EVALUATION OF THE ORGANIC MATTER AND CLAY CONTENT CONTRIBUTION TO THE CORRECTED REMEDIATION VALUES OF THE TRACE ELEMENTS MAXIMUM ALLOWED CONCENTRATIONS IN THE AGRICULTURAL SOILS OF PROKUPLJE MUNICIPALITY, SERBIA

Radmila Pivić, Aleksandra Stanojković-Sebić, Zoran Dinić, Jelena Maksimović

Institute of Soil Science, Teodora Drajzera 7, Belgrade, Serbia
e-mail: drradmila@pivic.com

Abstract
In the samples of Prokuplje Municipality agricultural soil, it was assessed the contribution of the organic matter and clay content influence on the corrected remediation values of the total forms of Cd, Cr, Pb and Ni maximum allowed concentrations (MAC). A total of 25 samples were analyzed, of which 8 samples were on Fluvisol type of soil, 3 samples were on Vertisol type of soil, 12 samples were on Eutric cambisol type of soil, and 2 samples were on Humofluvisol type of soil. In composite soil samples, taken from a depth of 0-30 cm, certain parameters of soil fertility (content of clay fraction and total forms of Cd, Cr, Pb and Ni), were determined.The interpretation of the obtained results was carried out in relation to the MAC of tested microelements defined in the Regulation on permitted levels of hazardous and harmful substances in the soil, and based on the formula for calculating threshold and remediation values according to Ordinance on the program of soil quality systematic monitoring, indicators for risk assessment from soil degradation, and methodology for developing remediation programs. A high correlative dependence related to the content of organic matter was determined for Vertisols and Humofluvisols, while it was low for Eutric cambisol and Fluvisol. The correlative dependence related to the content of clay fraction showed a strong correlation, for all examined soils.

Introduction
The origin of heavy metals in soil can be geochemical and anthropogenic. The geochemical origin refers to the practical, natural origin of heavy metals in the soil. Certain igneous rocks are characterized by a high content of some heavy metals, especially those that contain ore minerals. Sedimentary rocks comprise about 75% of the rocks that are located near the surface of the earth's crust and therefore have primary importance as the parent substrate of the soil [1]. According to Daskalopoulou et al. [2], high concentrations of trace elements in the soil can affect soil fertility and thus represent an ecological and human health risk if they enter the food chain or are washed into the aquifer.
The mobility of trace elements is influenced by the content of the clay fraction, organic matter and soil pH value [3,4]. In the soil pH interval from 5.50 to 8.00, Cr is almost insoluble, while the solubility of Cd decreases with increasing pH, so that at pH values higher than 7.50, its immobilization occurs. In soils with pH values from 3.80 to 7.10, Cd is less mobile than Ni [5]. The value of organic matter and clay fraction content in the ratio 1:3 influence the mobility of Cd to an insignificant extent. The mobility of Cr and Ni is not affected by the content of organic matter in the soil, while the mobility of Pb is equally affected by the content of clay and organic matter [6]. Based on the data obtained as part of the research [1], the results of organic matter and clay fraction content analysis were processed and their contribution to the assessment of the maximum allowed concentrations (MAC) of investigated trace elements corrected values was determined in accordance with Official Gazzetes of RS [7,8]

Experimental

The municipality of Prokuplje forms the central part of the Toplica sub-region in Serbia, which geographically lies in 43˚10' and 43˚20' of north latitude, and 21˚00' and 21˚50' of east longitude. It covers 75,896 ha, of which agricultural soil occupies 45,083 ha or 60% of the area. The study area has a moderately continental climate with mild transitions between seasons in the basin and long and harsh winters in the mountainous region [1].
The locations of the sampled soil and the type of soil are shown in Table 1.

Table 1. Sampling points and soil type

Sampling point	Coordinate		Soil tipe	Sampling point	Coordinate		Soil tipe
	X	Y			X	Y	
1.	4790957	537876	Fluvisol	14.	4787859	538423	Fluvisol
2.	4784989	530198	Fluvisol	15.	4787338	540137	Humofluvisol
3.	4791875	543018	Vertisol	16.	4787900	537437	Eutric cambisol
4.	4793753	542981	Vertisol	17.	4787938	537389	Eutric cambisol
5.	478768	537310	Eutric cambisol	18.	4791118	549879	Eutric cambisol
6.	4791055	537796	Eutric cambisol	19.	4789092	534040	Fluvisol
7.	4789104	550116	Eutric cambisol	20.	4790716	550010	Eutric cambisol
8.	4790791	532767	Fluvisol	21.	4792163	542846	Vertisol
9.	4784843	529900	Eutric cambisol	22.	4794467	542419	Eutric cambisol
10.	4792496	542907	Eutric cambisol	23.	4796588	547347	Eutric cambisol
11.	4786837	541028	Humofluvisol	24.	4794110	547390	Eutric cambisol
12.	4788473	536928	Fluvisol	25.	4792246	534794	Fluvisol
13.	4788369	536468	Fluvisol				

From the 25 soil samples, sampled and tested, 8 samples are on Fluvisol type soil, 3 on Vertisol type soil, 12 samples on Eutric cambisol type soil, and 2 samples on Humofluvisol type soil [9]. Soil sampling in a disturbed state was done from a depth of 30 cm, according to the instructions, which refer to standard sampling methods [10, 11].
In 25 composite soil samples, prepared in accordance with standard method [12], soil acidity was analyzed potentiometrically, using glass electrode [13], calcium carbonate by volumetric method [14], total C content was analyzed on elemental CNS analyzer Vario EL III [15], SOM (soil organic matter) was calculated using the formula: SOM content (%) = organic C content (%) x factor 1.724 [16]. Granulometric composition was analyzed by determination of particle size distribution in mineral soil material [17]. Determination of the total trace elements forms (Cd, Cr, Pb, Ni) was done by inductively coupled plasma-atomic emission spectrometry - THERMO iCAP 6300 Duo (radial/axial view versions) ICP-OES, after the digestion of the samples with aqua regia [18,19].
The interpretation of the trace elements content in soil samples was carried out based on the guidelines [8], where the following parameters are defined: MAC for Cd = 3 mg kg^{-1}, MAC for Cr = 100 mg kg^{-1}, MAC for Pb = 100 mg kg^{-1}, MAC for Ni = 50 mg kg^{-1}.
For adjusted established MAC [7] it was applied the equation defined by Official Gazzete of RS [8], as follows:

$$\mathbf{(SW, IW)_b = (SW, IW)_{sb} * \frac{A + (B * \%\ clay) + (C * \%\ SOM)}{A + (B * 25) + (C * 10)}}$$

In the equation, A, B and C present the constants dependent on the type of trace element; $(SW, IW)_b$ is corrected threshold or remediation value for a particular soil; $(SW, IW)_{sb}$ is threshold or remediation value from the table of Official Gazzete of RS [7], which determines the corrected MAC value.

Results and discussion

Soil organic matter (SOM) is a complex, naturally occurring material, and plays a critical role in soil fertility, the global carbon cycle, and the portion of pollutants in soil [20]. The level of organic carbon in the soil is closely related to the structure of the soil and is one of the main factors of aggregation [21]. With an increased content of clay particles, the content of organic carbon in the soil tends to increase.

Table 2 shows the values of the examined chemical parameters and the content of clay fraction depending on the soil type and the corresponding statistical parameters. The research results showed that the reaction of the soil solution of the tested samples ranges from acidic to neutral in Eutric cambisol, Fluvisol and Vertisol, while in Humifluvisol it is in the range of slightly acidic to neutral. According to the carbonate content, only certain Vertisol samples are highly carbonated, while samples of other soil types are classified as weakly carbonated and carbonate-free soils. The content of organic matter in the examined samples of all soil's ranges from medium to high, depending on the content of the clay fraction (Table 2).

Table 2. Tested chemical parameters depending on the soil type and clay fraction content

Soil tipe	Parameter	pH 1M KCl	$CaCO_3$	SOM	Clay (<0.002 mm)
			%	%	%
Eutric cambisol	Min	4.80	0.42	2.20	11.40
	Max	6.80	0.42	4.03	53.00
	Average	5.52	0.42	2.76	31.84
	STDEV	0.61	IGDM	0.57	13.02
	CV	0.35	IGDM	1.59	7.52
Fluvisol	Min	5.20	0.04	1.84	18.60
	Max	7.20	2.73	4.31	51.30
	Average	6.19	1.20	3.04	39.03
	STDEV	0.78	1.16	1.03	10.79
	CV	0.45	0.67	1.75	6.23
Vertisol	Min	4.60	10.90	2.98	28.30
	Max	7.20	10.90	5.48	49.10
	Average	5.83	10.90	3.83	36.37
	STDEV	1.31	IGDM	1.43	11.16
	CV	0.75	IGDM	2.21	6.44
Humofluvisol	Min	5.70	0.46	2.11	31.60
	Max	6.80	0.46	3.12	33.60
	Average	6.25	0.46	2.62	32.60
	STDEV	0.78	IGDM	0.71	1.41
	CV	0.45	IGDM	1.51	0.82

The content of Ni in the tested soil types was in the great majority of samples above the MAC (in Eutric cambisol in 6 samples, Fluvisol in all tested samples, in Vertisol in 2 out of 3 tested samples, and in Humofluvisol in 1 of the 2 tested samples. By analyzing the content of trace elements in soil samples, the content of Cd, Cr, Pb in all samples on the tested soil types was below the MAC [8].

By applying the equation for determining the corrected MAC value, taken from Official Gazzete of RS [7], which includes the coefficients of the organic matter content and the clay fraction in the calculation, it was determined that the content of the tested elements in no type of soil exceeds the corrected MAC value. The determination coefficient between the ratio of the corrected MAC value for each element and each type of soil and the MAC value determined by the Regulation [19] and the content of organic matter, i.e. the content of the clay fraction, was determined (Table 3).

Table 3. The average content of the total forms of tested trace elements depending on the soil type and determination coefficient between the ratio of the corrected MAC value for each element and each type of soil and MAC value determined by the Regulation [8] and the content of organic matter and clay fraction, respectively

Soil type	Average content of element mg/kg - R^2			
	Organic matter content			
	Ni	Pb	Cr	Cd
Eutric cambisol	46.96	15.93	50.36	0.29
	y = 0,0066x + 2,6868 R^2 = 0,1396	y = 0,0174x + 2,8206 R^2 = 0,1727	y = 0,0094x + 2,6868 R^2 = 0,1396	y = 0,026x + 3,152 R^2 = 0,242
Fluvisol	66.81	16.23	68.71	0.32
	y = 0,0101x + 2,6268 R^2 = 0,1432	y = 0,0278x + 2,8036 R^2 = 0,1945	y =0,0145x + 2,6268 R^2 = 0,1432	y =0,0425x + 3,2977 R^2 = 0,3012
Vertisol	46.43	16.83	49.7	0.29
	y = 0,0445x + 2,3819 R^2 = 0,9808	y = 0,096x + 3,2399 R^2 = 0,9849	y = 0,0636x + 2,3819 R^2 = 0,9809	y = 0,1036x + 4,4875 R^2 = 0,99
Humoflu-visol	63.35	45.95	65.15	0.35
	y = 0,1768x - 1,223 R^2 = 1	y = 0,2852x + 2,5429 R^2 = 1	y = 0,2525x - 1,223 R^2 = 1	y = 0,2252x + 5,5376 R^2 =1
Clay fraction content				
Eutric cambisol	46.96	15.93	50.36	0.29
	y = 0,35x + 25 R^2 =1	y = 0,8326x + 32,179 R^2 = 0,9979	y =0,5x + 25 R^2 = 1	y = 1,0435x + 45,544 R^2 = 0,9828
Fluvisol	66.81	16.23	68.71	0.32
	y = 0,35x + 25 R^2 =1	y = 0,8222x + 32,196 R^2 = 0,9953	y =0,5x + 25 R^2 =1	y =0,994x + 45,107 R^2 = 0,9633
Vertisol	46.43	16.83	49.7	0.29
	y = 0,35x + 25 R^2 = 1	y =0,754x + 31,76 R^2 = 0,9998	y = 0,5x + 25 R^2 =1	y =0,8107x + 41,538 R^2 = 0,9985
Humoflu-visol	63.35	45.95	65.15	0.35
	y = 0,35x + 25 R^2 = 1	y =0,5648x + 32,457 R^2 = 1	y =0,5x + 25 R^2 = 1	y =0,4459x + 38,387 R^2 =1

Conclusion

In the Serbian legislation, screening values in soil are defined as the maximum allowed concentrations, maximum limit values, corrective maximum limit values, remediation values and corrected remediation values. The obtained results indicate that the constant C, related to the product, which is used in the calculation for a specific element (C=0.021 for Cd; C=0 for Cr; C=1 for Pb; C=0 for Ni) has a greater dependence on sandy soils, which is expected considering the source of the formula, which is primarily intended for the studied soils. The highest determination coefficient related to the content of organic matter was determined for Vertisol and Humofluvisol soils, while it is low for Eutric cambisol and Fluvisol soils. The correlative dependence related to the content of the clay fraction shows a strong correlation, for all tested soils, which is in agreement with the assigned constants B for the tested elements (B=0.007 for Cd; B=2 for Cr; B=1 for Pb; B=1 for Ni). Soil is a "complex matrix" that is affected by many factors, but also their mutual influences, which depending on the conditions and factors at a given moment, can be from completely synergistic to completely antagonistic [22]. Monitoring and interpreting the condition of such a matrix requires a more complex interpretation compared to the current interpretation based on simple relationships between the values of soil condition parameters defined by the legislation of the Republic of Serbia.

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References

[1] Institute of Soil Science, Hazardous and harmful substances in agricultural soil, irrigation water and cultivated crops of the Municipality of Prokuplje in order to obtain health-safe products, Study, 2019 (in Serbian).
[2] K. Daskalopoulou, S. Calabrese, S. Milazzo, L. Brusca, S. Bellomo, W.D'Alessandro, K. Kyriakopoulos, F. Tassi, F. Parello, Ann. Geophys. 57 (2014) 1.
[3] A. Kabata-Pendias, Trace Elements in Soils and Plants, 4th ed. CRC Press, Taylor & Francis Group, Boca Raton, Florida, 2011.
[4] R. Pivić, Z. Dinić, J. Maksimović, D. Poštić, R. Štrbanović, A. Stanojković-Sebić, Matica Srpska J. Nat. Sci. Novi Sad 138 (2020) 97.
[5] D.C. Adriano, Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability, and Risks of Metals, 2nd ed. Springer Science, 2001.
[6] The Dutch Environment Ministry, Soil Remediation Circular 2009, Ministry of Housing, Spatial Planning and Environment Directorate-General For Environmental Protection, 2009.
[7] Official Gazzete of RS, Regulation on the Program of Systematic Monitoring of Soil Quality, Indicators for Assessing the Risk of Land Degradation and Methodology for Developing Remediation Programs, "Sl. *glasnik* RS", 30/2018 and 64/2019, 2019 (in Serbian).
[8] Official Gazzete of RS 23, Regulation on Permitted Quantities of Dangerous and Harmful Substances in Soil and Water for Irrigation and Methods of Their Testing, "Sl. *glasnik* RS", 23/94, 1994 (in Serbian).
[9] WRB, World Reference Base for Soil Resources, World Soil Resources Reports, 106, FAO, Rome, Italy, 2014.
[10] ISO 18400-102:2017, Selection and application of sampling techniques, Geneva.
[11] ISO 18400-105:2017, Packaging, transport, storage and preservation of samples, Geneva.
[12] SRPS ISO 11464:2004, Soil quality-Pretreatment of samples for physico-chemical analyses, Belgrade.
[13] SRPS ISO 10390:2007, Soil quality - Determination of pH, Belgrade.
[14] SRPS ISO 10693:2005, Soil quality - Determination of carbonate content, Belgrade.
[15] SRPS ISO 13878:2005, Determination of total nitrogen content by dry combustion (“elemental analysis”), Belgrade.
[16] R. Džamić, D. Stevanović, M. Jakovljević, Agrochemistry Manual, Faculty of Agriculture, University of Belgrade, 1996 (in Serbian).
[17] ISO 11277:2009(E), Determination of particle size distribution in mineral soil material-Method by sieving and sedimentation, Geneva.
[18] ISO 11466:1995, Soil quality-Extraction of trace elements soluble in aqua regia, Geneva.
[19] ISO 22036:2008, Soil quality - Determination of trace elements in extracts of soil by inductively coupled plasma-atomic emission spectrometry (ICP-AES), Geneva.
[20] M.J. Simpson, A.J. Simpson, In: In: J.C. Lindon, G.E. Tranter, D.W. Koppenaal, (Eds.), Encyclopedia of Spectroscopy and Spectrometry, 3rd ed. Academic Press, Oxford, 2017, pp. 170.
[21] C.J. Bronick, R. Lal, Geoderma 124 (2005) 3.
[22] M. Manojlović, Diffuse pollution of agricultural soil, prevention and management. Guide Book, Increasing national capacities to assess the risk of diffuse agricultural soil pollution, TCP/SRB/3803/C3, 2022.