American Journal of Environmental Sciences

Original Research Paper

Utilization of Sewage Sludge in Agricultural Soil as Fertilizer in the Republic of Benin (West Africa): What are the Risks of Heavy Metals Contamination and Spreading?

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Article history
Received: 11-06-2015
Revised: 08-08-2015
Accepted: 02-01-2016

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Abstract: Biosolids are the treated organic residuals, also known as sewage sludge, which are generated from domestic wastewater treatment plants. It is an organic matter and nutrients [phosphorous (P) and nitrogen (N)]-rich material. Due to these properties, it is has been reported to be a suitable fertilizer or soil amendment which can valuably replace synthesized NPK. Unfortunately, this matter is heavily loaded with inorganic pollutants, namely heavy metals which limit its land application. Here, we evaluated the quality of treated sewage sludge from Wastewater Treatment Plants (WWTP) in the republic of Benin; and assessed the eco-toxicological risks of heavy metals contamination and spreading related to the use of sludge as fertilizer in agriculture. Results revealed a slightly alkaline (pH ≥6.5) and high electrical conductivity (EC >4 mS cm^{-1}) of the sludge. Heavy metals including Cd, Co, Cu, Zn, Ni, Cr, Pb, Fe and Mn contents were at high level: 27.1, 18.6, 777.1, 1271.7, 165.5, 297.0, 131.2, 3184.0 and 394.2 mg kg^{-1} DM, respectively. Further fractionation of metals showed high mobility of metals classified as follow: Cu > Cd > Pb > Cr > Ni > Fe > Mn > Co > Zn. As a consequence, although the sludge is rich in organic matter and phosphorous, its high value of EC and heavy metals contents, with high mobility do not favor its used in agriculture soils. In addition, metals were enriched in the sludge; meaning that anthropogenic sources, human activities greatly contributed to the accumulation of metals in the sludge.

Keywords: Sewage Sludge, Heavy Metals, Chemical Fractionation, Mobility, Pollution

Introduction

Biosolids also known as sewage sludge are the treated organic residuals generated from domestic wastewater treatment plants. With development and population growth, the production of waste and sewage sludge steadily increases from a year to year across countries in the world. In advanced countries like China, over 11.2 million tons of dry sludge is generated (Chu *et al*., 2009); while Approximately 6×10^6 metric tons is reported in the U.S each year, of which about 60% is applied to agricultural soil and land application (WEF and NACWA, 2013). Sludge management has become a problem with growing importance due to it potentially environmental hazard and high cost for disposal. It has been reported to be an excellent fertilizer and a potential source of organic substances and essential nutrimental elements such as nitrogen and phosphorus for plants. As a consequence, sewage sludge can valuably replace synthetic N and P fertilizers (Kelter *et al*., 1997; Gao *et al*., 2008; Roca-Pérez *et al*., 2009). However, the potential of pathogen transmission and the presence of toxic and persistent organic chemicals and inorganic pollutants (heavy metals) in biosolids; have for the most part limited its valorization. Considerable amount of numerous biodegradable compounds is contained within

sewage sludge which gives rise to secondary pollution (Lee and Han, 2013). Anaerobic digestion and aerobic composting technology are widely used for sludge stabilization. During both processes, some organic pollutants are well remediated; while common sludge treatment process such as anaerobic digestion or composting cannot remove heavy metals from sewage sludge (Chipasa, 2003). Metals can thus be accumulated in the sludge and its long-term application can affect the productivity of soils (McBride, 1995). Therefore it is critical to pay due attention to this matter for the sake of environment safety.

In the republic of Benin, the management of wastewater and sewage sludge remains a great challenge. Talking of wastewater treatment plant, there is only one well known WWTP existing in the republic of Benin, which is located in most populated town (Cotonou) of the country. Now, old of 25 years, the WWTP was supposed to treat the wastewater from 300,000 inhabitants; which is the equivalent of 180 m^3 sludge/day. Nowadays, the population has grown up and the WWTP has to deal with wastewater 3 times greater (600 m^3sludge/day) than that it was supposed to normally deal with. Unfortunately, while the volume/quantity of wastewater knew a drastically increase, the capacity of the WWTP did not significantly increased. Such situation let put a doubt on the quality of the final effluent and produced sewage sludge. Besides, it is important to note that the WWTP was not built to treat and removed metals from sewage sludge. Yet, at the date, the sludge from the WWTP is already being used in agriculture as soil amendment. It would therefore be urgent to investigate the eco-toxicological risks that would be related to the use of sludge as agricultural fertilizer.

To our knowledge, no report on the risk of heavy metals contamination related to the use of sewage sludge from the WWTP in agricultural soils is reported in the republic of Benin these recent years. Therefore, the current work aims at first to investigate and quantify the of heavy metals including Cd, Co, Cu, Zn, Ni, Cr, Pb, Fe and Mn contents in the treated sewage sludge; and secondly, to proceed to their sequential fractionation in order to evaluate the eco-toxicological risks related to the use of sludge as fertilizer in agriculture.

Materials and Methods

Samples and Pretreatment

Dewatered sewage sludge collected from municipal WWTP was used in this study. Collected sludge was primary air dry, then under the oven at 105°C until constant mass and water content was determined. After drying, sludge was ground in a mortar and passed through a sieved size ≤2 mm. The sludge powder was stored in a plastic bag for further physicochemical characterization and heavy metals determination.

Physicochemical Characterization

Physical and chemical parameters included pH, Electrical Conductivity (EC), organic Matter Contents (OM), Total Phosphorus (TP) and metals contents. pH and EC were determined in the supernatant of dissolved sludge sample in reagent water ratio 1/10 (m/v) by the mean of a multi-parameters (HACH, HQ40d), OM was determined by weight ignition at 550°C for 5h. For TP determination, sludge sample was digested via aqua regia digestion according to ISO 11464, EN 12880 and quantify via Flow Injection Analysis (FIA).

Metal Total Concentration

Sludge sample was digested according to Dong *et al*. (2013). Briefly, a mixture (16 mL) of HCl (36%): HNO_3 (67%): HF (49%) ratio 4:1:1 (v: v: v) was added to 0.5 g of sludge sample. The mixture was brought to 110°C using a hot plat under hood and the digestion was performed until dryness. The residue was dissolved with 2% of HNO_3, filtered and collected into 50 mL polyethylene centrifuge tube and finally brought up to the volume. Samples were stored at 4°C until analysis. Samples were in triplicate and the average values were used. Let's call C_0 the concentration of a given metal.

Sequential Fractionation

Sequential fractionation of metals was performed according to the modified method of Tessier *et al*. (1979) as reported by Aikpokpodion *et al*. (2013) (Table 1). Metals, in all extracted samples were determined using Atomic Adsorption Spectroscopy (AAS). Samples were in triplicate and the average values were used.

Sequential Extraction Efficiency (SEE) and Quality Control (QC)

The sequential extraction efficiency SEE (%) for a given metal was calculated as the ratio of the sum of the metal content in all extracted fractions (C_1) and it concentration obtained by three strong acids digestion (C_2) brought to 100 (Equation 1). The digestion of a certified reference material GBW07309 (GSD-9, grey sediment) (0.5 g) and blank were also performed for quality control. The recovery ratios (R) were calculated as the ratio of the extracted concentration (Cex) and its corresponding reference value (Cs) brought to 100 (Equation 2). R values were comprised between 88.5% and 105.5% (Table 3). The supplement concentration responsible of R values greater than 100% could be attributed to some slight errors and uncertainty during manipulation and the preparation of samples:

$$\mathrm{SEE}(\%) = \frac{C1}{C0} \times 100 \quad (1)$$

$$R(\%) = \frac{Cex}{Cs} \times 100 \quad (2)$$

Pollution Indicators

To better understand and assess the impact of pollutants in the environment, several parameters such as Mobility Factors (MF), Pollution Indexes (PI), Pollution Load Index (PLI) and Enrichment Factor (EF) were evaluated.

Mobility Factors (MF)

MF is defined as the ability of a metal to pass from the most stable form to unstable ones, where it is less energetically retained (Achiba *et al*., 2010). In order to access the mobility and bioavailable metals in soil, the MF was calculated as a ratio of metal concentration in the mobile fraction to the sum of all fractions: High MF values is interpreted as symptoms of relatively high mobility and biological availability of heavy metals in soils (Achiba *et al*., 2010):

$$MF = \frac{\sum_{i=1}^{3} Fi}{\sum_{i=1}^{6} Fi} \times 100 \quad (3)$$

Pollution Indexes (PI)

Pollution Index (PI) is used to provide a relative ranking of contamination levels. It is calculated according to (Lee *et al*., 2006) via the equation (Equation 4) below; where *Cj* is the concentration of a given element *j* in soil samples (mg kg^{-1}) and Coj is its corresponding concentration (mg kg^{-1}) in a reference soil or sludge. In this study, the reference sludge for the environment most protective European countries such as Netherlands, Sweden and Denmark (EC, 2001; Salado *et al*., 2008; Olofsson *et al*., 2012) (Table 2) was considered in the present study:

$$PI = \frac{Cj}{Coj} \quad (4)$$

Table 1. Metals sequential extraction method according to Aikpokpodion *et al*. (2013)

Fractions	Reagents	Temperature	Duration
F1 (Water Soluble)	1g dry ground and sieved sample +15 mL reagent water.	Ambient	2 h
F_2 (Exchangeable)	F1 residue +8 mL of 1 M $MgCl_2$ (pH 7.0)	Ambient	1 h
F3 (Carbonate-Bound)	F2 residue +8 mL of 1M Ammonium acetate (Adjusted to pH 5.0 with Acetic acid)	Ambient	5 h
F4 (Fe-Mn Oxides-Bound)	F3 residue +20 mL 0.04M $NH_4OH.HCl$ in 25% (v: v) Acetic acid with occasional agitation.	96°C	6 h
F5 (Organic-Bound)	F4 residue +3 mL of 0.02 M Nitric acid and 5 mL of 30% H_2O_2 (adjusted to pH 2 with HNO_3) with occasional agitation.	85°C	3 h
	A second 3 mL aliquot of 30% H_2O_2 (pH 2 with HNO_3) heat at 85°C with intermittent agitation. Then Cool	85°C	3 h
	Add 5 mL of 3.2 M NH_4OAc in 20% (v:v) HNO_3, make up the volume to 20 mL reagent water and agitated continuously	Ambient	30 min
F6 (Residual)	F5 residue after drying transverse to conical flask +10 mL of 7M HNO_3 on a hot plate for 6 hours. After evaporation at 170°C, 1 mL of 2M HNO_3 was added and the residue after dissolution was diluted to 10 mL. The residue was washed with 10 mL reagent water.	Evaporation 170°C	6 h

Table 2. Standard heavy metals contents in the sludge in the EU countries with far more stringent limits than EU provisions (EC, 2001; Salado *et al*., 2008; Olofsson *et al*., 2012)

Elements	Concentration (mg kg^{-1} DM)	Average (mg kg^{-1} DM)
Cd	0.8-2	1.4
Co	NR	NR
Cu	75-600	337.5
Zn	300-800	550
Ni	30-50	40
Cr	75-100	87.5
Pb	100-120	110
Mn	NR	NR
Fe	NR	NR

NR - Not Reported

Table 3. Physicochemical characterization total metals contents of the sludge

Metals contents and speciation (mg kg^{-1} DM)

Parameters	pH		EC (mS cm^{-1})			OM (%)		TP (%)	
Values	7.6		4.7		TS (%) 22.6	52.5		0.76	
Elements	Cd	Co	Cu	Zn	Ni	Cr	Pb	Fe	Mn
F1	0.40	1.10	20.6	49.1	16.2	12.2	3.6	163.1	30.1
F2	1.30	0.90	69.5	115.8	8.7	46.3	11.9	577.1	59.0
F3	9.40	2.80	360.1	95.7	29.3	27.3	37.9	164.0	15.3
F4	2.30	1.65	55.8	469.2	5.1	37.6	13.0	1630.8	156.6
F5	7.40	3.80	180.4	173.7	65.5	49.0	55.6	153.7	60.9
F6	3.80	7.40	77.9	355.6	34.4	98.2	13.8	446.5	63.7
C1	24.60	17.70	764.6	1259.2	159.4	270.6	136.1	3136.1	285.6
C2	27.10	18.60	777.1	1271.7	165.5	297.0	131.2	3184.0	394.2
Cs	0.26	14.40	32.0	78.0	32.0	85.0	23.0	-	620.0
Cex	0.27	15.20	28.8	80.3	30.9	80.6	23.5	-	610.1
SEE (%)	91.10	94.90	98.4	99.0	96.3	91.1	103.6	98.5	97.8
R (%)	103.80	105.50	90.0	102.9	96.5	88.5	102.2	-	98.3

Note: R was not calculated for Fe because the concentration of free Fe wasn't reported in the standard material. SEE could be considered for it recovery appreciation. Cex and Cs are respectively the extracted concentration and it corresponding reference value in the standard sediment for a given metal

Table 4. Pollution factors

Elements	Cd	Co	Cu	Zn	Ni	Cr	Pb	Fe	Mn
EF	5318.0	19.1	490.7	335.6	62.3	57.1	136.5	1.0	7.3
MFs (%)	41.1	26.2	57.9	20.5	32.7	28.8	40.8	28.4	26.5
PI	19.3	-	2.3	2.3	4.1	3.4	28.9	-	-
PLI							3.4		

Note: PLI was calculate for Cd, Cu, Zn, Ni, Cr and Pb

Pollution Load Index (PLI)

PLI is used to assess the overall pollution status for a given sample (Lee *et al*., 2006). In the current study, PLI was calculated according to (Tomlinson *et al*., 1980; Luo *et al*., 2012; Lu *et al*., 2014) equation (Equation 5). Seven levels of pollution were reported by Zhang *et al*. (2011): Background concentration (PLI = 0), unpolluted (0 < PLI ≤1), unpolluted to moderately polluted (1< PLI ≤ 2), moderately polluted (2 < PLI ≤ 3), moderately to highly polluted (3 < PLI ≤ 4), highly polluted (4 < PLI ≤ 5) and very highly polluted (PLI > 5):

$$PLI = \sqrt[n]{PI1 \times PI2 \times PI3 \times \ldots \times PIn} \quad (5)$$

where, *n* is the number of heavy metals.

Enrichment Factor (EF)

Enrichment Factor (EF) is used to apportion the sources of trace metals in the sediment, soil and biosolids. EF of an element is obtained by comparing the abundance of a given trace element in the sludge relative to that same trace element in a reference material. Specifically, the EF of an element (X) is generally calculated relative to the average composition of crustal abundance (Taylor, 1964; Rudnick and Gao, 2003) using Al or Fe as the reference element (Y). In this study, EFs of selected elements relative to crustal abundance using Fe as the reference element were calculated according to the Equation 6 below:

$$EF = \frac{(X / Fe)Sludge}{(X / Fe)Crust} \quad (6)$$

Statistical Analysis

Origin 8 and SPSS 20.0 ANOVA one way were used for data analysis.

Results and Discussion

Physicochemical Characterization

The investigated dewatered sludge exhibit a slightly alkaline character (pH >6.5) and high electrical conductivity denoting high concentration of organic and inorganic ions such as Cl^-, Na^+, K^+, NH_4^+, NO_3^-, SO_4^{2-}, HCO_3^- in the sludge; which does not favor plant growth despite it is rich in organic matter and phosphorous (Table 3). Indeed, in previous study (Marchese *et al*., 2008), it has been reported that high EC values from 2.5-3.0 mS

cm^{-1} is harmful for fruits and values between 4.5-5 mS cm^{-1} is harmful for the stems; which result into the low germination rate, withering of the plants.

Metal Contents

Data (Table 3) showed varied range of metal contents in the sludge. Metals contents are as follow: 27.1, 18.6, 777.1, 1271.7, 165.5, 297.0, 131.2, 3184.0 and 394.2 mg kg^{-1} DM for Cd, Co, Cu, Zn, Ni, Cr, Pb, Fe and Mn, respectively. It can thus been noted that Cd and Co are at the lowest concentration and Cu, Zn and Fe at the highest concentration. The high concentration of Fe could be explained by the fact that Fe is known to be the earth crust's one of most abundant elements on one hand; and its wide utilization in our daily life on the other hand. The approach of EF is commonly to apportion the sources of trace metals in the sediment, soil and biosolids. As shown in the Table 4, no element shows consistently an EF <1; enrichment values are greater than 10 except for Mn (5318.0, 19.1, 490.7, 335.6, 62.3, 57.1, 136.5 and 7.3, respectively for Cd, Co, Cu, Zn, Ni, Cr, Pb and Mn). This suggests anthropogenic sources of elements than crustal source (Upadhyay *et al*., 2011). Co is commonly used in ceramic and glass materials. It can also be found in rechargeable batteries and electrical and electronic appliances. To promote growth rate, Zn and Cu are used as macronutrient elements in foodstuff additives (Xiong *et al*., 2010), which resulted to their accumulation in the sludge via excreta. In addition, other sources such as galvanized materials and car washes were reported for Zn and leaching from the newer plumbing systems was reported as the source for Cu (Sörme and Lagerkvist, 2002; Rule *et al*., 2006). Ni, Cr, Pb and Mn are detected at moderate concentration. The used of Cd, Ni and Cr, as microfunction elements in additives to enhance muscle productivity and immunity to diseases (Li *et al*., 2010); could explained their accumulation in the sludge. To better understand and appreciate the level of the metals in the sludge, comparison of their concentration in the sewage sludge and their corresponding value in the recommended reference biosolids (Table 2) is needed. Thus, although Cd, owns the lowest concentration in the biosolids compared to others elements, it is at the very high concentration in the sludge as it value is fixed at <2 mg kg^{-1} DM in the recommended reference biosolids (EC, 2001; Salado *et al*., 2008; Olofsson *et al*., 2012). Cu, Zn, Ni, Cr and Pb concentrations are also beyond the recommended values. As a consequence the use of such sludge in agricultural lands would lead to metals spreading and accumulation in the soil. The sequential chemical fractionation of metals carried out in the sludge (discussed below), provided more information and permitted to better appreciate and access the environmental eco-toxicological risk; as the bioavailability and toxicity of heavy metals in the environment depends on their chemical forms (Filgueiras *et al*., 2004). ANOVA one way statistical analysis revealed significant variation between metals concentration in the sludge ($p<0.05$). This suggests that metals in the sewage sludge may have some sources in common. Only Cd and Co did not show any dependency ($p = 0.858$) suggesting the possibility of not having a common source.

Sequential Extraction and Eco-Toxicological Risks

The results of the sequential fractionation of metals in term of mg kg^{-1} DM is shown in the Table 2. However, for better and easier appreciation of metals' level in the sludge, we are going to talk in the term of percentage (Fig. 1). Data showed that chemical forms distribution of metals varies from one to another. Cd, Cu, Ni and Pb are predominant in carbonates and organic bonds forms (F3 and F5), their concentration reached (34 and 27%), (46% and 23%), (18 and 39%) and (29 and 42%), respectively. It is widely said that organic bonds metals are relatively stable; however, under oxidizing condition which lead into the degradation of organic maters, metals could be released (Tessier *et al*., 1979) and easily be available for plants uptake. As it was predictable, Zn, Fe and Mn are predominately bonded to iron and manganese (F4): 37%, 51 and 40%, respectively. F4 is known as reducible fraction (Álvarez-Valero *et al*., 2009) can easily be reduced and converted to exchangeable fraction; especially in anaerobic condition as it use to be in agricultural soil. As a consequence, due attention should be paid to metals stabilization in the sewage sludge to enhance and promote its agricultural use. Co and Cr are strongly bonded to silicates particles (F6): 44.6% and 42%, respectively. It can also be noted that remarkable proportion, up to 23, 29 and 24.5% of Cd, Zn and Ni, respectively are bonded to silicates particles. Otherwise, F1 and F2 fractions of metals are the lowest; nevertheless, their sum reached up to 5% (Cd) to 20%. Such varied distribution of metals in the sludge has a very strong influence on the pollution indicators. Indeed, MFs PI and PLI widely vary from one metal to another (Table 4). Except Zn, all others metals MF is beyond 20%, this reveals the instability of metals and their potential mobility and migration in the sludge. Cu is the most mobile metal in the sludge (MF = 58%) followed by Cd (41%), Pb (40.8%) and Ni (32.7%). Co, Cr, Fe and Mn tend to exhibit similar mobility with MF ranging 26-29%. In the soil, F1, F2 and F3 fractions of metals are very sensitive to the environmental conditions (pH and Temperature) (Achiba *et al*., 2010; Mingot *et al*., 1995). As a consequence these elements can easily be released to the environment and uptake by plants.

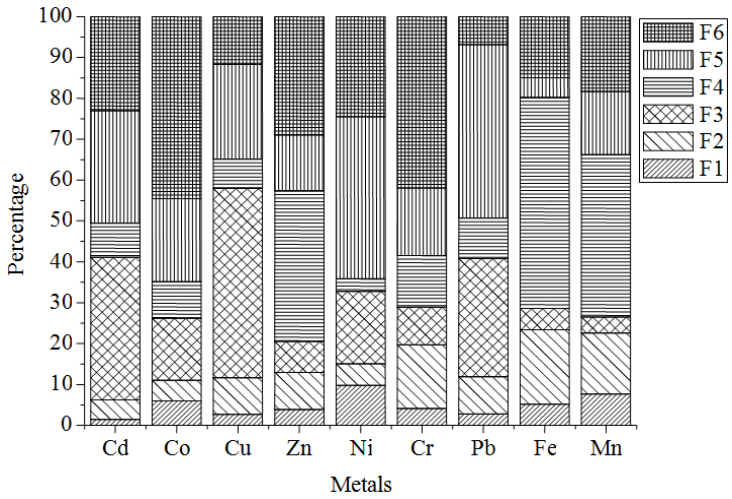

Fig. 1. Percentage distribution of different fractions of studied metals in the sludge

Moreover, the level of pollution's risk by metals is highlighted by the Pollution Index (PI). PI data showed that the application of such sludge in agricultural soil, would lead to a heavy Cd and Pb pollution (Lee *et al*., 2006) due to their high PI value (19.3 and 28.9, respectively). Repeated land application of such sludge would cause severe heavy metals pollution; as the PLI value (3.4) already indicated moderate heavy metals pollution of the sludge (Zhang *et al*., 2011).

Conclusion

Treated sewage sludge's physicochemical characterization, heavy metals contents determination and chemical fractionation have been investigated. The main conclusions are as follow:

- Sewage sludge is slightly alkaline and exhibited high electrical conductivity (EC >4 mS cm^{-1})
- Heavy metals concentration are at high level concentration beyond the recommended values in the sewage sludge
- Metals exhibit very high mobility with MFs ranging 20 to 41%, mainly for Cd, Cu, Ni and Pb
- Land application of such sludge will lead to a severe secondary environmental pollution, with its various negative impacts on the ecosystem

The improvement of the treatment process is highly recommended for better metals' stabilization within sludge before agricultural use or land application.

Acknowlegement

The authors acknowledged the finacial grant from the ministry of High Education and Scientific Research of the republic of Benin.

Author's Contributions

Fidèle Suanon, Lyde A.S. Tomètin and Ignace C. Agani: Equally contributed in designing and performing the experiments, samples analysis, data analysis, manuscript writing and the manuscript reviewing all through the publication process.

Biaou Dimon, Daouda Mama and Eni Coffi Azandegbe: Equally contributed in designing the experiments, data analysis, manuscript writing and reviewing during the publication process.

Conflict of Interest

This manuscript is original and contains not any published material. The corresponding author confirms that all of the others authors have read and approved the manuscript and thus declare no conflicts of interest.

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