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The impact of sewage sludge treatment on the content of selected heavy metals and their fractions

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ABSTRACT

The aim of the study was to assess the physicochemical properties of compost made of municipal sewage sludge from selected Municipal Sewage Treatment Plant. Content of basic macroelements and heavy metals (Zn, Cu, Cr, Cd, Ni, Pb, Hg, Mg, Ca, N, P, K, Na) and their fractions was determined by means of BCR method. Based on the analyzes, it was found that the content of heavy metals in compost did not exceed the limits set by natural land management of sewage sludge; the compost is very abundant in biogenic elements - nitrogen and phosphorus – and it can be also considered a significant source of calcium and magnesium. The analysis of results obtained from the three-stage chemical extraction revealed that deposits subjected to aerobic stabilization and composting accumulate metals (in descending sequence) in fractions III and II, i.e. fractions virtually inaccessible to the ecosystem in optimal conditions of use.

1. Introduction

The sewage treatment process leads to considerable amounts of sludge. Appropriate processing of sewage sludge eliminates their harmful effects and allows for natural utilization (Baran, 1997; Ignatowicz, 2011a,b; Kogut et al., 2014). Processes of sludge treatment and disposal consist in carrying out the aerobic or anaerobic stabilization, and then dehydrating to a dry matter content of about 20–30%. The resulting sludge is abundant in fertilizing substances such as biogenic compounds and organic matter, which improves the soil structure. However, the natural use of such sewage sludge is not possible, because they often contain toxic substances and may pose some health risks. A good process of preparing the sludge for further development is composting. It allows to obtain a wholesome organic fertilizer, abundant in nitrogen, phosphorus, potassium and organic matter, as well as safe in sanitary terms.

Chemical composition is an important aspect of a compost, which is shaped by macroelements and microelements. Among microelements necessary for the natural environment, following are essential: Cr, Sn, Zn, F, J, Co, Si, Mn, Cu, Mo, and V. These elements present in optimum quantities are not harmful for living organisms. Metals occurring in excessive amounts such as Cd, Pb, Hg, As, are extremely harmful to the environment. Toxicity of individual elements introduced along with compost to soil can cause changes in its fertility, reduce the prolificacy and quality of plants. It can also lead to the contamination of surface and groundwater by infiltration of metals.

The content of heavy metals in waste materials allows to determine the suitability of these substances for the natural purposes, including agriculture. Total content of heavy metals is not a reliable indicator of heavy metals bioavailability from the material brought to the soil. Such an assessment can be made by determining the share of metals in the mobile or immobile fractions. The method commonly used for this purpose is the sequential analysis, identifying the groups of compounds the metal is bound to. A common method of sequential extraction of sewage sludge is method by Tessier et al. (Arain et al., 2008; Tessier et al., 1997), that allows to identify the following operationally defined fractions: exchangeable, carbonate, reducible, oxidizable (bound to organic matter) and residual. Inorganic and organic matter is responsible for binding the heavy metals in sewage sludge (Bernacka and Pawłowska, 2000; Merrington et al., 2003). The inorganic matter of sewage sludge consists of: carbonates, phosphates, sulfides, and largely non-crystalline oxides and hydroxides of Fe, Al and Mn (Merrington et al., 2003). The organic matter in the sludge is mainly composed of living organisms, decayed organic debris (detritus) and a layer of the mineral particles (Rao et al., 2008); it has a high affinity to heavy metals. A simpler method of determining the metal fractions is a BCR method (Arain et al., 2008).

The aim of the study was not only the assessment of compost from municipal sewage sludge from selected Municipal Sewage Treatment Plant for the natural use based on the content of essential macronutrients and heavy metals (Zn, Cu, Cr, Cd, Ni, Pb, Hg, Mg, Ca, N, P, K, Na), but also determination of the content of mobile heavy metals forms in sewage sludge and compost.

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Table 1
Total content of nutrients (mean ± SD, n=3) [g/kg DM].

Sewage sludge	Na	K	Ca	Mg	N	N-NH$_4^+$	P	C
Stabilized after centrifuge	0.66 ± 0.04	0.41 ± 0.01	25.30 ± 0.46	8.43 ± 0.38	40.61 ± 1.12	0.4 ± 0.02	42.54 ± 1.12	450.50 ± 9.13
Stabilized with sawdust	0.80 ± 0.04	0.41 ± 0.01	14.40 ± 0.21	5.45 ± 0.21	18.58 ± 0.43	0.4 ± 0.02	63.52 ± 2.14	490.14 ± 8.16
Composted for 4 months	0.60 ± 0.02	0.45 ± 0.01	10.01 ± 0.19	3.98 ± 0.12	18.95 ± 0.42	0.4 ± 0.02	51.78 ± 1.89	485.67 ± 8.56
Mature compost	0.59 ± 0.02	0.45 ± 0.01	9.50 ± 0.19	4.02 ±	11.08 ± 0.35	0.4 ± 0.03	41.40 ± 2.56	482.22 ± 8.42

2. Material and methods

The study was carried out on the basis of sewage sludge and compost samples containing municipal sludge produced in selected wastewater treatment plant. Mechanical and biological sewage treatment plant purifies the household and industrial wastewater - mostly of dairy origin. The wastewater treatment plant is one of the few such facilities located in the Podlasie province (Poland), where the problem of sludge has been long completely solved. The presented composting method is anaerobic – aerobic type. Dehydrated sewage sludge was mixed with sawdust from deciduous trees in the centrifuge to obtain the correct C:N ratio in the compost. In the case of studied sewage sludge, quantity of dosed sawdust was approximately 30% of compost. Total time of composting and aging of an individual sludge batch was about 60–70 days.

The study was conducted in 2016 in samples of stabilized sewage sludge collected after a decanter centrifuge, sludge mixed with sawdust, compost after 4 months of aging, and mature compost. The fractionation was made in average samples (three individual dried samples were mixed and homogenized). In collected samples the following determinations were made macroelements, which are the nutrients for plants (Na, K, Ca, Mg, N, N-NH$_4^+$, P,), total content (Ni, Zn, Cr, Cu, Pb, Cd, Hg) and metal fractions (Ni, Zn, Cr, Cu) (Rao et al., 2008; Shrivastava and Banerjee, 2004; Dąbrowska and Nowak, 2014; Ignatowicz, 2011a,b; Rorat et al., 2017; Wiater and Łukowski, 2014).

Metals were determined by means of inductively coupled plasma atomic emission spectrometry (ICP-OES; Varian apparatus VISTA MPX) after sample digestion with concentrated HNO_3. Samples were digested using microwave digestion. Hg was marked on the AMA-254 spectrum analyzer directly through the sample's catalytic incineration in oxygen. In order to check the process of mineralization, the labeling of each sample was confirmed with a certified material for sewage sludge reference BCR-146 R and material for confirming curie and the whole analytical process SPS-SW2. Moreover, blind samples were used to control the limit of quantification. The metals were tested on interference lines: Cd – 214,439 nm, Cr-267,716 nm, Cu-327,395 nm, Ni-231,604 nm, Pb-220,353 nm, Zn-213,857 nm (PN-EN ISO 11885:2009).

Modified BCR method with a use of ultrasonic probe Sonics VCX 130 was used to evaluate fractional composition of metals in sludge samples (Łukowski, 2014; Rao et al., 2008; Shrivastava and Banerjee, 2004). Extraction included four stages:

1. Acid soluble and exchangeable fraction (F1) – 1g of sludge in 100 cm^3 centrifuge tube with 40 cm^3 of 0.11 mol dm^{-3} acetic acid was sonicated for 7 min (power – 20 W) at temperature 22 ± 5 °C. Then, the mixture was centrifuged for 20 min at 3000*g*. The extract was separated for analysis. Residue with 20 cm^3 of deionized water was sonicated for 5 min (power – 20 W) and centrifuged for 20 min at 3000*g*. Water was discarded.
2. Reducible fraction, bound to Fe/Mn oxides (F2) – to the residue from the first step was added 40 cm^3 of 0.5 mol dm^{-3} hydroxylamine hydrochloride fresh solution, pH 1.5, and sonicated for 7 min (power – 20 W) at temperature 22 ± 5 °C. Then, the mixture was centrifuged for 20 min at 3000*g*. The extract was separated for analysis. The residue was rinsed with deionized water, alike in the first step.
3. Oxidizable fraction, bound to organic matter (F3) – to the residue from the second step was added 20 cm^3 of 30% hydrogen peroxide and sonicated for 2 min (power – 20 W) at temperature 22 ± 5 °C. Then, the volume of H_2O_2 reduced to approx. 1 cm^3 using water bath. 50 cm^3 of 1 mol dm^{-3} ammonium acetate and sonicated for 6 min (power – 20 W) at temperature 22 ± 5 °C was added to the moist residue. Then, the mixture was centrifuged for 20 min at 3000*g*. The extract was separated for analysis. The residue was rinsed with deionized water, alike in the previous steps.
4. Residual fraction (F4) – residual fraction (option) F4 was calculated from the difference between 100% and summarized percentage of other fractions.

Results are represented as arithmetic mean of three replicates. The differences between the obtained values were determined by one-way ANOVA with Tukey's post-hoc test at confidence level $p < 0,05$.

3. Results and discussion

Agricultural utilization of sewage sludge is associated primarily with its abundance of organic matter and nutrients. This creates the real prospects for improving the negative balance of organic matter in Polish soils (mainly light soils). From an economic and ecological point of view, an important parameter is the sludge hydration, and thus the dry matter content. In the analyzed compost, the dry matter was 41.33% and moisture 58.67%. Mature compost was characterized by a high organic matter content −73.2%. The amount of carbon varied from 450.50 g/kg DM in stabilized sludge to 490,14g/kg DM in sludge mixed with sawdust. Contents of selected macroelements (N, P, K, and Ca) in studied organic materials is presented in Table 1. From ecological point of view, not only organic nitrogen in sewage sludge, but also the form of ammonium directly available to plants is important (Gorlach and Gambus, 1998). The compost from Sokółka contained total nitrogen at the level of 11.08g/kg DM, and ammonia nitrogen available to plants 0.4g/kg DM. The nitrogen content in sewage sludge and compost varied (Table 1). In the case of sewage sludge, more of total nitrogen (more than 2-fold) was found in the sludge that was stabilized with aerobic and dehydrated in centrifuge. After adding the sawdust, the amount decreased to 18.58g/kg DM, after 4-month composting process to 18.95, while in mature compost decreased to 11.08g/kg DM, which is associated with the dilution effect and gaseous loss. The second biogenic element (after nitrogen) is phosphorus. Given the importance of phosphorus for plants and its circulation in nature, more and more attention is paid to the need to re-inclusion of this element contained in the sewage sludge into circulation within food production (Quan-Ying Cai et al., 2007). The tested compost had a high phosphorus content, which was 41.40g/kg DM. However, the largest quantity of phosphorus characterized sludge mixed with sawdust 63.52g/kg DM (Table 1). Chemical analysis of sludge indicates that it should be considered also as a significant source of calcium (9.50–25.30g/kg DM) and magnesium (3.98–8.43g/kg DM). It was observed that the content of calcium decreased in the sludge after adding the sawdust, from 25.30 to 14.40g/kg DM, and the lowest value was reached after the composting process (9.50g/kg DM). The most scarce ingredient in sewage sludge is potassium, therefore using the sludge, additional fertilization with this component should be applied. Low