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Chemical Composition of Municipal Sewage Sludge: A Tool for Risk Assessment of Agricultural Land Application

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Abstract: A number of studies have shown that the application of sewage sludge to agricultural soils has a positive effect on plant nutrition. However, frequent application has been shown to result in soil contamination with potentially toxic metallic elements. The present research was conducted with the objective of establishing the chemical composition of sewage sludge from three urban wastewater treatment plants in Algerian's north region. We determined chemical parameters that account for their nutrient concentration and total content of Cr, Cu, N and Pb.The analysis revealed that the municipal sludge collected exhibited a high organic content, as well as significant concentrations of nitrogen, phosphorus, and potassium. This finding suggests that the use of sludge for agricultural purposes may be a beneficial application. The total contents of the five metals in the sludges were found to be significantly lower than the limit values that would be considered suitable for agricultural soil. However, it was observed that Ni concentration was already above the standards set by

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AFNOR, while Cr was found to be equivalent to 50% of the limit. Furthermore, the results obtained by means of the sequential extraction protocol demonstrate that a significant proportion of the total content of Cu and Pb is associated with fractions (acid-soluble, carbonates, oxides, organic matter) exhibiting higher levels of bioavailability under soil conditions. In contrast, Ni and Cr have been found to be bound to the residual fraction in up to 80–90% of the total concentration, making it the least bioavailable form for environmental impact.The results indicated that regulatory guidelines require refinement to account for the bioavailability of heavy metals in relation to soil properties.

Keywords: Municipal sewage sludge, Nutrients, Heavy metals

Introduction

Increasing urbanisation, industrialisation and population pressures have resulted in growing challenges in wastewater management globally (Allaoui et al., 2015). In several countries, Sewage sludge generated from wastewater treatment plants are being usually reused in light of their potential for improving soil properties and for containing significant plant nutrients (Cherfouh et al., 2018; Peyton et al., 2016). It is now well recognized that, the disposal by landfills or by incineration are feasible options adept in many parts of the world, but both these strategies are expensive cost and able to lead environmental problems (Walter et al., 2006; Amir et al., 2005). The spreading on the agricultural lands of dewatered sludge has therefore become an attractive opportunity and disposal option. Sewage sludge is a good source of valuable components: organic matter, N, P and other plant secondary and micronutrients (Cherfouh et al., 2022; Martìnez et al., 2003, Zufiaurre, 1998).

The greater amounts of organic matter can improve the biological activity and the physical properties of the soil (Logan and Harrison, 1995). However, the presence of heavy metals in municipal sludge is probably the main obstacle to bear in mind, when sewage sludge its use as organic amendments for agricultural purposes (Zhang et al., 2017). Thus, it has been notified that applying sewage sludge to soil might provide metals in potentially toxic, labile forms (McBride, 1995). Although the determination of the total amount of heavy metals of a sludge as an important information and useful as overall contamination level of metals in sludge. However, such parameter it delivers no indication about the solubility of metals, which depends on their chemical ionic forms (Su & Wong, 2003). Sequential extraction protocol of heavy metals or their chemical speciation from soil and sediments is a useful technique for determining the mobility of heavy metals, their bioavailability, and leaching rates when sludges are applied to soils (Fluentes et al., 2004). These characteristics depend strongly on the metals specific chemical forms or positions of binding. It partitions elements into five operationally-defined geochemical fractions including: exchangeable; carbonates (acido-soluble); Fe and Mn oxides (reducible); organic matter (oxidisable); and residual (Merdy et al., 2024).

The objective of the present study was to evaluate the probable characteristics of sludge from sewage treatment plants by examining agronomical relevant parameters, concentrations, and the speciation of heavy metals. This investigation aimed to furnish a tool to assist in determining the most effective management of urban sewage sludge.

Material and Methods

The sludge samples materiel include sludge obtained from three treatment wastewater plant which are described in table1. The sludge produced from all treatment wastewater plant is obtained with using the biological wastewater process. A composite sample was collected after mixed of five primary samples and stored at 4°C. The samples were dried at 65°C, finely ground in an agate mortar, the material was sieved through a sieve with a mesh size of 160 µm and stored in polyethylene containers at 4°C until analysis.

The agronomical pertinent parameters of sludge such as pH and EC were measured in sludge extracts (sludge/water ratio 1:10 [w/v]) using a pH and conductivity meter, respectively. At last, three sample replicates and three analysis replicates for each sample were performed in order to meet statistical acceptance requirements. The organic matter was calculated from the total organic carbon (TOC) using the formula: OM (%) = TOC (%) x 1.724The sequential extraction scheme was performed using four step procedure inspired by Tessier et al. (1979). However, the hydrosoluble fraction was realized in the water extraction by using sludge/water ratio 1:10 (w/v). The concentration of metals was quantified by the inductively coupled plasma atomic emission spectrometry (ICP-AES).

Table 1. General characteristics of the wastewater treatment plants (DWTP) where sampling took place.

	Location	To be work	Treatment process (biological)	Capacity (eq/hab)	Natural outlet
PBT	Tizi-Ouzou	July 2000	medium discharge	120 000	Sébaou River
BLF	Boukhalf	November 2006	less discharge	2 5000	Sébaou River
TMT	Tadmaît	May 2007	less discharge	13 000	Sébaou River

Results and Discussion

Nutrients and Key Chemical Properties

The results of the analysis of sludge samples collected from the three wastewater treatment plants are presented in Table 2. The rate for N total were evaluated range 4.39% to 3.00%; equivalent to 44 to 30 kg/tons of sludge dread matter. The available phosphorous content is down in most of the sewage samples analysed having phosphorous contents be varied between 0.9 and 1.6 $g.kg^{-1}$. The sludge show important agronomic properties contained high major nutrients, and the values N, P and K are presented were increasing in the following order PBT > BLF > TMT.

The EC of the EST sludge was higher one, indicating a high salt content, it was some two at five times higher than others sludge. This indicates that the sludge can be lead important content of salts can be a source of soil salinization under poor soil leaching or low irrigation management. The organic matter content shows range of variation between 39% and 44%. The organic matter and nutrient contents were found mostly in high concentrations in the majority of sludge samples investigated irrespective of the type of wastewater treatment plant. The pH of sludge has been similar (7.65 to 7.73), slightly alkaline ranges. Sludge application may reduce the pH of soils due to humic acid release and may increase the electrical conductivity of soils. In another hand, the pH of soils may increase due to the exchangeable calcium and other cations present in sewage sludge. Agricultural crops grow well when soil pH is between 6 and 7 because nutrients are available more at pH of around 6.5 (Smith, 1994).

Table 2. Nutrients content and chemical properties of urban sludge

	pH	**CE** (µs.cm-^{1})	**Nt** (%)	**PO4^{---}** ($g.kg^{-1}$)	**K^{+}** ($g.kg^{-1}$)	**CEC** $cmol.kg^{-1}$	**OM** (%)	**C/N**
BLF	7,65	946,5	3,69	0,90	2,49	38,5	39,3	6,2
PBT	7,70	1843,7	4,39	1,66	3,66	35,7	43,7	5,8
TMT	7,73	409,4	3,00	0,43	0,55	32,6	39,4	7,6

Total Concentration of Heavy Metals

The total content of the heavy metals copper (Cu), chromium (Cr), lead (Pb) and nickel (Ni) is presented, in addition to the threshold limits for these metals in sludge, as stipulated in the French AfNor standard (table 3). It was found that the total content of heavy metals in the sludge was generally low, and it was determined that there was a significant opportunity for its use as a fertiliser in agricultural soils. Nevertheless, TDM sludge poses a significant risk of potential pollution for Ni, Cr and Cu, given that their total contents are predominantly near the corresponding limit values. The highest metal content, attributable to the significant presence of chemical factories, which discharge their wastewater into the unban wastewater network. As indicated by the total content, the sludge resulting from BKH and EST could be utilised as effective organic fertilisers. Conversely, the TDM should not be used directly unless chemical remediation and bioremediation had been performed (Wong et al., 2000; Veeken & Hamelers, 1999).

The elevated concentrations of Ni (243 mg/kg) in the TDM sludge sample exceed the prescribed limits. The total content of Ni in all sludge samples ranged between a proportion of 54% and 120% of the set limit. The concentration of chromium (Cr) was found to be elevated (449 $mg.kg^{-1}$), attaining nearly 45% of the established limit value. This finding suggests the possibility of an ecological risk to agricultural land. Although the copper (Cu) concentration was below the limit value, the sludge from TMT poses a significant risk of contamination to agronomic soils.Despite their similar provenance, the three sludges exhibit distinct characteristics, including variations in heavy metal and organic matter content. It is imperative to employ the sludges in a manner that aligns with their unique characteristics. Consequently, the comprehensive analysis constitutes the foundation for the sustainable utilisation of sludge as a fertiliser within the agricultural land. The strict regulation and control of wastewater discharges, coupled with the development of an industry that has minimal environmental impact, will facilitate the acceptance of these sludge for agricultural use.

Table 3. Total concentrations of heavy metals in sludge and permitted values of AFNor 44-041)

Metal	BLF	PBT	TMT	AFNor 44-041
Cr	246.7	294.3	448.6	1000
Cu	119.7	145.4	210.4	1000
Ni	107.1	137.9	242.9	200
Pb	91.7	108.9	90.0	800

The Speciation of Heavy Metals

The process of speciation in the context of metals signifies the distribution of the total quantity of metal present across the various metal-bearing fractions. Figure 2 provides a visual representation of the proportion of each of the five fractions in relation to the total content of the metals that have been investigated. The bioavailability and ecotoxicity effects of metals are contingent on their speciation in sludge. The quantity of heavy metal bound to the residual fraction (F-res) is frequently designated as the stable fraction and is considered to be unaffected by environmental processes. However, it is important to note that certain fractions, including the hydrosoluble (F-wat), acid soluble/exchangeable fraction (F-ac), reducible fraction (F-red), and oxidizable fraction (F-oxi), have the potential to become bioavailable under natural soil conditions.

The total copper concentration exhibited a partition of 59 to 77% in the F-wat, F-ac, F-red and F-oxi fractions. In the TMT sludge, F-oxi represents 45%, while F-red is dominant in EST and BKH with proportions of 32% and 37% respectively. The stability of Cu-organic matter complexes is a well-documented phenomenon (Walter et al., 2006; Walter & Cuevas, 1999). It can be hypothesised that the local environment, with its oxidising soil conditions, may facilitate the availability of the Cu bound to F-oxi. The total lead (Pb) concentration was predominantly present in the F-red fraction, accounting for 56 to 67%, while the F-res remained significant at 30 to 40%. Consequently, this Pb partitioning has the potential to predict the high potential bioavailability after sludge application the agricultural in soil.

The results obtained from this study indicate that Ni is predominantly bound to F-RES within the range of 80-85%, thereby suggesting its limited bioavailability in the environment. However, the Ni total concentration in TMT (243 mg.kg^{-1}) sludge exhibited a more significant increase according to limits values (200 mg.kg^{-1}) and may pose a greater environmental hazard. It is important to note that Ni is present as the soluble chemical form (15 at 20%), which is significant given its status as a toxic heavy metal and a potential contaminant. Conversely, the Ni content in BLF (107 mg.kg^{-1}) and EST (137 mg.kg^{-1}) is more suitable for agricultural use. Chromium (Cr) speciation has been found to be concentrated in the F-res, with a proportion of over 92%, indicating minimal direct environmental impact. With regard to Cr fractionation, the following order has been observed: F-res > F-oxi > F-red > F-wat > F-ac. Consequently, it is imperative to assess the quality of both soils and sludges prior to their utilisation in agriculture.

Conclusion

From an agronomic point of view, analysis of the physico-chemical parameters reveals sludge with similar chemical compositions. The results obtained from the analysis of the samples of sludge revealed that the pH level was most frequently between 6.4 and 8. This finding suggests that the process of sludge stabilisation may not be necessary when the sludge is applied to soil. The content of nitrogen, phosphorus and potassium were high in all three sludges, with the EST plant exhibiting the highest concentrations. The C/N ratios of the sludge samples were recorded as between 5 and 8, indicating that nitrogen mobilisation by incorporation into the cell mass may be less efficient. The elevated cation exchange capacity (CEC) of the sludge is advantageous for utilisation in agricultural contexts, as it indicates the material's potential for application as a fertiliser.In the case of the wastewater treatment plant at BLF and PBT, the total concentration of heavy metals in the sludge was found to be well below the thresholds stipulated by European and American regulations concerning the application of sludge on agricultural land.

Conversely, the sludge emanating from the TMT facility poses significant risks of contamination by heavy metals including nickel (Ni) and chromium (Cr). The cumulative Ni concentration in this instance exceeds the established limit of 200mg/kg. Nonetheless, the analysis of speciation reveals that Ni and Cr are predominantly linked to the residual fraction, accounting for 83% and 93% of the total content, respectively. This finding suggests that the bioavailability of these metals in the soil environment may be low.

The current chemical composition of BLF and PBT municipal sludge has appreciable levels of nutrients, interesting properties for agricultural use and a low risk of heavy metal contamination of the soil. These results argue in favour of spreading the sludge on agricultural soils, with strict management in terms of doses and frequency of spreading. In order to ensure the sustainable utilisation of urban sludge, it is imperative that agricultural practices are appropriately regulated, on account of the fact that metals introduced into soil have the potential to accumulate over extended time periods.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

Conflict of Interest

* The authors declare that they have no conflicts of interest

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