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STUDY OF HEAVY METAL DYNAMICS IN SOIL

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Abstract

The paper covers the results of a study, carried out during 2005 and 2018, regarding the impact of sludge dump of a wastewater treatment plant from Iasi city, Romania, on the soil characteristics. Experimental research was conducted to highlight the evolution of the heavy metal content of both the material in the storage site and the soil in its proximity. The following heavy metal concentrations were analyzed with atomic adsorption spectrometry method: Zn, Ni, Cr, Pb, Co, Cu and Cd. Research has also addressed other physical (particle size composition and soil moisture) and chemical (pH, sludge and soil reaction, organic carbon content, nitric nitrogen concentration, total nitrogen, mobile phosphorus and potassium content) properties that influence the mobility and retention of chemical compounds in the soil.

The results of this study showed that the material consisting of sludge, on the depth of 0-20 cm, shows well-developed structural aggregates, with a structure between granules and subangular polyhedra, with a medium level of development. The analyzed material has good hydrophysical properties that give it mechanical and hydronic stability. Following the analyzes carried out during 2005 to 2018, we can say that there has been an increase in the humidity and the zinc content in the soil due to the sludge dump from the wastewater treatment plant in Iasi.

Research results can be used as a scientific basis for developing an appropriate soil management system in the study area.

Key words: concentration, effects, evolution, heavy metals, soil

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1. Introduction

The application on soil of treated sludge has been adopted worldwide as a sustainable economic option for sludge management. At European Union (EU) level, there are countries where the greatest percent of sludge disposal is for agricultural use. For example, in 2012, Spain, Germany and United Kingdom were the largest sludge producers (2577.2, 1844.4, 1078.4 thousand tones dry matter, respectively, of which 74.5%, 29.3% and 78.2% were used in agriculture) (Smith, 2005). In other countries such as Hungary, Greece and Romania, despite the fact that they produce considerably amounts of sludge, its utilization in agriculture is limited (157.7, 118.6, 48.4, thousand tones dry matter total production of which 9.5%, 11.8% and 4.1% are used in agriculture). Even though in 2013 the total production of sludge increased in Romania to 172400 tones dry matter, only 8000 tones (4.65%) dry matter was used in agriculture (Eurostat, 2016).

The reasons why in some countries of the European Union the agricultural use of sludge is limited are the lack of awareness about the benefits of using it agricultural, fear of contaminating the land with heavy metals, the costs of sludge transportation on agricultural land and costs of monitoring the quality of sludge and of the land on which it is used.

Most scientific papers show positive effects of sludge on improving plant yield because of the macro nutrient content in the sludge (Chrysargyris and Tzortzakis, 2015; Cornfield et al., 1976; Özyazıcı,

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2013; Vaca et al., 2011), but also of the better physico-chemical properties of soils on which they are used, by altering the bulk density of the soil, aeration and stabilization of eroded soils (Gu et al., 2013; Holz et al., 2000; Mihalache et al., 2014; Ros et al., 2003). There are also articles that show some negative effects, concerning the increase in heavy metals in plants and soils, pathogens and esthetic alteration of the environment through smell (Collivignarelli et al., 2015; Mazen et al., 2010; Singh and Agrawal, 2007; Vaitkute et al., 2010).

The study area is a sludge dump in Tomeşti, where the sludge comes from the wastewater treatment plant, Iasi. It was built in 1994 by removing the fertile soil layer from an area of 9.1 hectares of land and building contour dams and subdivisions. The dump is surrounded by a draining channel, which ensures its drainage (Lăcătuşu et al., 2012). The dump is located in the major river bed of the Bahlui River, on its right side. The straight line distance to Iaşi wastewater treatment plant is about 2000 m (Cojocaru et al., 2010). The dump (Fig. 1a, b) was divided into 11 compartments, with variable areas delimited by the partition dams. Between the compartments there were breaches of water and sludge circulation. The height of the sludge dumping layer is 1.5-1.8 m. The total volume of the dump is 225.000 m^3 (Neagu, 2007).

The research carried out in the study area involved the concentration of the following heavy metals: Zn, Ni, Cu, Co, Cr and Pb. The total concentration of heavy metals in the soil is a relevant indicator of the risk to human health and the environment (David and Janez, 2018). The knowledge of the total load of the soil with heavy metals is the basis to justify the remediation of the contaminated soil. In an attempt to minimize uncertainty in the decision-making process, this has gone from the total heavy metal loading to the bioavailable fraction (Lăcătuşu et. al., 2017). The metals present in the soil are generally mobile and present higher potential risks to potential receptors. Therefore, the research of the free metal ions together with the soil properties is vital for understanding the mechanisms of their absorption by the roots of the plants (Lăcătuşu, 2017).

The physical and chemical properties of the soil, which have been determined in this work are: pH, humidity, sludge and soil reaction, organic carbon content, nitric nitrogen concentration, total nitrogen content, mobile phosphorus and mobile potassium, these can influence the mobility and retention of chemical compounds in soil. Soils are influenced by stand composition and hydrological regime as well as by abiotic stress factors (Onet et al., 2019).

Growing plants in polluted areas can be a remedial solution and serve as an alternative tool in sustainable agriculture. Plants can influence the accumulation of heavy metals in soils, either by decreasing or increasing their accumulation (Boglárka et al., 2018).

(a)

(b)

Fig. 1. Sludge storage in Tomeşti (a) and the dump divided into 11 compartments (b)

2. Case studies

2.1. Objectives of research

The studies were conducted in order to highlight heavy metal content, both of the material within the dump and of the soil in its vicinity during the period of 2005-2018.

The physical and chemical properties of the soil and the content of the heavy metals were analyzed: Zn, Ni, Cr, Pb, Co, Cu and also the influence of the sludge dump on the soil.

2.2. Sampling

The distribution of soil sampling zones, harvesting technique and field practice are presented in Figs 2a-2b and 3. In the dump there were placed 5 collecting spots (named S1, S2, ..., S5) and a drilling spot (named F1 - control drill, located outside the battlefield but close to it).

Fig. 2a. Harvesting soil samples

Fig. 2b. Soil samples from land

Fig. 3. Distribution of soil sampling points

The sample collection, of the 5 collecting spots, was done on three standardized depths (0-20, 20-40, 40-60), while the drilling sample was from 20 cm to 20 cm to a depth of 140 cm. Nearly 5 polls were encoded in the vicinity (named SE1, SE2, ..., SE5), plus a drill (named F2 – dump drilling, carried out in the 8th compartment of the sludge dump, to which the infiltration water flows from compartment 1 to 8, so that the samples from this drilling characterize the sludge).

The sampling of the outdoor collecting spots was carried out in the same way as those in the dump, on three standardized depths (0-20, 20-40, 40-60), and in the case of drilling, the same as in the dump drill starting from 0 cm (20 cm distance from each other) to 140 cm deep.

2.3. Experimental technique

Soil physical and chemical properties were analyzed. For the characterization of the physical properties, the granulometric composition and humidity was determined by laboratory analysis, (determined gravimetrically, by drying the samples in the laboratory oven, at 105°C and then cut down în mortar and pestle) and observations were made in the field. For chemical analyzes they were determined by the Walkley-Black and Kjeldahl method, with atomic absorption spectrometry (Sudip et al., 2018), the total content of heavy metals (Zn, Ni, Cr, Pb, Co, Cu) was determined in the solution obtained by disaggregating soil samples with a mixture of perchloric acid, nitric acid and sulfuric acid.

The research would also target other physical and chemical soil properties (humidity, pH and heavy metal content) that influence the mobility and retention of chemical compounds in the soil. For the physical parameters the particle size and soil moisture were determined, which was determined gravimetrically, by drying the samples in the oven, at 105℃.

Phosporus, calcium and heavy metals (Zn, Ni, Cr, Pb, Co, Cu) were determined in the solution obtained by disaggregating soil samples with a mixture of perchloric acid, nitric acid and sulfuric acid in the laboratory located within the Faculty of Hydrotechnics, Geodesy and Environmental Engineering of the "Gheorghe Asachi" Technical University of Iasi, Romania, using an Atomic Absorbtion Spectometer (AAS ZEEnit 700) (Fig. 4).

The research aimed at determining other physical and chemical properties of the soil that influence the mobility and retention of chemical compounds in the soil:

- the reaction of sludge and soil, evidenced by the pH value, was potentiometrically determined in aqueous suspension, at a sludge-water ratio of 1: 2.5, using a combined glass-calomel electrode;
- the organic carbon content was determined according to the Walkley-Black method (FAO, 2019), with the Gogoasa modification (Edu et al., 2013);
- the mobile form of nitric nitrogen ($N\text{-}NO_3$) was determined potentiometrically, with an ion selective electrode for $N\text{-}NO_3$. The determination of total nitrogen content was performed by the Kjeldahl method.
- the content of mobile phosphorus (P_{AL}) and mobile potassium (K_{AL}) were determined in ammonium acetate-lactate solution at pH - 3.7 (Domingo et al., 2015) and the dosage by spectrophotometry and photometry in flame.

3. Results and discussions

The samples (S1, S2, S3, S4, S5, FD) consisting of soil and sludge, sampled at the 0-20 cm depth, showed well-developed structural aggregates with a structure ranging from grain to subangular, polyhedron, with an average development level. The analyzed material has good hydrophysical properties which give it mechanical and hydraulic stability, moderate dry, moderate adhesive, loose, medium-sized and large macroporous medium.

These physical and mechanical properties determine good aeration porosity and optimum aerohydricity. In the case of the S2 and S4 surveys, where the material layer consisting of municipal sludge is well drained and without groundwater entrainment between it and the upper horizon of the soil prior to dumping. Also, the FD drilling (where groundwater occurs at approximately 70 cm) identified traces of intense meso-faunistic activity, especially an intense activity of earthworms. In the range of 0-20 cm and even below this depth, the soil material is relatively well structured, with smaller structural aggregates, lack of groundwater causing an increase in consistency, plasticity and reduction of aggregate interstices.

At the bottom of the last sampling segment (40-60 cm), but also in the case of drilling (which continues to a depth of 140 cm), the soil material is still under the influence of water, the hydromorphism influencing the degree of aggregation and structure of elementary particles. The plasticity is reduced and gleization characteristics appear on the surface.

Fig. 4. Atomic Absorbtion Spectometer (AAS ZEEnit 700)

In the rest of the samples collected from the dump (S1, S3 and S5) the presence of water at approximately 25-30 cm from the surface and in the second half of the FD drilling (from 70 cm) determines a relatively structured soil material, but once with the appearance of water, it becomes from very poor cohesive to noncoating, sometimes non-plastic, very adherent to the depth of water harvesting.

Samples collected from the landfill (FM, SE1, SE2, SE3, SE4, SE5) did not show water in the control section, with visible gleyzation traces being identified at the base (40-60 cm). The soil is well-structured, with medium-sized aggregates, with a grainy structure in the first part, sub-angled polyhedral in the sub-surface. The humidity parameters, the reaction and the content of macroelements from 0-60 cm layer of the sewage sludge from the Tomești basin are presented in table no. 1.

Laboratory analyzes determined heavy metal concentrations in soil samples. For the sampling depth of 0-20 cm, the values corresponding to the 2 drillings are shown in the diagrams of Figs 5 to 10. In graphical representations, the alert threshold values for less sensitive soils (P.A. SMP) were used as comparative limits according to MAPPM Order 756/1997.

Following the data presented graphically, it can be noticed that since 2010 the heavy metals: Ni, recorded small concentrations close to the normal ones in the soils while for Zn, Cr, and Pb the concentrations varied from one analysis period to another, but remained above the normal soil value. The 2018 drought conditions have led to the preservation of a high content of soluble salts in the upper horizons, both at the level of the dump and the alluvial soil around them. Research has shown that some physical and chemical properties of the sludge have been transmitted to the soil that it stagnates. Thus, soil moisture under the sludge layer increased by up to 20% relative to the moisture content of the neighboring soil, which was not influenced by the presence of sludge.

The advanced clayiness of up to 83% of colloidal clay below 2 μ, constituted a geochemical barrier to the leaching of the chemical elements in the sludge with the liquid sludge phase. At the same time, it also constituted an absorption medium for many cations and anions.

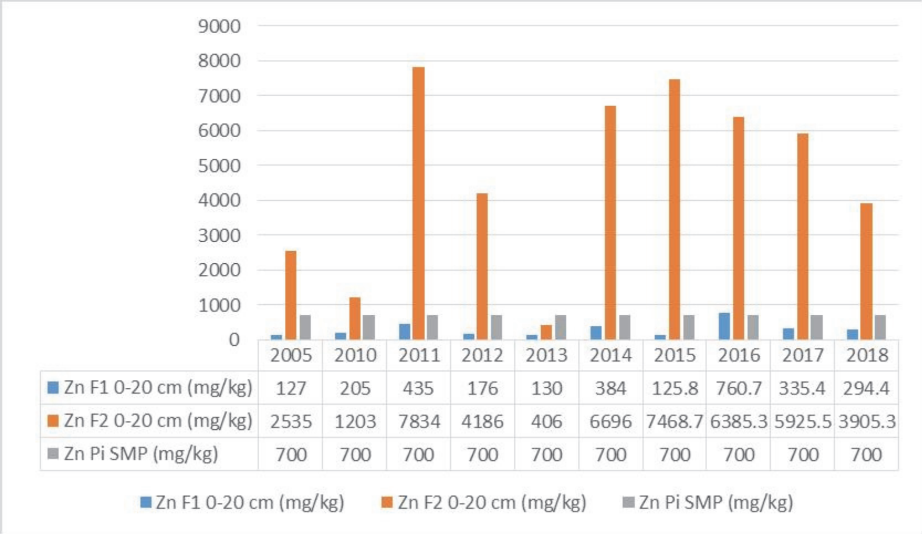
The sludge liquid phase contributed on one hand to the washing of salts from the first two horizons of the soil on which the sludge stagnated and on the other hand to the pH decrease by up to 0.61 pH units but the reaction field remained the same: weak-alkaline. Natural salt washes to about 1000 mg / 100g of soil, but the level of salinization remained the same, namely strong and very strong salinization.

From the group of heavy metals analyzed (Zn, Ni, Cr, Pb, Co), the only chemical element present at the pollutant was zinc. In the harvested samples, the total Zn content varies between 49 and 127 ppm with an average of 91 ± 23 ppm, while the zinc content range in the soil under the sludge dump varies between 3236 ppm in the horizon of contact with sludge and 78 ppm in the horizon of 280-300 cm. Therefore, a Zn load of the soil under the sludge layer was produced 7.7 times against the control soil.

Other chemical elements of metallic character, which exhibit a certain degree of load without reaching the maximum admissible limit values, are Pb, Ni and Cr. They have slightly increased content levels in the first soil horizon beneath the sludge layer. The high clay content did not allow them to migrate, resulting in reduced content levels, on a 20 cm thickness, from 100 to 120 cm. The only heavy metal polluting in the sludge of the Iasi wastewater treatment plant is zinc. The zinc pollution level is maintained at a thickness of 40 cm, from 100 to 140 cm. In the first horizon, the Zn content exceeds the LMA value by 10.8 times and in the second horizon by 1.6 times.

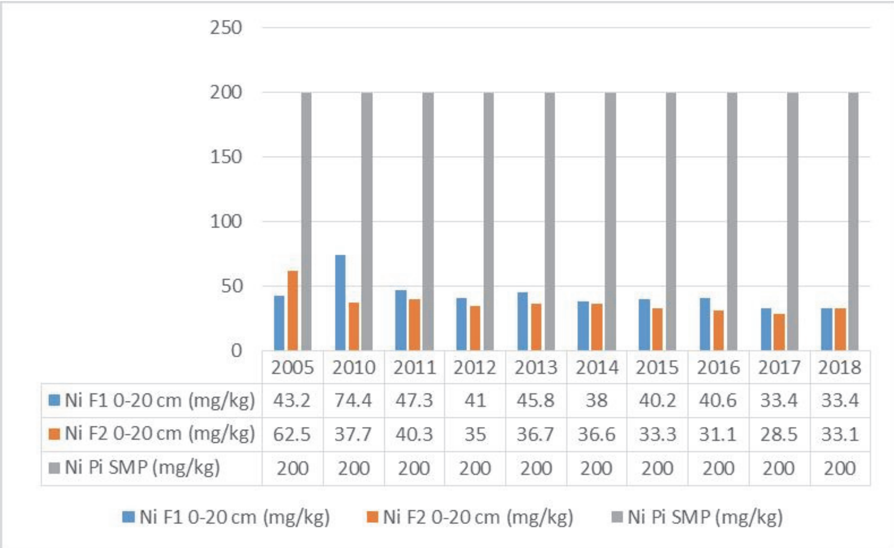
Table 1. Statistical parameters of the moisture, the reaction and the content of macroelements in the 0-60 cm layer of the sewage sludge from the Tomești basin, Iasi county

Statistical parameters	***Humidity (%)***	***pH***	$C_{organic}$	N_t	***C/N***	$N\text{-}NO_3$	P_{AL}	K_{AL}
		unit. pH	%	%		mg/kg	mg/kg	mg/kg
Min. value	19	6.55	1.17	0.229	1.6	19	333	356
Max. value	85	7.95	18.00	1.460	38.6	792	1.777	1.982
Arithmetic mean	58	7.20	8.33	0.641	16.0	275	1.087	849
Standard deviations	19	0.37	5.75	0.279	10.9	213	377	440
Geometric Mean	56	7.20	5.79	0.590	11.5	186	1.013	757
Coefficient of variation (%)	33	5.08	69.04	43.51	68.18	77.57	34.67	51.82
Median values	60	7.26	8.59	0.610	13.6	232	1.107	771
Module values	63	7.29	3.12	0.555	7.5	147	1.099	533



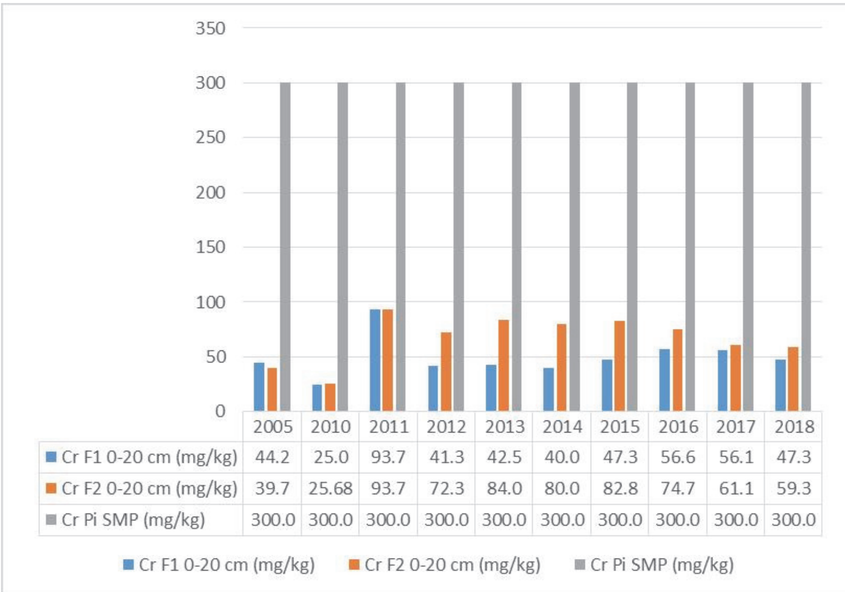
	2005	2010	2011	2012	2013	2014	2015	2016	2017	2018
Zn F1 0-20 cm (mg/kg)	127	205	435	176	130	384	125.8	760.7	335.4	294.4
Zn F2 0-20 cm (mg/kg)	2535	1203	7834	4186	406	6696	7468.7	6385.3	5925.5	3905.3
Zn Pi SMP (mg/kg)	700	700	700	700	700	700	700	700	700	700

Fig. 5. Dynamics of Zn content in soil



	2005	2010	2011	2012	2013	2014	2015	2016	2017	2018
Ni F1 0-20 cm (mg/kg)	43.2	74.4	47.3	41	45.8	38	40.2	40.6	33.4	33.4
Ni F2 0-20 cm (mg/kg)	62.5	37.7	40.3	35	36.7	36.6	33.3	31.1	28.5	33.1
Ni Pi SMP (mg/kg)	200	200	200	200	200	200	200	200	200	200

Fig. 6. Dynamics of Ni content in soil



	2005	2010	2011	2012	2013	2014	2015	2016	2017	2018
Cr F1 0-20 cm (mg/kg)	44.2	25.0	93.7	41.3	42.5	40.0	47.3	56.6	56.1	47.3
Cr F2 0-20 cm (mg/kg)	39.7	25.68	93.7	72.3	84.0	80.0	82.8	74.7	61.1	59.3
Cr Pi SMP (mg/kg)	300.0	300.0	300.0	300.0	300.0	300.0	300.0	300.0	300.0	300.0

Fig. 7. Dynamics of Cr content in soil

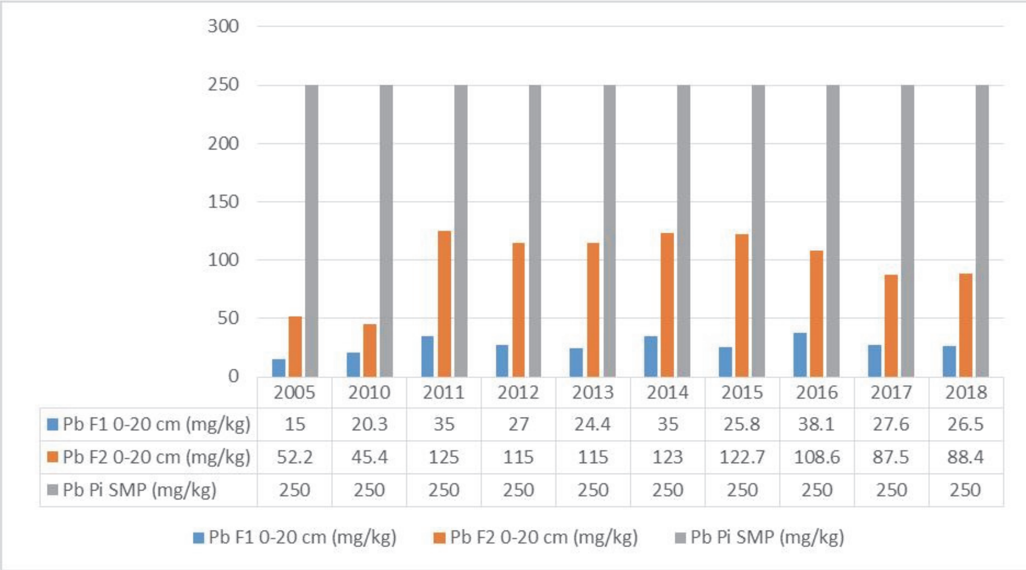


Fig. 8. Dynamics of Pb content in soil

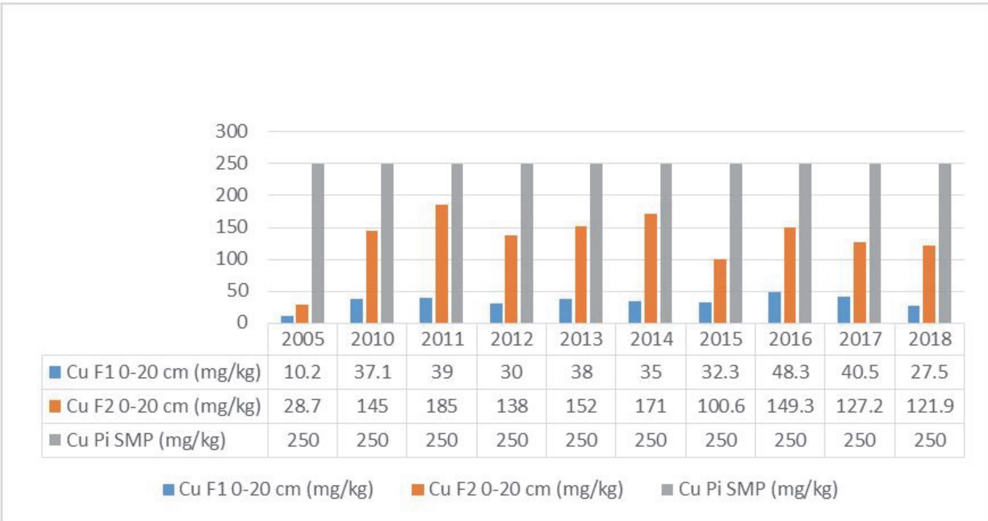


Fig. 9. Dynamics of Cu content in soil

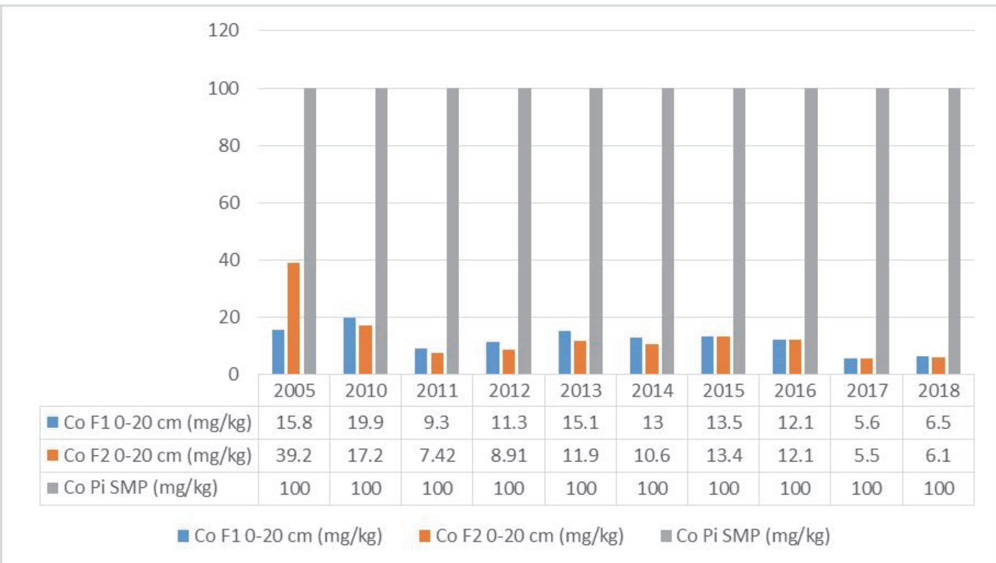


Fig. 10. Dynamics of Co content in soil

4. Conclusions

The extensive study to highlight the impact of sludge storage at the Iasi wastewater treatment plant is a necessary and useful material for risk analysis.

The results of this study showed that the soil material, consisting of sludge, on 0-20 cm depth, presents well-developed structural aggregates, with a structure between granules and subangular polyhedral, with a medium level of development. The analyzed material has good hydrophysical properties that give it mechanical and hydronic stability.

The chemical analyzes showed a neutral low alkaline reaction accompanied by high contents of organic Carbon, mobile phosphorus and mobile potassium. Also, there were high concentrations of mineral forms of nitrogen (N-NO_3 and N-NH_4) and high concentrations of total N.

The results showed that the increase in humidity, and some degree of loading is noted, without reaching the maximum limit values allowed for Pb, Ni, and Cr, but the Zn content exceeds the LMA value by 10.8 times, and in the second 1.6 times.

As a result of the analyzes carried out, we can say that the sludge storage at the Wastewater Treatment Plant in Iasi has a minor impact on the soil.

The surface area occupied by the dump can be introduced into the natural circuit by using a technological solution, namely the planting of rapidly growing trees of Populus, Salix or Paulownia species. They will also solve the problem of excess moisture, which still exists at depths greater than 60 cm or more, and at the same time it will decrease the zinc content of the sludge, by absorbing it and removing it from the system by cutting of the trees to be used for other purposes.

The results of this research can be used as a scientific basis for developing an appropriate soil management system in the study area.

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