STUDIA UBB CHEMIA, LIX, 1, 2014 (p. 87-98)
(RECOMMENDED CITATION)

MINERALOGICAL CHARACTERISATION AND HEAVY METALS ASSESSMENT OF SOILS FROM URBAN RECREATIONAL AREAS IN CENTRAL TRANSYLVANIA

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ABSTRACT. Forty-five soil samples collected from fifteen intensively visited recreational areas in four different sized urban settlements in central Transylvania, Romania were investigated through X-ray powder diffraction for mineralogical characterization and analyzed using atomic absorption spectrometry in order to identify Cd, Cu, Co, Pb, Zn, Mn and Ni contamination. Pollution indexes were calculated and revealed that one-third of the recreational areas studied requires immediate remediation measures in order to reduce potential risks for human health.

Keywords: *urban soil, recreational areas, mineralogy, heavy metals*

INTRODUCTION

In urban settlements a particular type of soil can be found that differs fundamentally from soil normally encountered in natural ecosystems, due to the fact that its properties are strongly influenced by anthropogenic activities [1]. The most common places where urban inhabitants come in contact with soils are recreational areas. Therefore soils in parks and playgrounds proved to be able to influence public health by transferring pollutants that tend to accumulate and persist over time endangering children or vulnerable persons [2]. In recreational areas residents can easily get in contact with contaminates through inhalation or ingestion of soil particles when outdoor activities are conducted.

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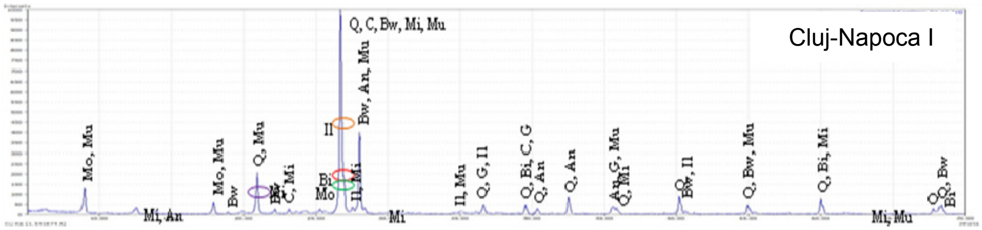
Heavy metals represent a particular class of contaminants, harmful to human health. In urban soils they have been identified as important markers of pollution [3] and therefore captured researchers’ attention worldwide. A consistent number of studies related to metal contamination in recreational areas have been conducted in China, Brazil, Chile, Australia, Sweden, Lithuania, Spain, England, Italy and Serbia [4].

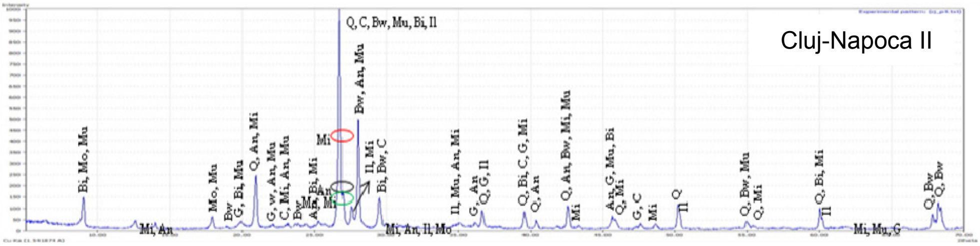
There is little research available on soils of recreational areas in urban settlements in Romania and therefore people are not aware of the potential risks that they impose. The aim of this study is to properly characterize soil mineralogy and to assess heavy metal contamination in this type of locations in central Transylvania.

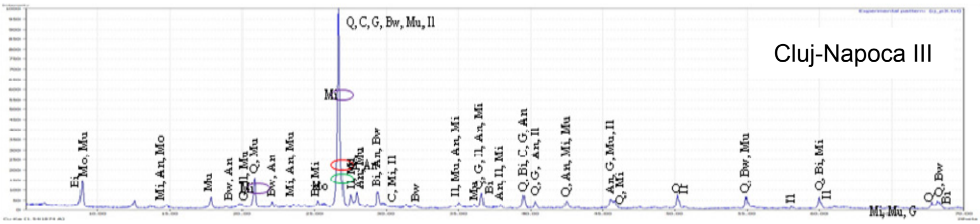
Transylvania is the region in the centre of Romania bounded by the Carpathian Mountains. Numerous cities, communes and villages developed here over time. The current study focused on four cities located in the centre of the region, respectively Cluj-Napoca, Turda, Câmpia Turzii and Târgu Mureş. Even though these cities have different surfaces they are densely inhabited and host various anthropogenic activities. This study will examine soils from recreational areas (parks and playgrounds) within these cities and will highlight potential environmental problems caused by soil contamination with heavy metals.

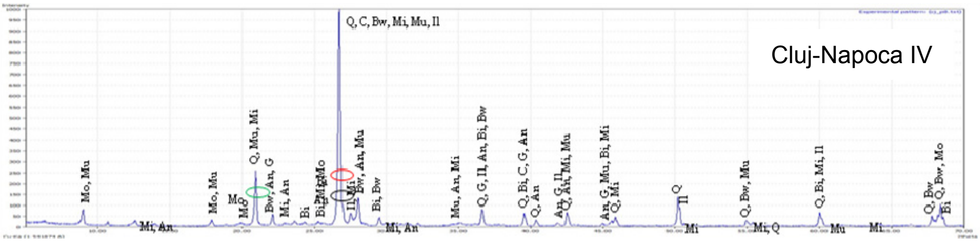
RESULTS AND DISCUSSION

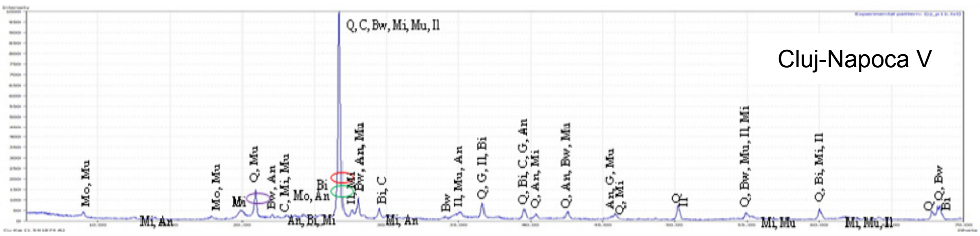
Characterizing the mineralogical composition of soil represents an important part in heavy metals contamination studies due to the fact that minerals may considerably influence the toxicity, bioavailability and leaching for this type of contaminates [5]. Using X-ray powder diffraction (XRPD), the mineralogical composition of recreational area soils samples can be identified and interpreted.

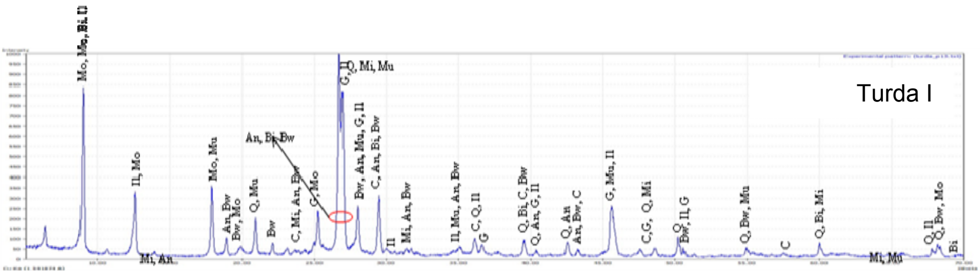



Cluj-Napoca II
Q, C, Bw, Mu, Bi, Il


Cluj-Napoca III
Q, C, G, Bw, Mu, Il


Cluj-Napoca IV
Q, C, Bw, Mi, Mu, Il


Cluj-Napoca V
Q, C, Bw, Mi, Mu, Il


Turda I
Q, Mi, Mu

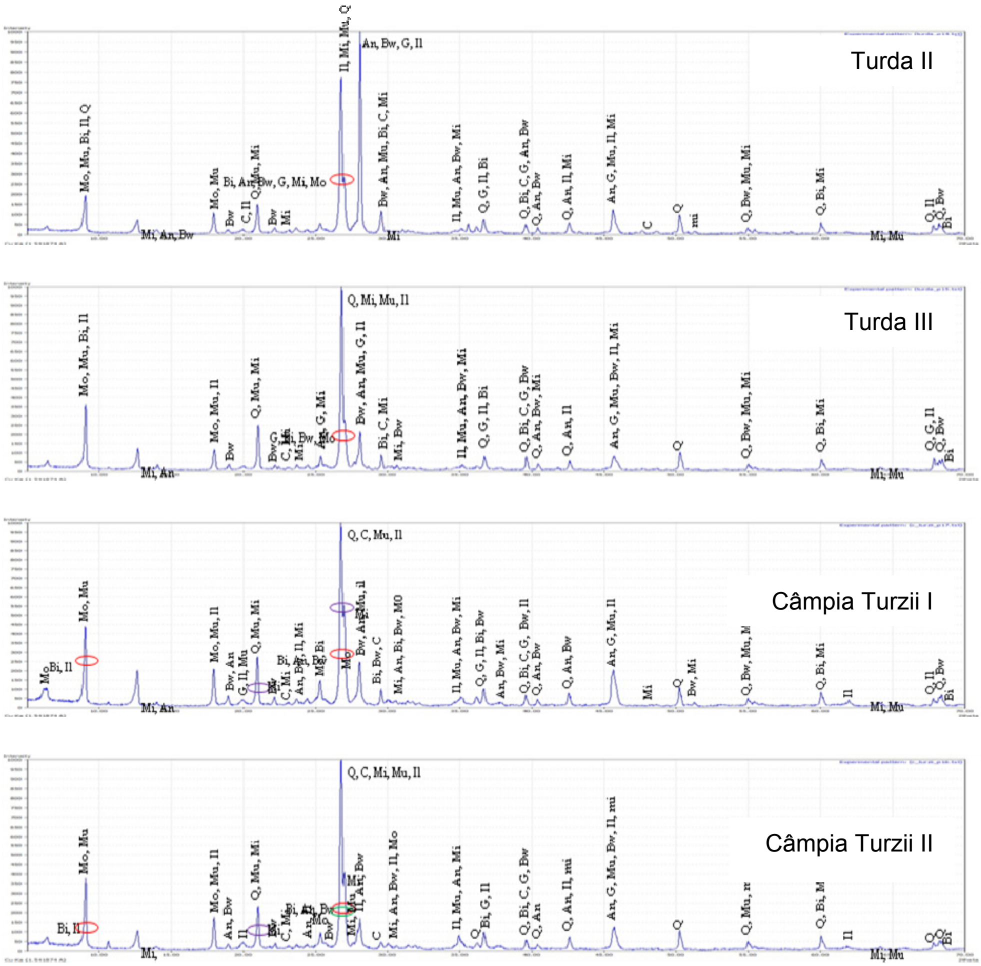


Figure 1. Mineralogical composition obtained by X-ray diffraction for all 15 locations analysed (Legend: An - anorthite, Bi - biotite, Bw - bytownite, C - calcite, G - gibbsite, Il - illite, Mi - microcline, Mo - montmorillonite, Mu - muscovite and Q – quartz)

Based on recorded changes in diffracted X-ray intensities the mineralogical composition of the soil samples was detected [6]. As a result, each of the diagrams included in Figure 1 expresses a sequence of diffraction peaks generated by recorded photon intensity versus a detector angle 2θ and generates information about the mineralogical composition that exists within a soil sample.

In the first diagram of figure 1 the mineralogical composition of the Cluj-Napoca I location is represented and the minerals contained were identified. Therefore it can be stated that the analyzed soil is a polymineral sample and contains a various type of minerals: anorthite biotite, bytownite, calcite, gibbsite, illite, microcline, montmorillonite, muscovite and quartz. Similar identifications were conducted for all the other fourteen locations analyzed. The results reveal that Cluj-Napoca II, Cluj-Napoca III, Cluj-Napoca IV, Cluj-Napoca V, Turda I, Turda II, Turda III, Câmpia Turzii I, Câmpia Turzii II and Târgu Mureş I present similar mineralogical compositions when being compared to sample Cluj-Napoca I. From a qualitative point of view, they all contain quartz, feldspars, clay minerals, carbonate minerals and hydroxides in various proportions. Samples collected from the locations referred to as Târgu Mureş II, Târgu Mureş III, Târgu Mureş IV, and Târgu Mureş V lack calcite and gibbsite. For better visualization qualitative mineralogical data was structured in Table 1.

Table 1. Mineralogical composition of recreational area soil samples

Recreational area	Mineralogical copmposition									
Cluj-Napoca I	Anorthite	Biotite	Bytownite	Calcite	Gibbsite	Illite	Microcline	Montmorillonite	Muscovite	Quartz
Cluj-Napoca II	Anorthite	Biotite	Bytownite	Calcite	Gibbsite	Illite	Microcline	Montmorillonite	Muscovite	Quartz
Cluj-Napoca III	Anorthite	Biotite	Bytownite	Calcite	Gibbsite	Illite	Microcline	Montmorillonite	Muscovite	Quartz
Cluj-Napoca IV	Anorthite	Biotite	Bytownite	Calcite	Gibbsite	Illite	Microcline	Montmorillonite	Muscovite	Quartz
Cluj-Napoca V	Anorthite	Biotite	Bytownite	Calcite	Gibbsite	Illite	Microcline	Montmorillonite	Muscovite	Quartz
Turda I	Anorthite	Biotite	Bytownite	Calcite	Gibbsite	Illite	Microcline	Montmorillonite	Muscovite	Quartz
Turda II	Anorthite	Biotite	Bytownite	Calcite	Gibbsite	Illite	Microcline	Montmorillonite	Muscovite	Quartz
Turda III	Anorthite	Biotite	Bytownite	Calcite	Gibbsite	Illite	Microcline	Montmorillonite	Muscovite	Quartz
Campia Turzii I	Anorthite	Biotite	Bytownite	Calcite	Gibbsite	Illite	Microcline	Montmorillonite	Muscovite	Quartz
Campia Turzii II	Anorthite	Biotite	Bytownite	Calcite	Gibbsite	Illite	Microcline	Montmorillonite	Muscovite	Quartz
Targul Mures I	Anorthite	Biotite	Bytownite	Calcite	Gibbsite	Illite	Microcline	Montmorillonite	Muscovite	Quartz
Targul Mures II	Anorthite	Biotite	Bytownite	/	/	Illite	Microcline	Montmorillonite	Muscovite	Quartz
Targul Mures III	Anorthite	Biotite	Bytownite	/	/	Illite	Microcline	Montmorillonite	Muscovite	Quartz
Targul Mures IV	Anorthite	Biotite	Bytownite	/	/	Illite	Microcline	Montmorillonite	Muscovite	Quartz
Targul Mures V	Anorthite	Biotite	Bytownite	/	/	Illite	Microcline	Montmorillonite	Muscovite	Quartz

The mineralogical composition plays an important role in adsorbing, oxidizing, reducing and precipitating chemicals such as heavy metals into pure or mixed solids. Clay minerals are the most responsible for restraining such contaminates, and can be divided into two major types: nonexpanding (1:1) and expanding (2:1). The major difference between the two types is that the nonexpanding clay minerals have one silica tetrahedral sheet bonded to one aluminum octahedral sheet while the expanding clay minerals have two silica tetrahedral sheets surrounding an aluminum octahedral sheet. The 2:1 type is attributed to minerals such as montmorillonite and illite [6] both contained in all soil samples collected for this study. Montmorillonite defines a class of soft clayey water-absorbent minerals. The water content in montmorillonite can vary so that the chemical formula is written as $(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2{\cdot}nH_2O$.

Due to the fact that only weak van der Waals type forces exist among the layers of expanding clay minerals the chemicals such as heavy metals often enter between them, where they remain immobilized [7]. Illite is a common phyllosilicate or layered alumino-silicate clay mineral. The general chemical formula for illite is given as $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$ but there is considerable ion substitution. The presence of montmorillonite and illite in the analyzed soil samples can be interpreted in two ways. On one hand the immobilization of metals in the upper soil layer limits vertical migration and reduces the threat of ground water contamination, but on the other hand it increases risks for human health due to the fact that in urban recreational areas children come in contact with top soil particles. Montmorillonite and illite were identified in all 15 locations analyzed.

Carbonate minerals such as calcite are widely available in soil and have considerable influence in the accumulation of various metals in the environment [8]. Calcite is the most stable polymorph of calcium carbonate ($CaCO_3$), has a rhombohedral crystal system and has been identified through experimental observation as being an absorption substrate with affinity for Zn and Cd [9]. Calcite is present in 11 of the 15 locations analyzed.

Aluminum hydroxides such as gibbsite often designed as γ-$Al(OH)_3$ are also important adsorbents of heavy metals in soils, making this mineral's presence in the upper layer of urban recreational areas noticeable [10]. As in the case of calcite, gibbsite was identified in 11 out of the 15 locations.

Quartz is also an important mineral present in all recreational area samples analyzed. It is also known for its ability to absorb trace metals from solutions. Experimental studies show that the reactive ability of metals on quartz follows the order Cd > Pb > Zn > Ni > Cu [11]. Taking this into account it can be affirmed that quartz also plays a key role in the accumulation of metal contaminants in soils.

Anorthite, biotite, bytownite, microcline and muscovite have limited or moderated influence on heavy metal retention in soil. Nevertheless, despite the mineralogical composition of soil, the fact should be taken into account, that metal adsorption and retention processes are strongly influenced by a series of chemical and physical parameters such as water or substrate pH that can vary substantially from one location to another. Also metals can be found in a pure form unattached to minerals.

In order to assess heavy metal contamination Cd, Cu, Co, Pb, Zn, Mn and Ni concentrations in the urban recreational area soil samples were determined using atomic absorption spectrometry. Due to the fact that in each recreational area under discussion three samples were analyzed average values were calculated. For better visualization heavy metal concentrations were structured into Table 2 that also included guideline values considered normal in Romania. For each location a general pollution index (PI) was calculated as the ratio between the heavy metal concentrations identified in the study and the normal reference value attributed for Romania. Each PI calculated vas classified as low if (PI ≤1), moderate if (1 ≤ PI ≤ 3) or high if (PI > 3) and highlighted in Table 3 [12].

Table 2. Heavy metal concentrations and Romanian guidelines for normal values

Identification	Cd (mg/kg)	Cu (mg/kg)	Co (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Mn (mg/kg)	Ni (mg/kg)
Cluj-Napoca I	0.17	87.9	10.7	11.9	80	496	40.9
Cluj-Napoca II	0.61	83.2	8.5	143.7	219	378	21.7
Cluj-Napoca III	0.82	115.4	13.3	73.9	262	576	47.7
Cluj-Napoca IV	0.24	36.9	8	72.1	319	607	21.1
Cluj-Napoca V	0.40	40.7	16.9	39.9	116	778	35.4
Turda I	0.16	141.2	15.2	172.4	343	1069	47.9
Turda II	0.46	39.5	13.4	55.1	140	826	30.4
Turda III	0.80	41.1	10.1	67.2	171	779	27
Campia Turzii I	0.38	50.3	12.5	93.4	205	1194	41.9
Campia Turzii II	0.49	39.8	14.4	44.7	140	825	33.8
Tg. Mures I	0.15	32.1	13.4	28.6	102	729	29.4
Tg. Mures II	0.17	28.7	13.3	26.3	98	725	24.3
Tg. Mures III	0.34	29.6	12.4	16.4	86	873	35.8
Tg. Mures IV	0.13	19.2	7.6	38.3	60	419	16.5
Tg. Mures V	0.14	22.2	13.4	19.4	73	659	27
Romanian Guideline Values [13]	1	20	15	20	100	900	20

The results presented in Table 2 demonstrate a general tendency to exceed normal values especially for Cu, Pb and Zn, heavy metals that are usually associated with anthropogenic pollution sources. Samples collected from recreational areas in Cluj-Napoca, Turda and Câmpia Turzii reveal higher metal levels than samples collected form Târgu Mureş.

Co, Mn and Ni concentrations exhibit levels comparable to the guideline values established as normal for Romanian soils. Cd concentration values are well maintained under the Romanian guideline values suggesting that in the Transylvanian cities investigated there is no sign of possible cadmium contamination.

Heavy metal concentrations identified in Târgu Mureş are homogeneously distributed for all locations investigated suggesting healthy environments that pose limited threats for recreational area users [14].

The recreational areas referred to as Cluj Napoca II, Cluj Napoca III, Turda I and Câmpia Turzii I reveal alarmingly high Pb concentrations indicating pour soil quality and a considerable threat for human health.

Table 3. Pollution Indexes (PI) calculated for heavy metal concentrations identified

Identification	PI - Cd	PI - Cu	PI - Co	PI - Pb	PI - Zn	PI - Mn	PI - Ni
Cluj-Napoca I	0.17	4.40	0.71	0.60	0.80	0.55	2.05
Cluj-Napoca II	0.61	4.16	0.57	7.19	2.19	0.42	1.09
Cluj-Napoca III	0.82	5.77	0.89	3.70	2.62	0.64	2.39
Cluj-Napoca IV	0.24	1.85	0.53	3.61	3.19	0.67	1.06
Cluj-Napoca V	0.40	2.04	1.13	2.00	1.16	0.86	1.77
Turda I	0.16	7.06	1.01	8.62	3.43	1.19	2.40
Turda II	0.46	1.98	0.89	2.76	1.40	0.92	1.52
Turda III	0.80	2.06	0.67	3.36	1.71	0.87	1.35
Campia Turzii I	0.38	2.52	0.83	4.67	2.05	1.33	2.10
Campia Turzii II	0.49	1.99	0.96	2.24	1.40	0.92	1.69
Tg. Mures I	0.15	1.61	0.89	1.43	1.02	0.81	1.47
Tg. Mures II	0.17	1.44	0.89	1.32	0.98	0.81	1.22
Tg. Mures III	0.34	1.48	0.83	0.82	0.86	0.97	1.79
Tg. Mures IV	0.13	0.96	0.51	1.92	0.60	0.47	0.83
Tg. Mures V	0.14	1.11	0.89	0.97	0.73	0.73	1.35

As it can be seen from Table 3 the pollution indexes differ considerably from one metal to another. For Cd, Co, and Mn low pollution indexes were calculated indicating that metal concentrations resemble values considered normal for soils in Romania and that there are no pollution problems that need to be further discussed.

Ni pollution indexes can be characterized as being medium in 14 out of the 15 locations analyzed. There is no alarming Ni contamination that has been identified in recreational area soils of centre Transylvanian cities since there are no locations where high values were recorded.

Zn pollution registered high values in 2 locations, medium in 7 and low in 6. These values reveal punctual Zn pollution directly linked to anthropogenic activities.

Cu and Pb contamination prove to be more serious since in the majority of locations studied pollution indexes are medium and high. For Cu there are 4 locations with high pollution indexes and 10 with medium while for Pb 6 locations have high pollution indexes and another 6 medium. These data highlight widespread Cu and Pb contamination in recreational areas within cities of central Transylvania. Therefore, it can be concluded that due to the fact that one-third of the locations analysed reveal significant Cu and Pb pollution problems, there is a great possibility that numerous parks and playgrounds within cities of Transylvania pose risks for human health and wellbeing due to heavy metal contamination.

Heavy metal pollution indexes were represented in Figure 3 for better visualisation for all locations investigated. Cu and Pb contaminations seem to have similar compositional patterns. Hotspots have been evidenced in Cluj - Napoca II, Cluj-Napoca III, Turda I and Câmpia Turzii I. Cluj-Napoca II is a middle size park in the former industrial area of Cluj-Napoca and Cluj-Napoca III is a small playground located near an intensively used roadway with great amounts of traffic. Turda I is the biggest park in the centre of the city Turda and Câmpia Turzii I is a medium sized playground near the steel plant. All four recreational areas are relatively old, and have a strong connection to anthropogenic activities.

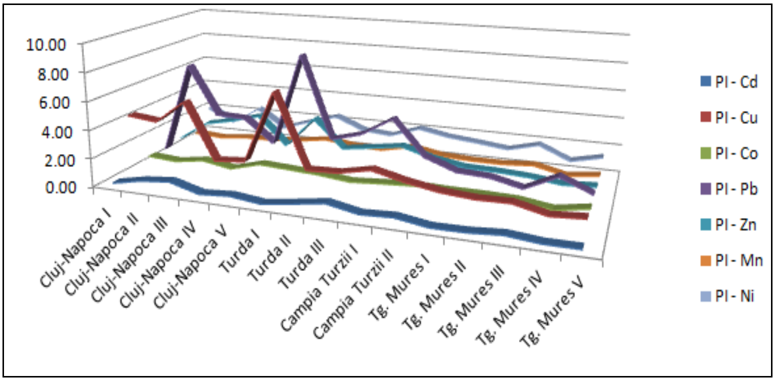


Figure 2. Heavy metal pollution in the investigated recreational areas

The Integrated Pollution Index (IPI) calculates the average of pollution indexes established for all seven metals in each recreational area [12]. Integrated pollution indexes vary between 0.77 and 3.41 and have been classified as low (IPI ≤ 1), middle (1 < IPI ≤ 2) or high (IPI > 2). The lowest values are recorded in Târgu Mureş II, Târgu Mureş III, Târgu Mureş IV, and Târgu Mureş V. These are the same locations that lack calcite and gibbsite, minerals known to have considerable influence in the accumulation of various metals in the environment. The integrated pollution index identified in the recreational areas named Turda I was the highest, followed by Cluj-Napoca III, Cluj-Napoca II and Câmpia Turzii I. Remediation measures need to be taken for these parks and playgrounds in order to reduce potential risks posed for human health.

CONCLUSIONS

The results obtained in this study characterise soils in recreational areas of 4 different cities in central Transylvania from a mineralogical point of view and assess heavy metal contamination.

All topsoil samples (0-15 cm) from parks and playgrounds in Cluj-Napoca, Turda, Câmpia Turzii and Târgu Mureş contain anorthite biotite, bytownite, illite, microcline, montmorillonite, muscovite and quartz, in various proportions. In 11 out of the 15 locations analyzed calcite, gibbsite, two minerals known to have considerable influence in the accumulation of various metals in the environment have been identified.

Heavy metal assessment reveals high concentrations especially for Cu, Pb and Zn in some locations associating contamination with anthropogenic pollution sources. Co, Mn and Ni concentrations exhibit levels comparable to the guideline values established as normal for Romanian soils. Cd concentration values are well maintained under the Romanian guideline values suggesting that in Cluj-Napoca, Turda, Câmpia Turzii and Târgu Mureş there is no sign of possible cadmium contamination.

Calculating pollution indexes for metals in all locations analyzed links Zn contamination directly to anthropogenic activities and highlights that one-third of the locations analysed reveal significant Cu and Pb pollution problems.

The integrated pollution index determined for all locations underlines the fact that in Târgu Mureş heavy metals are homogeneously distributed and values do not exceed national guidelines. Therefore it can be stated that these parks and playgrounds represent healthy environments that pose no threats to for recreational area users. In contrast, in Cluj-Napoca, Turda and Câmpia Turzii there are some locations that require immediate remediation measures in order to reduce potential risks posed for human health. In order to minimize exposure to the contaminated topsoil, contaminated areas should be restricted and soil quality annually controlled [15].

The data presented within this study represents a starting point for recreational areas quality assessments and clearly indicates that in urban settlements in Romania more attention should be paid to heavy metal contamination of parks and playgrounds.

EXPERIMENTAL SECTION

The study area comprises 15 diverse, intensively visited locations described as follows. Cluj-Napoca I is a frequently used playground located near a highly circulated street in Manastur neighborhood, Cluj-Napoca II is an old park known as knows as “The railway park”, Cluj-Napoca III is a playground on Muncii street, situated in the industrial area, Cluj-Napoca IV is the Central Park, the biggest park in the city and Cluj-Napoca V is a playground in Gheorgheni neighborhood. Turda I is the oldest and biggest park in Turda City, Turda II is a newly renovated park and Turda III is a recreational area located near the river bank. Câmpia Turzii I is a playground located near the former steel plant and Câmpia Turzii II is an old park in the center. Târgu Mureş I, II, III and V are playground located in different neighbourhoods of the city while Târgu Mureş IV is a extended recreational area with a big adventure park and a zoological garden.

In order to identify the mineral compositions and Cd, Cu, Co, Pb, Zn, Mn and Ni concentrations of soils from recreational areas mentioned above, 45 topsoil samples, were collected. Each sample is consisted of a number of sub samples mixed together and was collected from the depth interval of 0-15 cm. Soil samples were air dried for 24 hours, sieved [16] and then redried using a drying stove at 110 ^{o}C [17] in order to eliminate physically bound water.

The mineralogical composition was identified through X-Ray diffraction using a Shimadzu XRD-6000 X-ray diffractometer. When analyzing soil samples, the diffraction phenomenon occurs when x-rays are scattered by a periodical array of atoms as the ones that can be found within the crystalline structure of a mineral. The scattering of X-rays from differently arranged atoms produces a unique diffraction pattern which contains information about the atomic arrangement within a crystal. The difference among crystalline structure of minerals determines the position and intensity of peaks in a diffraction pattern [6]. A qualitative computer analysis of the peak positions and intensities associated with each sample was conducted. Mineralogical composition and its influence on heavy metal adsorption and retention were highlighted and explained using scientific literature examples.

Heavy metal concentrations from soil samples digested in aqua regia were analysed through atomic absorption spectrometry using a Solaar S4 Atomic Absorption spectrometer. This is an extremely accurate technique for metal determinations in solutions, with a wide range of detection that allows the identification of a spectrum of 70 metallic elements. Data obtained was structured into tables and for each location a general pollution index (PI) was calculated as the ratio between the heavy metal concentrations identified in the study and the normal reference value attributed for Romania. Each PI calculated vas classified as low if (PI ≤1), moderate if (1 ≤ PI ≤ 3) or high if (PI > 3). The arithmetical mean of the pollution indexes calculated for each location generated the integrated pollution index (IPI) witch was classified as low (IPI ≤ 1), middle (1 < IPI ≤ 2) or high (IPI > 2). Using the pollution index and the integrated pollution index, conclusions could be drawn in terms of heavy metal soil contamination.

ACKNOWLEDGMENTS

This paper has been completed with the support of the Doctoral School within the Technical University of Cluj-Napoca, Romania.

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