# Approach to reporting heavy metal, metalloid and toxic element contamination in land evaluation of reclaimed soils

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### Abstract

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In the background of the existing officially validated "Methodology of Work in the Cadaster of Agricultural Land in Bulgaria" (Petrov. E., et al, 1988), which does not treat the issues of evaluation of remediated and contaminated soils, the present article presents an element of a future common system of land evaluation, which should be developed and applied into practice.

The national standards of accounting for the soil contamination as well as the international experience (FAO recommendations) in the field have been taken into consideration. Algorithms of land evaluation of remediated soils, contaminated by heavy metals, metalloids and toxic elements, have been devised.

The algorithms lead to an Equation, through which the "leading" contaminator is established as well as two land evaluation scales (Method accounting for the number and severity of limitations), serving as "actual" and "potential" assessments. An example for working with the standards, the equation and the scales has been provided in the article.

Keywords: land evaluation; agricultural lands; reclaimed soils; soil contamination

#### Introduction and Aim of the Article

Land evaluation equalizes to determination of the optimal conditions for land use on a certain territorial unit and accounts for the ecological, social and economic conditions. Land contamination with heavy metals and toxic elements is an unfavorable phenomenon, most frequently caused by certain types of anthropogenic activities in the field of industry, agriculture, human way of life, etc. It could be direct or indirect consequence of the aforementioned human activities. Apart from being a local one, this problem is increasingly outlined as a global one; therefore, the inclusion of soil pollution indicators in the assessment of agricultural land is becoming more and more urgent.

The above is especially true in the case of land of remediated soils provided for agricultural use. (Ordinance № 26., State Gazette, Issue 30/22, March, 2002). It must also be emphasized that the "Methodology of Work on the Cadaster of Agricultural Lands in the Republic of Bulgaria" (Petrov et al., 1988), does not refer to cases of contaminated soils or those of agricultural lands of remediated soils. In this regard the aim of the present research is as follows:

Compiling algorithms for relative assessment of the land characteristic "soil contamination" on the basis of existing normative documents, which algorithms will subsequently be included in a subtle new methodology for evaluation of lands of remediated soils in Bulgaria.

## **Materials and Methods**

The peculiarity of parameterization of land characteristic of this type is that they are most frequently related to certain mandatory standards (for environment, plant and animal produce, etc.), legally adopted on national and international level. In most cases these are not single legislative acts.

To cover its aims the present research has been focused on the normative base underlying Ordinance  $N_{\Omega}$  3 (Ministry of Environment and Waters, 2008) "Standards of Admissible Content of Harmful Substances in Soils".

In its meaning, this ordinance determines that:

"Harmful substances" are the heavy metals, metalloids (HMM), organic contaminators and petroleum products (OCPP), enumerated in the appendices of the ordinance. In order not to complicate the exposition, only examples with heavy metals and metalloids are considered below. In regard to organic contaminators and petroleum products, the proposed algorithms work identically.

In the present article all above mentioned contaminators will be referred to as "soil contaminators" (SC). The establishment of the concentrations of the individual contaminators in the reclaimed soils for the purposes of agriculture is done by taking soil samples according to a uniform methodology (Table 1) and their subsequent laboratory determination.

Table 1. Depth of soil sampling according to land use types

Land use type	Depth of soil sampling, cm
Anahla landa	0-20
Arabie lands	20 - 40
Permanent Grasslands	0-10
	- 40

"Precautionary concentration" (PC) is the content of a harmful substance in the soil in mg/kg, the exceeding of which does not lead to disturbance of soil functions and to endangering environment and human health (Table 2).

"Maximum admissible concentration" (MAC) is the content of a harmful substance in the soil in mg / kg, the exceeding of which under certain conditions leads to disturbance of soil functions and to endangering environment and human health (Table 3).

"Interventional concentration (IC) is the content of a harmful substance in the soil in mg/kg, the exceeding of which leads to disturbance of soil functions and to endangering environment and human health.

Ordinance № 3. (MEW, 2008) refers to a total of 40 soil contaminators – 9 for heavy metals and metalloids and 31 for persistent organic contaminators and petroleum products. Not all of the latter apply to agricultural land. However, in order to make an accurate assessment, based on the condition of the soil before remediation, it is necessary to perform sampling, laboratory analyses and the results obtained to be processed according to Equation 1 for each potential contaminator, determining the "leading" one on this particular basis.

In regard to land evaluation this article uses devised and enhanced FAO recommendations for a longer period of time (1976 – 2001) namely "Method of limitations, accounting for their number and severity".

For the actual assessment of the "soil contamination" land characteristic the following 5 levels are accepted:

- L<sup>CO</sup><sub>0</sub> no limitations;
- $L_{2}^{co}$  unsubstantial or slight limitations;  $L_{2}^{co}$  moderately exposed limitations;
- L<sup>CO</sup><sub>3</sub> strict limitations;
- $L^{co_4}$  very strict limitations.

For each level of restriction (from  $L^{CO}_{1}$  to  $L^{CO}_{4}$ )), according to the existing possibilities for remediation, it is possible to reach a potential assessment.

#### **Results and Discussion**

In practice, soil contamination with several soil contaminants is often observed (SC $_{123}$ ). The article, as already

Soil	Heavy metals and metalloids								
	Arsenic	Cadmium	Cuprum	Chromium	Nickel	Plumbum	Zink	Mercury	Cobalt
	As	Cd	Cu	Cr	Ni	Pb	Zn	Hg	Со
Background concentrations									
Standard soil of pH ( $H_2O$ ) <= 6.0	10.0	0.4	34.0	65.0	46.0	26.0	88.0	0.03	20.0
Precautionary concentrations									
1. Clayey-Sandy and Sandy soils	15.0	0.6	50.0	90.0	60.0	40.0	110.0	0.05	30.0
2. Sandy-Clayey soils	15.0	0.6	60.0	110.0	65.0	45.0	160.0	0.07	35.0
3. Clayey soils	20.0	1.0	70.0	130.0	70.0	50.0	180.0	0.08	40.0
4. Soils of increased natural content of HMM	Determined (if necessary) on the basis of local background values								

Table 2. Standards of Precautionary Concentrations (PC) for Heavy Metals and Metalloids (HMM in Soils (determined as total content in mg/kg of dry soil at extraction with aqua regia)

Notes: At pH > 6.0 the precautionary values for soils of sandy-clayey mechanical composition are applied for clayey soils, and the values for clayey-sandy and sandy soils - for soils of sandy-clayey mechanical composition. For Plumbum the borderline of pH is 5.0

Table 3. Standards for Maximum Admissible and Interventional Concentrations (MAC, IC) for Heavy Metals and
Metalloids (HMM) in the Soils of Arable Lands and permanent grasslands (determined as total content in mg/kg of dry
soil at extraction with aqua regia)

HMM	pH (in H <sub>2</sub> O) <sup>(1)</sup>		Interventional con-			
	-	Arable lands	Permanent grasslands	Co-efficient of correction – KK <sup>(2)</sup>	centrations	
Arsenic (As)	-	25.0	30.0	1.2	90.0	
	<6.0	1.5	2.0			
Cadmium (Cd)	6.0 - 7.4	2.0	2.5	1.3	12.0	
	>7.4	3.0	3.5		1	
	<6.0	80.0	80.0			
Cuprum (Cu)	6.0 - 7.4	150.0	140.0	1.2	500.0	
	>7.4	300.0	200.0			
Chromium (Cr)		200.0	250.0	1.2	550.0	
	<6.0	90.0	70.0			
Nickel (Ni)	6.0 - 7.4	110.0	80.0	1.2	300.0	
	>7.4	150.0	110.0		]	
	<6.0	60.0	90.0			
Plumbum (Pb)	6.0 - 7.4	100.0	130.0	1.3	500.0	
	>7.4	120.0	150.0		]	
Mercury (Hg)		1.5	1.5	1.2	10.0	
	<6.0	200.0	220.0			
Zinc (Zn)	6.0 - 7.4	320.0	390.0	1.3	900.0	
	>7.4	400.0	450.0		]	

*Notes:* 1 pH, determined at soil/water ratio of 1:5 and time of interaction with water -5 hours; 2. CC – correction co-efficient is applied for soils of content of physical clay (particles < 0.01 mm) > 60 % in the arable horizon (depth 0 - 20 cm) and/or horizon A (0 - 10 cm) of non-arable lands by multiplication of the values of maximum admissible concentrations of arable lands and grasslands by the CC. Data of physical clay content are taken from soil maps or essays or by on-site tests

mentioned, involves working with one of them, the so-called "leading soil contaminator" – the SCx, the measured concentration of which (it can be denoted by MCSC) exceeds at most the corresponding precautionary concentration (PC).

In order to determine the degree of soil contamination (DSC) with individual SCx, an algorithm shown in Equation 1 below, is proposed:

$$DSC_{x} = 100(MCSC_{x} - PC_{x})/(MAC_{x} - PC_{x})$$
(1)

where:

 $DSC_x - Degree of soil contamination by SC_x (%).$   $MCSC_x - Measured concentration of SC_x (mg/kg).$   $PC_x - Precautionary concentration of SC_x (mg/kg).$  $MAC_x - Maximum admissible concentration of SC_x (mg/kg).$ 

As a matter of fact the developed Equation 1 determines the degree of soil contamination (DSC), expressed as a percentage between the fixed precautionary concentration of the contaminator (SC, for which we purposefully accept limitation level of  $L^{CO}_{0}$ ) and its maximum admissible concentration (MAC – accepted for a maximum limitation level of  $L^{CO}_{4}$ ). Therefore with DSC  $\leq 0$  it is taken that the evaluated land has no limitations in regard to the soil contamination, but when the DSC values are  $\geq 100$ , i.e. they exceed the maximum admissible concentration, the most restrictive assessment of level  $L^{CO}_{_{a}}$  is assigned.

In order to clarify the performance of the proposed algorithms we will use the following random example:

Land evaluation is performed of agricultural land of remediated soil, used as "arable". The soil reaction (pH measured in water slurry) is 5.5, and the content of physical clay is < 60 %.

After relevant sampling and laboratory analyses the following soil contaminators (SC) and their concentrations (MCSC) are established: SC Arsenic (As) in MCSC 14.6 mg/kg of dry soil; SC Cuprum (Cu) in MCSC 78.3 mg/kg of dry soil. After solving Equation 1 through the standard values exposed in Tables 2 and 3) and bearing in mind the measured concentrations, the following results about the two contaminators are obtained:

DSC As = 100(14.6-10)/(25-10) = 30.67 %

DSC Cu = 100(78.3-34)/(80-34) = 96.30 %

Therefore, we consider Cuprum (Cu) as a leading contaminator in the evaluation.

 Table 4a. Assessment of soil contamination

Land evaluation Scale 1a.								
DSC leadi	ng contami	Limitation levels L <sup>co</sup>						
< 0		L <sup>CO</sup> 0						
0	÷	30	L <sup>CO</sup> 1					
30	÷	65	L <sup>co</sup> <sub>2</sub>					
65	÷	100	L <sup>CO</sup> <sub>3</sub>					
>100 L <sup>co</sup> <sub>4</sub>								
Levels could be corrected								

Table 4a displays the devised scale for actual assessment of the following characteristics (Land evaluation Scale 1a.) of agricultural lands – ''soil contamination with heavy metals, metalloids, organic contaminators and petroleum products''. To work with this table many specific primary analyses are needed to identify the "leading contaminator". Any neglect of such studies and replacement with expert data carries risks of an inadequate final assessment of this characteristic. In many cases, although it is expensive, remediation of such soils is economically justified. in Bulgaria. The necessity of related research arose on the background of the existing and officially validated "Methodology of Work on the Cadaster of Agricultural Lands in the Republic of Bulgaria" (Petrov et al., 1988), which does not treat any of these problems and is generally inapplicable in the case of remediated soils.

With reference to the specificity of the problems, the present article is in itself an element of a future general system of land evaluation, which should be created and applied into practice.

The national standards of accounting for the soil contamination and international experience (FAO recommendations) in the field have been complied with. Algorithms of evaluation of lands contaminated with heavy metals, metalloids and toxic elements have been created.

Algorithms equalize to an Equation, which determines the "leading" contaminator, and to two land evaluation scales (a method of accounting for the number and severity of limitations) serving for an "actual" and "potential" assessment.

Table	4b.	Corrections	in the	e assessment	of so	oil cor	ntaminatio	n in	actual	conditions	for	remediation
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Land evaluation Scale 1b.												
		Corrections according to actual conditions for remediation, %										
	DSC le	ading contam	inator %	0	25	50	75	100				
	< 0		L <sup>co</sup> <sub>0</sub>	L <sup>CO</sup> 0	L <sup>CO</sup> 0	L <sup>CO</sup> 0	L <sup>CO</sup> <sub>0</sub>					
Levels	0	÷	30	L <sup>co</sup> 1	L <sup>CO</sup> 0	L <sup>CO</sup> 0	L <sup>CO</sup> 0	L <sup>CO</sup> 0				
of miniations L	30	÷	65	L <sup>CO</sup> <sub>2</sub>	L <sup>CO</sup> 1	L <sup>CO</sup> 0	L <sup>CO</sup> 0	L <sup>CO</sup> 0				
	65	÷	100	L <sup>co</sup> <sub>3</sub>	L <sup>CO</sup> <sub>2</sub>	L <sup>CO</sup> 1	L <sup>CO</sup> 0	L <sup>CO</sup> 0				
			>100	L <sup>co</sup> <sub>4</sub>	L <sup>co</sup> <sub>3</sub>	L <sup>co</sup> <sub>2</sub>	L <sup>co</sup> 1	L <sup>co</sup>				

In Table 4b Land evaluation Scale 1b is devised, which can serve for a potential assessment of remediated soils.

In return to the example, according to what is exposed in Table 4a (Land evaluation Scale 1a), it is seen that the actual assessment of the "soil contamination" characteristics is  $L^{CO}_{3}$ , i.e. it is within the scope of actual strict limitations for land use.

However, if there are conditions for remediation and it is applied (Table 4b, Land evaluation Scale 1b.), the potential assessment would be within the scope of moderately exposed ( $L^{CO}_{2}$ ), insignificant and ( $L^{CO}_{1}$ ) limitations, and would even reach a level with no limitations ( $L^{CO}_{0}$ ).

# Conclusions, Consequences and Recommendations

The problems of the relative assessment (land evaluation) of remediated soils have been dealt with insufficiently The actual scale responds to the query: ""What exactly is the situation like?", and the potential one – to the query: "What would happen if there is the opportunity of applying remediation?" An example of working with the standards, the equation and the scales has been provided.

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