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ANALYSIS OF METAL CONTENT IN SOIL IN TIMIS COUNTY

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Abstract

The paper reports on the presence of various metals in soil in Timis county. A set of 18 samples were collected from different points of interest. The metal content of the samples was investigated using a handheld XRF Niton XLp 300 GOLDD analyzer. Special attention was paid to the metals with harmful potential to humans. Based on the obtained results, a set of conclusions on the environment's health was drawn.

1. Introduction

The soil is a natural layer on the top of Earth's surface, having specific properties and functions, developed naturally in a long period of time, but influenced more and more by human activities at present. It is a very complex medium, having an important role in supporting the vegetation, balancing the flow of water, reducing air pollution and recycling the dead organic matter and pollutants. At the same time, it is a limited resource and its improper use in various human activities may result in damaging large areas beyond recovery.

Heavy metals are natural elements in Earth's surface. Some of them play an essential role in the metabolism of living organisms, including the human one. Iron, cobalt, copper, manganese, molybdenum, and zinc are required by humans [1].They get into the organism in small quantities, along with food, water or even air [2]. In larger quantities, though, metals can become toxic [3]. The negative effect of metals on humans can build up, due to their tendency of bioaccumulation, by ingesting contaminated plants or drinking contaminated water. Pollution of soil with heavy metals originates mainly from industrial wastes. Some of these metals, like Pb, Cr, Co, Ni and Se are known for their carcinogen effects. They are commonly present in industrial environment [4], but have also been found in the air in the vicinity of industrial areas [2, 5]. Pb reaches the atmosphere by means of exhaust gases, paints or pesticides, and then it enters the soil or water and gets absorbed by plants, mainly in roots. From the atmosphere it can also deposit directly on the leaves of plants [2]. Once inside the organism, it partially accumulates in bones or hair, and partially in liver [6]. Cd has also a strong toxic effect on living organisms. It enters through skin or along with food, and accumulates in tissues, partially bonding to proteins [6]. The content of Cd and Pb in the edible part of the fresh root vegetables (carrots, radish, potatoes) or in leafy vegetables (lettuce, parsley, dill) collected in some polluted areas in Romania, exceeded several times the normal concentration, reaching up to 7 times for Cd, or 17 times for Pb [7]. Co and Ni are also used in many human activities, and can alter the health in excessive quantities.

This paper reports on the metal content in soil in Timis county, a region in the western part of Romania.

2. Samples and method

2.1. Sample Locations and Characterization

A set of 18 soil samples were collected from different locations in Timis county (see figure 1), in urban or rural areas, including various types of soils (see table 1). The soil samples were finely grinded, homogenized and then analyzed.

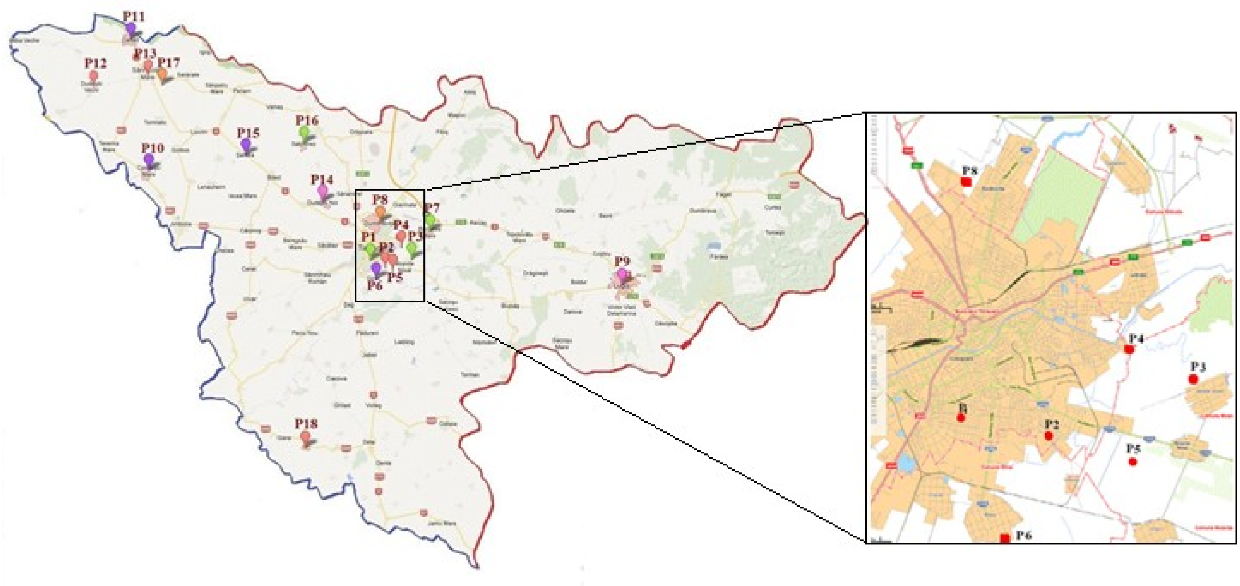


Fig. 1. Location of samples on the map of Timis county. The detail represents the city of Timisoara

TABLE 1. The sample locations and their geographic coordinates.

Samples	Location	Coordinates	Type of soil
P1	Timisoara	N 45^0 43' 46.9'', E 21^0 13' 25"	Sand, fine, gray, medium dense
P2	Giroc (Calea Urseni)	N 45^0 43' 13.5'', E 21^0 16' 1.5"	Sandy clay, plastically consistent
P3	Mosnita Veche	N 45^0 44' 21.6'', E 21^0 19' 34.6"	Sand, fine, gray, medium dense with clay lenses
P4	Ghiroda	N 45^0 45' 16.7'', E 21^0 18' 22.8"	Loam, plastically consistent, with iron oxides
P5	Mosnita Noua	N 45^0 43' 02.3'', E 21^0 17' 22.2"	Medium sand, gray, medium dense with pebbles
P6	Giroc (Str. Timis)	N 45^0 41' 28.1'', E 21^0 14' 33.1"	Medium sand, brown, medium dense with pebbles
P7	Remetea Mare	N 45^0 47' 03.8'', E 21^0 23' 08.2"	Clay, gray, plastically consistent, with Fe oxides and altered carbon concretions
P8	Dumbravita	N 45^0 47' 43.76'', E 21^0 13' 38"	Clay, brown, plastically stiff, with Fe oxides and iron-manganese concretions
P9	Lugoj	N 45^0 43' 03.4'', E 21^0 52' 55.6"	Medium sand, gray, dense
P10	Comlosu Mare	N 45^0 53'49.2'', E 20^0 36' 49.7"	Sand, brown, medium dense
P11	Cenad	N 46^0 07' 44.6'', E 20^0 31' 12.9"	Sand, medium fine, gray, medium dense, with rotten vegetal pieces
P12	Dudestii Vechi	N 46^0 03' 07.8'', E 20^0 29' 14.7"	Sand, fine, gray, medium dense
P13	Sannicolau Mare	N 46^0 00' 10.6'', E 20^0 33' 10.8"	Loam clay, plastically consistent
P14	Dudestii Noi	N 45^0 48' 59.7'', E 21^0 06' 10.4"	Clay, gray, plastically stiff, with Fe oxides
P15	Uihei (Sandra)	N 45^0 54' 42.2'', E 20^0 51' 39.2"	Sand, brown, medium fine, medium dense
P16	Satchinez	N 45^0 56' 59'', E 21^0 03' 28.9"	Silty clay, brown, plastically stiff with altered carbon concretions
P17	Sanpetru Mare	N 46^0 04' 13'', E 20^0 49' 09.6"	Sand, brown, medium fine, medium dense
P18	Livezile	N 46^0 21' 54.6'', E 21^0 03' 11.7"	Sand, fine, gray, with Fe oxides

2.2. Measurement Method

The samples were measured using a handheld Thermo Scientific Niton XL3t GOLDD analyzer. The measurement technique is based on X-ray fluorescence (XRF) which consists on the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays. The rate of generation of secondary photons is proportional to the element concentration.

The GOLDD (Geometrically Optimized Large Area Drift Detector) technology permits to identify elemental concentrations from low levels to high level of contaminated soil, on-site, in real time.

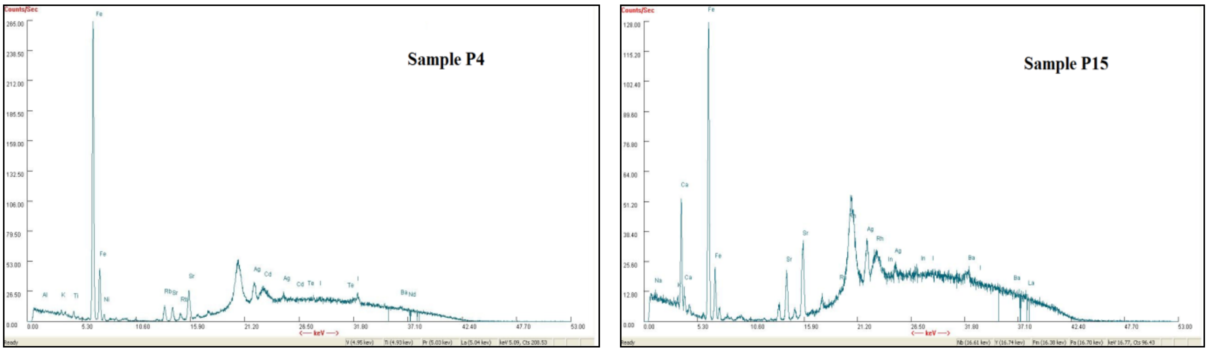
The analyzer is equipped with a 50 kV X-ray tube sample excitation system, a high-performance thermoelectrically cooled detector, 80 MHz real-time digital signal processing, and dual state-of-the-art embedded processors for computation, data storage, communication, and other functions.

The measurements were performed "ex-situ" in order to have the possibility to carefully prepare the samples. The "matrix effects" are minimized by pressing the soil grains into a pellet for improving the homogeneity of the sample. The measuring time was 10 to 15 second, which assures accurate results. The analyzer provides both the metal concentrations and the specific XRF spectrum for each sample.

3. Results and disscussions

3.1. FRX Spectra

For each sample a FRX spectrum was obtained, and the concentrations of metals were determined. The XRF spectra of the most and less abundant in Fe samples are presented in figures 2 a) and b), respectively, as examples.



a) b)

Fig. 2. FRX spectra of the a) most abundant in Fe sample (P4) and b) the less abundant in Fe sample, P15

3.2. Measurement Results

The measurement results are presented in Table 2. For emphasizing the significant values, the largest metal concentration, i.e. the highest value on each column, is bolded, and the lowest non zero metal concentration is underlined.

The metal concentrations presented in Table 3 were measured and found to be zero for all samples.

The results show that Zn is present in all locations in low to normal concentrations; Pb is generally absent in the investigated samples, excepting sample (P4), which contains Pb in a concentration 1.3 times the normal value; only two samples present As, both in concentrations approximately 1.5 times the normal value; three samples contain Ni, (P6, P11 and P13) all having concentrations exceeding the normal value 2.4 and 3 times, respectively;

Cu is either missing (5 samples) or exceeding the normal value (the other 13 samples), by a factor of as much as 2.5 (sample P3); Mn is generally present, in moderate concentrations, with only two exceptions which exceed the normal concentration (P8 and P13).

For the other investigated metals, there are no normal concentrations indicated by law.

A comparison between urban, suburban and rural sites indicates that samples P4 and P8 from suburbia of Timisoara (the first being also close to the airport) are the champions of the polluted sites, having four maximum values each, for Rb, Pb, Zn and Cu (P4) and As, Cu, Mn and Bi (P8). At the opposite, the most remote rural sites show the smallest metal concentrations in soil: sample P15 with four minimal non zero values and five zeros, and sample P10, with one minimum value and seven zero concentrations.

The contamination/pollution index (C/P index) as defined in [9], representing the ratio between the heavy metal content effectively measured in soil by chemical analysis and the reference value **A** (obtained by calculation for each sample using the formulae of the Dutch system), computed for each sample for Pb, Zn, Cu and Ni is presented in Table 4. The multiple pollution index is computed as a sum of individual indices. The significance of the values of the C/P index is as follows [9]:

- Contamination: very slight (C/p<0.1), slight (0.1-0.25), moderate (0.26-0.50), severe (0.51-0.75) and very severe contamination (0.76-1.00)

- **Pollution**: slight (1.1-2.0), moderate (2.1-4.0), severe (4.1-8.0), very severe (8.1-16.0) and excessive (>16.0).

As far as the C/P index for the four metals is concerned, the most polluted sites are the ones corresponding to samples P6, P11 and P13, while the less polluted are confirmed to be P10 and P15, as also resulted from Table 2.

TABLE 2. Metal concentration in samples.

Sample	Location	Unit	Zr	Sr	Rb	Th	Pb	As	Zn	Cu	Ni	Fe	Mn	Ti	Nb	Bi
P1	**Timisoara**	ppm	183.75	72.88	54.26	11.7	14.32	0	70.23	**24.31**	0	27887.67	**0**	2557.62	13.32	11.21
P2	**Giroc** (Calea Urseni)	ppm	195.86	79.5	44.51	13.38	17.76	0	63.92	0	0	**36702.38**	394.83	1532.98	13.59	11.33
P3	**Mosnita Veche**	ppm	186.13	67.92	56.23	14.47	15.19	0	69.55	**49.44**	0	30664.42	250.53	2204.27	13.88	14.65
P4	**Ghiroda**	ppm	120.69	57.64	**60.38**	12.45	**26.09**	0	**98.72**	47.74	0	30343.60	255.29	1663.87	13.67	**9.93**
P5	**Mosnita Noua**	ppm	209.98	63.55	42.48	12.55	0	0	44.14	38.75	0	20957.29	378.07	2226.54	15.68	11.88
P6	**Giroc (**Str. Timis)	ppm	187.84	73.69	44.1	13.68	0	0	51.81	0	**71.56**	22288.52	344.79	2726.92	**16.94**	0
P7	**Remetea Mare**	ppm	**213.37**	57.1	52.94	12.2	0	0	57.03	32.15	0	30368.86	689.65	2368.18	12.04	0
P8	**Dumbravita**	ppm	208.63	58.18	51.16	16.38	0	**7.78**	62.83	34.76	0	26662.14	**1029.19**	1938.05	13	**14.66**
P9	**Lugoj**	ppm	145.03	76.91	46.33	**17.33**	11.06	0	54.06	44.76	0	26957.70	704.53	2556.31	15.72	18
P10	**Comlosu Mare**	ppm	122.62	76.31	**32.49**	0	0	0	44.74	0	0	20473.25	561.34	0	8.57	0
P11	**Cenad**	ppm	134.41	79.9	56.34	11.35	16.79	0	79.04	29.64	59.39	32608.10	877.14	**2749.69**	12.78	11.63
P12	**Dudestii Vechi**	ppm	**97.56**	76.92	41.44	6.97	0	0	70.24	0	0	18934.24	486.34	0	6.86	0
P13	**Sannicolau Mare**	ppm	117.33	**116.92**	41.33	6.36	0	0	58.22	34.5	59.17	21345.71	**948.26**	1780.54	**6.78**	0
P14	**Dudestii Noi**	ppm	207.89	50.68	44.36	11.71	0	7.46	47.94	35.35	0	23532.07	**211.39**	2626.74	12.09	0
P15	**Uihei**	ppm	152.26	107.9	33.65	**6.1**	0	0	**39.82**	0	0	**14172.93**	393.61	**1098.55**	7	0
P16	**Satchinez**	ppm	204.33	**50.13**	45.88	11.66	0	0	47.62	26.49	0	23357.55	493.35	2040.65	12.65	0
P17	**Sanpetru Mare**	ppm	143.66	83.05	52.2	11.39	13.19	0	78.47	46.19	0	33689.27	587.17	2033.22	13.97	0
P18	**Livezile**	ppm	166.56	67.33	58.2	13.73	0	0	49.4	27.97	0	24546.11	323.26	2346.90	12.72	14.38
Normal value	**[8]**	**g/kg**					**20**	**5**	**100**	**20**	**20**		**900**			
Alert Threshold urban soil	**[8]**	**g/kg**					**250**	**25**	**700**	**250**	**200**		**2000**			
Alert Threshold rural soil (garden)	**[8]**	**g/kg**					**50**	**15**	**300**	**100**	**75**		**1500**			

TABLE 3. Metal concentrations measured and found to be zero in all samples

Element	**U**	**Se**	**Hg**	**Au**	**Cr**	**Sb**	**Sn**	**Cd**	**Pd**	**Ag**
Concentration [ppm]	0	0	0	0	0	0	0	0	0	0
Normal value [ppm] [8]		1	0.1		30		20	1		2

TABLE 4. Contamination/Pollution index for Pb, Zn, Cu, Ni and multiple pollution for all samples. Abbreviations used in table: **S.p.** – slight pollution; **M.p**. – moderate pollution; **Sev.p** – severe pollution; **V. Sev.p** – very severe pollution

Sample	Location	C/P index Pb	C/P index Zn	C/P index Cu	C/P index Ni	Multiple pollution index
P1	**Timisoara**	0.29	1.40 (S. p.)	1.62 (S. p.)	0	3.31 (M.p)
P2	**Giroc**	0.36	1.28 (S. p.)	0	0	1.63 (S.p)
P3	**Mosnita Veche**	0.30	1.39 (S. p.)	3.30(M.p.)	0	4.99 (Sev.p)
P4	**Ghiroda**	0.52	1.97 (S. p.)	3.18(M.p.)	0	5.68 (Sev.p)
P5	**Mosnita Noua**	0	0.88	2.58(M.p.)	0	3.47 (M.p)
P6	**Giroc**	0	1.04 (S. p.)	0	7.16 (Sev.p)	**8.19 (V.Sev.p)**
P7	**Remetea Mare**	0	1.14 (S. p.)	2.14(M.p.)	0	3.28 (M.p)
P8	**Dumbravita**	0	1.26 (S. p.)	2.32(M.p.)	0	3.57 (M.p)
P9	**Lugoj**	0.22	1.08 (S. p.)	2.98(M.p.)	0	4.29 (Sev.p)
P10	**Comlosu Mare**	0	0.89	0	0	0.89
P11	**Cenad**	0.34	1.58 (S. p.)	1.98 (S. p.)	5.94 (Sev.p)	**9.83 (V.Sev.p)**
P12	**Dudestii Vechi**	0	1.40 (S. p.)	0	0	1.40 (S. p)
P13	**Sannicolau Mare**	0	1.16 (S. p.)	2.30(M.p.)	5.92 (Sev.p)	**9.38 (V. Sev.p)**
P14	**Dudestii Noi**	0	0.96	2.36(M.p.)	0	3.32 (M.p)
P15	**Uihei**	0	0.80	0	0	0.80
P16	**Satchinez**	0	0.95	1.77 (S. p.)	0	2.72 (M.p)
P17	**Sanpetru Mare**	0.26	1.57 (S. p.)	3.08(M.p.)	0	4.91 Sev.p)
P18	**Livezile**	0	0.99	1.86 (S. p.)	0	2.85 (M.p)
Ref. value A [9]		50	50	15	10	

4. Conclusions

A set of measurements regarding the metal contents in soil in Timis county is presented. Comparison with normal concentrations established by law is made and the contamination/pollution index is computed for Pb, Zn, Cu and Ni for each sample. The locations with minimal metal concentrations are Comlosu Mare and Uihei, both having brown sandy soils. The locations with the maximal metal concentrations are Ghiroda and Dumbravita, and the locations with the largest multiple pollution index are Cenad and Sannicolau Mare.

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