BABEȘ-BOLYAI UNIVERSITY
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-Summary of PhD thesis-

SOIL POLLUTION BY HEAVY METALS. HEALTH AND ENVIRONMENTAL IMPACT ASSESSMENT.

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Key Words: *Copșa Mică, soil pollution, heavy metals, health programs.*

CONTENTS

CAP. 1. INTRODUCTION

After 1990, Copșa Mică became known as *”the most polluted town in Europe”.* The main cause of the pollution is tied to the industrial past of the town. After numerous cases of occupational diseases within the metallurgic industry (I.M.M.N.), due to lead exposure (Bardac, 1999), environment protection and population health became important topics.

Over the last years, the activity of metallurgical plant has scaled down, being almost shut down entirely, due to this, atmospheric emissions have decreased significatively. However, the soil of Copșa Mică continues to be polluted with heavy metals (Lăcătușu, 2014; Szanto et al., 2012), having a long persistence, between decades and thousands of years (Kabata-Pendias, 2001), which means that the exposure to heavy metals remains a risk for the population health.

Health studies conducted in the area (Gurzău et al., 2010; Gurzău&Neamțiu, 2010; Gurzău&Bardac, 2002) showed that in Copșa Mică blood lead levels in children is approximately 7 times higher than the reference level set by CDC (Centers for Disease Control and Prevention USA). According to the study conducted by Gurzău et al. (2010), the main exposure pathways to heavy metals are throught ingestion of soil particles, ingestion of home-grown vegetables, inhaling of dust, the children being most exposed.

In the context of low atmospheric emissions and the polluted soil wich is a permanent exposure source for the population, assessment of the levels of heavy metals in the soil and the dust were made, along with analyses statistics regarding the correlation between them and assessment of the exposure doses of the population to heavy metals in the soil. The results are important for having a scientific foundation in order to create and implement health programs, the purpose being to stop or decrease the exposure of heavy metals and improving the population health of Copșa Mică.

1.1. Thesis structure

In order to achieve the purpose and objectives of the PhD thesis, it was structured into two parts, as follows:

The first part, theoretical one, presents a synthesis of specialized literature regarding the non-ferrous metallurgic industry, the environment aspects and associated health problems, the general framework for the research that was outlined and the industrial history of the town that was described.

In the second part, which presents personal contributions to the thesis, analysis have been conducted regarding the quality of the soil, the content of heavy metals from the indoor and outdoor dust. Next, it has been established if there was a statistic correlation between them. The exposure of the population to the heavy metals in the soil was evaluated. The results of researches can be used in order to develop future health program for the population of Copsa Mică, starting from a scientific base.

The first part of PhD thesis consists of three chapters:

- **Ch. 1 Introduction**
- **Ch. 2 Review of specialized literature. Non-Ferrous Metallurgy. Environmental pressures and population health effects.**

  In this chapter an analyses of specialized literature has been conducted regarding the non-ferrous metallurgy and its environmental effects in correlation with the production of Pb, Zn and Cd.

  An analysis has been conducted concerning the pollution of the soil with heavy metals and their transfer, especially through dust and the health effects was detailed.

  A synthesis of studies from polluted areas due to non-ferrous metallurgy has been conducted at a regional level (in Europe) and a local level (in România: Zlatna, Baia Mare, Copșa Mică).
- **Ch. 3 General framework of research. The town of Copșa Mică**

  In this chapter, the analysis of the general framework of the research, of the physico-geographical conditions of the town with the local particularities that favor the transport or the stagnation of atmospheric pollutants in the area was carried out. The industrial past of the town has been investigated in order to identify its particularity pollution sources and a synthesis has been performed regarding the pollution of the soil with heavy metals, the levels of heavy metals within the dust and the evolution of the health of the population of Copșa Mică.

The second part of PhD thesis consists of six chapters:

- **Ch. 4 Personal contribution. Motivation, purpose, objectives, research methodology.**

  The chapter details personal contribution to the PhD thesis, showing the framework of the problem, the purpose, objectives, the study model and the research methodology.

- **Ch. 5 Assessment of heavy metals content in the soil**

  The chapter details the field research methods, the laboratory analytical methods and the statistical analysis methods for the data obtained in the laboratory.

  The soil quality was assessed for the two research campaigns, 2014 and 2018, the results of the statistical analysis for the Pb, As, Cd, Cu and Zn contents being presented, which are compared with the environmental standards; the soil pollution level was evaluated with the pollution indices method (PLI and PI) and distribution maps of heavy metals for soil of Copșa Mică town being created.

- **Ch. 6 Assessment of heavy metals content in indoor and outdoor dust of the houses**

  The chapter details the field research methods, the laboratory analytical methods and the statistical analysis methods for the data obtained in the laboratory.

  The heavy metals content in indoor and outdoor dust of the houses was analyzed, in 2014, the results of the statistical analysis for the content of Pb, Cu and Zn in the dust being presented and the distribution maps for the heavy metals in the dust of Copșa Mica town being created.

- **Ch. 7 Statistical analysis of the relationship between the heavy metals content in the soil and dust.**

  The chapter presents the results of the statistical analysis by the simple linear regression method and the correlation for the level of heavy metals in the soil and in the dust, as well as for the level of the heavy metals in the outdoor and indoor dust from the houses.

- **Ch. 8 Assessment of exposure to heavy metals and health programs in Copșa Mică.**

  This chapter presents a summary description of the population of Copșa Mică, the results of the exposure assessment to heavy metals from the soil, and the distribution maps for the exposure doses for the population groups: adults, children and *pica child*.

- **Ch. 9 Conclusions.**

  The last chapter presents general conclusions of the research and possible solutions for implementation a health program in Copșa Mică in order to stop or decrease the population exposure to heavy metals in soil and dust.

1.2. The purpose and objectives of the PhD thesis

The purpose of the PhD thesis *"Soil pollution by heavy metals. Health and Environmental Impact Assessment."* is to obtain a current image regarding the concentration of heavy metals in the soil and dust and to establish a correlation between the two, to evaluate the exposure of the population to heavy metals in the soil, to obtain a scientific base for future health programs in Copșa Mică.

Objectives of the PhD thesis:

1. The analysis of the specialized literature and researches carried out in the field of heavy metal pollution from non-ferrous metallurgy and obtaining an image regarding the pollution history in Copșa Mică.
2. The analysis and processing of new data sets obtained from Copșa Mică, in order to assess the quality of the soil and heavy metal content of the dust from outdoor and indoor the houses.
3. Establishing a relationship between the heavy metal content in soil and outdoor and indoor dust, to understand the percentage in which the heavy metal content in the soil could be determinant for the heavy metal content in the dust.
4. Assessment of population exposure to heavy metals in soil.
5. Identification of future measures to stop or reduce the exposure to heavy metals in soil and dust in order to improve the population health of Copșa Mică.

1.3. Stages of the research

The research it was carried out in four stages, as follows:

In the first stage of the research, the specialized literature and the available studies of heavy metal soil pollution in the areas affected by non-ferrous metallurgy were analyzed. Along with that, studies carried out in Copșa Mică were consulted, the annual reports on the state of the environment published by the Environmental Protection Agency Sibiu and the projects implemented by authorities in the area.

In **the second stage of the research, in 2014**, there were field activities for soil and dust sampling from population households and laboratory activities for the preparation and analysis of samples. A number of 60 soil samples and 80 dust samples were obtained from households.

In **the third stage of the research, in 2018**, field activities were conducted for soil sampling from public areas and laboratory activities for sample preparation and analysis. A number of 27 soil samples were obtained from the public areas (schools, kindergartens, playgrounds, sports fields, market-supermarket, etc.).

In **the fourth stage of the research, in 2018 and 2019**, the results obtained in the laboratory were processed and the present thesis was elaborated.

1.4. Research methodology

In Table 1 is an overview of the methodology used in the research, with references to the corresponding chapters of the thesis where the detail was made and arguments for the method were presented.

Table 1 – Research metodology

Thesis Chapter	Thesis Objective	Research methodology	Method detailed and motivation / chapter
Ch. 5.	**O2:** The analysis and processing of new data sets obtained from Copșa Mică, in order to assess the quality of the soil and heavy metal content of the dust from outdoor and indoor the houses.	The method to analysis of soil samples: X-Ray fluorescence (XRF) spectrometry, US EPA Method 6200. The method of calculation pollution indices – PLI, PI. The method of statistical analysis and geostatistical: descriptive statictis, histograms, correlation, Kriging interpolation for distribution maps (soft ArcGIS).	**Ch. 5.2.**
Ch. 6.		The method of sampling dust in accordance with *OSHA Techical Manual (OTM), Section II, Chapter 2, Apendix C Procedure for Collecting Wipe Samples*. The method of analysis of dust samples – X-Ray fluorescence (XRF) spectrometry. The method of statistical analysis and geostatistical: descriptive statistics, histograms, correlation, Kriging interpolation for distribution maps (soft ArcGIS).	**Ch. 6.2.**

Thesis Chapter	Thesis Objective	Research methodology	Method detailed and motivation / chapter
Ch. 7.	**O3:** Establishing a relationship between the heavy metal content in soil and outdoor and indoor dust, to understand the percentage in which the heavy metal content in the soil could be determinant for the heavy metal content in the dust.	The advanced statistical analysis: the correlation and simple linear regression, ANOVA test.	**Ch. 7.2.**
Ch. 8.	**O4:** Assessment of population exposure to heavy metals in soil.	The calculation method of population exposure to heavy metals: software used by ATSDR. The geostatistical method: Kriging interpolation for distribution maps in the town of Copșa Mică.	**Ch. 8.2.**

CAP. 2. REVIEW OF SPECIALIZED LITERATURE. NON-FERROUS METALLURGY. ENVIRONMENTAL PRESSURES AND POPULATION HEALTH EFFECTS

Following the synthesis of the specialized literature, it was found that the main environmental aspect associated with non-ferrous metallurgy is heavy metal pollution (Nriagu, 1996; Ettler, 2015; Cusano et al., 2017), with important concentrations being monitored in the soil, where they accumulate and have a long persistence (Wuana et al., 2011).

The pollution of soils with heavy metals from non-ferrous metallurgy occurs directly through the storage of raw materials and waste, but also indirectly through atmospheric deposits. If soil pollution has occurred through atmospheric deposition, the degree of soil pollution decreases with distance from the source, but it has also been identified over long distances, pollutant transport being influenced by the prevailing winds (Ettler, 2016). Such an example is soil pollution reported in the area of Micăsasa locality in Sibiu, a locality situated at approx. 9 km distance from Copșa Mică, downstream on the Tarnavei Mari valley, because the prevailing winds are by corridor of the river. Soil pollution was detected up to the area of Mediaș municipality, located upstream on the Târnavei Mari valley.

Regional and local studies conducted in areas affected by the non-ferrous metallurgical industry, have concluded that heavy metals pollution is higger on top soils, here being recorded the highest concentration of de Pb, As, Cd, Cu and Zn (Derome&Lindroos, 1998; Steckerman et al., 2000; Kabala&Singh, 2001; Burt et al., 2003; Ettler et al., 2004; Martley et al., 2004; Neaman et al., 2009; Kribek et al., 2010; Li et al., 2011, Chrastny et al., 2012; Vanek et al., 2013; Podolsky et al., 2015, citați de Ettler, 2016). In case of agricultural soils, lower concentrations of heavy metals have been explained through interventions on the soil, through agricultural work has the effect of *dilluting* the concentration of pollutants from topsoil (Rieuwerts&Farago, 1996; Ettler et al., 2005; Douay et al., 2009; Chrastný et al., 2012; Vanek et al., 2013, citați de Ettler, 2016).

The transfer of heavy metals from the soil are through depth *migration*, through the transport of surface water, through bioaccumulation inside living organisms, but also through particle suspension an resuspension from the surface. A series of studies (Young et al., 2002; Harris&Davidson, 2009; Hillel, 2008; Sullivan&Ajwa, 2011) have shown that heavy metal (Pb) transfer by air it is possible through particle suspension on the surface of the soil, in favorable conditions with soil dryness and mechanical agitation, denuded lands can become important pollution sources.

In areas with non-ferrous metallurgy, the population is exposed to heavy metals mainly by ingesting soil particles, or by consuming home-grown vegetables, by ingesting and inhaling dust from surfaces or from the air (Gurzau et al. 2008, 2010).

The most vulnerable population groups to exposure to heavy metals are children, pregnant women and also adults over 50 years (Gurzau et al. 2008, 2010). Children are exposed to higher amounts of heavy metals than adults due to the habit of hand-to-mouth, by putting their hand or toys in or around their mouths, by playing on the surface of the soil, by having behaviors that favor ingestion of particles with heavy metal content. In their case, the absorption of heavy metals in the body is higher than in adults because of the higher daily ingested doses and lower body weight.

The effects of heavy metals on population health have been documented through a series of researches (Wani et al., 2015; CDC, 2014), finding that chronic exposure leads to the accumulation of heavy metals in the body and serious diseases, some even lethal. Heavy metals such as Pb, Cd and As have extremely serious effects on population health at chronic exposure, even at low concentrations, for instance, the saturnism that appears at exposure to Pb, or Itai-Itai at exposure to Cd. Arsenic can have lethal effects upon intense exposure, such as the inorganic As form, recognized as poison in history. Cu and Zn are considered to be essential elements for health, but at high concentrations, they can produce toxic effects.

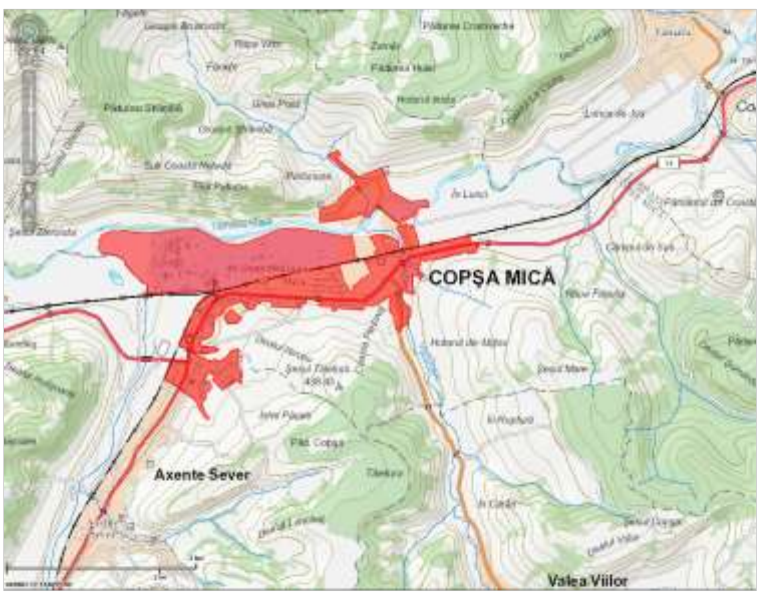
Due to the long persistence, the exposure of the population to heavy metals in soil and dust is a current health problem in Copșa Mică, generating health risks, even if industrial activities have been reduced.

CAP. 3. GENERAL FRAMEWORK OF RESEARCH. THE TOWN OF COPȘA MICĂ

Chapter 3 described the general framework of Copșa Mică and the local aspects that favor or not the transport of atmospheric pollutants over long distances. The industrial development and the history of pollution in the area were documented and a synthesis of the researches that investigated the soil pollution, the content of heavy metals in dust and the effects on the health status of the population in Copșa Mică was made.

From the physical-geographic point of view, Copşa Mică is located in the geomorphological *unit of the* Transylvanian Depression, in the central-southern part, the subunit of the Târnavelor Depression, a region drained by the middle course of the Târnava Mare. The town has a central position on the Târnava Mare river corridor, in a developed area with with well-defined river meadows.

Figure 1 – Location of Copșa Mică (*Source: ancpi.geoportal.ro*)



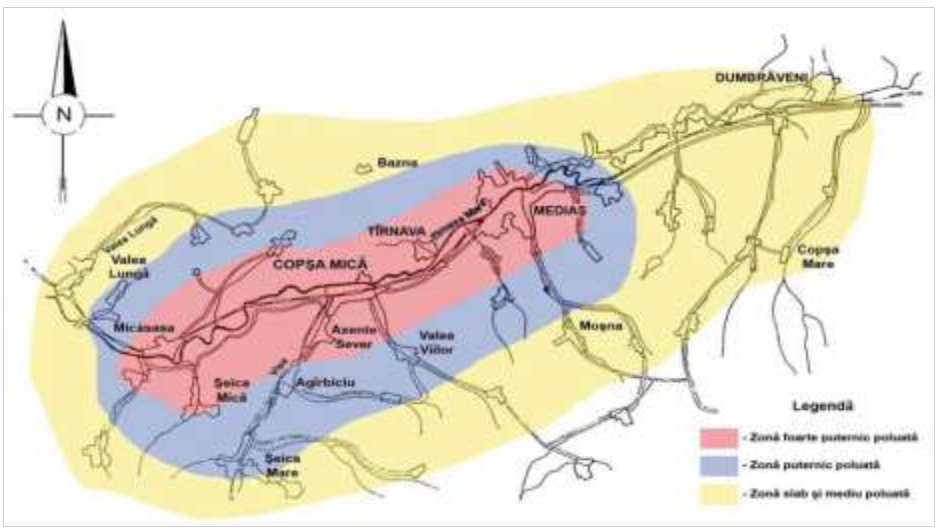
The town has developed predominantly on the left side of Târnava Mare. On the right side is present just the neighborhood of Târnăvioara, which in the past was an isolated village. The industrial platform where the chemical and metallurgical units functioned – CARBOSIM and SOMETRA, and nowadays ROMBAT, is located on the left bank of Târnava Mare, between the confluence with the stream Valea Viilor (la E, upstream) and the confluence with the river Visa (la W, downstream). The residential area of the town is mostly developed on the left side of the river, at S of the railway and the national road (DN14).

The relief of the area is specific to the valley, with an E - V orientation on the Târnavei Mare valley, a position that favors both stagnation and the transport of pollutants in the longitudinal direction. The transport of pollutants is influenced by the flow of the river and the seasonal climate data.

The soils in the area belong to the class of protisols (aluvisoil, entiantrosoil, regosoil), the pH of the soils is in the range 7-8 UpH (Szanto et al., 2012).

According to the documents published by the Environmental Protection Agency Sibiu (APM, 2010), it turned out that along the Târnava Mare valley, the area of polluted land amounted to 180,750 ha, of which 31,285 ha from forest fund and 149,465 ha agricultural land. Of these, a highly polluted area was estimated at 21,875 ha. In the Figure 2 are highlighted by distinct colors areas with different levels of pollution, as presented by APM Sibiu.

Figure 2 – Map of polluted area Copşa Mică-Mediaş (*Source: APM Sibiu – Integrated air quality management program in the area Copșa Mică-Mediaș, Sibiu, 2010*)



It can be observed that up to the area of Micăsasa, downstream from the source, but also upstream to Mediaș, at approx. 9-10 km away, the lands were classified as very heavily polluted, the transport of pollutants being made longitudinally on the Târnava Mare river path.

Regarding the land use, following field research, it has been observed that the majority of the population living in houses use gardens for fruit trees, vines and other crop plants that they use in their own households or for animals.

Regarding the groundwater, within Copșa Mică, it is at -3.0 - -4.5 m. Following the monitoring of groundwater body *ROMU05 - Meadow and the terraces of the Târnava Mare river,* in the area, the Cd concentration measured were higher than threshold value established by H.G. no. 53/2009 and by Order no. 137/2009 (limit value for Cd - 0.005 mg / l).

Following the field research it was highlighted that the majority of the population living in houses uses the groundwater (from wells) for watering the gardens and for cooking, as resulted from the discussions with the subjects included in the research.

In Copșa Mică (partial) the water supply and sewerage project has been implemented, unfinished investment yet, so the town owns at this moment, partially, a centralized system of drinking water supply to blocks and houses, or ponds and wells in the area of houses, this being another public health problem.

The average annual liquid precipitation is approx. 570 l/mp. The total annual level of precipitation is relatively low, which is a favorable factor for the presence of pollutants in the atmospheric air (APM Sibiu, 2010), but also for the suspension of fine particles from the soil surface.

Regarding the air quality in the area of Copșa Mică, the monitoring carried out by APM Sibiu showed the improvement of the air quality since 2009, which was due to the temporary cessation of the SOMETRA activity and, on restarting due to the reduction of the activity and the fact that a series of measures have been implemented: installation of filters with bags and scrubbers, casing and sealing of the main equipment for the elimination of fugitive emissions and the automation of the emissions.

As a result of the analysis, it was found that through the inadequate construction and placement of the industrial units in an area where the local physical-geographical and climatic conditions favored the accumulation, but also the long-distance transport of the atmospheric pollutants, it was registered the situation where an extended area to be affected by heavy metal pollution. The pollutants are found in concentrations that exceed the alert thresholds and sometimes the intervention thresholds for sensitive land use for Pb, Cd, Cu, Zn, and As (Damian F. et al., 2008).

Previous studies in the area (Lăcătușu, 2014; Szanto et al., 2012) have shown a high level of soil pollution and consequently effects on population health are present, especially in the case of the vulnerable groups (children). It is known that in the historically polluted areas there are registered statistical health data that exceed the national averages for the specific diseases caused by the presence of heavy metals in the environment, in Copșa Mică this being a current problem.

CAP. 4. ASSESSMENT OF HEAVY METALS CONTENT IN SOIL

4.1. Introduction

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 F. 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.

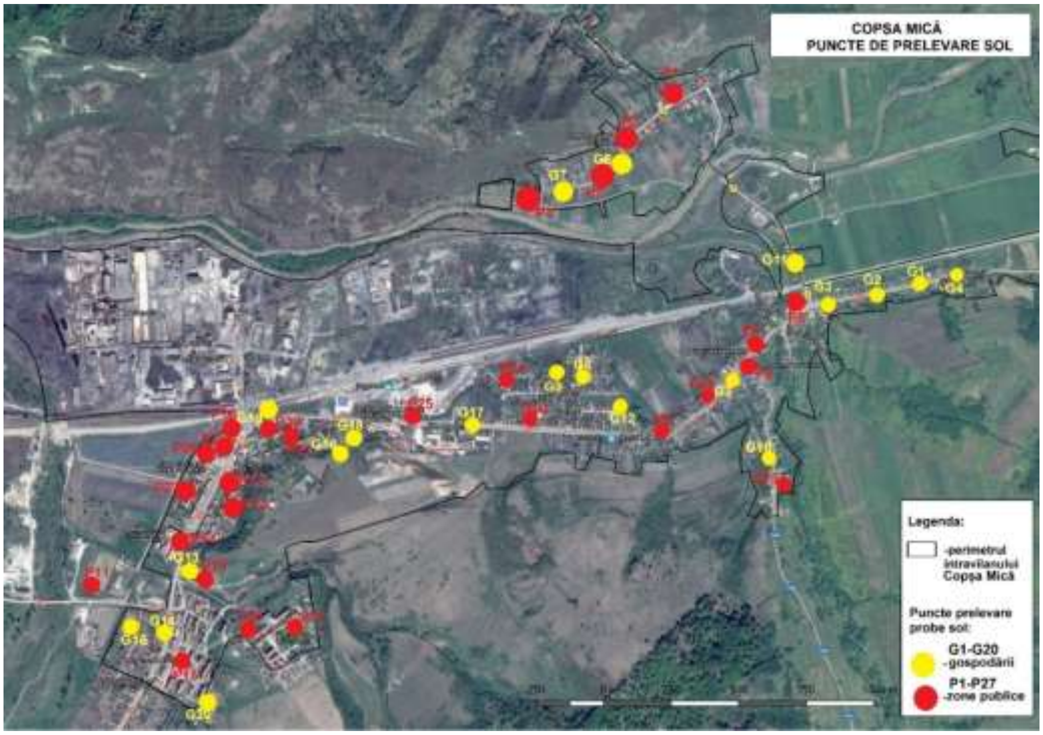
4.2. Materials and methods

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 E. 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 3.

Figure 3 – Copşa Mică, soil sampling points, 2014 and 2018



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:

$PLI = n\sqrt{}\ (PI_1 \times PI_2 \times PI_3 \times ...\ PI_n)$ (19)

where: n – number of pollutant assesses; PI – single pollutant index of each metal assesses.

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

$PI = Cn / GB$ (19)

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

PI levels and significance: $PI \leq 1$ – non polluted; $1 < PI \leq 2$ – slightly polluted; $2 < PI \leq 3$ – 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 (Uterman et al., 2006).

4.3. Results and discussions

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

Table 2 – *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 3 – *Values of the minimum, mean and maximum concentrations for cadmium (Cd), copper (Cu) and zinc (Zn) in soil, in different function areas (mg/kgSU)*

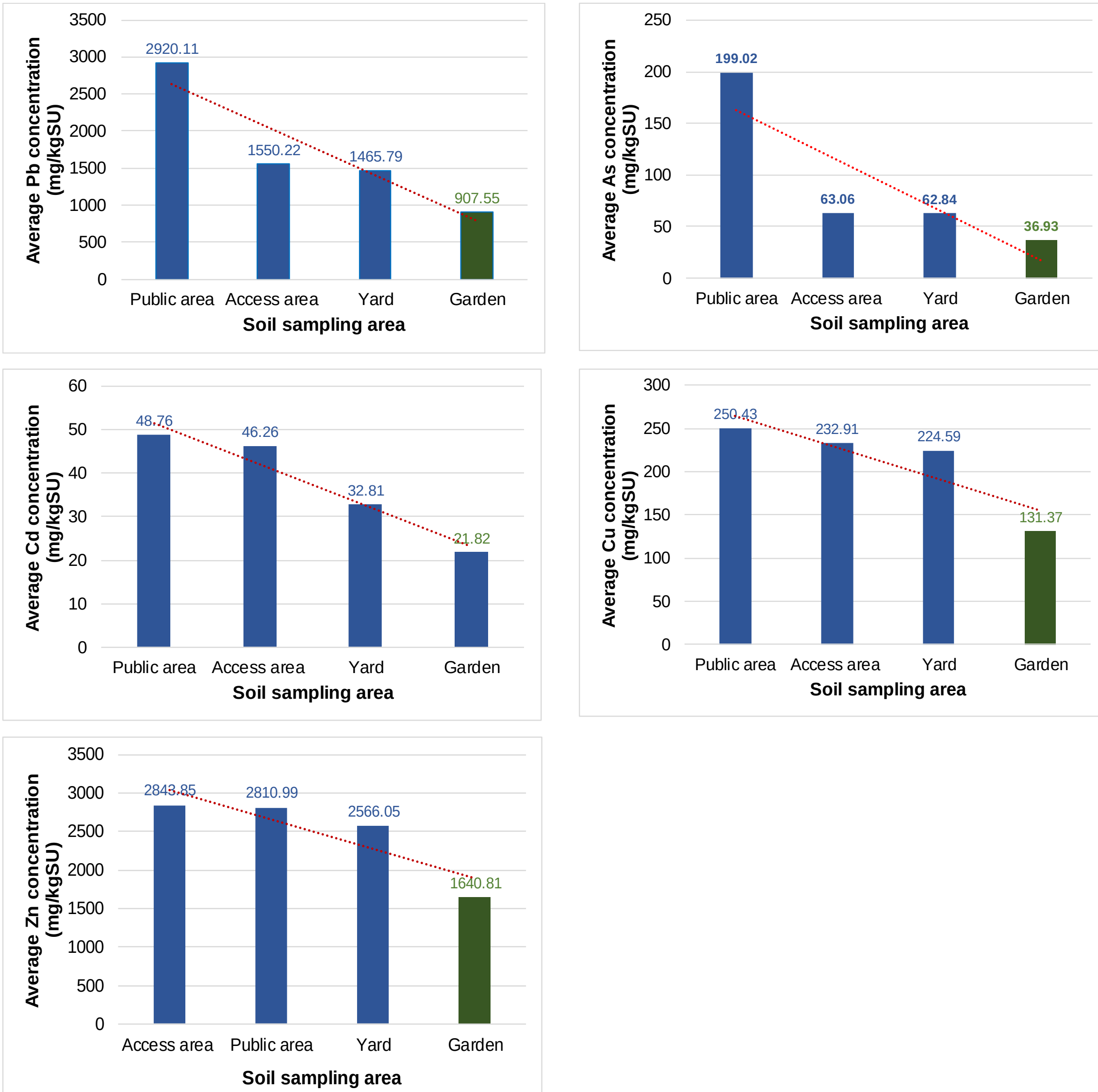
Sampling area	Cd			Cu			Zn		
	min	med	max	min	med	max	min	med	max
Access area (street)	9.54	46.26	236.90	57.68	232.91	1123.46	543.75	2843.85	17661.06
Yard	11.33	32.81	84.84	56.19	224.59	1373.17	531.21	2566.05	8221.26
Garden	8.84	**21.82**	53.28	61.76	**131.37**	233.87	610.00	**1640.81**	3599.07
Public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

Figure 4 – 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).

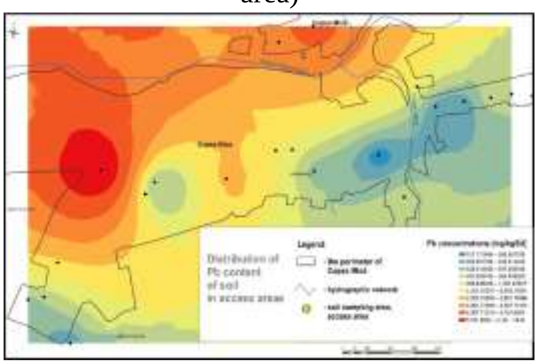
Spatial distribution of heavy metals content of soil in Copșa Mică

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.

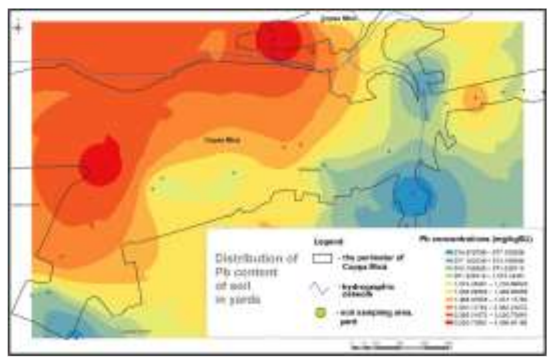
We can see a rule on average concentrations of heavy metals depending on the field of land use. The highest concentrations being recorded in 2018 in public areas, with the lowest concentrations in 2014 in gardens (except Zn, insignificant difference). It was considered relevant to generate separate distribution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

Figure 5 – The distribution map of Pb content of soil in different areas, Copșa Mică

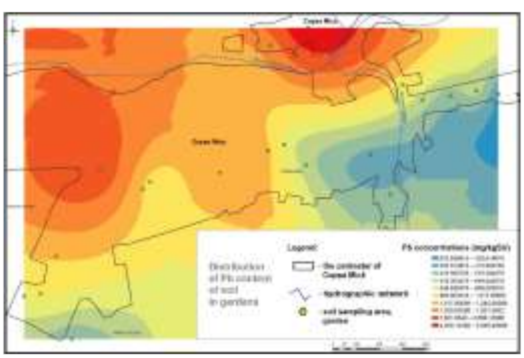
The distribution map of Pb in soil (acces area)



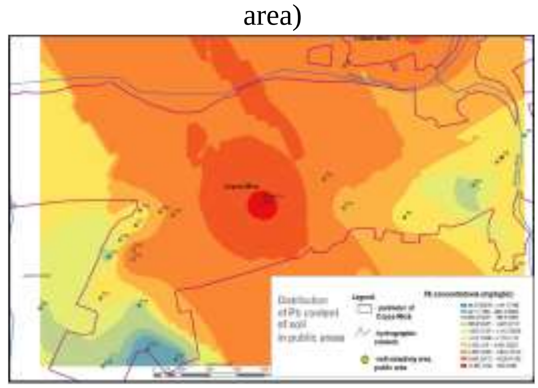
The distribution map of Pb in soil (yard)



The distribution map of Pb in soil (garden)



The distribution map of Pb in soil (public area)



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.

After developing the distribution maps for the other metals, it was observed that 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.

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 4 – 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

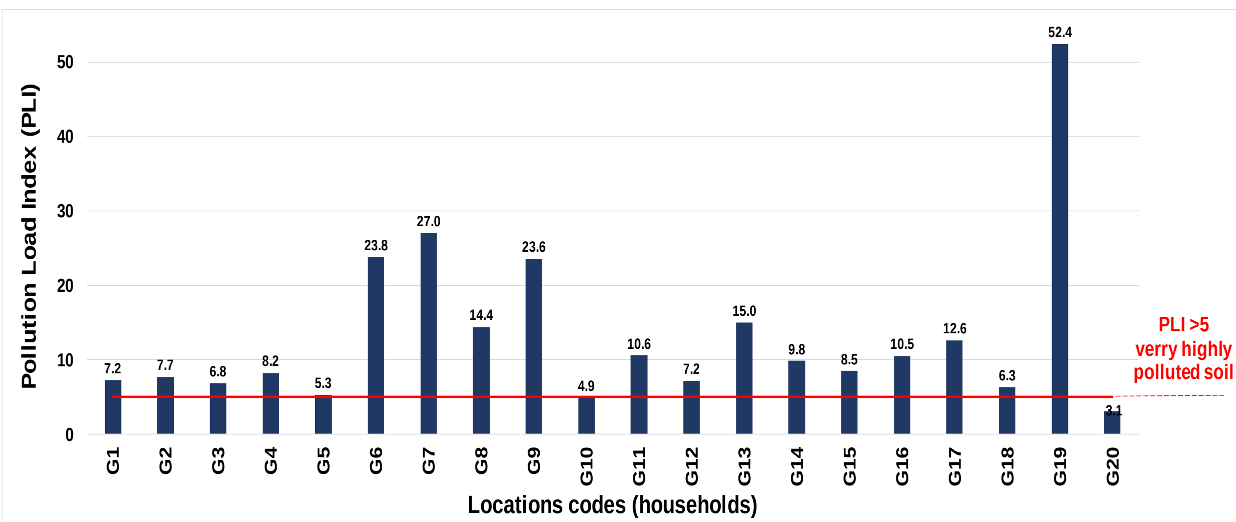
There is a very strong correlation between the concentrations of heavy metals for Zn-Cd, a strong correlation for Pb-As, Pb-Cd, As-Cd, As-Cu, As-Zn, Cu-Cd și Cu-Zn, a moderate correlation between Pb-Cu and Pb-Zn. The lowest values of the correlation coefficients are for Pb and Cu in relations with the 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 Copşa Mică.

Calculation of pollution indices (PLI, PI)

The figures 6 to 9 present the results of the calculations for PLI, for all samples taken in 2014 and 2018.

Figure 6 – Values of PLI for soil, Copşa Mică, 2014



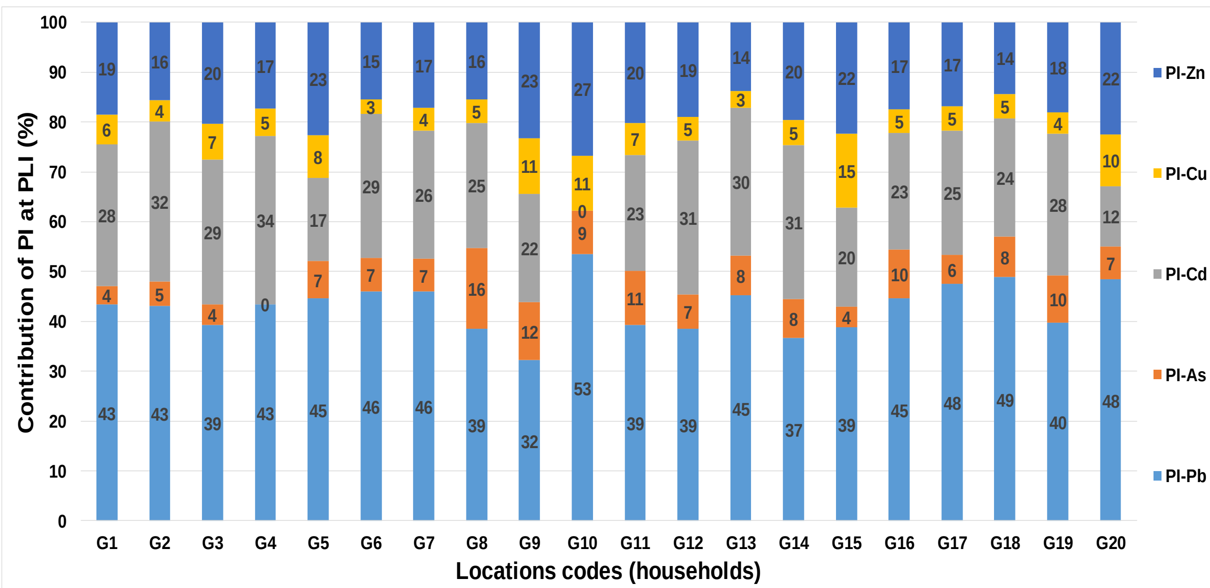
PLI values indicate a moderately to highly polluted soil in one of the investigated households G20 (PLI = 3.1), a highly level of pollution in one household G10 (PLI = 4.9) and very highly polluted soil in the remaining of 18 households investigated.

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.

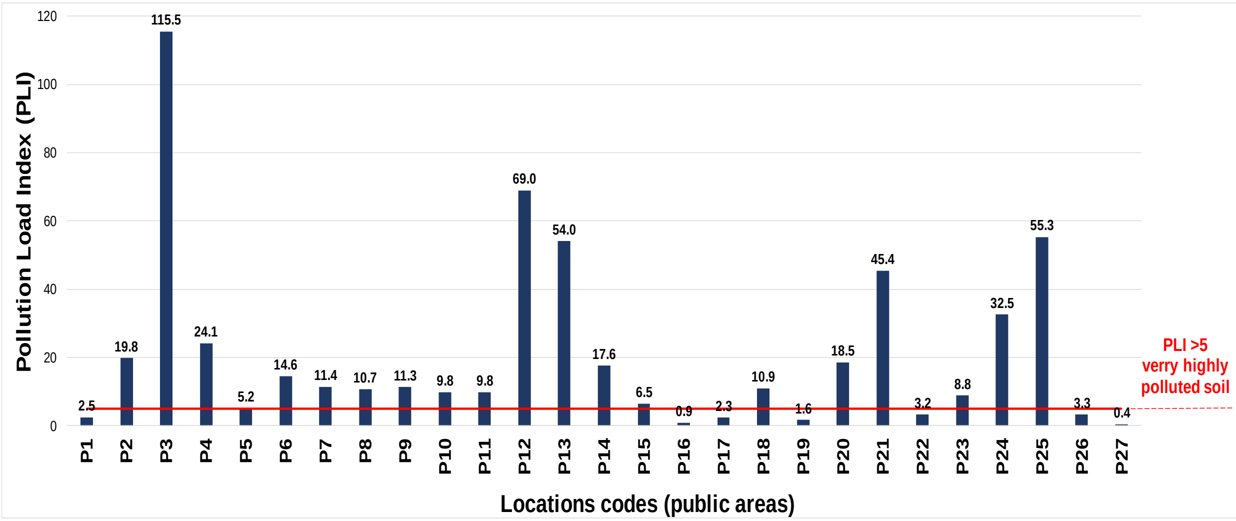
To highlight the contribution of each metal to the total level of PLI in the soil (2014), graphical and percentage indices of individual pollution (PI) were represented in figure 7.

Figure 7 – Percentage contribution of PI at the level of PLI for soil, Copșa 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%.

Figure 8 – Values of PLI for soil in Copşa Mică, 2018



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.

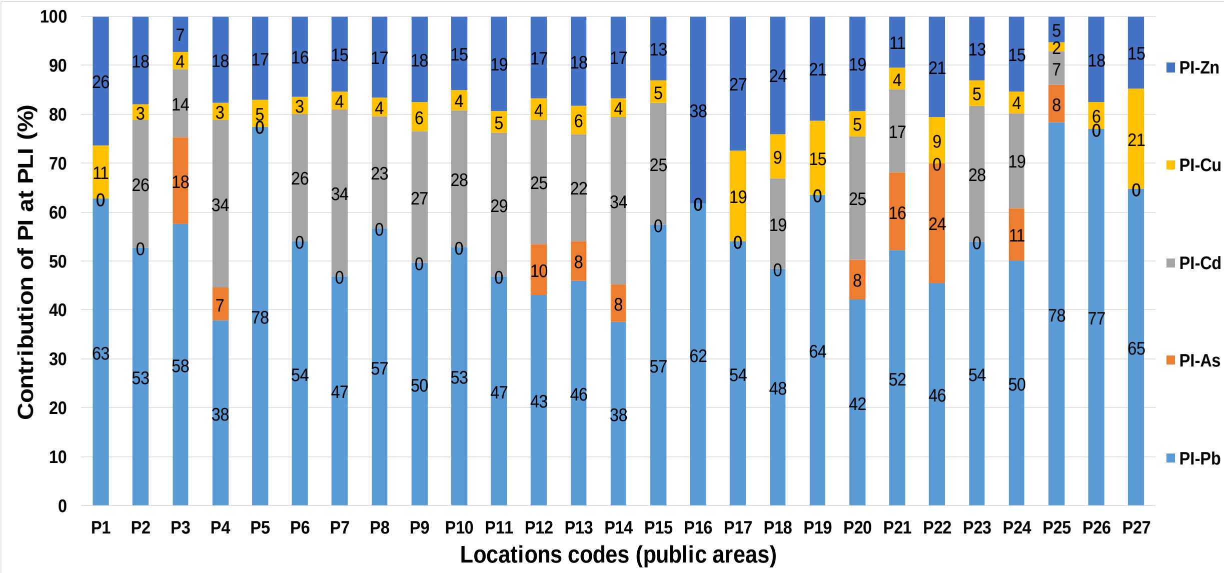
For an investigated point P19, there was a low level of pollution (PLI=1.62), being the Copşa Mică Orthodox cemetery area. For two investigated points resulted a moderately polluted soil P1 (PLI=2.48) and P17 (PLI=2.34) – these were located in Tarnăvioara (playground) and playground no.2 in Copşa Mică,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

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-Copşa 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 9.

Figure 9 – 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 5 – 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.

5.4. 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.

CAP. 5. ASSESSMENT OF HEAVY METALS CONTENT IN INDOOR AND OUTDOOR DUST OF THE HOUSES

5.1. Introduction

Because the persistence of heavy metals makes the soil a permanent source of exposure for the population and because previous studies (Young et al., 2002; Hillel, 2008; Harris et al., 2009) have shown that under certain conditions the soil can become a significant source of particles (by suspension and resuspension), I have continued present research by assessing the level of heavy metals in the outdoor and indoor dust.

In the year 2014, from the 20 households from which soil samples have been analyzed, dust samples were taken and the same metals were analyzed (Pb, As, Cd, Cu, Zn). The results of the analyzes allow the statistical verification of a possible significant relationship between the two variables: the level of heavy metals in the soil and the level of heavy metals in the dust.

5.2. Materials and methods

Dust samples were taken from the floors indoor (kitchens, bedrooms), from outdoor the households (on the access area) and from the right hand of the investigated subjects (one person/household). Four dust samples were obtained from each household ($G_{1\text{-}20}$), that is mean that 80 dust samples were analyzed.

Figure 10 – Copșa Mică, dust sampling points, 2014

Sampling method: *OSHA Technical Manual (OTM), Section II, Chapter 2, Apendix C – Procedure for Collecting Wipe Samples.*

Prelevarea probelor de praf s-a efectuat cu servețelele speciale (Lead Wipe) impregnate cu apă deionizată, polyorbate 20, methylparaben și propylparaben, care fixează o serie metale grele (Pb, Zn, Cu, Cd, Cr, Ni etc.).

The dust samples were taken with Lead Wipes impregnated with deionized water, polyorbate 20, methylparaben and propylparaben, used for a series of heavy metals (Pb, Zn, Cu, Cd, Cr, Ni etc.).

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

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

Interpretation of laboratory results was performed by descriptive statistics of the data, distribution maps of heavy metals from dust were built using the Kriging interpolation model, in ArcGIS and an image was obtained regarding the spatial distribution of heavy metals in the dust of the town. Potential similarities between distribution maps of heavy metals in soil and distribution maps of heavy metals in dust have been studied.

5.3. Results and discussions

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

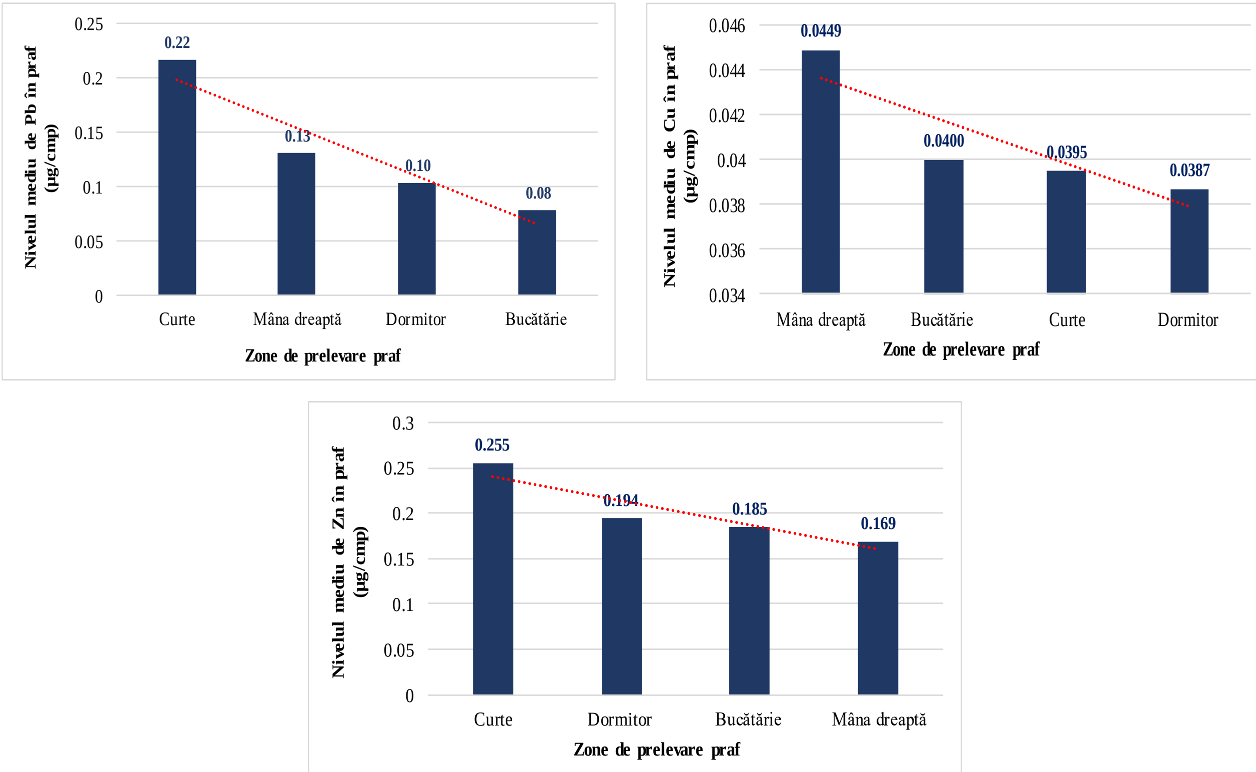
Table 6 – Values of minimum, mean and maximum levels for lead (Pb), cooper (Cu) and zinc (Zn) in dust, in different function areas (µg/cm^2)

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 3 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 > P b> Cu > As > Cd.

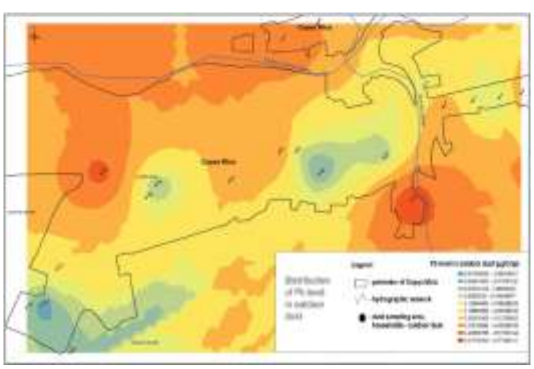
Figure 11 – Average levels of heavy metals content of dust in different areas (µg/cm^2)



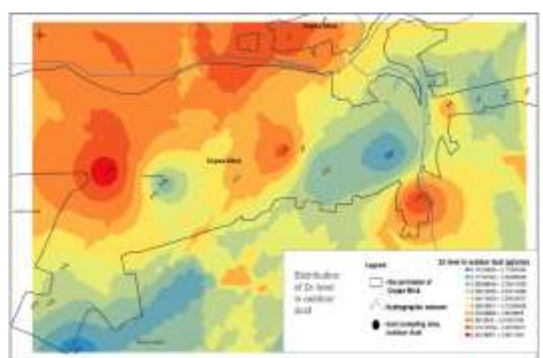
Unlike the concentrations of heavy metals in soil, where there is a order in functional areas, with the highest average of the access (street) and the lowest average in the gardens, there is no order for dust. The highest average content of Pb and Zn in the dust were recorded outside the households area, while for Cu the highest average being recorded on the right hand of the investigated subjects.

Figure 12 – The distribution maps of heavy metals content in outdoor dust (yard), Copșa Mică, 2014

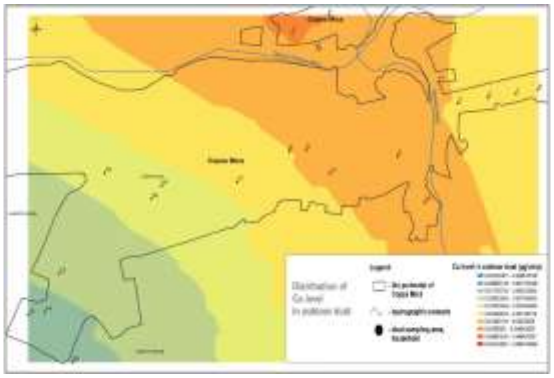
The distribution map of Pb in outdoor dust



The distribution map of Zn in outdoor dust



The distribution map of Cu in outdoor dust



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

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 metals distribution in the soil.

The distribution maps show a correlation regarding the highest levels in the SE of the town (figure 12). This area does not overlap areas with high concentrations of heavy metals in the soil.

Correlation test for heavy metal in dust

Using the DataAnalysis tool in Excel, correlation matrix was obtained

Table 7 – 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.

5.4. Conclusions

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 3 metals (Pb, Cu, Zn) in dust recorded average levels in a decreasing order **Zn > Pb > Cu**, with the following values ($\mu g/cm^2$): 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** > A s > 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 3 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.

CAP. 6. STATISTICAL ANALYSIS OF THE RELATIONSHIP BETWEEN THE CONTENT OF HEAVY METALS IN SOIL AND DUST

6.1. Introduction

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.

6.2. Statistical methods of analysis, correlation and regression

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.

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.

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%.

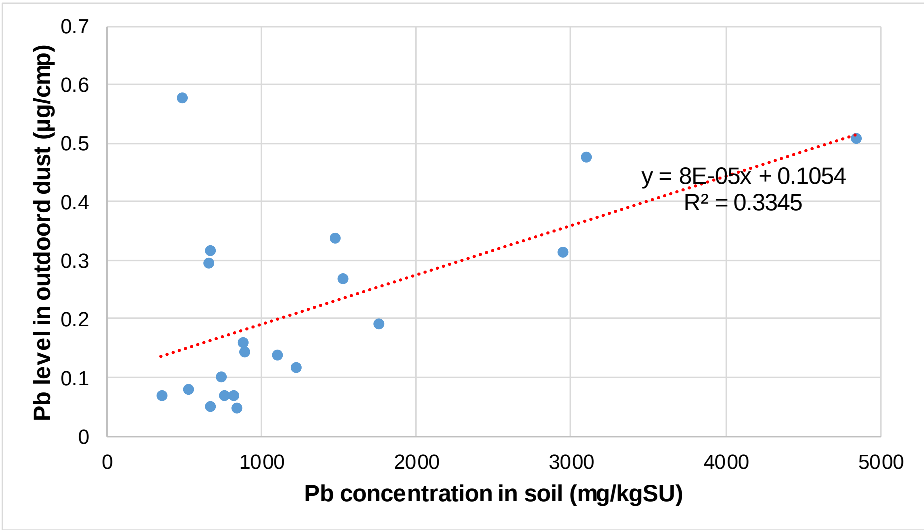
6.3. Results and discussions

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 3 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

Figure 13 – Scattering diagram for Pb concentration in soil and Pb level in 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 13).

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).

Table 8 – 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-sol medie	8.462E-05	2.813E-05	3.008148124	0.007550401	2.55E-05	0.000144

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.

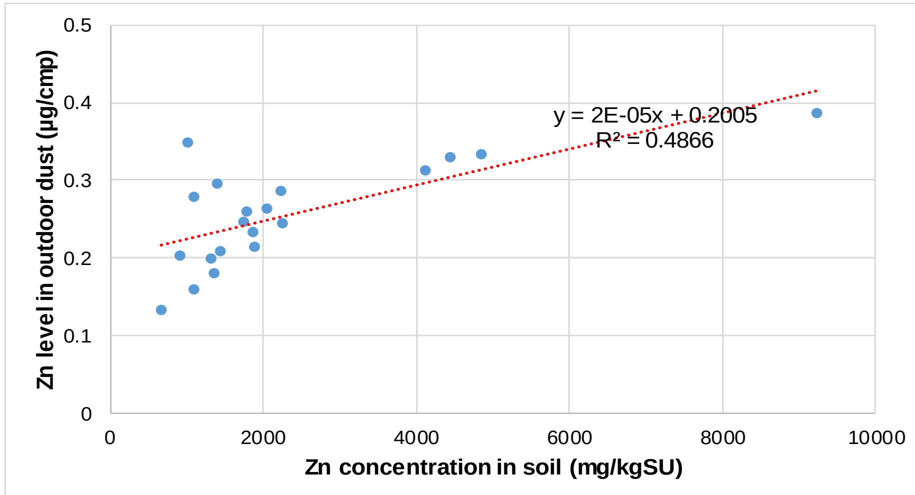
In the ANOVA test, p value (*Sig. F*) is less than 0.05, so the hypothesis of the lack of significance of the independent variable is rejected, in favor of the hypothesis that the regression model is statistically significant.

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.

Zinc in soil and in outdoor dust

Figure 14 – Scattering diagram for the concentration of Zn in soil and Zn level 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 14).

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 9 – 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.

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-sol medie	2.33E-05	5.64E-06	4.130638569	0.000627934	1.1442E-05	3.51286E-05

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.

6.4. Conclusions

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.

Having demonstrated the role of contaminated lands in dust emission with heavy metals content, the relationship between the analyzed data series is statistically significant, for the implementation of future population health programs it must be taken into account that the areas with high levels of heavy metals in the soil (Pb, Zn) overlap with areas with higher levels of heavy metals in the dust. Thus, when designing health programs, the exposure pathways through ingestion and inhalation must be taken into consideration.

CAP. 7. ASSESSMENT OF EXPOSURE TO HEAVY METALS AND HEALTH PROGRAMES IN COPȘA MICĂ

7.1. Introduction

This chapter includes information about the sensitive receptors of pollution - the population of Copșa Mică. The interest is in the habits, the local peculiarities of the population and its spatial distribution in the urban area, and the exposure to heavy metals in the soil by ingestion was assessed.

The information obtained from the assessment will underpin future measures to stop or reduce the exposure of the population to heavy metals in the soil in order to obtain positive results for the population health.

7.2. Materials and methods

The calculation for the daily exposure dose of contaminants via ingestion exposure pathway, it was used a program of the Agency for Toxic Substances and Disease Registry (ATSDR) of the Center for Disease Control and Prevention (CDC), which is also used in the United States of America. Exposure doses were calculated for adults, children, and *pica child.*

Daily Exposure Dose Equation is:

$ED=(C \times IR \times EF \times BF \times CF)/BW$ *[mg/kg, day]* (1)

Where: ED – exposure dose (mg/kg, day), C – contaminant concentrație (mg/kg), IR – intake rate of contaminated medium (mg/day), EF – exposure factor (without a unit of measure), BF – bioavailability (without a unit of measure), CF – conversion factor (without a unit of measure), BW – body weight (kg).

7.3. Results an discussions

The assessment of human exposure to heavy metals in soil by ingestion pathway has been done for adults, children and pica child. The analysis was conducted for household (2014) and public areas (2018). For the entire town, one average exposure dose was calculated for each metal.

Table 10 – The average exposure doses to heavy metals in soil by ingestion pathway, in households (mg/kg, day)

	Adult 70 kg (100 mg/day)	**Child 1-6 ani 16 kg (200 mg/day)**	**Pica child 1-6 ani 16 kg (5000 mg/day)**
Pb	0.00186	0.016348	0.408704
As	0.000066	0.000576	0.014393
Cd	0.00004	0.00036	0.00923
Zn	0.00335	0.02937	0.73444

Table 11 – The average exposure doses to heavy metals in soil by ingestion pathway, in public areas (mg/kg, day)

	Adult 70 kg (100 mg/day)	**Child 1-6 ani 16 kg (200 mg/day)**	**Pica child 1-6 ani 16 kg (5000 mg/day)**
Pb	0.00417	0.03650	0.91253
As	0.00028	0.00249	0.06220
Cd	0.00007	0.00061	0.01524
Zn	0.00402	0.03514	0.87844

A summary analysis of the average exposure doses shows that:

- for all metals, the group of pica child, have an average exposure doses 218.7 times higher than for adults and 25 times higher than for children;
- for all metals, children have an average exposure doses 8.7 times higher than for adults;
- for Pb in public areas, the average exposure doses are 2.2 times higher than the average exposure doses in households;
- for As in public areas, the average exposure doses are 4.3 times higher than in households;
- for Cd in public areas, the average exposure doses are 1.65 times higher than in households;
- for Zn in public areas, the average exposure doses are approx. 1.2 times higher than in households.

It can be noticed that in public areas the exposure doses are significantly higher than the exposure doses in households perimeter. Both children and adults are more exposed in public areas. Future health intervention programs in Copșa Mică should be focus on the most susceptible population to exposure - children and public areas frequented by them: playgrounds, sports fields, kindergartens, schools etc.

For households, where adults and children are exposed for a long time, using Kringing interpolation, distribution maps of daily exposure doses were created. For children, exposure maps to Pb and Zn in the soil are presented, indicating that for As and Cd, they are similar.

Distribution maps of exposure doses, by ingestion pathway to Pb and Zn in the soil of households perimeter have revealed critical areas in some neighborhoods - such as Târnavioara, where the quality of living visually appreciated is poor. Here, the dominance of the population with a low living standard is obvious, the most vulnerable population group being well represented (the children).

Regarding adults, since the metallurgical unit drastically reduced its activity, the occupational exposure is significantly reduced, the main problem being related to the source of exposure in the soil.

Because extended areas are affected by pollution, green reconstruction is not feasible. An appropriate solution is considered the one proposing measures to decrease or stop exposure in order to achieve population health improvement. The main measures to be applied should be focus on:

- children, in functional areas with the highest daily exposure doses (playgrounds, kindergartens, schools, sports fields etc.);
- adults, in functional areas where they are frequently exposed: in their own households and in public areas.

7.5. Conclusions

According to the Public Health Assessment Guidance Manual (2005 update), Cap. 9, developed by the Agency for Toxic Substances and Disease (ADSDR), health intervention programs must be developed and implemented after the health risk assessment. The main measures must refer to health advices for decreasing or stopping exposure, health education, and health surveillance studies.

Based on the results of present study, health intervention programs should be targeted at children in order to reduce exposure in public areas and households. This involves measures aimed to change behaviours that favour the ingestion of soil and dust particles: hand and toys washing, administration interventions at playgrounds and kindergardens etc.

For adults, occupational exposure became a secondary issue. This means health intervention programs must be targeted to changing attitudes, behaviors and practices that favor exposure such as: health education (hygiene), wet cleaning in households, abandonment of home-produced vegetables and watering gardens from the underground water source, stopping the marketing of local food plants etc.

At the administrative level, health intervention programs should propose measures implemented in public areas such as sanitation and street sweeping and washing, decreasing uncovered land areas who favoring the suspension of surface dust particles, grassing, pavement, asphalting and irrigation of green spaces to prevent dryness etc. Knowing the children's tendency to play at ground level, sandboxes can be arranged for playgrounds and kindergartens, brought from controlled sources and regularly changed.

It is important to take into account the residential areas where the highest exposure doses were recorded in 3 neighborhoods: in the South of the industrial platform (Colonia Laborator, with blocks), Târnăvioara and the neighborhood Est – South-Est of the industrial platform (with Muncitorilor Street, Nicovalei Street etc.). Another thing to take into account is that in some areas with high exposure doses to heavy metals in soil, population has a quality of life below the community average. Here the group of children is well represented, and the health intervention programs must be addressed properly to the cultural and educational level of the community.

Health intervention programs should be promoted at the administrative level, through public information, in kindergartens and schools, the way of communication being appropriate to the public to whom it is addressed. Monitoring of results and their perpetuation should be ensured by monitoring health indicators in target population groups, for example by regularly measuring the BLL in children and adults.

Future implemented programs and periodic analyses of health indicators (BLL) should provide results that establish strategic decisions for public health in Copșa Mică.

CAP. 8. CONCLUSIONS

8.1. General conclusions

In each chapter of the thesis, the general conclusions were presented. A summary of the most important aspects are presented briefly, as follows:

Analysis of soil quality in households and in public areas showed that the highest average concentrations of Pb, As, Cd and Cu are found in decreasing 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 access areas in households is slightly higher than the average recorded for public areas, but the difference is insignificant (1.16%).

It is highlighted that in the public areas (schools, kindergartens, playgrounds, sports fields, etc.), where the interventions on the ground are not regular, the highest concentrations of heavy metals in the soil are recorded. These areas are frequented by children, the level of exposure being high for this populational group.

The concentrations of heavy metals in the soil show exceedances of the normal values and of the regulated thresholds for the analyzed metals (Pb, As, Cd, Cu, Zn). The regulated intervention thresholds for sensitive land use were exceeded for all the metals analyzed, as shown: for Pb - in 100% of the analyzed samples; for Zn - in 95% of the samples; for Cd - in 85% of the samples; for As - in 55% of the samples; for Cu - in 23.3% of the samples.

Calculation of pollution indices (PI and PLI) shows a moderate to very high level of soil pollution. The highest contribution to the general pollution index (PLI), by individual pollution indices (PI) are in descending order: Pb, Zn and Cd.

Distribution maps for heavy metals in the soil highlighted the areas most affected by pollution in the town of Copșa Mică: in the vicinity of the industrial platform, to South of it; in the neighborhood situated to Est – South-Est of industrial platform; in the Târnăvioara neighborhood, to North-Est of the town.

Following the analysis of the soil quality in the inner town of Copșa Mică, it was found that the risks for the health status of the population are still present, the soil is a permanent source of exposure for the resident population, especially for the most vulnerable group - children. Because a large area of land is affected by pollution, measures are not feasible for greening the area, but it is feasible to implement targeted measures to reduce or stop the exposure of the population to heavy metals in the soil and within certain functional areas.

Analysis of the dust heavy metals content showed for Cd and As levels that were below the limit of detection. For Pb, Zn and Cu, average levels were recorded in decreasing order Zn> Pb> Cu. The decreasing level of the average levels for the heavy metals in the dust is similar to the decreasing order of the average concentrations for the heavy metals in the soil (Zn> Pb> Cu> As> Cd).

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

The average levels of Pb and Zn in the outdoor dust are higher than the average levels of the indoor dust.

According to the distribution maps for heavy metals in outdoor dust, the highest levels for Pb and Zn were registered in the vicinity of the industrial platform in the South, in the North-Est in the Târnăvioara neighborhood, in the South-Est at the exit to the town of Valea Viilor and in the neighborhood situated to Est – South-Est of industrial platform. The highest levels of Pb and Zn in outdoor dust have been recorded in the three areas where the highest concentrations of Pb and Zn have been recorded in the soil. Exception is the SE part of the town, at the exit towards Valea Viilor.

Statistical analysis by correlation snd simple linear regression showed that in households there is a statistically significant relationship between the level Pb and Zn in the soil and the level Pb and Zn in the outdoor dust (yard). The simple linear regression model shows that in areas where high levels of heavy metals are recorded in soil, high levels of heavy metals in dust are expected to be found in relation to them. This relationship was also highlighted on the distribution maps of heavy metals in the soil and from the outdoor dust.

Statistical analysis by correlation and simple linear regression has not highlighted a statistically significant relationship between the levels of heavy metals from indoor dust and outdoor dust, or from the dust on the hands of the investigated subjects. Cleaning activities in homes and hand washing influence the level of heavy metals from indoor dust and on the hands of the subjects.

The assessment of the exposure of the population to the heavy metals in the soil, by ingestion, showed high values of the exposure doses in children and in the subgroup *pica* child, in relation to the exposure doses calculated for adults. Higher exposure doses are recorded in public areas compared to the exposure levels within households.

As a result, health programs should be targeted at the population group most vulnerable to exposure to heavy metals in the soil - children, in order to reduce exposure in public areas by targeted measures to change behaviors that favor the ingestion of soil and dust particles. For adults, health programs must be oriented on all functional areas of the town in order to change current attitudes, behaviors and practices.

8.2. Recommendations for future research

It is documented that historically polluted towns have low potential for socio-economic development, these being *"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. A polluted urban environment, in which the health of the population has been historically affected, does not provide the premises for the development of communities and represents the territories with a negative population growth, being areas destined for demographic, social and economic crises. Therefore, the implementation of health programs in the town of Copșa Mică is appropriate, as the programs should target the population groups:

- **children,** on the functional areas with the highest doses of exposure (playgrounds, kindergartens, schools, sports fields, etc.);
- **adults,** on the functional areas where they are frequently exposed: in their own households and on public areas.

The measures for health population status improvement to be applied must be oriented in the following directions:

- reducing or stopping exposure by modifying adult attitudes, behaviors and practices through:
    - stopping the cultivation of home-grown vegetables in their own gardens and replacing them with other plant categories;
    - stopping the consumption and marketing of home-grown vegetables;
    - obtaining edible vegetables from other sources;
    - stopping using water from its own sources (fountains) and stopping irrigating gardens with water from wells;
    - changing behaviors related to personal hygiene and wet housekeeping;
    - frequent washing of children's toys and other objects belonging to them etc.
- in the case of children, it must be followed:
    - changing behaviors that favor the ingestion of soil and dust;
    - hand washing;

    - frequent washing of toys and other personal items etc.
- approving decisions of the local administration for reducing or stopping exposure, through the following:
    - for playgrounds and in kindergartens/schools rubber mats and sand areas can be arranged, which will be brought from controlled sources and which will be changed periodically;
    - street sweeping and washing;
    - the decreasing of denuded land surfaces which favors the suspension of dust from the surface, thru grassing, paving or asphalting works;
    - irrigation of green spaces to prevent soil drying;
    - ensuring the drinking water infrastructure for all neighborhoods;
    - raising awareness and stimulate the population in order to give up the cultivation, consumption and marketing of home-grown vegetables.

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