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MACRO- AND MICROELEMENTS ABUNDANCE IN SOME URBAN SOILS FROM ROMANIA

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Abstract: The paper present dates concerning the macro- (N, P, K) and microelements (Mn, Cu, Zn, Cd, Cr, Co, Ni, Pb) in some urban soils from three large Romanian cities: Bucharest, Iasi and Baia-Mare. The soil samples from different locations as park areas, along the streets areas, and gardens for vegetables and fruits were collected. The chemical elements contents varied in a large range, from a low up to excessive pollution level. The majority of investigated urban soils are soils with carbonates, sometimes with soluble salts and alkaline reaction. Also, are rich in phosphorus and calcium. The soils located along the streets areas with intense cars traffic and/or in influence zones of some industrial objective with chemical or non-ferrous processing activities recorded heavy metals loading. In these soils the heavy metals concentration outrun by 3-4 times the maximum allowable limits. In urban soils located in Baia-Mare area, 70-80% from the total heavy metals content (Cd, Cu, Pb, and Zn) is mobile forms that could be absorbed by plants.

Key words: urban soils, abundance, macroelements, microelements, heavy metals

1. INTRODUCTION

Urban soils derive from those natural pursuant to anthropic influence caused by human settlement construction and their development. The transformation level is directly proportional with urbanization process intensity, with its nature and civilization degree reached by the inhabitants. On the strength of these reasons, the urban space will be separated in zones. Some zones in which natural soil has been strongly modified, sometimes removed as consequences of civilian and industrial buildings, urban equipment, and communication routes systems constructions, and zones where the soil has been less modified, but it received and still receiving impacts, moreover negative, caused by daily household or industrial activities. The soils belonging to this category are soils from green spaces less modified by urbanism, soils from gardens of peripheral and suburban areas denizens. At last, a final category, seldom meted, is represented by soils from urban space integral keeping its natural character. These, are soils existing under the woods included in urban space as parks along the time, soils that have been suffered any anthropic modification.

Is indubitable the fact that the abundance of chemical elements in urban soils is a result of geogenic abundance and anthropogenic ones. Many times, anthropogenic influence is decisive for urban soils properties modification, mainly those chemicals. Having in mind that the urban soils going into different use, among vegetable and/or trees cultivation in the small gardens around the houses, the nutritive chemical elements level knowledge is usefully.

In this context, studies concerning urban soil chemistry, especially about macro- and microelements contents as premise for urban agriculture developing, were carried out in Romania. Some of these studies results are presenting further.

2. MATERIALS AND METHODS

From urban zone of three big Romanian cities: Bucharest, Iassy and Baia Mare, samples have been taken from upper horizon of soil, at up to 20 cm depth. Samples were collected from the parks, gardens and from the green zones located along the streets.

Soil samples have been analyzed from physical and chemical point of view. Clay content, soil reaction (pH in aqueous solution), carbonates and organic carbon content, the primary order macroelements (N, P and K) and the mainly nutritive microelements (Mn, Cu, Zn, Co) have been determined, also, the metallic chemical elements without plant nutrition contribution but with pollutant potential (Cd, Cr, Ni, Pb).

Total macro- and microelements content has been determined through physico-chemical methods as spectrophotometry in visible light (P), flame emission photometry (K), atomic absorption spectrometry (Mn, Cu, Zn, Co, Cd, Cr, Ni, Pb) and steamed distillation (Kjeldhal method for nitrogen). Total contents of heavy metals were determined in hydrochloric acid solution obtained after soil mineralization with $HClO_4$ and HNO_3, and mobile contents by extraction at equilibrium with K_2SO_4 0.1n (N-NH_4; N-NO_3); ammonium acetate lactate (AL) for P and K.

Statistic analyze was applied on dates, and grouping center parameters, statistical spreading parameters, and correlative bounding between different chemical properties.

3. RESULTS AND DISCUSSIONS

3.1. The Nature of Urban Soils from Bucharest, Iassy and Baia Mare

Romanian metropolis Bucharest, with a surface about 228 square kilometers, over 2 billions inhabitants, is located in southeastern part of country in a plain zone. The developing of city has occurred on natural soils belonging to the different types as Chernozems and Brown Redish types. By anthropic action, these natural soils have becoming urban soils as Urbic Regosols, Regosols and Humic Regosols.

Iassy is locating in extreme eastern part of country, in a hilly zone, having 340,000 inhabitants, and 93.9 square kilometers surface. The urban soils belonging to

Urbic and Mixic Entiantrosols have been deriving from natural soils belonging to Chernozems or Alluvial Soils types, some of them saline.

Baia Mare, located in the north-eastern part of Romania, having 148,263 inhabitants, and stretches on a surface about 35,73 square kilometers, is a city well known for its complex sulfide ores extraction and processing industry. The natural soil, which on the settlement has been developed are Albic Luvisols type and Brown Acid type, both, being acid soils. In those strongly modified zones have been resulted Urbic, Mixic and Urbic-Alluvic Entiantrosols.

3.2. Reaction and Mainly Analyzed Urban Soil Properties

Different reaction domains defined by pH ranges values (table 1), varying from slightly (medium) alkaline for Bucharest and Iassy urban soils to moderate acid up to neutral reaction for Baia Mare urban soils. Analyze of grouping center parameters values establishing a slightly alkaline soil reaction in the first two cases and slightly acid soil reaction in the last case. The carbonates presence in these urban soils generated from natural soils without carbonates, could be explain only by anthropic influence link by building activities, especially. Thus, in these three locations the carbonate content varied from zero up to high values, in Bucharest and Iassy, and up to medium values in Baia Mare. Generally, the carbonates content in all three locations is medium (table 1).

Table 1. Statistical parameters of the main chemical and physical indicators in urban soils from Bucharest (B), Iassy (I) and Baia Mare (BM)

Parameter	pH_{H2O}			$CaCO_3$ (%)			Corg. (%)			Clay (<2μ) (%)		
	B	I	BM	B	I	BM	B	I	BM	B	I	BM
X_{min}	6.3	6.4	5.2	0	0	0	0.59	0.50	0.31	12	10	15
X_{max}	8.2	8.5	7.0	29.0	35.0	4.0	2.22	2.80	1.27	31	34	40
X	7.8	7.9	6.1	7.4	8.7	0.8	1.74	1.80	0.88	24	26	30
σ	0.5	0.6	0.4	5.1	7.4	0.6	0.51	0.6	0.3	8	7	10
CV (%)	6.4	7.6	5.3	68.0	85.0	75.0	29.3	33.0	34.0	33	27	33
Me	7.4	7.3	6.0	7.3	8.5	0.6	1.70	1.8	0.8	21	23	29
Mo	7.3	7.4	5.9	7.1	8.4	0.7	1.65	1.6	0.7	20	22	27

Although, organic carbon content is small, with medium values about 1.7%, sometimes, this element is present in large quantities in urban soils from Bucharest and Iassy, up to values higher than 2%. In Baia Mare, the organic carbon content is smaller than in the first two cities reaching only 1.27% value. The medium organic carbon content is about 0.8% that means very small value of this chemical indicator (table 1). The colloidal clay content (θ < 2 mm) indicating predominant loamy texture of urban soils from Bucharest and Iassy, and a clayey texture of Baia Mare urban soils (table 1).

3.3. The Main Macroelements Abundance

Dates concerning total contents of main macroelements (N, P and K) analyze revealing close and higher values in Bucharest and Iassy and smaller in Baia Mare. Considering the values range and grouping center parameters resulting that urban soils from Bucharest and Iassy have medium nitrogen content, and those from Baia Mare have the small one (table 2). In spite of this differentiation, the nitric azote content is relative uniform, with a maximum value up to 18 mg kg^{-1} N-NO_3 and with grouping center values between 7 and 12 mg kg^{-1} N-NO_3 (table 3). These values meaning a low level of nitric azotes supplying, are specific for the soils that have not received any organic or mineral fertilizers. Therefore, in normal conditions, the urban soils are poorly supplied with mobile nitrogen forms, that representing one of the specific chemical property of these soils (Lacatusu R., 2005).

Table 2. Statistical parameters of main order macro-elements total content (%)

Parameter	N			P			K		
	B	I	BM	B	I	BM	B	I	BM
X_{min}	0.074	0.089	0.031	0.044	0.052	0.027	0.72	0.92	0.56
X_{max}	0.251	0.264	0.167	0.194	0.241	0.093	3.54	3.82	3.20
X	0.169	0.165	0.120	0.120	0.172	0.069	2.70	2.66	1.97
σ	0.035	0.047	0.024	0.040	0.032	0.011	0.83	0.70	0.54
CV (%)	21	28	20	33	19	16	31	26	27
Me	0.143	0.157	0.112	0.106	0.148	0.052	2.56	2.43	1.80
Mo	0.138	0.156	0.110	0.101	0.140	0.047	2.51	2.37	1.76

From former researches (Bennett, 2003; Foy et al., 2003; Lacatusu et al., 2005; Yuan et al., 2007) resulted those urban soils containing significant phosphorus quantities. In deed, the soils analyzed by us having high phosphorus content, too, recorded values up to 0.241% and medium values about 0.172% in Iassy urban soils. However, Baia Mare urban soils recorded medium values about only 0.069% (table 2). Mobile forms phosphorus values over than 600 mg $\cdot kg^{-1}$ recorded in Bucharest and Iassy urban soils and about 367 mg kg^{-1} in Baia Mare urban soils. Medium values of mobile phosphorus in urban soils from all three locations ranging between 91 and 149 mg kg^{-1}, values that, without exception, defining a very high content domain.

Regularly, the potassium there is in large quantities in urban soils. In natural soils case, developed on loess, the potassium content is superior to in other soil types. Bucharest and Iassy urban soils belonging to this category, higher total potassium contents that exceeding by all odds 3% being a prove for that. Medium total potassium values, rounding about 2.5%, are revealing a very good soil supplying with this macroelement. In addition, the mobile potassium content is very high, reaching a maximum value about 882 mg kg^{-1} in Iassy urban soils. Medium values of mobile potassium from Bucharest and Iassy urban soils are ranging between 366 and 429 mg kg^{-1}, making point very high mobile potassium content in soil. Analytical and statistical dates of mobile potassium content values in Baia Mare urban soils are lower than recorded in the other two studied locations. However, the 300 mg kg^{-1} mobile potassium is the value round about all statistical dates (table 3), that is designating the lower limit of very high mobile potassium soil supplying domain.

Therefore, analyzed urban soils are containing low quantities of mobile mineral nitrogen as nitrates, but very large quantities of mobile phosphorus and potassium.

Table 3. Statistical parameters of mobile forms of macro-elements (mg ·kg^{-1})

Parameter	$N\text{-}NO_3$			P_{AL}			K_{AL}		
	B	I	BM	B	I	BM	B	I	BM
X_{min}	2	3	1	4	2	5	73	114	95
X_{max}	18	16	15	608	649	367	728	882	640
X	11	10	9	124	149	107	429	395	311
σ	4	5	6	156	170	96	252	206	179
CV (%)	36	50	66	125	114	89	58	52	57
Me	9	12	11	103	131	88	389	340	274
Mo	7	9	10	91	109	87	374	366	248

3.4. Microelements Abundance

The analyzed microelements were divided in two groups: the first including chemical elements with biogenic role (Co, Mn, Cu, Zn), and the second without biogenic role, having even toxic effect on environment (Cd, Cr, Ni and Pb). According to content level or their abundance, the chemical elements belonging to the first group could produce negative effects on environmental factors. In fact, from environmental sciences point of view, all these chemical elements are included in heavy metals generic terms.

Table 4 Statistical parameters of total microelements content (mg · kg^{-1})

Parameter	Co			Mn			Cu			Zn		
	B	I	BM	B	I	BM	B	I	BM	B	I	BM
X_{min}	16	18	12	407	322	453	21	4	23	126	41	180
X_{max}	183	254	151	794	925	884	70	904	404	321	1344	2695
X	28	34	24	565	501	597	39	31	166	212	131	585
σ	23	28	19	153	83	174	18	102	193	65	145	622
CV (%)	82	84	79	27	17	29	47	334	116	31	110	106
Me	24	30	20	520	502	524	37	26	143	193	93	507
Mo	23	33	19	510	501	231	30	21	247	184	125	481

Table 5 Statistical parameters of total heavy metals content (mg · kg^{-1})

Parameter	Cd			Cr			Ni			Pb		
	B	I	BM	B	I	BM	B	I	BM	B	I	BM
X_{min}	0.3	0.1	0.30	11	15	12	11	22	18	5	23	151
X_{max}	4.6	33.3	16.60	41	71	31	44	79	50	359	524	3261
X	1.8	2.1	3.30	30	35	21	33	47	25	61	62	834
σ	0.7	5.3	3.70	5	12	6	6	9	6	45	77	857
CV (%)	39	252	113	17	35	29	18	19	30	74	125	103
Me	1.7	0.7	3.21	25	32	20	30	47	24	57	45	794
Mo	1.6	2.3	3.27	24	31	18	31	47	22	53	57	807

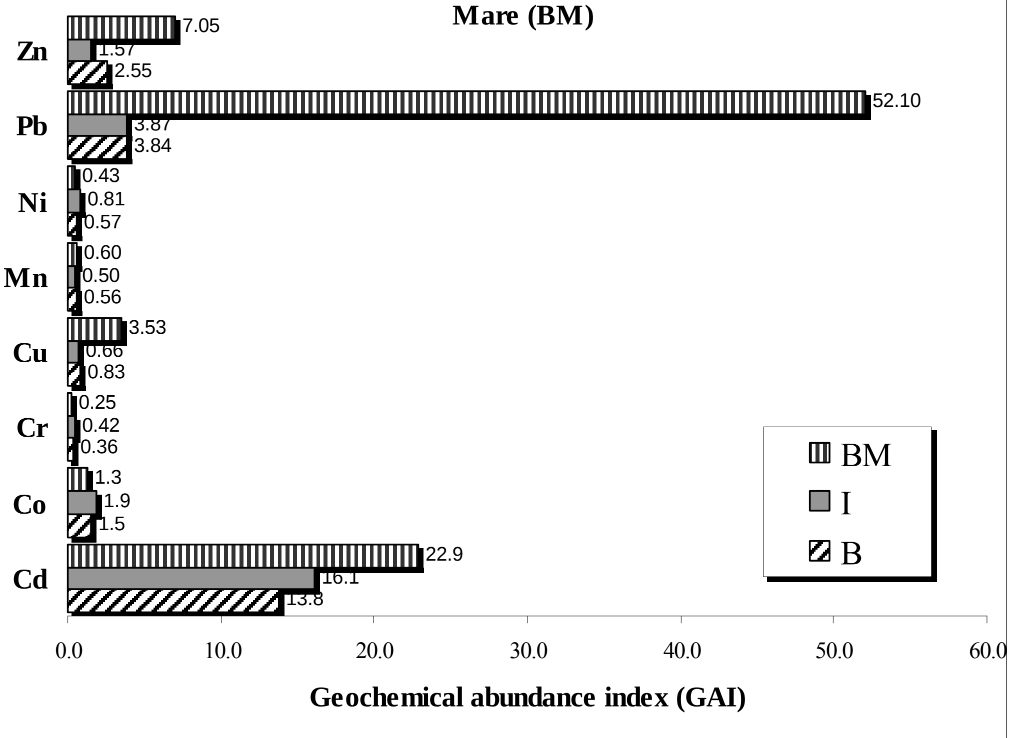
Analytical dates, statistically calculated, have been reveal differences between both chemical elements and locations (table 4 and 5). Thus, if a chemical elements as

Co, Mn, Cr and Ni ranging between closely limits for all three locations, having as consequence the groping center parameters values nearly, too, not the same aspects were recorded about other analyzed elements: Cd, Cu, Zn and Pb (table 4 and 5). In those last mentioned chemical elements case, there are contrasting values between locations, recorded normal and nearly values for Bucharest and Iassy urban soils, and very high, pollutant, values, for Baia Mare urban soils. If we comparing the medium values of Cd, Cu, Zn and Pb total contents from Bucharest and Iassy urban soils with those from Baia Mare urban soils, we finding out that this latter are higher than the first by 13.7 times for Pb, 4.7 times for Cu, 3.4 times for Zn and 1.7 times for Cd.

For a correctness and better evaluation of microelements abundance in urban soils of this three locations, geochemical abundance index (GAI), pedogeochemical abundance index (PAI) and anthropogenic abundance index (AAI), were calculated (Lacatusu & Ghelase, 1992).

We could observe the pollutant character of Cd, Cu, Pb and Zn, expressed in high values (figure 1-3), in Baia Mare urban soils.

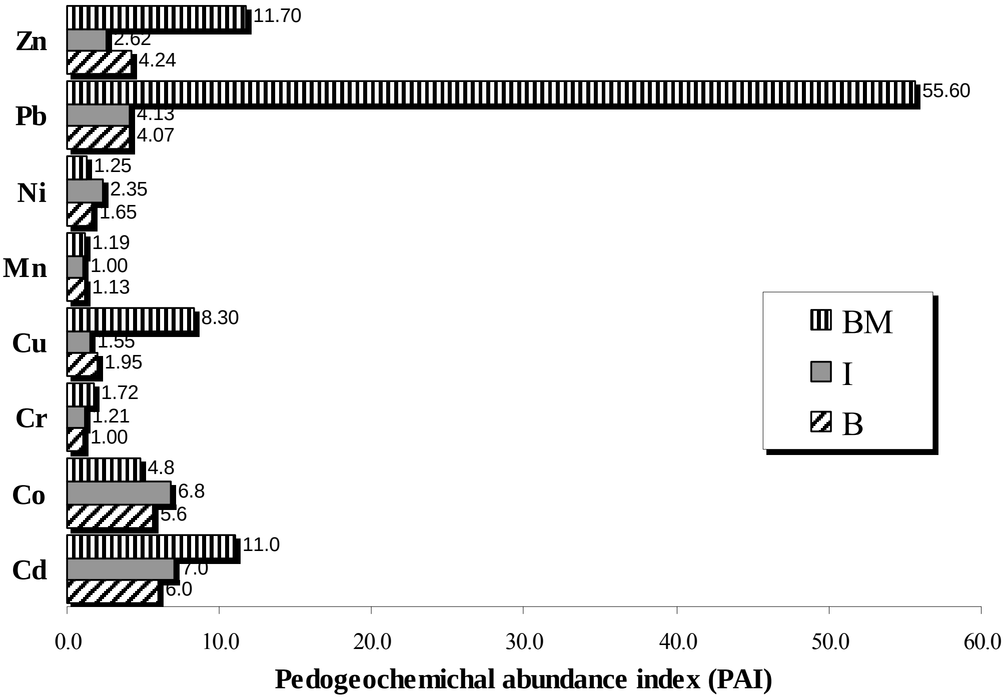
Figure 1. Geochemical abundance index (GAI) of heavy metals in urban soils from three cities: Bucharest (B), Iassy (I) and Baia Mare (BM)



Geochemical abundance index (GAI) clearly showing that elements as Cd, Co, Pb and Zn and in part Cu (for Baia Mare urban soils) having a superior abundance as comparing with clark values (that reliving the lithosphere abundance), while Cr, Mn and Ni having in analyzed urban soils an inferior abundance as comparing with those of lithosphere (figure 1).

As comparing with general content level of analyzed microelements in urban soils from the three chosen cities, we could observe that the abundance of Cd, Cu, Pb and Zn from Baia Mare soils is superior, reaching maximum values (figure 2).

Figure 2. Pedogeochemichal abundance index (PAI)of heavy metals in urban soils from three cities: Bucharest (B), Iassy (I) and Baia Mare (BM)

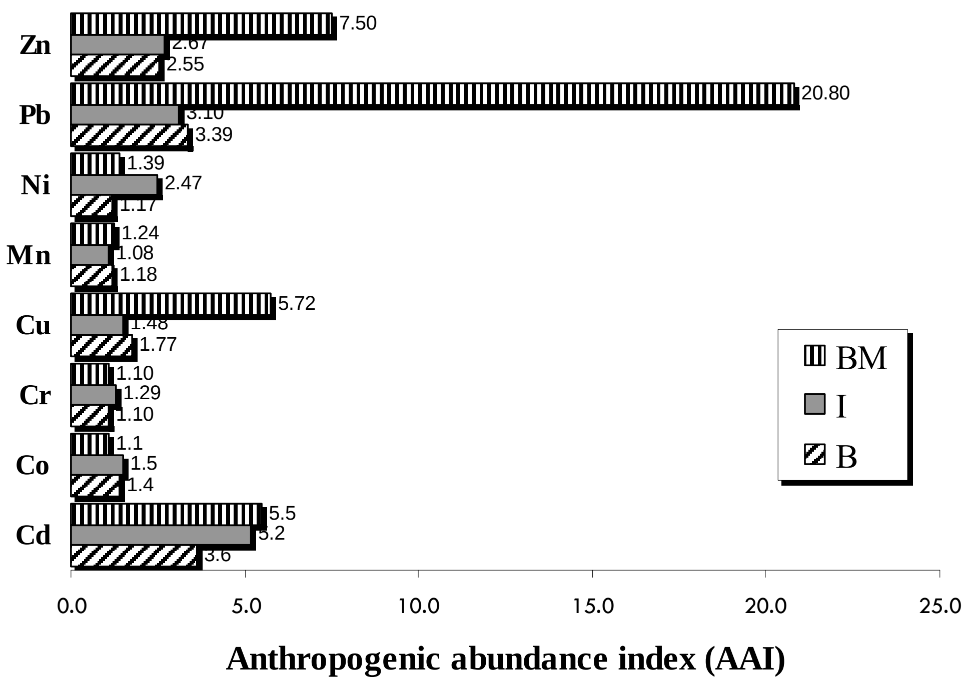


Anthropogenic abundance index (AAI) revealing the analyzed chemical elements level in urban soils as comparing with content level in natural soils located in suburban zones. As we expected, those indexes values are over the unit, but, regularly, and smaller than the values of pedogeochemical abundance index. This dates showing that natural soils from suburban zones having a microelements content level higher than those generally meted in soil cover (Fiedler & Rosler, 1988). Again, those four chemical elements: Cd, Cu, Pb and Zn, distinguish between the others, and in Baia Mare having a pregnant pollutant character (figure 3).

The lead content in urban soils from Baia Mare recorded for abundance indicators values that exceeding by 13.5 (GAI), 11.3 (PAI) and 6.5 times (AAI) the values established in other two locations. A differential measurement of abundance indicators values for other three heavy metals (Cd, Zn, Cu) has relieved the following decreasing order: cadmium, zinc and copper.

If analyze only the values of microelements abundance indicators for Bucharest and Iassy urban soils we could seeing that they are closely, but in majority of cases values recorded in Iassy urban soils are higher, although, without an evident significance (figure 1-3).

Figure 3. Anthropogenic abundance index (AAI) of heavy metals in urban soils from three cities: Bucharest (B), Iassy (I) and Baia Mare (BM)



4. CONCLUSIONS

1. The urban soils from the three Romanian cities belonging, firstly, Entiantrosols type, generated from different natural soils types as: Chernozems, Brown Reddish soils (Bucharest), Cernozems, Alluvial soils (Iassy) and Albic Luvisols, Brown Luvic soils (Baia Mare).
2. Total nitrogen abundance recorded small (Baia Mare) and medium content levels (Bucharest and Iassy), while mobile nitrogen abundance, as nitrites, was low.
3. Urban soils from all three cities having very high phosphorus and potassium contents, originated from anthropic activities.
4. Metallic microelements abundance is connected with the chemical element nature and its location. Normal content levels from cobalt, chrome, nickel and manganese in all analyzed urban soils, were determined. However, cadmium, copper, lead and zinc reached strong and very strong pollutant levels in urban soils from Baia Mare.

BIBLIOGRAPHY

Bennet E. M., 2003, *Soil phosphorus concentrations in Dane county, Wisconsin, USA: an evaluation of the urban-rural gradient paradigm*, Environ. Manage., 32, 476-487.

Fiedler H. J., Rösler H. J., 1988, *Spurenelemente in der Umwelt*, Ferdinand Enke Verlag, Stuttgard.

Foy R. H., Lennox S. D., Gibson C. E., 2003, *Changing perspectives on the importance of urban phosphorus inputs as the cause of nutrient enrichment in Long Neugh*, Sci. Tot. Environ., 310, 87-89.

Lacatusu R., Ghelase Ileana, 1992, *On abundance of heavy metals in soil*, Med. Inconj., vol III, 4, 45-52 (published in Romania).

Lacatusu R., 2005, *Consideration on urban soils,* Factori si procese pedogenetice in zona temperata. Serie noua, vol. 4, 69-78 (published in Romania).

Lacatusu R., Rasnoveanu I., Breaban Iuliana, Rusu C., Lungu Mihaela, Kovacsovics Beatrice, 2005. *Urban soils in Iassy municipium.* Factori si procese pedogenetice in zona temperata. Serie noua, vol 4, 135-143 (published in Romania).

Yuan Gang-Da, Zhang G. L., Gong Z. T., Burghardt W., 2007, *Variations of soil phosphorus accumulation in Nanjing, China as affected by urban development,* J. Plant Nutr. Soil Sci., 170, 244-249.

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