Scientific Papers, UASVM Bucharest, Series A, Vol. LIII, 2010, ISSN 1222-5339

# ISSUES REGARDING THE ECOLOGICAL RESTORATION OF LAND COVERED WITH SLUDGE PIT AT TOMEȘTI-IAȘI

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Keywords: sludge, ecological restoration, soil, plant

## Abstract

Sludge from the water treatment station Iasi, one of the largest in the country, was stored for ten years, between 1995 and early 2006, on an area of 18.920  $m^2$ .

The wet sludge has a negative impact on environment by: anaerobic fermentation gas emissions, the presence of heavy metals, soluble salts and pathogens; it was necessary to close the deposit.

The variant of land ecological restoration through phytoremediation is plausible as long as the water regime from the deposit is check up. First, it is necessary to accelerate the drainage, in order to install vegetation throughout the area.

In this paper there were analyzed and presented some aspects regarding the phytoremediation as the least costly method, with a high probability of land ecological restoration affected by wet sludge deposits.

For this purpose three sludge samples were collected and analyzed. First is a reddish sludge due of trivalent iron oxides and hydroxides under water excess conditions. The second sample, the darker, is a transient state sludge oxidation and the third sample was collected from an area with reeds where begins the humification process. Also, plant samples were collected from seven species: Atriplex sp., Rumex acetosela, Phragmites australis, Chenopodium album, Aster panonicum, Solanum nigrum, Galinsoga parviflora. Plants were separated for analysis in organs: root, stem and leaves.

## INTRODUCTION

The sludge deposit was built by removing the layer of soil over an area of 9.1 hectares with planning surrounding and partitions dams. The deposit was divided into 11 compartments of different sizes. Between the compartments there are lapses of movement of water and mud. The total deposit volume is 225,000 m<sup>3</sup> with a total active area of 15 hectares. The deposit is located in the major bed of Bahlui River, on its right side the distance in straight line until water treatment station Iasi is approximately 2000 m [2].

## MATERIAL AND METHODS

To investigate the sludge three samples were collected and analyzed. First was a reddish sludge due of trivalent iron oxides and hydroxides under water excess conditions. The second sample, the darker, was a transient state sludge oxidation and the third sample was collected from an area with reeds where begins the humification process. Sampling depth of sludge was between 20 and 30 cm. Sludge samples were dried at room temperature and then were minced.

Plant samples were collected from seven species: *Atriplex* sp., *Rumex acetosela*, *Phragmites australis, Chenopodium album, Aster panonicum, Solanum nigrum, Galinsoga parviflora.* Plants were separated in organs: root, stem and leaves.

The main chemical properties determined on sludge samples were: sludge reaction (pH determined potentiometrically in aqueous suspension), organic matter content (Walkley and Black method), C/N ratio, contents of total nitrogen (Kjeldahl method), and content in mobile forms of phosphorus and potassium in acetate-soluble solution of ammonium lactate at pH 3.7 (Egner-Riehm-Domingo method). Also, were determinate the total contents of heavy metals (measured with flame atomic absorption spectrometer in hydrochloric solution resulted by digestion of soil samples in  $HCIO_4$ -HNO<sub>3</sub> mixture). Those parameters were determined according to the ICPA methodology.

Plant samples were dried in the oven for several hours, at a temperature of 70°C, after which they were crushed. Total nitrogen was determined by Kjeldahl method, macro elements (P, K, Ca, Mg) and microelements (heavy metals) were determined hydrochloride solution obtained after solubilisation plant ash produced by burning plants, several hours, at 450°C. Measurements were made by spectrometry in the visible (P), flame photometry (K, Ca) and atomic absorption spectrometry for Mg, Cd, Co, Cr, Fe, Mn, Ni, Pb and Zn.

## **RESULTS AND DISCUSSION**

#### The chemical composition of sludge

The reaction values (pH), determined in aqueous suspension at a ratio dry sludge: water of 1:5, indicated a weak alkaline reaction in reddish sludge and a weakly acid reaction in the other two samples. The reaction was slightly alkaline due to the presence of hydroxides and carbonates (Table 1).

The organic matter content was 3.06% in the reddish sludge and 27.1% in sludge sample collected near the dam. A high content of organic matter was found in the sludge with reed vegetation. Reed vegetation helped to reduce the amount of water and influenced favorable the humification process. The ratios C/N value of 11.5 showed a good evolution of the mineralization process. In sample 1, organic matter content and total nitrogen content was low. Although, the C/N is 13, mineralization

had a very low intensity. Sludge sample taken near the dam, had a high nitrogen content which significantly reduced the value of the ratio C/N.

Table 1

Sample	Identification	pН	Organic matter	N <sub>t</sub>	C <sub>org.</sub>	C/N	P <sub>AL</sub>	K <sub>AL</sub>
number		H <sub>2</sub> O		%		pp	om	
1	Reddish sludge	7.91	3.06	0.158	1.8	13.1	1233	1526
2	Sludge dam area	6.75	27.1	4.633	15.7	4.0	504	558
3	Sludge with reed vegetation	6.78	22.4	1.321	13.0	11.5	600	549

Reaction and content of macro elements sludge samples collected from the Tomești deposit

The total nitrogen content of sludge samples, compared to the limits of interpretation of content classes in soil, showed different levels namely: very low (reddish sludge sample), small (sludge sample with reed vegetation) and very high (sludge sample collected from dam are). The content of mobile forms of P and K was high.

The total heavy metal content (Table 2) showed a significant loading of heavy metals. If the analytical data are compared with Clark values, in the three samples of sludge, heavy metal content, with the exception of two chemical elements (Co and Mn) were larger than Clark. Zinc values were 125 times, 54 times, respectively 85 times higher than the Clark. Also, cadmium levels in the three samples were 54 times, 23 times, respectively 38 times higher than Clark. Pb had a major accumulations between 6 and 11 times the value of Clark. Other elements analyzed (Cr, Ni), in some cases exceeded three times Clark values.

## Table 2

Total neavy metal content (mg/kg) of studge samples Tomeşti, compared with									
Clark values (C), with normal values in soil (NV) and with the alert threshold									
values (PA) and intervention threshold values (PI) for a less sensitive land use									
Identification	Cd	Со	Cr	Cu	Fe	Mn	Ni	Pb	Zn

Total beaux motal content (mg/kg) of sludge samples Tomosti, compared with

Identification	Cd	Со	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Reddish sludge	7	14	106	141	34525	542	65	186	10409
Sludge dam area	3	10	52	144	26632	486	39	95	4473
Sludge with reed vegetation	5	14	107	130	22653	427	134	141	7088
Clark values C <sup>1</sup>	0.13	18	83	47		1000	58	16	83
normal values NV <sup>2</sup>	0.30	5	30	20		500	20	15	50
alert threshold values PA <sup>3</sup>	5	100	300	250		2000	200	250	700
intervention threshold values PI <sup>4</sup>	10	250	600	500		4000	500	1000	1500

<sup>1</sup>Fiedler and Rösler (1988); <sup>2</sup>Lăcătuşu and Ghelase (1992) <sup>3, 4</sup>Order 756/1997 of MAPPM (1997)

Comparing the data analysis of heavy metals content in sludge with the alert thresholds and intervention thresholds for a less sensitive land use showed that most heavy metal content are lower than these thresholds. This variant of comparison was chosen because it is not recommended to cultivate this land with plants used in human or animal nutrition, after ecological restoration.

If we consider the pH sludge samples range variation, from a slightly acid reaction to a slightly alkaline, with predominance of neutral reaction, we observe that the mobility of heavy metals is lower than in moderately acid or strongly acid pH range of variation.

## Absorption of chemical elements by plants from spontaneous flora installed on sludge at Tomești

The analytical data on the content of primary (N, P, K) and secondary (Ca and Mg) macro elements showed that plants have received sufficient amounts of these nutrients. This was demonstrated by the levels of these chemicals in the sludge substrate, founded in various physical and chemical stages of maturation (Table 1) and by the concentrations of these nutrients in leaves, stems and roots of seven types of plants from ruderal flora, which were analyzed (Table 3).

#### Table 3

Nr.	Species		Ν	Р	K	Ca	Mg
					%		
1		leaves	3,75	0,339	2,75	2,16	0,598
2	Atriplex sp.	stems	0,91	0,097	1,25	0,31	0,055
3		roots	0,92	0,149	1,92	0,27	0,180
4		leaves	3,11	0,237	2,92	5,23	0,569
5	Rumex acetosela	stems	1,18	0,064	2,62	1,00	0,097
6		roots	1,77	0,365	1,25	1,72	0,273
7		leaves	3,40	0,231	3,10	0,60	0,140
8	Phragmites australis	stems	1,07	0,088	1,42	0,18	0,050
9		roots	2,77	0,331	2,09	0,73	0,180
10		leaves	3,22	0,292	5,39	1,99	1,070
11	Chenopodium album	stems	0,70	0,070	2,13	0,44	0,085
12		roots	0,71	0,168	1,21	0,40	0,171
13		leaves	3,46	0,257	1,51	2,91	0,503
14	Aster panonicum	stems	1,65	0,105	1,95	1,50	0,116
15		roots	0,80	0,148	1,92	0,57	0,100
16		leaves	6,00	0,462	4,92	3,22	0,344
17	Solanum nigrum	stems	2,03	0,278	4,25	1,26	0,204
18		roots	1,31	0,218	2,27	0,97	0,152
19		leaves	5,61	0,857	4,86	4,23	1,554
20	Galinsoga parviflora	stems	3,22	0,220	4,39	1,10	0,213
21		roots	2,51	0,379	7,07	5,07	0,311

Macro elements content of plant organs collected from Tomești

The nitrogen concentration was close to 3.5% in leaves of *Atriplex* spp., *Rumex* acetosela, *Phragmites australis, Chenopodium album, Aster panonicum* and high with values of 6.0% and 5.6% in leaves of *Solanum nigrum* and *Galinsoga* parviflora. Nitrogen absorption in these species leaves is a typical characteristic of

these plants [3]. The nitrogen contents of stems and roots analyzed between 0.7% and 2.77% are normal. Higher values, in stems and roots of *Solanum nigrum* and *Galinsoga parviflora*, between 1.31% and 3.22% are specific to these species.

The absorption of larger quantities of nitrogen in these two species was accompanied by a proportional uptake of other macro (P, K, Ca and Mg), particularly in leaves.

The accumulation of P, K, Ca and Mg in stems and roots of species analyzed was produced in accordance with the requirements of a chemical element of each species. Thus, in terms of macro elements nutrition of analyzed plants, there are no morphological or biochemical signs which may indicate aspects of deficiency or excess.

#### Accumulation of heavy metals (microelements)

Unlike macro elements, heavy metals have accumulated in large quantities, some quite large in comparison with plants needed for a balanced nutrition (Table 4).

Analyzing the obtained data, it is noted that some heavy metals were at a high level of content, others at a medium level and some at normal levels. Thus, Zn content was 37 times higher than the normal limit (60 ppm) in leaves of *Rumex acetosela*. Similarly, high levels of zinc were recorded in leaves of *Aster panonicum* and *Galinsoga parviflora* (19 times then the value of 60 ppm).

Table 4

Nr.	Species		Zn	Cu	Fe	Mn	Pb	Cr	Ni	Со	Cd		
				mg/kg									
1		leaves	664	10	269	242	10	sld	1,60	1,36	3,10		
2	Atriplex sp.	stems	147	4	75	20	7	sld	sld	1,46	2,36		
3		roots	309	7	135	21	10	sld	sld	1,27	3,05		
4		leaves	2246	9	349	676	10	sld	0,81	1,45	3,53		
5	Rumex acetosela	stems	351	3	98	54	9	sld	sld	1,59	2,56		
6		roots	1391	35	121	128	21	15,72	11,32	3,41	3,94		
7		leaves	158	5	191	150	11	sld	1,10	1,61	2,81		
8	Phragmites australis	stems	140	4	88	40	10	sld	sld	1,61	2,63		
9		roots	685	13	1043	108	13	2,18	1,38	2,37	3,10		
10		leaves	899	9	291	268	13	sld	sld	1,72	2,71		
11	Chenopodium album	stems	192	4	61	30	13	0,73	sld	1,56	4,36		
12		roots	372	7	388	23	13	1,08	sld	2,27	2,96		
13		leaves	1151	12	685	517	14	1,57	sld	2,81	3,20		
14	Aster panonicum	stems	220	3	69	54	14	0,81	sld	2,15	2,89		
15		roots	460	9	1136	43	14	2,49	0,81	2,88	2,93		
16		leaves	608	38	121	505	14	1,46	1,15	2,33	3,67		
17	Solanum nigrum	stems	527	7	98	118	13	1,15	sld	2,27	3,24		
18		roots	901	17	1670	63	17	6,42	2,49	3,10	3,28		
19		leaves	1171	28	481	252	16	2,91	0,87	3,82	3,54		
20	Galinsoga parviflora	stems	225	5	98	14	14	2,69	sld	2,55	4,13		
21		roots	1671	15	1920	50	19	5,90	2,57	2,42	3,49		
	Levels of normal co	ntent*	20-60	5-30	20-600	50-200	5-10	0,02-0,2	0,1-2,0	0,1-0,5	0,01-0,1		

## Microelements (heavy metals) content of plant organs collected from Tomești

\*from Pendias, 2001

The average zinc content of the seven plants analyzed was approximately 11 times higher than the right limit of the range of content. Also, the content of Cd in all plants analyzed is 32 times higher than normal content.

From the second category, in which chemical elements were in the medium levels of content were: Fe, Mn, Pb, Cr and Ni. Thus, the Fe content was high in roots of *Phragmites australus, Aster panonicum, Solanum nigrum, Galinsoga parviflora.* Larger amounts of Fe were accumulated in the leaves of *Aster panonicum* and *Galinsoga parviflora.* In the third category, of normal contents, was Cu and Co.

Of all the chemical elements analyzed zinc content of plant organs was very high. In descending order of concentration were the iron and then the rest of heavy metals.

The variant of land ecological restoration through phytoremediation is plausible as long as the water regime from the deposit is check up. First, it is necessary to accelerate the drainage, in order to install vegetation throughout the area [3]. *Phragmites* plants are an early solution to remedy this field. These, together with other species, help to reduce the amount of water and of chemicals in excess by absorption. The yields obtained for several years can significantly reduce both excess of moisture and chemical elements.

## CONCLUSIONS

- 1. The sludge samples had a slightly acid reaction to slightly alkaline, a significant content of organic matter and total nitrogen and high concentrations of mobile forms of phosphorus and potassium. In some areas the mineralization of organic matter and the humification process began.
- 2. Sludge contained excessive amounts of zinc, well above the intervention threshold value and larger amounts of Cd. Other heavy metals (Cr, Cu, Ni, Pb) have levels content nearly the normal contents.
- 3. In the plants from spontaneous flora, increased on the sludge from Tomeşti the accumulation of macro elements were done in the normal level of content, depending on the nature of species.
- 4. The variant of land ecological restoration through phytoremediation is plausible as long as the water regime from the deposit is check up.
- 5. *Phragmites* plants, together with other species, help to reduce the amount of water and of chemicals in excess by absorption. The yields obtained several years can significantly reduce both excess of moisture and chemical elements; at least a few years after the installation of solification process, the land will not be used for growing plants for animal or human feed.

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