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SOIL AND SLUDGE SAMPLES CHEMICAL PROPERTIES AND VEGETATION MINERAL COMPOSITION MONITORIZATION ON THE IAȘI SEWAGE TREATMENT-PLANT PONDS PRECINCT (TOMEȘTI)

Mihaela LUNGU, Radu LĂCĂTUŞU, Andrei VRÎNCEANU, Rodica LAZĂR, Ilie CALCIU

National Research and Development Institute for Soil Science, Agrochemistry and Environment - ICPA Bucharest, 61 Marasti Blvd, District 1, Bucharest, Romania

Corresponding author email: mihaelalungu.icpa@gmail.com

Abstract

Sludge quality resulted from the Iași sewage treatment-plant and deposited in the Tomești ponds has been studied over several years, starting 2005, with the aim of land greening. The main general chemical properties of the sewage treatment sludge in process of soil formation showed that it offers normal conditions for vegetation development even though upper horizons salinization was detected that year due to drought occurrence. Zinc contents were very high in the upper horizons. The sampled plants accumulated normal macro elements quantities and only zinc out of the heavy metals in higher concentrations, especially in the roots, without prejudice to vegetation development. As compared to this situation the Tomești sewage treatment pond had reached an incipient soil formation stage in 2020 following several greening measures and the draining phenomenon which had a certain intensity and determined vegetal cover changes, from a mainly hygrophytic vegetation to a less humidity loving one.

Key words: *sewage treatment sludge, soil quality, macro elements, salinization, heavy metals.*

INTRODUCTION

For several years, from 2005 to 2020, research has been carried out on the sludge produced by the Iași wastewater treatment plant and deposited in the Tomești sludge pond.

Their purpose was to draw up level II environment balance and risk assessment (2005), ponds phyto-rehabilitation (2007), environment impact assessment and monitoring of the soil heavy metals contents in samples from ponds bordering soil, ponds mud, and vegetation grown on the pond's precinct (2012, 2013, and 2014).

Further research continued soil chemism monitorization, especially that of salinization and heavy metals contents, of the zinc one by choice, from the pond mud, soils around it, and vegetation grown on them.

This paper presents the evolution of pond bordering soil quality as influenced by the phyto-rehabilitation operations during the 2015-2020 period.

MATERIALS AND METHODS

In 2015 observations were made after completing the garbage heap arrangement and greening works which aimed at changes monitoring of the water condition, flora composition, surface aspect and morphometry of the deposited material within the pond consisting of urban sludge. A retrenchment of the water covered areas was ascertained. Also, the water volume in the precinct south and east edging drainage was reduced as compared to the observations made in the previous years. The only drainage branch still in an overflow state was that of the north side.

As ascertained in the previous years starting 2010 it was noticed that the material stratum deposited in the pond, consisting of urban waste, evolved in a slow and lengthy process towards outlining a soil material. At the same time the botanic composition of the Tomești urban waste pond's specific surface continues to progressively change towards a natural wild flora similar to that which existed before changing the land use and creating the pond. The presence of some shrubs specimens was identified in 2014 consisting of elderberry arbores (*Sambucus nigra*) around the dams' ramps, where the slightly higher ground offered a better drained soil material stratum. This eutrophic, mezophytic - mezo hygrophytic species developed very well and occupied a significant area in the pond's precinct centre (Lăcătușu et al., 2017b).

Thenceforth arboreal species number enhancement could be identified beside the elderberry one not only around dams' banks but also in the areas where the slightly higher pond surface levels offered a better drained soil material stratum.

The general direction of the material stratum consisting of urban waste was thenceforth that of levelling and equalization of the specific surface, even if small depressions will still exist randomly disseminated on the whole precinct surface which would be filled with water in times of excessive water inputs, which is frequently encountered in the river's major beds and as natural as it gets.

The mud pond greening process and the mud material development towards a soil one also influenced the bordering area. The quality of these soils was also monitored over time, in five soil profiles (SE1-SE5) located in Figure 1.

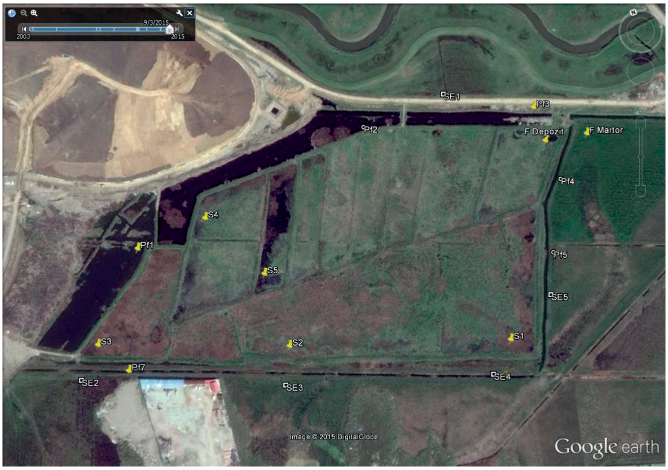

Figure1. The mud, vegetation, soil and water sampling points within the Tomești, Iași County, urban sludge deposit

Soil samples were taken by geometric horizons, by the 0-20; 20-40; and 40-60 cm depths. They were dried and grounded according to specific technical procedures and analytical determinations were carried out according to dedicated methodology and standards commonly used in the laboratories for pedological and agrochemical studies (Lăcătușu et al., 2017a), as follows:

- Water content was determined gravimetrically by drying the samples in a stove at 105°C.
- Soil reaction (pH) was determined through potentiometric analysis, in aqueous suspension, using a combined glass-calomel electrode.
- Organic carbon content was assessed by the Walkley-Black method modified by Gogoașă.
- The nitrate nitrogen ($N\text{-}NO_3$) mobile form was determined by potentiometric analysis with ion-selective electrode. The nitrogen total content was determined by the Kjeldhal method.
- The mobile phosphorus (PAL) and potassium (KAL) contents were determined in an ammonium acetate lactate solution with 3.7 pH (after Egnér-Riehm-Domingo) by spectrophotometry and flame photometry respectively.
- The totals soluble salts contents were determined through conductometric analysis.
- Total heavy metals contents (cadmium - CD, cobalt - Co, chromium - Cr, copper - Cu, iron - Fe, manganese - Mn, nickel - Ni, lead - Pb, and zinc - Zn) were determined by atomic absorption spectrometry in the solution obtained after digesting the samples with a concentrated perchloric, nitric, and sulphuric acids).

RESULTS AND DISCUSSIONS

Water content, reaction, and macroelements contents of the soil samples from around the purging mud ponds

The dry climate accompanied by high temperatures contributed to the water content spectacular decrease in soils. The very low soil water content, up to 44% in 2015 (Table 1) clearly shows the drought period through which the area was going at the time. Actually, the whole water content range of 18-44% with a 29 ± 9% average is significant in this respect. In 2016 the soil had, down to 60 cm depth, an average 33% water content, a relatively constant value as the 6% standard deviation shows.

In July 2017 the soil also had a high aridity degree, the water content didn't go beyond 32% of the water holding capacity.

Worth noticing that the grouping centre parameters ($\underline{x}$, Me, Mo) varied in a narrow range (18-32%) and the higher values were specific for the 40-60 cm layer.

Table 1. Average values of water content, reaction, and macro elements contents in the soil samples from around the purging mud ponds

Year of study	Water content at 105°C %	pH	$C_{org.}$	Nt	C/N	$N\text{-}NO_3$	P_{AL}	K_{AL}
			%			mg/kg		
2015	29	8.02	3.15	0.31	11.1	70	61	132
2016	33	7.94	3.20	0.26	11.1	5	58	633
2017	23	8.12	3.14	0.25	15.2	13	30	473
2018	54	8.11	3.18	0.21	17.5	85	81	550
2020		8.19	2.16	0.22	11.1	10	26	318

The arid sludge water content also reflected on the pond mud samples water content values so that in 2018 the bordering soil water content was similar to the pond mud one which demonstrates a balanced state existence between the two. It's enough to say that the average values were 58% and 56%, respectively.

The ***reaction*** (Table 1) varied very little along the research years and was constantly slightly alkaline due to the intrinsic chemical characteristics of the Calcaric Fluvisol strongly salinized in-depth. Alkalinity is also brought about by the carbonates and soluble salts presence. The pH varied in 2015 between 7.55 and 8.22 with an average 8.02 ± 0.15.

By comparing the statistical parameters of the pond sludge and the surrounding soil, it can be concluded that there is no influence of the former on the chemical and physical condition of the latter. A slight pH increase was noticed in-depth with approximately 0.2 units.

The ***organic carbon*** and ***total nitrogen*** contents (Table 1) of the bordering soil are normal for that Calcaric Fluvisol. The analytical data signify a low – average organic carbon content and an average total nitrogen one. It contains 4timesless organic carbon and 4.4 times less total nitrogen than the pond's mud. So, neither the soil organic carbon nor its total nitrogen content is influenced by the pond's mud.

In 2017 the soil had, in its upper horizon (0-20 cm), a high organic carbon content (4.81%) but much lower (2.5 times) than the mud. Worth noticing that in the soil underlying horizons the organic carbon content decreases by 45 and 61%, respectively.

The organic carbon statistical data in 2018 though presented high contents ranges with 3.18% average values. The values of the other two grouping centre parameters (M_e, M_o) and of the dispersion indices were also close to one another showing thus a levelling of the land around the pond from this point of view.

A depletion of the organic carbon was noticed in 2020 down to an average content of 2.20% in the upper horizon which was 5.4 times lower than that of the soil from inside the precinct. It also decreased in-depth.

Total nitrogen contents in the pond's bordering soil were medium in 2015 with an average value of 0.31%. In 2016 the values ranged from 0.34% in the 0-20 cm layer to 0.17% below 60 cm depth with a 0.29 ± 0.14% average value in the upper horizon which shows a high total nitrogen content soil. And it continued to be high in 2017 with 0.19 and 0.46% values in the upper horizon and a 0.33% average. Although the values decrease in the lower layers to 0.24 and 0.18% respectively, they belong to the same content class. These high contents are characteristic for the Calcaric Fluvisol which the pond lies on and there's no question about being influenced by the neighbouring mud.

Alike the total nitrogen contents ranged between 0.29 and 0.45% in the upper horizon with a 0.37% average value.

The values and statistical parameters of the ***nitrogen mobile forms: N-NO_3 (nitrate) and N-NH_4 (ammonium)*** (Table 1) stand proof that no ammonium nitrification reactions take place in the soil. The fact that ammonium nitrate can't be detected in soil samples by the analytical method in use shows that the main factor for triggering this phenomenon is missing. Furthermore, the nitrate nitrogen contents are also low, at the limit of soils unfertilized with nitrogen.

In 2016 the soil had a very low nitrates content, normal for a soil on which no fertilizers were spread, and it was 25.4 times lower than the purging mud nitrates content.

The soil C/N ratio (Table 1), 10.8 ± 2.0 in the upper horizon (0-20 cm) in 2015, shows a normal organic matter mineralization rate (Davidescu & Davidescu, 1999). In 2018 though the 16-18 average values and also 9-12 singular ones show a diversity of the soil organic matter mineralization degree.

Mobile forms of macro elements are sufficient for plants nutrition. Thus, nitrate nitrogen ranged in 2015 between 55 and 188 mg/kg with a 67 ± 34 mg/kg average value. Mobile phosphorus, soluble in the al solution (Table 1), ranged between 25 and 245 mg/kg with a61 ± 53 mg/kg average value, showing a high supply level with this plant nutrition macro element and also a great variability of it. The mobile potassium values soluble in the same conventional reagent ranged between 70 and 314 mg/kg with a 132 ± 73 mg/kg average value showing a medium supply level with this chemical element. In 2016 mobile phosphorus and potassium supply was still very good although the soil contained 20 times less mobile phosphorus and 1.3 times less mobile potassium than the purging mud.

Analytical data in 2017 highlighted, on an average, a high mobile phosphorus supply in the first layer (0-20 cm), average in the next one (20-40 cm) a lower in the third. Accordingly, a normal distribution for this type of soil. Mobile potassium supply is very high, with 363 mg/kg average values in the 40-60 cm layer and up to 606 mg/kg in the first one. Again, the very good supply of these two elements is not influenced by the neighbouring pond mud. The average values in 2018 were higher than agricultural soil normal contents namely: N-NO_3 2 times, P_{AL} 1.1 times, and K_{AL} 1.8 times.

Salinization level of the soil samples from around the purging mud ponds

Data regarding conductometric residue analysis (Table 2) highlight a moderate salinization below 60 cm depth of the Calcaric Fluvisol and below that, at 80-100 cm depth, the salinization level is very strong, with a 1.574 mg/100 g soil value of the conductometric residue. High contents of soluble salts, in the hundreds and thousands of mg/100 g soil, were registered in the samples collected from around the pond which signify a strong salinization. This salinization could have two causes: the capillary water rising loaded with salts proceeded from the strongly salinized soil base or the saline influence of the neighbouring purging mud deposit.

Sulphates predominate in the soluble salts composition in other proportions than in the mud, namely: 32% sodium sulphate (Na_2SO_4), 24% Calcium sulphate ($CaSO_4$), and 19% magnesium sulphate ($MgSO_4$); chlorides: 12% sodium ($NaCl$) and 5% potassium (KCl). Bicarbonates also occur in significant quantities: calcium 14% and occasionally magnesium or sodium.

The accented salinization of the soil bordering the ponds didn't negatively influence the area's characteristic vegetation development.

The total soluble salts contents in 2016 were 115 mg/100 g soil in the 0-20 cm layer and 1.088 mg/100 g soil in the 120-140 cm layer of the control profile. That is because of the vicinity of the pool with levigated water from the waste deposit. Another cause for the high soluble salt's contents of the bordering soil, starting even with the 20-40 depth, could be the scraping of the soil surface horizon to build the pond surrounding the dam.

Table 2. Average values of the total soluble salts contents in the soil samples collected from around the purging mud ponds

Year of study	Conductometric residue mg/100 g sol
2015	801
2016	1.098
2017	810
2018	364
2020	550

The salts also consist of mostly sulphates, this time the natrium one (Na_2SO_4) is predominant. The sulphates range in a decreasing order as follows: 44% Na_2SO_4, 21.4% $MgSO_4$, 10.0% $CaSO_4$. The difference is completed by 11.5% calcium bicarbonate ($Ca(HCO_3)_2$) and sodium (NaCl) and potassium chloride (KCl).

Data regarding the total soluble salt's contents in the pond bordering soils clearly highlight the strongly in-depth soil salinization reaching up to 2.275 mg/100 g soil values 40-60 cm deep as compared to 66 mg/100 g soil which was determined in the 0-20 cm layer which is consistent with a non-salinized soil material. The sulphate anion (SO_4^{2-}) is predominant and the Na^+ cation, followed by magnesium (Mg), calcium (Ca), and sometimes potassium (K) in much lower quantities. Consequently, the dominant salt is sodium sulphate (Na_2SO_4) with a 42 ± 22% average content. The magnesium sulphate ($MgSO_4$) has a 22 ± 8% average content, and the calcium one ($CaSO_4$) 21 ± 10%. The other soluble salts: potassium sulphate (K_2SO_4), calcium bicarbonate ($Ca(HCO_3)_2$), sodium chloride(NaCl), and potassium chloride (KCl) have much lower contents.

So, if calcium sulphate ($CaSO_4$) was the predominant salt in the mud, sodium sulphate (Na_2SO_4) is to be found in the largest quantities in the bordering soil. But then their sources differ too, anthropic in the first case and natural in the latter.

Considering that high soluble salts concentrations are in the soil depth and in the upper layer the salinization degree is practically null, a specific grassland vegetation developed with plants whose root system didn't penetrate below 40-45 cm depth.

The same slight salinization of the upper layer is noticed in 2018 and a very strong one in the deep ones. But the pond bordering soil salinization is 36 times lower in the upper horizons and 7 times lower in the deep horizons than that of the mud. The predominant anion is sulphate.

The predominant anion is the sulphate (SO_4^{2-}), decreasingly followed by bicarbonate (HCO_3^-), and chlorine (Cl^-). Among the cations sodium is predominant (Na^+), followed by magnesium (Mg^{2+}) and calcium (Ca^{2+}) with similar values, and finally potassium K^+) with the lowest content. The predominance of sodium resulted in its salts predominance namely the sulphate (Na_2SO_4), the bicarbonate ($NaHCO_3$), and the chloride (NaCl). The sulphates and the bicarbonates come next in the soluble salts hierarchy in the purging mud pond bordering soil represented by $CaSO_4$, $MgSO_4$, $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$. The smallest contribution to the total soluble salts content comes from the potassium chloride (KCl). The total soluble salts contents reach 2.114 mg/100 g soil in 2020 in the 80-100 cm layer of the control profile as compared to a minimum 60 mg/100 g soil determined in the 0-20 cm layer and which shows a non-salinized soil material.

But salts percentage composition differs, qualitatively in the first place: magnesium ($Mg(HCO_3)_2$) and sodium bicarbonates ($NaHCO_3$) occur. The sulphate anion (SO_4^{2-}) and sodium cation (Na^+) predominate, followed by calcium (Ca) and magnesium (Mg), and potassium (K) in extremely low quantities.

The calcium bicarbonate ($Ca(HCO_3)_2$) is the predominant salt which has a 59.2 ± 25.9% concentration in the first layer; the sodium chloride is next (29.8 ± 17.8%), magnesium sulphate ($Mg(SO_4)_2$) with 16.9 ± 3.6% values, sodium sulphate (Na_2SO_4) with 18.6 ± 14.5, and potassium chloride (KCl) with 7.7 ± 7.3%. The great variability of the salt's percentage composition is to be noticed reflected in the very high standard variation values and in the fact that some of the salts are not to be found in all the collected samples (the magnesium and sodium bicarbonates, the calcium and magnesium sulphates).

Consequently, if calcium sulphate ($CaSO_4$) was predominant in the samples collected from inside the precinct the calcium bicarbonate ($Ca(HCO_3)_2$) is to be found in the largest quantity in the bordering soil. And again, their source differs, anthropic in the first case, natural in the latter.

Heavy metals contents of the soil samples from around the purging mud ponds

Analytical data regarding total heavy metals of the pond bordering soils (Table 3) highlight the fact that the mud heavy metals contents didn't influence the same elements concentration in the bordering soil. Thus in 2015 the zinc content of the bordering soil is much lower than the alert threshold, although it outruns the soil normal value by 86 mg/kg. Its concentration can be seen as normal for this kind of soil.

Table 3. Average values of total heavy metals contents in the soil samples from around the purging mud ponds

Year	Zn	Cu	Fe	Mn	Pb	Cd	Cr	Co	Ni
	$mg \cdot kg^{-1}$								
2015	3.937	77.9	26.990	470	98.2	4.00	69.4	12.7	38.0
2016	142	51.1	33.591	560	19.1	0.80	52.6	5.6	43.9
2017	182	38.7	31.788	573	29.3	0.82	57.0	14.7	35.0
2018	196	38.6	28.615	490	18.9	0.48	45.1	9.5	49.8
2020	83.3	28.5	29.685	420	14.7	0.34	49.8	7.8	3.8

The other determined heavy metals (copper, nickel, lead) all have lower contents than the alert thresholds although they have higher values, sometimes double as compared to the normal soil contents. It's worth noticing that the cadmium and manganese average concentrations are lower than the normal values encountered in soils.

Consequently, the Tomești Calcaric Fluvisol on which the purging mud ponds are placed has normal heavy metals contents not influenced by the pond's mud.

Out of the analysed heavy metals range only the zinc concentrated to a higher degree in the purging, namely 27 times more than in the pond surrounding soil and 91 times more than the general soil average content. As long as the pond surface was covered with *Phragmites* sp. it absorbed important zinc quantities from the mud, namely 2.000-3.000 mg/kg. But as the *Phragmites* plants were not harvested the zinc absorbed quantities returned to the mud in the process of soil formation along with the plants which were mineralized and contributed to the new zinc content increase. Actually, the phenomenon is ongoing although not at the same intensity as during the *Phragmites* plants mineralization. In spite of these high zinc content values the present vegetation growth is not negatively influenced.

The described phenomenon took place for other heavy metals too (copper and cadmium) but at much lower intensities. Thus, the copper content of the mud in the process of soil formation is 2.6 times higher than in the bordering soil and 6.4 times higher than the general soils average concentration. The mud lead concentration is 5.6 times higher than that of the pond surrounding soil and 11.7 times higher than the soils average content. Finally, the cadmium concentration in the mud is 9.5 times higher than the surrounding soil average content and 14 times higher than the general soils average concentration. It must be mentioned that heavy metals mobility in the neutral - slightly alkaline soil is much lower than in acid soils so these elements absorption in plants will be much reduced and will have no effect on plants growth and development on the purging mud in the process of soil formation.

Zinc content decrease was registered in the following years below the maximum allowable limit (MAL). Concentrations decrease with the profile depth. The low level of the other heavy metals (copper, iron, manganese, cadmium, chromium, cobalt, nickel) contents in the bordering soil is a consequence of these elements' presence in the purging mud at low levels too.

The heavy metals concentrations in the Tomești Calcaric Fluvisol on which the purging mud ponds are located were already around soil normal contents by 2018.

Although slightly increased average values were sometimes registered between 2010 and 2018, as in 2014-2016, a sure influence of the mud deposited in the pond can't be ascertained. Likewise it can be noticed that other heavy metals (copper, nickel) have average concentration values double as compared to the general average values reported for common soils.

Other heavy metals (cobalt, chromium, lead) have the determined average values practically equal to those known from literature (Baker & Brooks, 1989; Filep, 1999; Kabata-Pendias & Pendias, 2001; Kim Tan, 1993), while others (cadmium and manganese) have average content values lower than these.

A slight increase of zinc and chromium contents was noticed in 2020 in the upper layer (0-20 cm) but without outrunning MAL. The concentrations generally decrease down the soil profile. It might be possible that this slight increase is due to the vicinity of the mud or to the diffusion phenomenon occurring once the drain water levels in the ditch around the pond increase, the more so that the contents values in the deeper horizons are higher than those at the surface.

The slightly increased zinc abundance in the pond bordering soil didn't impede the development of a vegetation consistent with the Calcaric Fluvisol strongly salinized in-depth in the area existing conditions.

CONCLUSIONS

The Calcaric Fluvisol on which the Tomești mud deposit lies has a slightly alkaline reaction, average organic carbon, total nitrogen, nitrate nitrogen contents, high mobile phosphorus content and average mobile potassium one. So, it offers good conditions for plant nutrition with macro elements.

It is slightly salinized in the upper horizons and very strongly salinized in the deep ones. The dominant salt is sodium sulphate (Na_2SO_4), while calcium sulphate ($CaSO_4$) dominates in the mud.

From these points of view the Calcaric Fluvisol strongly salinized in-depth is a fertile soil, not influenced by the Tomești pond purging mud presence.

The Calcaric Fluvisol strongly salinized in-depth contains heavy metals at concentrations levels around the known normal values for soils. The slightly increased zinc abundance in the pond bordering soil didn't impede the development of a vegetation consistent with the Calcaric Fluvisol strongly salinized in-depth and with the environment conditions existing in the area.

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