pollution is the presence of a large number of sources of emissions (Rocha and Palma, 2019).

In the last time, different researches were carried out on this subject. The conclusion is that the isomeric ratio of PAHs seems to be the most convenient methodology for the identification of the sources of PAHs in the environment because it allows the differentiation of PAHs from petrogenic and pyrogenic sources (Tobiszewski and Namieśnik, 2012; Yunker et al., 2002).

The aim of this work was to investigate the occurrence of PAHs in sediments from the Someș River, in 13 points, before and after the entrance of the river in major urban agglomerations in its river basin area and to establish the pollution emission sources, applying different diagnostic ratios.

MATERIAL AND METHODS

Chemicals and reagents

For qualitative and quantitative analysis, a PAH standard mixture was used and it contained 16 priority congeners listed by the United States Environmental Protection Agency (US EPA): naphthalene (Nap), acenaphthylene (Acy), acenaphtene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF),

benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP), and indeno[1,2,3-cd]pyrene (IcdP) in concentration of 1.0 µg mL^{-1} of each compound was obtained from Sigma Aldrich (Germany).

Silica, alumina and granular anhydrous sodium sulphate used for the extract clean-up were purchase from Merck (Germany). All solvents used for sample processing (dichloromethane, n-hexane, acetone) were HPLC grade. Highly purified deionized water used in the chemical analysis was prepared using a Direct-Q UV 3 system (18.2 MΩ/cm) from Millipore (Molsheim, France).

Sample collection and geographical coordinates

A total of thirteen surface sediment samples were collected in May 2017 from different location of the Someș River watershed. The name of the sampling point, assigned number and the geographical coordinates are given in table 1, and in the map of the studied watershed (figure 1).

Table 1. Sampling points, abbreviation and the geographical coordinates

Sampling point	Number	Geographical coordinates	
		Latitude (N)	Longitude (E)
Entrance in Cluj-Napoca city, Someșul Mic River	P1	46°75´9.47”	23°53´5.04”
Exit of Cluj-Napoca city, Someșul Mic River	P2	46°78´7.51”	23°70´8.68”
Entrance in Gherla city, Someșul Mic River	P3	47°01´6.78”	23°88´5.65”
Exit of Gherla city, Someșul Mic River	P4	47°06´1.15”	23°91´6.32”
Entrance in Dej city, Someșul Mic River	P5	47°14´4.32”	23°91´6.78”
Entrance in Dej city, Someșul Mare River	P6	47°14´6.24”	23°91´2.87”
Exit of Dej city, Someș River	P7	47°17´0.98”	23°84´7.62”
Entrance in Jibou town, Someș River	P8	47°24´4.66”	23°28´4.52”
Exit of Jibou town, Someș River	P9	47°30´5.92”	23°27´5.26”
Before confluence with Lăpuș River, Someș River	P10	47°65´5.12”	23°40´1.74”
After confluence with Lăpuș River, Someș River	P11	47°65´9.25”	23°39´9.25”
Entrance in Satu Mare city, Someș River	P12	47°78´2.58”	22°92´1.68”
Exit of Satu Mare city, Someș River	P13	47°79´8.17”	22°83´7.43”

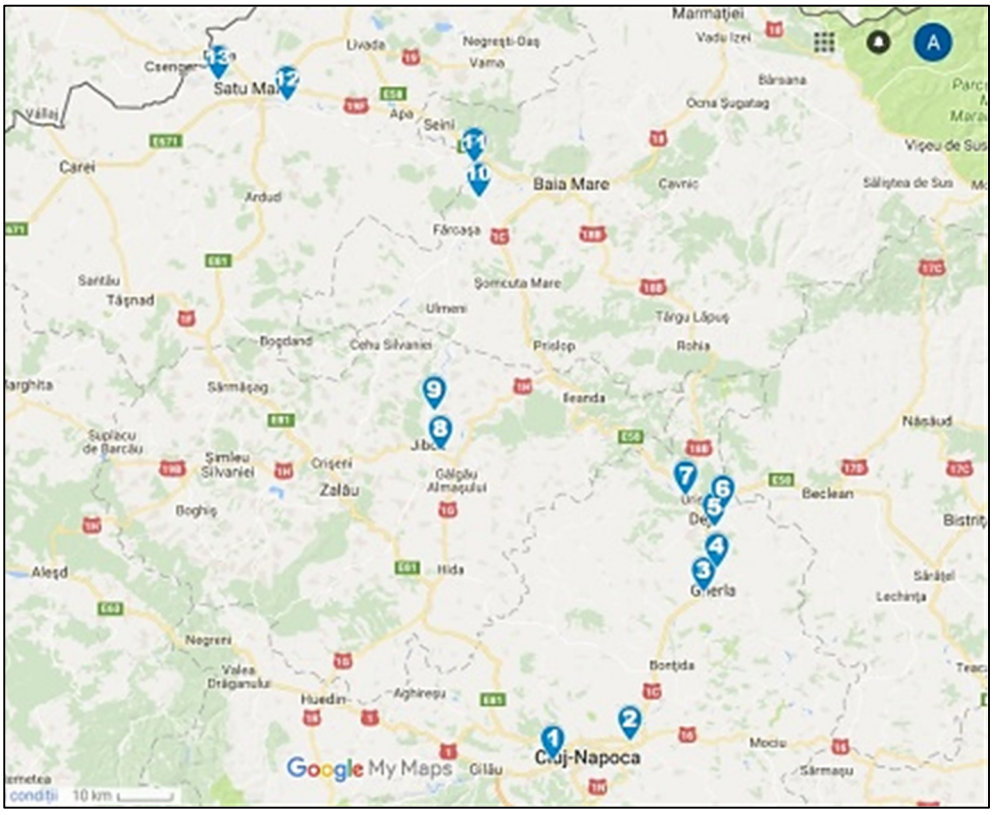

Fig. 1. Map of the studied watershed and the location of sampling point

Samples were collected using a stainless steel shovel at about 0.5 – 2.5 m water depth, sealed in clean polyethylene bags and stored at 4℃ until analysis. Before extraction, samples were oven-dried at 40°C, ground up in a gear mortar, and then sieved through a 2 mm-mesh sieve to remove the large stones, roots or other coarse particles.

Instrumentation

PAHs compounds were analysed by gas chromatography coupled with mass spectrometry (GC–MS) using a Focus GC-DSQII, (ThermoElectron) equipped with a DB-5 MS column (25 m × 0.25 mm × 0.25 μm) and operating

in electron impact (EI) ionization mode (70 eV). Helium of high purity at a constant flow rate of 1.2 mL min^{-1} was used as carrier gas. A volume of 1.0 µL sample was injected in the splitless mode using a TriPlus autosampler. The injector, detector, ion source, and transfer line temperatures were 280, 310, 200 and 300ºC, respectively. The separation of the compounds was performed with a gradient temperature program of 10ºC min^{-1} from 120 to 220ºC, and of 3ºC min^{-1} from 220 to 300 ºC, with a holding time of 1 min. Identification of individual PAH compounds was based on the selected ion monitoring (SIM) mode by the comparison of retention times between sample and the standard mixture. Quantification was carried out using external standard method. All data acquisition was performed using the Xcalibur™ software.

Sample extraction and clean-up

The extraction of PAH from sediment samples were performed by ultrasound extraction procedure (Beldean-Galea et al., 2016) using the follow protocol: 5 g of dry sediment samples were placed into a 50-mL conical vial and after the addition of 20 mL acetone:hexane mixture (1:1, *v/v*), the vial were capped and sonicated for 20 min using an ultrasonic bath, model Elmasonic acquired from Elma Schmidbauer GmbH, Germany. After sonication, the sample was centrifuged and the upper layer (solvent extract) was transferred in a round flask. The extraction procedure was repeated two more times with fresh solvent and finally the all three extracts were reunified together. The resulted extract was, concentrated to approximately 2 mL using a rotary evaporator.

For the purification of the extract, silica-alumina column (10 mm i.d., made of glass) was prepared by filling from bottom to top with 4 g activated silica, 4 g activated alumina and 1 g dehydrated sodium sulphate. The column was then conditioned with 20 mL of n-hexane and used for extract purification. For purification, the concentrated extract was loaded to the column and the target compounds (PAH) were eluted with a mixture of 40 mL n-hexane/ dichloromethane (80:20 *v/v*). The collected fraction was concentrated by rotary evaporation to approximately 2 mL and then reduced down to 1 mL under nitrogen stream.

The obtained extract was then subjected to GC-MS analysis.

RESULTS AND DISCUSSIONS

PAH concentrations in sediment samples

The concentration of the PAHs in the analysed sediment samples were situated between 33.25 and 251.6 μg kg^{-1} (table 2). The highest value was obtained in the sampling point P2 (Exit from Cluj-Napoca city, Someșul Mic River), while the lowest value in the sampling point P1 (Entrance in Cluj-Napoca city, Someșul Mic River).

Table 2. PAH concentrations in the analysed samples

Compound	**Sampling point/concentration (μg kg^{-1})**												
Abreviation	**P1**	**P2**	**P3**	**P4**	**P5**	**P6**	**P7**	**P8**	**P9**	**P10**	**P11**	**P12**	**P13**
Nap	2.57	39.4	10.7	13.3	6.27	4.16	6.07	10.6	4.34	4.90	13.4	3.00	2.20
Acy	0.24	nd*	nd	1.78	nd	nd	0.53	nd	nd	nd	nd	nd	nd
Ace	0.76	nd	nd	0.62	nd	nd	1.66	3.20	4.74	1.03	0.46	2.71	0.49
Fl	1.01	7.76	1.59	2.26	3.41	1.80	9.64	1.68	3.17	5.13	2.11	1.23	2.52
Ant	5.93	21.2	19.1	15.3	22.2	10.0	25.4	14.5	25.7	15.5	26.8	13.9	11.9
Phe	0.98	9.28	7.43	7.76	7.00	3.69	12.6	5.69	13.4	5.07	7.77	4.51	4.07
Flu	6.42	43.8	18.0	20.2	17.6	3.91	20.4	11.8	36.2	8.71	8.04	8.51	10.8
Pyr	6.31	42.8	17.8	18.9	17.8	4.47	25.7	13.7	37.2	8.62	8.34	7.91	11.3
BaA	0.74	15.5	3.95	1.53	1.16	0.11	1.44	2.93	1.78	0.44	1.46	1.68	1.12
Chr	3.26	24.3	6.53	4.52	4.96	0.88	3.55	6.13	5.65	1.81	6.48	3.21	3.95
BbF + BkF	2.00	13.4	4.38	7.48	2.94	0.15	11.0	2.33	7.02	2.71	0.11	1.20	2.07
BaP	**1.56**	**10.4**	**2.33**	**7.36**	**2.11**	**0.56**	**4.52**	**1.59**	**5.93**	**1.37**	**8.31**	**0.54**	**25.1**
IcdP	0.80	4.42	1.33	2.81	1.06	0.42	3.20	0.71	2.44	0.97	0.57	2.48	8.12
DahA	1.06	8.82	2.78	4.81	1.69	1.47	8.68	1.06	2.25	1.45	0.74	0.75	0.83
BghiP	0.61	10.6	1.92	4.85	2.13	2.20	7.68	1.12	1.63	2.03	0.76	2.05	2.51
Total PAH	33.3	251.6	97.8	113.6	89.3	33.8	142.1	77.1	151.7	59.8	85.3	53.7	87.1
$\sum_{LMW}/\sum_{HMW}$	0.53	0.45	0.66	0.57	0.77	1.39	0.65	0.86	0.51	1.13	1.45	0.89	0.32
Ant/(Ant+Phe)	0.86	0.70	0.72	0.66	0.76	0.73	0.67	0.72	0.66	0.75	0.78	0.75	0.75
Flu/(Flu+Pyr)	0.50	0.51	0.50	0.52	0.50	0.47	0.44	0.46	0.49	0.50	0.49	0.52	0.49
IcdP/(IcdP+BghiP)	0.57	0.29	0.41	0.37	0.33	0.16	0.29	0.39	0.60	0.32	0.43	0.55	0.76
BaA/(BaA+Chr)	0.25	0.39	0.38	0.25	0.23	0.11	0.29	0.32	0.24	0.20	0.18	0.34	0.22

**nd* - not detected

It can also be observed that the compounds mentioned in the Romanian legislation referred to PAHs in sediment (benzo[a]pyrene, naphthalene, anthracene, phenanthrene, fluoranthene, benzo[a]anthracene, crysene, indeno(1,2,3-cd)pyrene and benz[k]fluoranthene) are presented in all analysed samples but, their concentrations do not exceed the maximum allowable concentration (1 mg kg^{-1}). This fact indicates that, PAHs cause no adverse ecological effects in studied area.

Anyway, the analysis of the PAH concentration in water or sediment samples provide information about the level of contamination and do not give information about the sources of pollution. In this way other research are necessary for the identification of the PAHs pollution sources and implicitly to establish ways to reduce PAH pollution of water courses.

Identification of PAH sources

In order to assess the sources of PAH discharged in the Someș River, ratios of $\Sigma_{LMW}/\Sigma_{HMW}$ (sum of PAH with low molecular weight (2-3 aromatic rings) (LMW) and PAH with high molecular weight (more than 3 aromatic rings), (HMW)), Ant/(Ant+Phe), Flu/(Flu+Pyr), IcdP/(IcdP+BghiP) and BaA/(BaA+Chr), were considered. According to the values obtained from these ratios, estimates of the sources of PAHs pollution can be made. (table 3).

Table 3. Diagnostic ratios used to identify the origin of PAHs

Diagnostic Ratio	Pyrolytic source	Petrogenic source	Fuel combustion	Grass/coal/ wood combustion	Reference
Ant/(Ant + Phe)	> 0.1	≤ 0.1	ndef*	ndef	Zhu et al., 2008
Flu/(Flu+Pyr)	> 0.5	< 0.4	0.4–0.5	> 0.5	Yunker et al., 2002
IcdP/(IcdP+BghiP)	> 0.5	< 0.2	0.2–0.5	> 0.5	
BaA/(BaA+Chr)	> 0.2	< 0.2	> 0.35	0.2-0.35	Tobiszewski & Namieśnik, 2012
$\sum_{LMW}/\sum_{HMW}$	< 1	> 1	ndef	ndef	

**ndef – not defined*

The obtained results suggest that mixed sources of pollution with PAH occurs in the investigated samples (table 4).

Table 4. Values of the diagnostic ratios obtained for the analysed sediment samples

	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13
$\sum_{LMW}/\sum_{HMW}$	Pyr[a]	Pyr	Pyr	Pyr	Pyr	Petr[b]	Pyr	Pyr	Pyr	Petr	Petr	Pyr	Pyr
Ant/(Ant+Phe)	Pyr	Pyr	Pyr	Pyr	Pyr	Pyr	Pyr	Pyr	Pyr	Pyr	Pyr	Pyr	Pyr
Flu/(Flu+Pyr)	Pyr	Pyr	Pyr	Pyr	Pyr	Pyr	Pyr	Pyr	Pyr	Pyr	Pyr	Pyr	Pyr
IcdP/(IcdP+BghiP)	Pyr	Pyr	Pyr	Pyr	Pyr	Petr	Pyr	Pyr	Pyr	Pyr	Pyr	Pyr	Pyr
BaA/(BaA+Chr)	Pyr	Pyr	Pyr	Pyr	Pyr	Petr	Pyr	Pyr	Pyr	Petr	Petr	Pyr	Pyr

where: Pyr[a] mean “Pyrolitic source” and Petr[b] means “Petrogenic source”

Thus, from the ratio of $\Sigma_{LMW}/\Sigma_{HMW}$ it can be observed that, excepting the sampling points P6, P10 and P11, the main source of pollution in the investigated sites is pyrogenic, and the obtained ratios exceed “1” in almost all sampling points. Similar results have been obtained for other used ratios which confirm that, the main sources of pollution in the investigated area are pyrogenic sources.

For a better estimation of the PAH sources the cross plot of the ratios of Ant/(Ant+Phe) against Flu/(Flu+Pyr) and IcdP/(IcdP+BghiP) against BaA/(BaA+Chr) were done (figures 3 and 4).

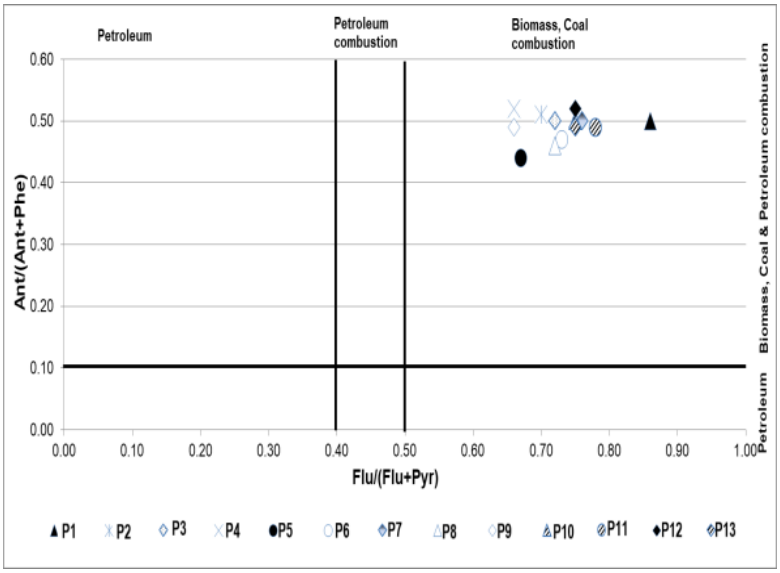

Fig. 3. The cross plot of the ratio of Ant/(Ant+Phe) against Flu/(Flu+Pyr)

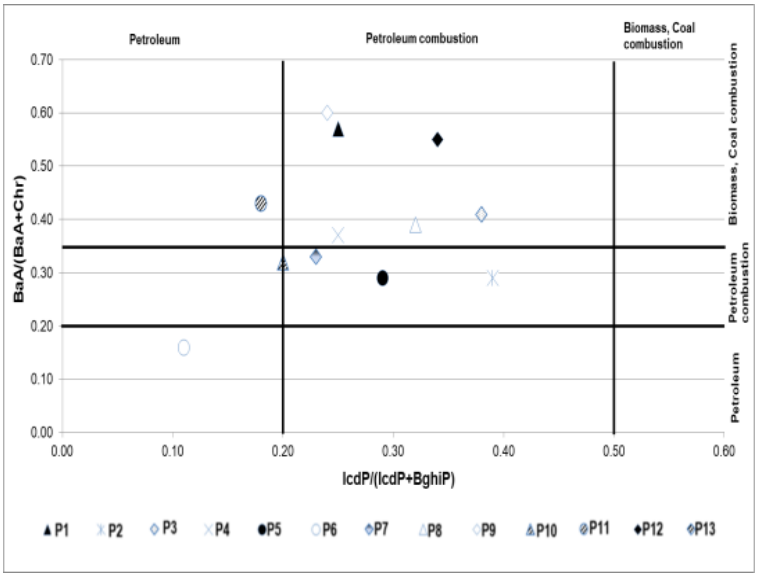

Fig. 4. The cross plot of the ratio of IcdP/(IcdP+BghiP) against BaA/(BaA+Chr)

Thus, from the cross plot of the ratio of Ant/(Ant+Phe) against Flu/(Flu+Pyr) it can be observed that the main source of PAH is the combustion of biomass, coal and petroleum products, while for the cross plot of the ratio of IcdP/(IcdP+BghiP) against BaA/(BaA+Chr) it can be observed that, in the sampling points P6, P10 and P11 the source of pollution has a petrogenic fingerprint while in other the petroleum combustion fingerprint.

Taking into consideration the obtained results, it can be concluded that the PAH pattern obtained for the analysed sediment are in connection with the anthropic activities, the petrogenic fingerprint being a result of the petroleum products leaks and to an inefficient removal during the wastewater treatment, while the pyrogenic fingerprint is given mainly by the burning of wood and coal necessary for houses heating and to the combustion of petroleum products generated by traffic or different industrial activities.

CONCLUSIONS

The results of the study showed that, in the studied area, the concentration of the PAH in sediment samples ranged between 33.25 and 251.6 μg kg^{-1} μg kg^{-1}. The lowest values were obtained at the entrance of the river into the urban agglomerations while the highest at the exit which indicate that the urban activities are the main reason for the PAHs contamination of the river.

The concentrations of the PAH in sediment samples do not exceed the maximum allowable concentration established by the Romanian legislation which indicated that PAH causes no adverse ecological effects in the area under study.

Regarding the PAH pattern, the obtained results indicate that mixed sources, petrogenic, and pyrogenic are present in the analysed sediment samples. The main sources of pollution are the leaks of petroleum products, the combustion of fossil fuels and biomass and coal combustions respectively.

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SPATIAL ANALYSIS OF LANDSLIDES USING GIS. CASE STUDY: TÂRNAVELOR PLATEAU

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ABSTRACT. Landslides represent one of the most important hazardous geomorphological phenomena in the Târnavelor Plateau. Geographically this unit is positioned on the southern part of the Transylvanian Depression. For the landslides distribution analysis, we used five criteria: geology, slope, altitude, exposition and the local administrative units. This type of studies is a must, on one hand to find out how the current landslides are distributed, and on the other hand to identify the areas which are prone to this type of hazardous geomorphological phenomena. By investigating the study area's ortophotoplans and topographic maps, 5797 landslides were vectorized to create a landslide inventory map. The study shows that lithologic conditions (the presence of friable rocks such as marls, clays, sand) and the land use (mostly agricultural lands) are the most defining factors for landslide to develop, it is believed that in the future landslides will appear on similar slope, orientation and geological conditions etc. In this situation, knowing the susceptible areas to landslides is beneficial for the territorial planning actions and also to avoid the building and expanding other civil engineering constructions on lands which are prone to landslides.

Key words: *landslides, spatial statistics, distribution, GIS.*

INTRODUCTION

One of the main hazardous geomorphological processes from the Târnavelor Plateau are represented by landslides. The Târnavelor Plateau is placed in the southern part of the Transylvanian Depression (figure 1) (Bilașco et al., 2011; Petrea et al., 2014). On its 780.916 ha surface there were identified 5797 landslides, which represent in total 47.930 ha.

This is, on one side the result of the characteristic geological substrates, and on the other side the result of the land use which is significantly influenced by the anthropic activities. Under lithological aspect it is especially noticeable the presence of friable rocks like marls, clays, clay marl, gritstone etc., as the result of sedimentation of eroded materials from the Carpathian Mountains, which delimitate the Transylvanian Basin (Sanders et al., 2002; Krézsek and Filipescu, 2005; Krézsek and Bally, 2006). We must mention that even if it is a depressionary space, it has the hilly aspect, which is the direct effect of fluvial modelling of the mentioned lithological formations.

The forest's place, which had also a slope retaining role, was initially taken by the grasslands (they were used as a meadows), and afterwards, as mechanization took over agriculture, these were transformed mostly in arable lands. Given these land use changes and considering also the friable lithology, landslides type geomorphological processes did not take long to occur (Roşian et al., 2010).

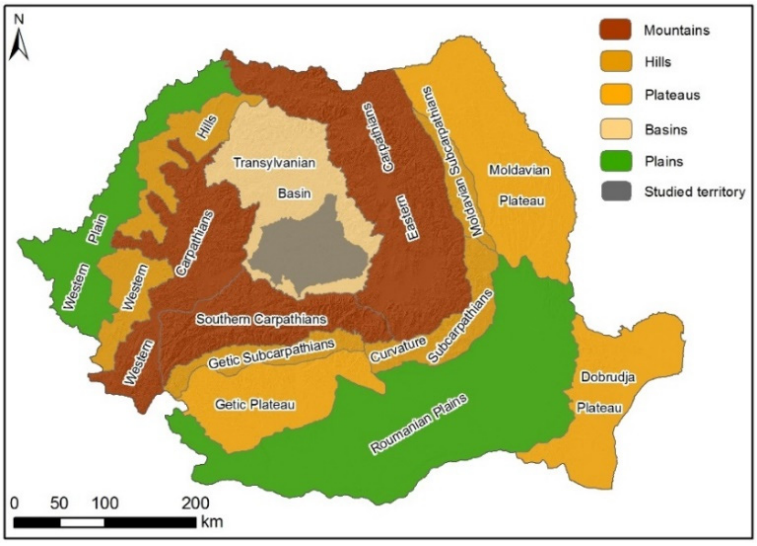

Fig. 1. Localization of the study area

Thus, the Târnavelor Plateau landslides distribution statistical analysis proves to be extremely useful, given the fact that the causes and triggering factors of these geomorphological processes are still the same nowadays. Therefore, we present the current distribution of landslide as well as data about possible areas that in the future might be affected by such processes.

METHODS AND RESOURCES

A spatial analysis methodology was used in order to identify the landslide distribution within Târnavelor Plateau based on five criteria (geology, altitude, slope, slope orientation and administrative units), taking into consideration also field Global Positioning System (GPS) observations (Roșian et al., 2016a).

Landslide identification was made using 1:5000 orthophotos, based on which, using a GIS software (ArcMap 10.2), landslides were vectorized using its Editor function. Also, field observations were made and where landslide delimitation was not possible by ortophotoplans, the GPS method was applied; the information from field observations were then downloaded and introduced into a GIS in order for them to be processed (Roșian et al., 2016b).

Subsequently, based on the classes of each criterion, (geological age, altitude intervals, slope values, orientation type etc.) the landslides were analyzed to identify their distribution and extension. For this purpose, we identified the areas exposed to landslides by using Esri's ArcGIS toolbox Spatial Analyst tools/Zonal/Tabulate Area tool which computes the areas for each class defined by the analysis, it uses the classes as defined zones and computes the area which is affected by the studied phenomena. We also analyzed the number of slides in each class, this was accomplished by identifying the gravitational point of every vectorised landslide polygon, and this point was used to compute density (Roșian et al., 2016a).

RESULTS AND DISCUSSIONS

After vectorizations of landslides from orthophotos, the statistics say that in the Târnavelor Plateau, there are 5.797 landslides which represent 47.930 ha. Given that the geographic unit surface is of 78.0916 ha, it results that 6,13% of its surface is affected by landslides.

From a landslide distribution perspective, starting from the five criteria taken into consideration, we reached the following results.

From a geological point of view, Burdigalian, Badenian (marls), Sarmatian (marl clay) and Pannonian deposits (clays) prevail along with the Quaternary deposits (Pleistocene and Holocene). As it results from figure 2 and table 1, landslides mostly affect the areas belonging to the Pannonian era.

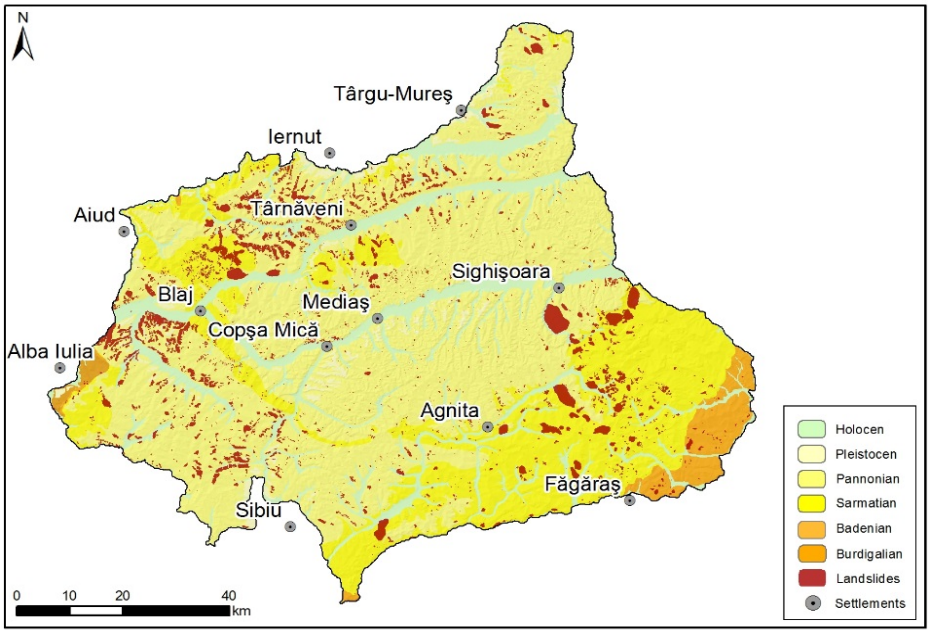

Fig. 2. Târnavelor Plateau Geological map

Table 1. Landslide distribution based on geological deposits

Geological deposits	Landslide number	Landslides area (ha)	Percentage (%)
Holocene	259	2228	6
Pleistocene	67	345	1
Pannonian	3765	29548	61
Sarmatian	1613	15110	30
Badenian	76	660	1
Burdigalian	17	39	1
Total	5797	47930	100

In order to observe landslide distribution from an altitude perspective, six altitude classes were chosen: 216 - 300 m, 300 – 400 m, 400 – 500 m, 500 – 600 m, 600 - 700 and 700 – 808 m (figure 3). As it results from table 2, the majority of landslides belong to the altitude range 400 – 500 m and the largest surface is also specific to the 400 – 500 m range.

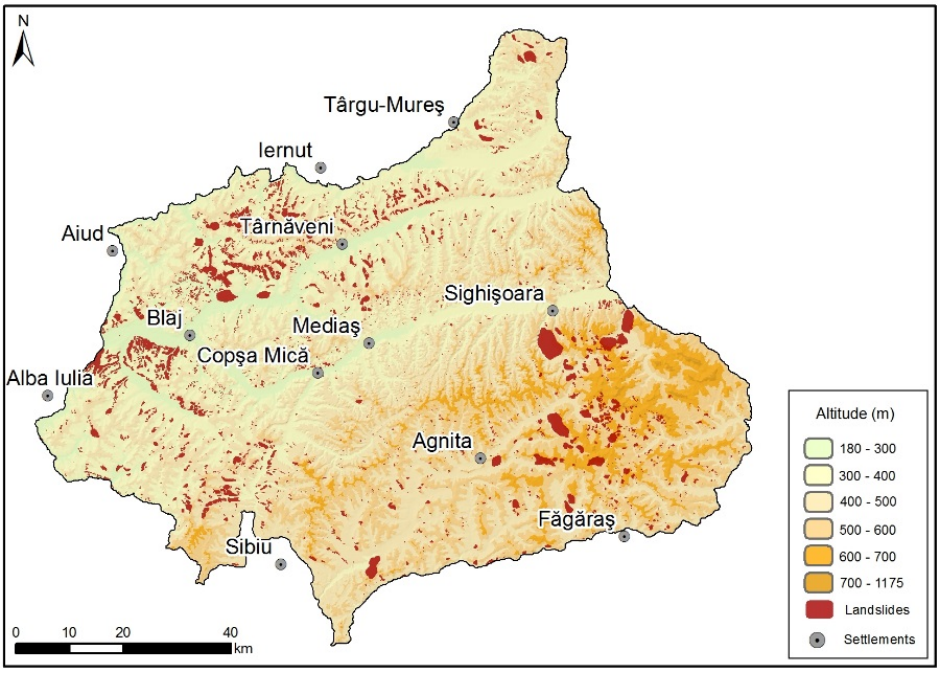

Fig. 3. The map of altitude range

Table 2. Landslide distribution based on altitude range

Altitude range (m)	Landslide number	Landslide surface (ha)	Percentage (%)
216 - 300	216	3070	6
300 - 400	2243	16493	34
400 – 500	2230	17593	37
500 – 600	973	9014	19
600 – 700	135	1760	4
700 - 808	0	0	0
Total	5797	47930	100

Another indicator of landslide distribution is represented by slope. Starting from the previous field classifications depending on slope, for the Târnavelor Plateau seven classes were chosen: 0 – 2º, 2 – 5º, 5 – 7º, 7 – 12º, 12 – 17º, 17 – 22º şi 22 – 45º (figure 4). As it can be noticed on table 3, the majority of landslides belong to the 7º – 12º slope category and the largest surface is specific to the same range.

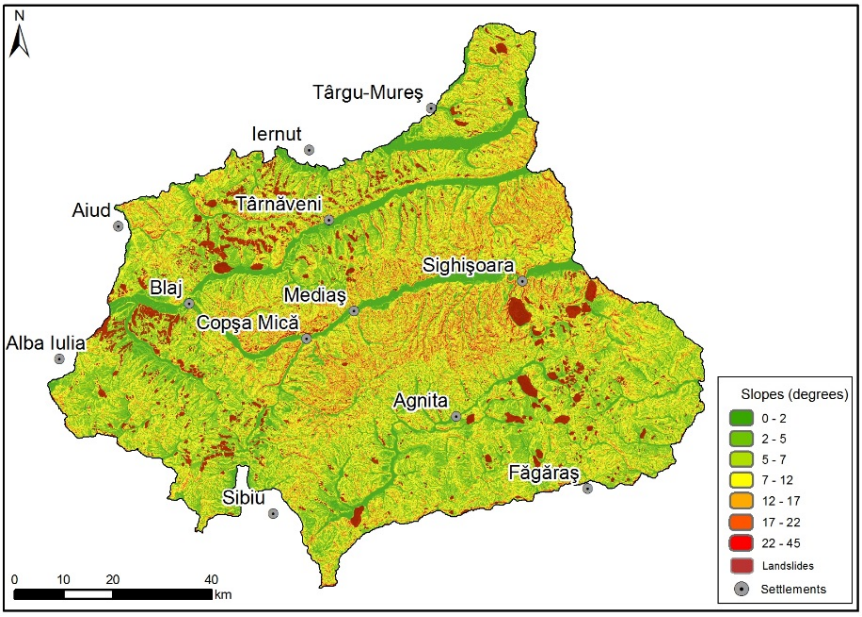

Fig. 4. Slope map

Table 3. Landslide distribution based on slope categories

Slope category (º)	Landslide number	Landslide surface (ha)	Percentage (%)
0 - 2	15	910	2
2 - 5	254	8,835	18
5 - 7	634	9,769	20
7 – 12	2,476	21,041	44
12 - 17	1,622	5,876	12
17 - 22	620	1,126	3
22 – 45	176	373	1
Total	5,797	47,930	100

An important criterion taken into consideration to observe landslide distribution is represented by slope orientation (figure 5). The exposure to the sun energy decisively determines the heat condition, soil and humidity, it influences the freezing-melting processes, the type and nature of the superficial deposits on the slopes and leads to qualitative differences in the ongoing processes preceding erosion (Jakab, 1979). In table 4, one can notice that the surfaces that have a southwest orientation are the mostly affected slopes by landslides. Also, from a surface perspective, the highest values are specific to western slopes. This means that on the southwest slopes are more landslides but they have smaller surfaces compared to those with a western exposure (less numerically, but have larger surfaces).

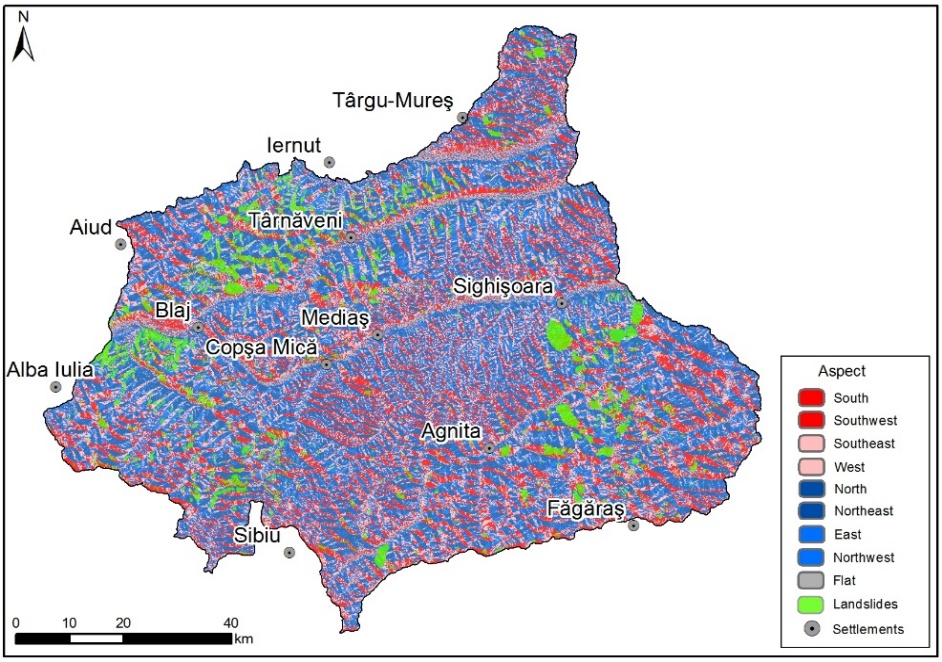

Fig. 5. Landform exposure map

In regards to landslide distribution we took into consideration also the local administrative units, for the Târnavelor Plateau. We considered this subdivision because al territorial planning and future interventions, with national or international budgets, are limited by the administrative hierarchy and so it represents a must in the present situation landslide and erosion analysis and statistics.

Table 4. Landslide distribution based on exposure

Exposure towards to the sun	Exposure towards compass directions	Landslide number	Landslide surface (ha)	Percentage (%)
Sunny	South	953	7,163	15
	South-West	1,243	8,837	18
Partial sunny	South-East	644	5,326	11
	West	1,103	9,380	21
Shady	North	396	3,720	8
	North-East	299	2,538	5
Partial shady	East	415	3,675	7
	North-West	744	7,291	15
Flat (unexposed)		0	0	0
Total		5,797	47,930	100

So, the following situation unfolded: there are 168 administrative units of which 149 are affected by landslides. The situation of the ten most affected administrative divisions from the landslide extent and number is shown in the tables 5 and 6.

Table 5. Landslide distribution at the local administrative units level by affected areas

Name	Studied territory surface (ha)	Landslide surface (ha)	Percentage of the affected surface (%)	Number of landslide
Şona	10,566	2,673	25	112
Apold	12,536	2,648	21	47
Saschiz	9,785	1,853	19	45
Şoarş	17,247	1,767	10	124
Loamneş	9,903	1,351	14	104
Fărău	7,984	1,334	17	140
Blaj	8,340	1,304	16	85
Iacobeni	10,326	1,256	12	48
Jidvei	10,495	1,168	11	69
Brădeni	8,156	1,150	14	60

Table 6. Local administrative units landslide distribution by landslide number

Name	Studied territory surface (ha)	Number of lanslide	Landslide surface (ha)	Percentage of the affected surface (%)
Jibert	16,481	188	1,107	8
Sâncel	5,171	166	354	7
Alma	3,423	163	111	3
Micăsasa	8,897	156	362	4
Fărău	7,984	140	1,334	17
Lopadea Nouă	9,226	133	396	4
Şoarş	17,247	124	1,767	10
Bîrghiş	9,986	114	206	2
Şona	10,566	112	2,673	25
Adămuş	8,115	112	1,119	14

The values showed in table 6 suggest that even if for some of the territorial-administrative divisions there are a high number of landslides, their surface is relatively small.

In regards to landslide type, in most of the cases, these are of a superficial and of medium depth according to Varnes classification (Varnes, 1978). Their large number is tightly bound, along with the land use, also to the geological characteristics. They are Miocene age formations that belong to Badenian, Sarmatian and Pannonian. For Badenian marls are typical, for Sarmatian marly clays, sand and tuff and for Pannonian clays, sands and poorly cemented sandstones. These clays have in their composition montmorillonite, illite and beidellite mineral which can retain water. Taking into consideration that it is a hilly area made of the mentioned lithology, there is a highly susceptibility to landslides.

Hence, from the perspective of a spatial distribution analysis, the conclusions that can be drawn are, that the most affected by landslides are the areas overlapped with Pannonian deposits, those on an altitude range of 400 - 500 m and those which have an angle of inclination of 7-12 degrees, but also those with a west orientation. At the administrative units level the most affected are: Șona, Apold, Saschiz, Șoarș, Loamneș, Fărău, Blaj, Iacobeni, Jidvei, Brădeni, Jibert, Sâncel, Alma, Micăsasa, Lopadea Nouă, Bîrghiș, Adămuș etc.

CONCLUSIONS

When all the observed landslide aggravation factors come together we need to take actions against landslides within the area of the Târnavelor Plateau. Considering also the susceptibility of the area to other type of hazardous geomorphologic phenomena, along with the combative measures, preventive measures are also necessary. It is recommended, in this regard, the change of the used agricultural technique, by preventing slopes hydric oversaturation with a quick drainage of precipitation, rivers or groundwaters.

Given the number of landslides and the areas affected by them, in the Transylvanian Depression, it is necessary to extend the research method to all the other regional subunits of Transylvania, trying to illicit information regarding all the factors affecting the landslide phenomena and to construct a general spatial GIS model for the areas susceptibility.

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OPTIMIZATION OF LIDAR SYSTEMS MEASUREMENTS FOR DETECTION OF CLEAR AIR TURBULENCE

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ABSTRACT. In this paper we analyse the optimization of lidar systems in order to investigate Clear Air Turbulence (CAT), which is a dangerous weather phenomenon affecting especially the commercial aircrafts. It is assumed that aircrafts can cause air turbulence that can be detected by lidar, since pressure gradients could cause slight variations of the molecular depolarization values. This study will assess the capability of the lidar systems to highlight air turbulence from depolarization profiles. In order to do this, lidar measurements were performed at two sites in Romania: one in Magurele, near Bucharest and one in Cluj-Napoca. The measurements were accompanied by continuous flight path monitoring to mark the incidence events above the measuring locations.

Keywords: *lidar, CAT- Clear Air Turbulence, aircrafts*

INTRODUCTION

One of the most dangerous aviation hazards is represented by the Clear Air Turbulence (CAT). CAT is defined as the turbulent movement of air masses in the absence of any visual clues, such as clouds. It is caused when bodies of air moving at widely different speeds meet (Stull, 1988). Usually this is a high altitude, sudden phenomenon encountered outside of convective clouds that causes violent buffeting of aircrafts. The part of the flight most prone to injuries from CAT is the cruising phase, because passengers and crew are often unbuckled (Sharman et al., 2006). CAT produces one of the largest causes of weather-related aviation accidents, accounting for 24% of all weather related accidents (Kim and Chun, 2011). Storer et al., in a 2017 study, noted that currently there are strong increases in the number of clear air turbulence over the entire globe, especially in mid latitudes where the busiest flight routes are located.

Remote sensing instruments, such as lidar systems and sun radiometers are currently widely used for measuring atmospheric dynamics and optical and microphysical properties of different components like clouds and aerosols (Calinoiu et al., 2018). Lidar techniques for atmospheric studies are one of the most powerful tools used in studying the composition and vertical structure of the atmosphere.

In this paper we analyse the optimization of lidar systems in order to investigate the Clear Air Turbulence phenomena. This work was done during the first measurements campaign within the CONTUR - Emerging Technologies to Counteract the Effects Induced by the Turbulent Flows of Fluid Environments 87PCCDI/2018 research project. This project aim is to develop emerging technologies to counteract effects induced by the turbulent flows. It is divided into two complementary component projects: the first one is dedicated to the study of the clear air turbulence, while the second is aimed at designing new active control technologies to reduce vibrations (Radu et al., 2018). The main objective of the campaign was to assess the detection capabilities of the Clear Air Turbulences by using the lidar systems from 2 sites in Romania: Măgurele, near the capital city of Bucharest and Cluj-Napoca in north-western part of Romania. The campaign focused on the detection of turbulences produced by large aircrafts – the wake turbulences.

EXPERIMENTAL

It is assumed that airplane's wings and engines can cause air turbulence that can be detected by lidar systems, since pressure gradients could cause slight variations of the molecular depolarization values. The Raman lidar systems detect the Raman backscattering radiation from atmospheric molecular nitrogen and water vapour and Mie / Rayleigh backscattering radiation from atmospheric molecules and aerosol particles. Two multi-wavelength Raman depolarization lidar systems capable of measuring molecular depolarization at 532 nm (Belegante et al., 2018, McCullough et al., 2017) were used during the CONTUR campaign.

One system – RALI – is located at the National Institute for Research and Development in Optoelectronics INOE 2000 in Măgurele, near Bucharest. The laser emission wavelengths are 1064 nm (90mJ), 532 nm (50mJ) and 355 nm (60mJ) and the detection channels are 1064, 532 cross, 532 parallel, 355 nm (elastic wavelengths), and 607, 387 and 408 nm (Raman channels). The laser pulse duration is 7-9 ns, repetition rate 10 Hz, and the beam diameter between 5.5-7 mm. The dynamic range covers 2-15 km depending on atmosphere transmission, with a 3.75 m spatial resolution. The reception has a 400 mm Cassegrain telescope with 1.73 mrad field of view, and the system acquisition is both analogue and photon counting, with a 20 MS/s analogue sampling rate and 250 MHz photon counting count rate. The output parameters are the backscatter coefficient, the extinction coefficient, water vapour mixing ratio (for 407 nm), particle depolarization ratio for 532 nm (Belegante et al., 2015).

The second LIDAR system – CLOP – is located at the Faculty of Environmental Science and Engineering within the Babes-Bolyai University, in Cluj-Napoca. The emission system is based on a Nd:YAG laser (Continuum INLITE II -30) with a repetition rate of 30 Hz. The laser beams at 1064 nm, 532 nm and 355 nm are simultaneously emitted into atmosphere. The dynamic range covers 2-12 km depending on atmosphere transmission, with a 3.75 m spatial resolution. The backscattered radiation is collected by a Raymetrics D300 Cassegrain type telescope with a focal length of 1500 mm. The signal detection unit has 4 detection channels, acquisition being both analogue and photon counting, for the elastically backscattered radiation at 1064, 532

(cross and parallel) and 355 nm and 2 detection channels for the Raman radiation backscattered from the N_2 molecules at 607 and 386 nm (Ajtai et al., 2017).

In order to obtain the lidar profiles, measurements were divided into data sets with 3 integration times: high (1 minute), average (30 seconds) and small (15 seconds), corresponding with the temporal scale of this type of turbulence. The measurements were accompanied by continuous flight path monitoring to mark incidence events above the measuring location. For this, an area of interest was defined, which included several degrees of incidence with flights in transit over stations (200, 500, 1000 and 2000 m) (figure 1).

Fig. 1. Distances of interest overlapping the 2 lidar systems:
a. Măgurele b. Cluj-Napoca

RESULTS AND DISCUSSION

The testing campaign to detect CAT events took place between 10 and 14 September 2018. The campaign was focused on the detection of turbulent phenomena caused by the passage of large - scale airplanes - wake turbulence. This type of turbulence can be marked in space and time by continuous air traffic monitoring over the two sites with lidar systems at INOE 2000 (National Institute for Research and Development in Optoelectronics, Bucharest and UBB (Babes-Bolyai University), Cluj-Napoca, Romania).

Profiles obtained during the campaign did not highlighted patterns that may be associated with turbulence events. At Cluj-Napoca station, out of a total of 86 flights, only 6 cases where within the 500 m radius as seen in table 1. At Bucharest station 5 cases where within the 500 m radius out of a total of 15 flights within the 2000 radius.

Table 1. Flights within a 500 m radius of the LIDAR sounding point at Cluj-Napoca station

Date	Time	Altitude (m)	Ground speed (km/h)	Airplane type	Estimated distance from LIDAR sounding point (m)
10.09.2018	14:23	9,140	770	Boeing 777	190
10.09.2018	14:58	9,750	760	McDonnell Douglas	200
13.09.2018	9:05	10,360	820	Airbus A 321	160
13.09.2018	10:35	876	285	Airbus A320	395
13.09.2018	11:39	1,700	390	Boeing 737	410
13.09.2018	13:43	2,725	330	ATR 42	175

In order to assess the performances of the lidar systems, the profiles with the shortest integration time (15 seconds) were analysed. The most suitable integration time for obtaining the LIDAR profiles coincided with the lowest possible statistical error as this was the main indicator for determining the quality of the signal.

The obtained lidar profiles show a good signal to noise ratio for altitudes up to 3 km in all cases. After the smoothing process was applied to the lidar profiles, one can observe an improvement in the signal, but even in this case, the systematic error shows a good signal up to maximum 4 km for Măgurele station (figure 2) and maximum 5 km for Cluj-Napoca station (figure 3). In the case of night measurements performed in 13.09.2018 at Măgurele station, one can observe that the relative error is improving and the profiles are useful up to 8 km as seen in figure 4. This is due to the reduced signal noise specific to the lidar night measurements.

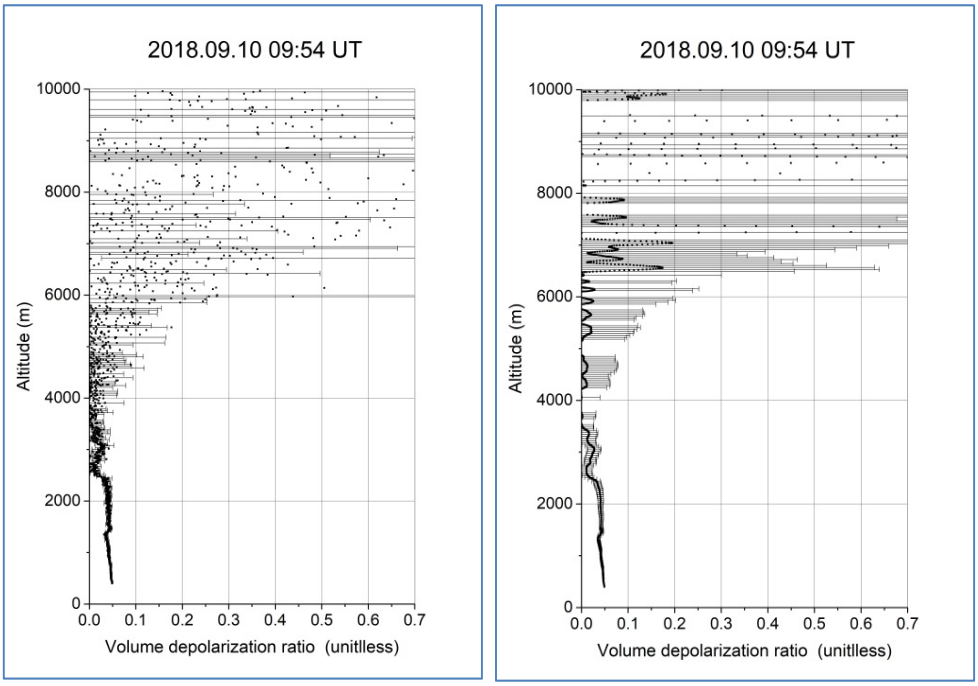

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Fig. 2. Volume depolarization ratios profiles for 10.09.2018, Măgurele, at 15 seconds: a. raw signal, b. smoothed signal

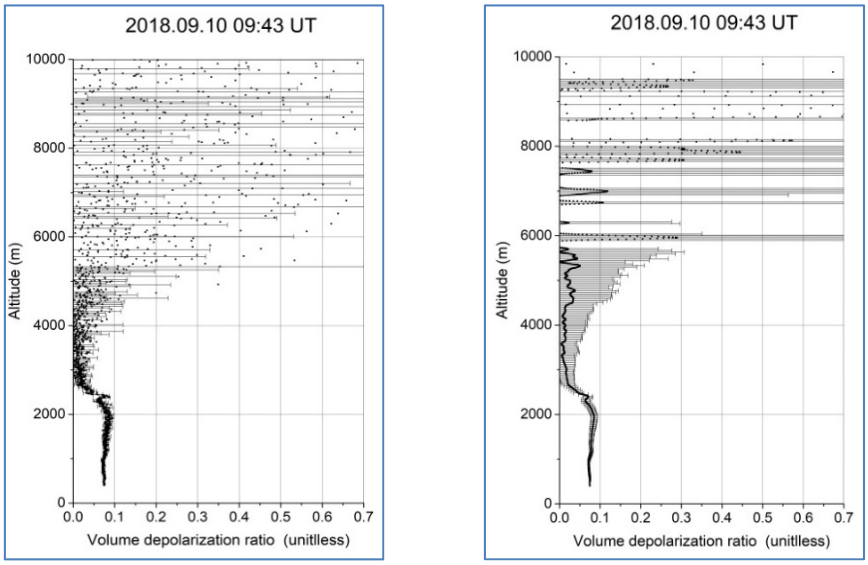

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Fig. 3. Volume depolarization ratios profiles for 10.09.2018, Cluj-Napoca, at 15 seconds: a. raw signal, b. smoothed signal

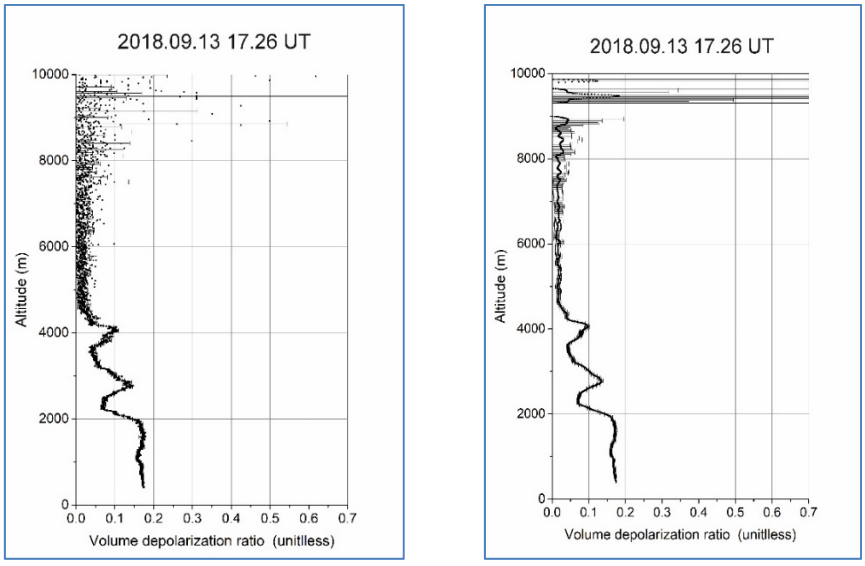

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Fig. 4. Volume depolarization ratios profiles for 13.09.2018, Magurele, at 15 seconds: a. raw signal, b. smoothed signal

CONCLUSIONS

During the first CONTUR ("Emerging Technologies to Counteract the Effects Induced by the Turbulent Flows of Fluid Environments 87PCCDI/2018 research project") campaign that focused on the investigation of air turbulence events, lidar depolarization profiles were used together with CCD imaging to monitor the airplane overpass occurrences over Măgurele and Cluj-Napoca for assessing the performance of CAT detection.

By analysing the measurements, we concluded that integration times of 15 seconds and lower should be used in the next campaigns in order to be able to identify the air turbulences. Lidar profiles indicated a useful signal up to 5 km for daytime for both lidar systems, while for night time the useful signal was up to 8 km. The contrails produced by aircrafts engine exhaust or changes in air pressure may have an influence on the depolarization profiles. Based on these findings the next campaign aims to conduct night-time measurements at low integration times, 15 seconds and lower, focusing on altitudes upwards of 6 km for a greater chance of turbulence detection.

Acknowledgements

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