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Heavy metals and pollution assessment in soils around major dumps in Akwa Ibom State

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Abstract

This study was conducted to assess the status of lead (Pb), arsenic (As), copper (Cu), cadmium (Cd) and mercury (Hg) in soils around the main dumps in Uyo, Eket and Ikot Abasi urbans in Akwa Ibom State and to assess the levels of contamination/pollution of the soils by the heavy metals. Nine composite samples were collected from the soils at 0 - 20 cm depth - three from each location. At each location, the soil samples were taken about 30, 60 and 90 m away from the dump and were designated A, B and C respectively. The concentrations of the heavy metals in the soil samples were extracted with 0.1 M HCl and measured by atomic spectrophotometry. Results showed that the concentrations of Pb (4.52 - 18.96 mgkg^{-1}), As (0.53 - 5.03 mgkg^{-1}), Cu (5.44 - 26.12 mgkg^{-1}), Cd (2.46 - 11.62 mgkg^{-1}) and Hg (0.01 - 3.81 mgkg^{-1}) were all less than the USEPA/NESREA maximum permissible limits for agricultural soils, but much higher than the WHO maximum safe limits for agricultural soils. All the soils were polluted by the heavy metals and Cd and Hg contributed mostly to the pollution, as indicated by the pollution index (PI) and pollution load index (PLI) values.

Keywords: Status, concentrations, heavy metals, contamination, pollution load index.

Introduction

Heavy metals are naturally occurring elements with densities that are at least five times higher than that of water. They include mercury (Hg), cadmium (Cd), chromium (Cr), thallium (Tl), lead (Pb), zinc (Zn), copper (Cu), iron (Fe), manganese (Mn) and metalloids like arsenic (As) (Tahar and Keltoum, 2011). According to Buekers (2007), these elements enter soil environments through natural and anthropogenic sources such as weathering of rocks and soil minerals, atmospheric deposition, runoff, agricultural inputs, oil spills, mines, smelters, untreated solid/liquid wastes and leachates from dumps and may remain for a long time because of their non-biodegradable nature undergoing chemical transformations which affect bioavailability (Raffa *et al*., 2021).

Although a small number of these elements (Mn, Cu, Zn, Fe, Cr, Se and Ni) are essential for proper plant growth and yields if taken up in trace quantities (Jung, 2008; Adelekan and Alawode, 2011), heavy metals are generally toxic in soil environments, particularly at concentrations above threshold levels, thereby reducing soil microbial activity and soil fertility, retarding seed

germination and root growth, compromising food and groundwater quality and impacting human and animal health negatively (Jung, 2008; Zhang *et al*., 2010). Besides, soils are contaminated by the mere presence of heavy metals or polluted when the metals are present at levels that individually or collectively cause harm or injury to resident communities, plants, animals or humans (Chapman, 2007).

Regular assessments of the status of these elements in soils are therefore necessary for ascertaining the extent or degree of pollution and developing strategies for remediation of the polluted soils. These can be achieved using various pollution indices. The single pollution index (PI), geoaccumulation index (I_{deo}), contamination factor (Cf) and enrichment factor (EF) are some of the indices commonly used to assess soil pollution by a single heavy metal, while the pollution load index (PLI), Nemerow pollution index ($PI_{Nemerow}$), sum of contamination (PI_{sum}) and average single pollution index (PI_{avg}) are some of the indices used to assess soil pollution that is collectively caused by two or more heavy metals (Kowalska *et al*., 2018).

Similar studies have been carried out in the past, but this present study sought to provide an update and additional information which might not only help remind people of the danger of improper solid waste disposal, but may also provide a guide to solving some of the environmental and health-related problems associated with soil contamination/pollution by heavy metals. Therefore, this study was aimed at assessing the status of Pb, As, Cu, Cd and Hg in soils around selected dumps in Akwa Ibom State and the levels of contamination/pollution of the soils by the heavy metals.

Materials and Methods

Study area

The study was conducted in Uyo. Eket and IkotAbasi Urbans in Akwa Ibom State, which is located between latitudes 4^{o} $32^{'}$ and 5^{o} $30^{'}$ N and longitudes 7^{o} $25^{'}$ and 8^{o} $25^{'}$ E. The state has the tropical moist climate with a wet season (April - October) and a dry season (November - March). The annual rainfall of the state is usually high ranging from about 2,500 mm in Uyo to > 3,000 mm in Eket and Ikot Abasi. Most of the soils in Uyo are derived from coastal plain sand, whereas most of the soils in Eket and Ikot Abasi urbans are derived from beach sand (Petters *et al*., 1989; Uduak, 2019).

Soil sample size and sampling technique

A total of nine composite samples were collected from the soils around Uyo, Eket and IkotAbasi main dumps at 0 - 20 cm depth with a soil bucket auger - three from each study location. At each location, the first composite sample, designated A, was taken at a distance of 30 m from the dump, while the second and third composite soil samples, designated B and C,

were taken at the distances of 60 and 90 m from the dump respectively.

Preparation of soil samples for laboratory analyses

Two sets of each composite soil sample were prepared for laboratory analyses. One (the larger set) was prepared with a 2 mm-mesh sieve, while the other set was prepared with a 0.5 mm-mesh sieve. The 2 mm-sieved samples were used for all the determination of the physicochemical properties and heavy metals except organic carbon and total nitrogen, while the 0.5 mm-sieved soil samples were for the determination of organic carbon and total nitrogen. All the soil samples were first air-dried and crushed in the laboratory before being passed through the appropriate sieves.

Determination of soil physicochemical properties

Soil physicochemical properties were determined by the routine methods described by Udo *et al*. (2009). Particle size distribution, organic carbon, total nitrogen and available phosphorus were determined by the Bouyoucos (hydrometer), Walkley and Black wet oxidation, Kjeldahl and Bray 1 methods respectively. Organic matter was determined as the product of organic carbon and van Bemmelan factor of 1.732.Soil pH was measured in water with a glass electrode pH meter in soil/water ratio of 1: 2.5.Exchangeable Ca, Mg, K and Na were determined after leaching soil samples with neutral ammonium acetate (1M NH4OAc). The K and Na concentrations were determined with a flame photometer, while the Ca and Mg concentrations were determined with an atomic absorption spectrophotometer. Exchangeable acidity was determined by the KCl extraction method, while the ECEC was determined by the summation method as follows: ECEC = TEB + EA, where ECEC, TEB and EA represent soil effective cation exchange capacity, total exchangeable bases and exchangeable acidity respectively.Base saturation was determined as the percentage of ECEC occupied by the exchangeable bases.

Determination of heavy metal concentrations in the soils

The heavy metals in the soil samples were extracted with 0.1 M HCl and their concentrations measured by atomic spectrophotometry as described by Udo *et al*. (2009). The concentrations of lead, cadmium, mercury or arsenic in the soils were rated based on USEPA/NESREA maximum permissible limits as well as FAO/WHO (2011) safe limits in agricultural soils. The USEPA/NESREA maximum permissible limits for Pb, As, Cu, Cd and Hg used were 200, 20, 100, 0.48 and 1.0 mg/kg (Pratt, 2014; Afolayan, 2018), while the WHO safe limits for Pb, As, Cd and Hg were 0.30, 0.20, 0.1 and 0.39 $mgkg^{-1}$ respectively (FAO/WHO, 2011). Copper was rated based on the FDALR (1990) critical level of 0.2 $mgkg^{-1}$.

Assessment of soil contamination/pollution by the heavy metals

Soil contamination or pollution by each heavy metal and by all the heavy metals was assessed using the single pollution index and the pollution load index

respectively, as reported by Kowalska*et al*. (2018). The single pollution index is mathematically expressed as follows:

$$PI = \frac{Cn}{GB}$$

Where;

PI represents pollution index,

Cn represents the soil content of the heavy metal studied and *GB* represents the geochemical background value of the heavy metal.

The local geochemical background values reported by Kabata-Kendias (2011) were used in the *PI* determination and they were as follows: Pb (27), As (0.67), Cu (38.9), Cd (0.41) and Hg (0.07). Soil contamination/pollution was rated based on *PI* values as follows:

PI < 0.1 (Very slightly contaminated),
0.10 - 0.25 (Slightly contaminated),
0.26 - 0.50 (Moderately contaminated),
0.51- 0.75 (Severely contaminated),
0.76-1.00 (Very severely contaminated),
1.10 - 2.00 (Slightly polluted),
2.10 - 4.00 (Moderately polluted),
4.10 - 8.00 (Severely polluted),
8.1 - 16.00 (Very severely polluted)
and > 16.00 (Excessively polluted).

The pollution load index (PLI) was mathematically expressed as follows:

$$PLI = (PI_1 \times PI_2 \times PI_3 \times \ldots PI_n)^{1/n}$$

Where *PLI, PI* and *n* represent pollution load index, single pollution index and total number of heavy metals studied, respectively.

Soil pollution was rated based on the *PLI* values as follows:

PLI < 1.0 (Slightly polluted),
1.1 - 3.0 (Moderately polluted),
3.1 - 5.0 (Highly polluted)
1.2 and > 5.0 (Very highly polluted).

Statistical analysis

Ranges and Pearson product moment correlation coefficients were the main statistical tools used. The correlation coefficients were computed using the SPSS package to establish the relationships between the heavy metals and some soil physicochemical properties.

Results and discussion

Physicochemical properties of the soils

The physicochemical properties of the soils are shown in Table 1. The sand, silt and clay contents of the soils respectively ranged as follows: 81.20 - 83.40, 4.40 - 6.40 and 10.40 - 14.40%. The soils generally exhibited loamy sand texture. Sand dominance in the soils could mostly be due to the sandy nature of the parent materials of the soils. The pH values of the soils ranged from 4.4 to 6.8 with most of the soils being moderately acidic, which could be attributed to aluminum hydrolysis, organic matter decomposition, acid rain, excessive leaching

and the acidic nature of the parent materials. The organic matter contents of the soils ranged from 2.36 to 5.33%, indicating low to moderate carbon/organic matter levels in the soils.

Total nitrogen (N) values ranged from 0.36 to 0.71% and were generally high, especially in the soils collected about 30 and 60 m away from the dumps, indicating the influence of the dumps. Low N contents were recorded mostly for soils collected about 90 m away from each of the dumps and might be due to low input. Available phosphorous contents ranged from 2.14 to 4.29 $mgkg^{-1}$ respectively, it could be attributed to the presence of high amount of organic matter and plants decomposition in the dumpsite. The available P contents of the soils were all less than the 7.00 $mgkg^{-1}$ critical level for crop production (FDLAR, 1990).

The exchangeable Ca concentrations in the soils ranged from 4.39 to 6.81 $cmolkg^{-1}$ indicating low to moderate levels. The exchangeable Mg contents ranged from 4.11 to 5.36 $cmolkg^{-1}$ in the soils studied which were all high to very high. The exchangeable K contents ranged from 0.15 to 0.21 $cmolkg^{-1}$ indicating low status of the element and poor K-fertility of the soils, as the values were below the 1.00 $cmolkg^{-1}$ critical limit of soil exchangeable K (FDALR, 1990). The soils had very low to low exchangeable Na contents (0.09 - 0.18 $cmolkg^{-1}$). The exchangeable acidity levels ranged from 3.08 to 6.40 $cmolkg^{-1}$. The ECEC ranged from 11.4 to 19.2 $cmokg^{-1}$) indicating moderate abilities of the soils to attract and hold nutrients and other cationic components of the soils. All the soil samples analyzed had medium base saturation (53.1 - 67.2%) and were higher than 50% regarded as the critical limit established for productive agricultural soils in the ecological zone.

Concentrations of heavy metals in the soils

The concentrations of the heavy metals in the soils studied are shown in Table 2. The concentrations of Pb, As, Cu, Cd and Hg ranged from 4.52 to 18.96, 0.53 to 5.03, 5.44 to 26.12, 2.46 to 11.62 and 0.01 to 3.81 $mgkg^{-1}$ respectively and decreased with distance from the dumps, indicating the influence of the dumps. The findings agree with earlier researchers (Ukpong *et al*., 2013; Jhothi *et al*., 2017). The concentrations of the individual heavy metals in all the soils studied were less than the internationally recognized maximum permissible limits for agricultural soils (especially those of USEPA and NESREA) suggesting that the heavy metals might pose no serious threats to the soil environments around the dumps individually. However, the concentrations of all the heavy metals were much higher than the maximum safe limits recommended by WHO which therefore

indicate that the heavy metals in the soils might pose serious health risks to plants, animals and humans. The various health issues associated with soil heavy metal toxicities have been widely reported (Jhothi*et al*., 2017).

Assessment of soil pollution by the heavy metals

The single pollution index (PI) and pollution load index (PLI) values used to assess the degree of pollution of the soils by the heavy metals are presented in Tables 3 and 4 respectively. The PI values of Pb, As, Cu, Cd and Hg, respectively ranged as follows: 0.27 - 1.12, 0.11 - 1.05, 0.19 - 0.93, 6.00 - 28.34 and 0.02 - 9.29 (Table 3). As indicated by the PI values, Cd and Hg individually polluted the soils, but the other heavy metals (Pb, As and Cu) only contaminated the soils, though at varied degrees. All the soils collected at the distance of about 30 m away from the dumps were excessively polluted by Cd; whereas those collected about 60/90 m away were either severely or very severely polluted by Cd. Pollution by Hg was very severe and severe in the soils collected about 30 and 60 m away from the Ikot Abasi main dump, respectively. The relatively high concentrations of these two highly toxic metals in the soils may not be entirely influenced by the dump but also by industrial emissions and atmospheric deposition considering that Ikot Abasi is a littoral settlement and host to the Aluminum Smelting Company and Ibom Power Power Plants in Nigeria.

All the soils were very strongly polluted, as indicated by the PLI of the heavy metals (Fig. 1), except those collected at about 90 m away from the three dumps which showed only baseline levels of pollution by the heavy metals. Baseline levels of pollution cause no serious deterioration of soil quality, but very strong soil pollution by heavy metals do (Kowalska *et al*., 2018; Masindi and Muedi, 2018).

Conclusions

The status of Pb, As, Cu, Cd and Hg in the studied soils were all below the USEPA/NESREA maximum permissible limits. However, the levels of the heavy metals were far above WHO maximum safe limits for agricultural soils, indicating health implications. As indicated by the PI values, Pb, As and Cu polluted none of the soils except the Ikot Abasi soil at 30 m-distance away from the dump which was slightly polluted by Pb and As. All the soils collected about 30 m away from the dumps were very severely polluted by Cd, whereas those collected about 60/90 m away were very severely/severely polluted by the heavy metal. Mercury showed very severe, severe and moderate pollution in the soils collected about 30, 60 and 90 m away from the dump in Ikot Abasi Urban, respectively. The

Uyo soils collected about 30 and 60/90 m away from the dump were moderately and slightly polluted by Hg, whereas the soils collected from Eket at about 30, 60 and 90 m away from the dump were moderately polluted, moderately contaminated and very slightly contaminated by Hg respectively. As indicated by the PLI values, all the soils collected about 30 m away from the dumps were highly polluted by the heavy metals.

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Table 1: Physicochemical properties of the soils around selected dumps in AkwaIbom State

Soil	Sand %	Silt %	Clay %	T	EC ds/m	pH	OM %	TN %	AP mg/kg	Ca cmol	Mg cmol	K cmol	Na cmol	EA cmol	ECEC cmol	BS %
Uyo A	82.20	5.30	12.50	**LS**	0.09	5.9	4.43	0.51	2.14	6.53	4.11	0.15	0.11	5.06	17.40	58.33
Eket A	83.40	6.20	10.40	**LS**	0.10	5.8	3.88	0.44	2.27	6.44	5.36	0.20	0.09	4.39	18.11	53.14
Ik. Abasi A	82.2	6.40	11.40	**LS**	0.10	6.0	5.33	0.71	2.83	6.81	5.13	0.21	0.21	5.12	19.22	59.87
Uyo B	81.20	6.40	14.40	**LS**	0.09	5.1	2.36	0.36	2.38	6.33	4.00	0.18	0.15	4.86	15.54	59.40
Eket B	83.40	6.20	10.40	**LS**	0.09	5.1	2.42	0.52	3.72	6.80	4.26	0.18	0.13	6.40	17.19	62.58
Ik. Abasi B	82.20	5.30	12.50	**LS**	0.10	5.8	4.09	0.59	3.11	5.18	4.66	0.17	0.17	6.18	17.38	67.16
Uyo C	82.20	5.50	12.30	**LS**	0.07	6.8	2.46	0.46	3.41	5.82	5.00	0.19	0.18	6.09	11.42	53.14
Eket C	83.40	5.20	11.40	**LS**	0.08	4.4	3.31	0.62	3.38	4.39	4.58	0.15	0.18	3.08	13.36	66.17
Ik. Abasi C	83.20	4.40	12.40	**LS**	0.07	6.0	4.16	0.65	4.29	5.26	4.52	0.19	0.14	4.32	15.25	62.59

A = Composite soil sample taken at 30 m distance from the dump, B = Composite soil sample taken at 60 m distance from the dump, C = Composite soil sample taken at 90 m distance from the dump, T = texture, LS = Loamy sand.

Table 2: Levels of the heavy metals in soils around some dumps in Akwalbom State

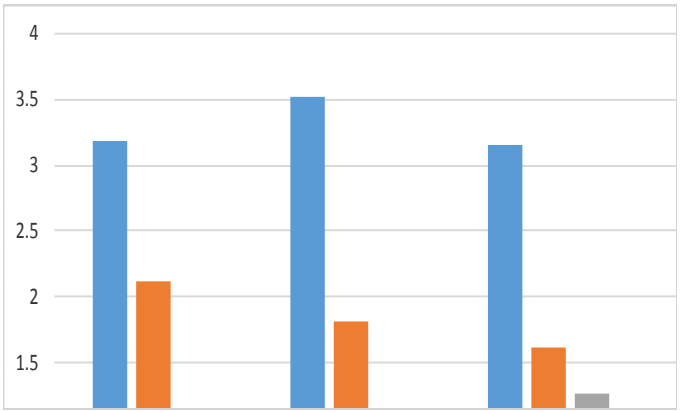
Soil	Lead mg/kg	Arsenic mg/kg	Copper mg/kg	Cadmium mg/kg	Mercury mg/kg
Uyo A	12.31	4.02	22.26	11.62	1.50
Eket A	10.28	2.96	10.58	8.55	1.14
Ik. Abasi A	18.96	5.03	26.12	10.33	3.81
Uyo B	5.40	2.88	13.31	6.49	0.51
Eket B	7.94	0.81	7.74	5.68	0.13
Ik. Abasi B	10.73	3.02	17.69	4.27	1.74
Uyo C	5.53	0.56	9.36	2.46	0.51
Eket C	4.52	0.53	5.44	2.84	0.01
Ik. Abasi C	8.43	1.94	10.78	3.54	1.66

A = Composite soil sample taken at 30 m distance from the dump, B = Composite soil sample taken at 60 m distance from the dump, C = Composite soil sample taken at 90 m distance from the dump.

Table 3: Single pollution index (PI) of the heavy metals

Soil	Lead	Arsenic	Copper	Cadmium	Mercury
Uyo A	0.73	0.84	0.80	28.34	3.66
Eket A	0.60	0.62	0.38	20.85	2.78
Ik. Abasi A	1.12	1.05	0.93	25.20	9.29
Uyo B	0.32	0.60	0.48	15.61	1.24
Eket B	0.47	0.17	0.28	13.85	0.32
Ik. Abasi B	0.63	0.63	0.63	10.41	4.24
Uyo C	0.33	0.12	0.33	6.00	1.24
Eket C	0.27	0.11	0.19	6.93	0.02
Ik. Abasi C	0.50	0.40	0.39	8.63	4.05

A = Composite soil sample taken at 30 m distance from the dump, B = Composite soil sample taken at 60 m distance from the dump, C = Composite soil sample taken at 90 m distance from the dump.



A = Composite soil sample taken at 30 m distance from the dump, B = Composite soil sample taken at 60 m distance from the dump, C = Composite soil sample taken at 90 m distance from the dump.

Fig. 1: A graph showing pollution load index (PLI) of the heavy metals