STUDIES TOWARDS THE DETERMINATION OF THE CONTAMINATION LEVEL WITH HEAVY METALS OF A SITU LOCATED IN IAŞI

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Abstract

The paper presents studies in order to determine the degree of contamination of a situ located in Iasi whose surface is about. 4 ha.
There are presented the pedological characteristics of the soil and outcome of the tests carried out towards Cd and Zn content in soil from depths of 5 cm, respectively, 30 cm. The analysis of the soil samples in terms of Cd and Zn content was done using atomic absorption spectrometry method. Taking as a basis for the classification of pollution (contamination) Order 756/1997, it was possible to identify the level of contamination of each sole that the area have been divided in.
Measurements revealed that for both contaminants Cd and also Zn at depth of 5 cm, the largest area is occupied by a significantly polluted land and at a depth of 30 cm, a significant potential polluted land predominates.
The results also highlight the need for undertaking of some the depollution measures in the investigated site because as follows from the work, it is often exceeded the intervention level on land whose use is less sensitive.

Key words: contamination, soil, cadmium, zinc

Cadmium (Cd) and zinc (Zn) are elements naturally presented in all kind of soils. On these lines, soils contain about 1.00 mg / kg d.s. for Cd and 100 mg / kg d.s. for Zn. Cadmium is to land, in terms of toxicity, the second contaminant metal after Hg. It has a high throughput in the plant and in terms of effect, plants are very sensitive to the presence of cadmium as it is more resistant plants. The negative effect of cadmium on plants is felt mainly by:

- braking the synthesis processes of atmospheric nitrogen, the processes of ammonification, nitrification and denitrification;
- blocking a large number of microbiological processes;
- agricultural production losses.

Zinc is not as toxic as cadmium but its presence in soils, in quantities exceeding natural levels, can cause the following negative character effects:

- it reduces the micro-processing of organic matter by braking the fermentation activity;
- it reduces the microorganisms activity in terms of decomposition processes of cellulose and of the respiration processes, etc.;
- It reduces mass production of higher plants;
- It exercises a relatively low toxicity upon humans and animals consuming plants grown on land contaminated with Zn.

Zinc gets into the plant quite easily and it is accumulated, especially in green bodies, but become toxic and cause crop losses only at concentrations exceeding 400-500 ppm.

In our country, the sites containing Cd and Zn are generally historical sites and there are represented by areas located near former industrial units which had the object of activity: mining, plating, manufacture of plastics, paint pigments, electric batteries. The most important sources of Cd and Zn are still mining and processes of zinc and cadmium plating of the household appliances, cars, trucks, agricultural tools, parts of airplane, industrial tools, hand tools and parts such as: nuts, bolts, screws, nails, etc. (Adriano, 2001, Cordero et al., 2004).

The only Romanian standard which specifies some elements towards the method of establishing the pollution level of a polluted site is Order 756/1997, which provides sufficient information for classification. On these lines, based on the indications and limits of contaminant concentrations from this standard, we were established the soles which need urgent implementation of remediation measures.

MATERIAL AND METHOD

Measurements towards Cd and Zn content in soil were conducted at a site, area of 4 hectares, located in Iasi (*fig.1)*.

Figure1 **Initial image of the contaminated area**

Initial pedological study revealed that investigated soil is a Entiantrosol and the main characteristics, determined by sampling and laboratory analysis, are presented in *table 1*.

Table 1

The characteristics of the investigated soil

The main characteristics of the soil	The analyzed soil sample	
	P1	P2
pH	6.86	6.98
Humidity (%)	10.95	9.32
Granulometry (%)	- sand: 23.20 - dust: 61.60 - clay: 15.20	- sand: 24.00 - dust: 61.20 - clay: 14.80
Total organic carbon (mg/kg d.s.)	6492	6986
Humus (mg/kg d.s.)	11361	12225
Total phosphorus (mg/kg d.s.)	299	308
Total potassium (mg/kg d.s.)	64	76
Total nitrogen (mg/kg d.s.)	586	602
Nitrate (mg/kg d.s.)	14.94	12.04
Nitrite (mg/kg d.s.)	0.62	0.84
Sulphate (mg/kg d.s.)	1232	1184
Chloride (mg/kg d.s.)	40.62	38.92

The land area studied was divided into soles, according to existing limits in territory and function of distance from the former source of Cd and Zn:

- *Sole S1*, with an area of 4255 sqm;
- *Sole S2,* with an area of 1734 sqm;
- *Sole S3,* with an area of 17,821 sqm, is composed of six subsoles (S3-1 S3-2 S3-3 S3-4 S3-5, S3-6).

Sole S4, with total area of 10,464 sqm., consists of three subsoles (S4-1, S4-2 and S4-3) covered entirely by dross (the area was not taking into account for the research).

- *Sole S5,* with an area of 1719 sqm;
- *Sole S6,* with an area of 1167 sqm;
- *Sole S7*, with an area of 1519 sqm;
- *Sole S8*, with an area of 2322 sqm.

An outline of the situ divided by soles is presented in *fig.2*.

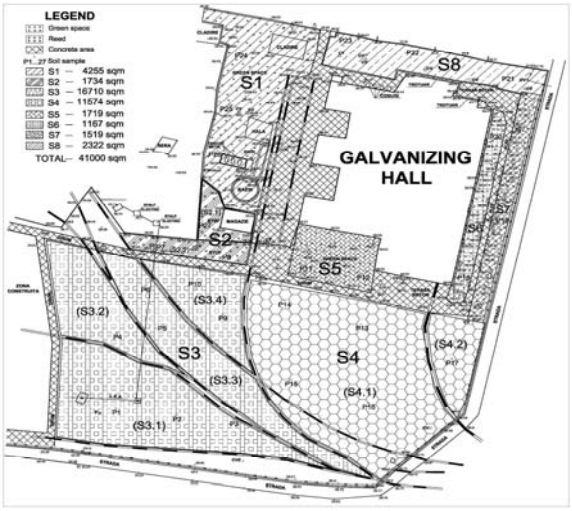

Figure 2 **Outline of the contaminated situ**

RESULTS AND DISCUSSIONS

Because since the beginning of the study, by reason of the environmental level I and II, conducted in the area under study, it was known the nature of heavy metals present in soil, our research began by collecting soil samples from depths of 5 and 30 cm, in this purpose in view for the determination of Cd and Zn content. Measurements were performed in the laboratory by a method of disaggregation of soil (ISO 14869-1/2001) and then by atomic absorption spectrometry [EN ISO 6869/2002]. Analyses result for the soil samples are presented in *table 2*.

The results presented in *table 2*, analyzed in connection with the Order 756/1997 towards: "The approval of the regulation upon the assessment of environmental pollution", revealed the following situations (*tab. 3*) towards the sole contamination level of the site investigated. Form *table 3*, we can observe that for cadmium, for 5 cm depth, the original pollution situation was as follows:

- the soles S1, S2-1 S2-2 S3-1 S3-2 S3-3, S4-2, S5, S6, S7 and S8 are significantly polluted. Summed area was 2.71 ha which represents 76% of the total site;
- the soles S3-4 and S4-1 are significantly potentially contaminated soils. Summed area was 0.85 ha which represents 24% of the total area of the site;
- there are no unpolluted soils.

Table 2

Analyses results for the soil samples

Sole	Depth (cm)	Metal content (mg/kg d.s.)	
		Cadmium	Zinc
S1	0 - 5	44.32	620.84
	20 – 30	77.58	548.90
S2-1	0 - 5	10.10	272.44
	20 – 30	6.74	180.24
S2-2	0 - 5	13.61	472.10
	20 – 30	12.24	438.64
S3-1	0 - 5	14.56	486.14
	20 – 30	14.22	462.18
S3-2	0 - 5	8.72	786.24
	20 – 30	16.94	842.10
S3-3	0 - 5	24.82	502.26
	20 – 30	11.02	398.21
S3-4	0 - 5	4.56	459.80
	20 – 30	9.94	340.12
S4-1	0 - 5	4.24	402.00
	20 – 30	2.36	368.02
S4-2	0 - 5	9.40	256.48
	20 – 30	8.82	196.00
S5	0 - 5	7.72	400.84
	20 – 30	12.60	398.08
S6	0 - 5	6.80	186.44
	20 – 30	5.50	144.08
S7	0 - 5	8.40	420.60
	20 – 30	4.32	286.90
S8	0 - 5	11.10	480.20
	20 – 30	17.30	320.10

Consequently, for 5 cm depth, the largest area of the site was significantly polluted with Cd.

For Cd, for 30 cm depth, the situation was as follows:

- the soles S1, S2-1 S2-2, S3-1, S3-2, S3-3 S3-4, S4-2, S5, S6 and S8 are significantly polluted. Summed area was 2.80 hectares which is 78.44% of the total site;
- the sole S7 is significantly potentially polluted. Area was 0.15 ha which represents 4.20% of total site;
- the sole S4-1 is unpolluted. Area was 0.62 hectares which is 17.36% of the total site.

Consequently, for 30 cm depth, the largest area of the site was significantly polluted with Cd.

For Zn, for 5 cm depth, the situation was as follows:

- the soles S1 and S3-2 are significantly polluted. Summed area was 0.75 hectares which is 21% of the total site;
- the soles S2-2, S3-1, S3-3, S3-4, S4-1, S5, S7 and S8 are significantly potentially polluted. Summed area was 2.35 ha which represents 65.85% of total site;
- the soles S2-1, S4-2 and S6 are unpolluted. Summed area was 0.47 hectares which is 13.15% of the total site.

Consequently, for 5 cm depth, the largest area of the site was significantly potentially polluted with Zn.

For Zn, for 30 cm depth, the situation was as follows:

- sole S3-2 is significantly polluted. The area was 0.32 hectares which is 9% of the total site;
- the soles S1, S2-2, S3-1, S3-3, S3-4, S4-1, S5 and S8 are significantly potentially polluted. Summed area was 2.62 ha which represents 73.60% of total site;
- soles S2-1, S4-2, S6 and S7 are unpolluted. Summed area was 0.62 hectares which is 17.40% of the total site.

Consequently, for 30 cm depth, the largest area of the site was significantly potentially polluted with Zn.

Now, if we analyze the results under the means of the contamination level showed before, we can make two main notations:

- Firstly, the main pollution, both in terms of toxicity and in terms of prevalence, for the studied area, is the one with Cd;
- secondly, the surface soil stratum (0-5 cm) is the most affected, no matter of the nature of metal ion.

Taking into account that we are dealing with a historical pollution the second observation highlights a very low mobility of Cd and Zn cations in the studied soil.

By the means of Order 756/1997, the soil surfaces which present "significantly pollution" level of contamination, have a metal content that exceeds the threshold for intervention and so require remediation measures. By analyzing the results, from this point of view, we can notice that from the total area of the site, over 78% need the application of remediation works.

A particularly interesting issue that we have observed, by the occasion of making these studies, was finding, all over the area, of a large number of species of herbs from the spontaneous flora.

These species have been identified and, for each of them, the prevalence level was determined by visual observations (*Tab. 4*). It could be observed that the most widespread plants were: *Ambrosia artemisifolia, Agropyron repens, Cirsium arvense, Calamagrostis epigeios şi Phragmites communis.*

Abundance of vegetation on the land polluted with Cd and Zn gave us the first hint of methodologies for decontamination: use of phytoremediation (Caraiman, P. et al., 2010).

Table 3

The soles contamination level from the area after the soles sample analyses

Nr. ctr.	Sole	Contamination level			
		Cadmium		Zinc	
		0 – 5 (cm)	20 – 30 (cm)	0 – 5 (cm)	20 – 30 (cm)
0	1	2	3	4	5
1.	S1	Significantly polluted	Significantly polluted	Significantly polluted	Significantly polluted
2.	S2-1	Significantly polluted	Significantly polluted	Unpolluted	Unpolluted
3.	S2-2	Significantly polluted	Significantly polluted	Significantly potentially polluted	Significantly potentially polluted
4.	S3-1	Significantly polluted	Significantly polluted	Significantly potentially polluted	Significantly potentially polluted
5.	S3-2	Significantly polluted	Significantly polluted	Significantly polluted	Significantly polluted
6.	S3-3	Significantly polluted	Significantly polluted	Significantly potentially polluted	Significantly potentially polluted
7.	S3-4	Significantly polluted	Significantly polluted	Significantly potentially polluted	Significantly potentially polluted
8.	S4-1	Significantly potentially polluted	Unpolluted	Significantly potentially polluted	Significantly potentially polluted
9.	S4-2	Significantly polluted	Significantly polluted	Unpolluted	Unpolluted
10.	S5	Significantly polluted	Significantly polluted	Significantly potentially polluted	Significantly potentially polluted
11.	S6	Significantly polluted	Significantly polluted	Unpolluted	Unpolluted
12.	S7	Significantly polluted	Significantly polluted	Significantly potentially polluted	Unpolluted
13.	S8	Significantly polluted	Significantly polluted	Significantly potentially polluted	Significantly potentially polluted

CONCLUSIONS

The conducted and presented research from the paper makes evident the following conclusions.

The studied site falls within the large area of historically polluted soils from our country.

The researches, towards the content of Cd and Zn cations from the studied soil, revealed the presence of a pollution level exceeding threshold of intervention (Order 756/1997), for a rate exceeding 78% of the total area.

The dominant cation, both in terms of toxicity and in terms of areal spread, is the Cd cation.

Cd and Zn contamination is, in principle, superficial which highlights the low mobility of these cations in the site-specific weather and pedological conditions (it have been passed many years since cessation of the activity that generated contaminants).

On the site area it was identified a large number of herb species whose development and density showed a good adaptation to the polluted environment.

For the site decontamination, given the presence of abundant spontaneous flora, it must be primarily taking into account the method of "phytoremediation".

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Table 4

The most prevalence species of identified herbs on the studied area

Nr. crt.	Specie	Popular name	S4-1	S4-2	S4-3	S5	S6	S7	S8	S 1	S2-1	S2-2	S3-1	S3-2	S3-3	S3-4	S3-5	S3-6
1.	*Ambrosia artemisifolia*	Ambrosia	FS	FS	-	FS	S	S	S	DS	-	DS	FS	DS	FS	FS	-	-
2.	*Agropyron repens*	Couch Grass	S	S	-	DS	FS	FS	FS	FS	-	DS	DS	DS	DS	S	FS	FS
3.	*Cirsium arvense*	Thisting	S	NS	-	S	S	NS	S	S	-	NS	NS	NS	NS	NS	NS	NS
4.	*Calamagrostis epigeios*	Chee Reed Grass	NS	NS	-	S	NS	NS	NS	NS	-	NS	NS	NS	NS	S	S	S
5.	*Lepidium latifolium*	Broadleaved Pepperweed	NS	NS	-	NS	NS	NS	NS	NS	-	-	-	-	-	-	NS	-
6.	*Galium tremifusum*	Robin-run-in-the-hedge	NS	NS	-	NS	NS	-	-	-	-	NS	NS	NS	NS	-	-	NS
7.	*Convolvulus arvensis*	Field Bindweed	NS	NS	-	S	NS	NS	NS	NS	-	-	-	-	-	-	NS	-
8.	*Xanthium italicum*	Cocleburr	DS	NS	-	NS	DS	NS	NS	NS	-	NS	NS	NS	NS	-	-	-
9.	*Cuscuta epilinum*	Dodder	-	-	-	NS	-	-	-	-	-	-	NS	NS	NS	NS	-	-
10.	*Plantago mmedia*	Hoary plantain	NS	-	-	NS	-	-	NS	NS	-	-	-	NS	-	-	-	-
11.	*Inula britanica helenium*	Horseheal	NS	NS	-	NS	NS	-	-	-	-	NS	-	-	NS	NS	-	-
12.	*Cichorium intybus*	Chicory	-	NS	-	-	-	-	NS	NS	-	NS	-	NS	NS	-	-	-
13.	*Phragmites communis*	Reed	DS	-	-	-	-	-	-	-	FS	DS	NS	NS	NS	S	S	NS
14.	*Caucalis platycarpos*	small bur-parsley	S	-	-	-	-	-	NS	NS	-	NS	-	-	-	-	-	-
15.	*Matricaria inodora*	Scentless chamomile	S	NS	-	-	NS	NS	NS	NS	-	-	NS	-	-	NS	-	-
16.	*Medicago sativa*	Lucerne	-	-	-	-	-	-	-	-	-	-						
17.	*Poligonium lapathifolium*	Curlytop knotweed	-	-	-	-	-	-	-	-	-	-	NS	NS	NS	NS	NS	-
18.	*Euforbia exigua*	Maltese Dwarf Spurge	S	NS	-	-	NS	-	NS	NS	-	-	-	-	-	-	-	-
19.	*Tussilago farfara*	Coltsfoot	NS	-	-	-	NS	NS	NS	NS	-	-	-	-	-	-	-	-
20	*Medicago lupulina*	Shamrock	NS	-	-	-	-	-	-	-	-	-	NS	NS	NS	-	-	-
21.	*Centaurea difusa cyanus*	Diffuse knapweed	NS	NS	NS	-	-	-	NS	NS	-	NS	-	NS	NS	-	-	-
22.	*Lathyrus tuberosus*	Tuberous Pea	-	-	-	-	-	-	-	-	-	-	NS	NS	NS	NS	-	-
23.	*Arrhenotherum elatius*	Oat-grass	NS	-	-	-	NS	-	NS	NS	-	NS	NS	NS	NS	NS	NS	NS
24.	*Pastinaca sativa*	Parsnip	NS	-	-	-	-	-	-	-	-	NS	NS	NS	NS	-	-	
25.	*Typha angustifolia*	Reed mace	-	-	-	-	-	-	-	-	-	-	NS	NS	NS	NS	NS	NS
26.	*Bolboschoenus maritimus*	Alkali bulrush	-	-	-	-	-	-	-	-	-	-	NS	NS	NS	NS	NS	NS
27.	*Inula helenium*	Horseheal	-	-	-	-	NS	NS	NS	NS	-	NS	-	-	NS	-	-	-

Note: The notations from the tabel have the following significance: NS – insignificant spreading (< 5 %); DS – significant distinctness spreading (15 – 25 %); S – significant spreading (5 - 15 %); FS – very significant spreading (> 25 %)