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RESEARCH ARTICLE

HEAVY METALS CONCENTRATION IN SOILS AND VEGETATION AROUND SELECTED WASTE DUMPSITES IN DELTA STATE

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ABSTRACT

Contamination levels assessment of potential toxic metals such as Ni, Cu, V, Cr, Cd, Pb and Ba in soils and vegetations (Americinthus Spinosus and Brachiria deflexa) around Agbor, Sapele and Warri waste dumpsites were carried out. The aforementioned metals were analytically determined by using the atomic absorption spectrophotometry of model GBC – Scientific A6358, Austira. The results show that all metals levels in soils were higher than their values in Ameranthus, Spinosus and Brachiria deflexa. The levels of Cd in soils from all waste dumpsites were greater than the DPR target values. Also Ni value in Sapele and Pb in Agbor sites were higher than the DPR target values. The contamination/pollution index calculated revealed that the soils were very severely contaminated except that Sapele and Agbor waste dumpsites were polluted with Ni and Pb respectively. All soil samples in this study were polluted with Cd. Metals such as Ni, Cu, Cr, Cd, and Pb showed evidence of metal transfer from the soil to vegetation, although the transfer factor varies from one metal to another.

INTRODUCTION

Pollution is one of the most important problems around the World in which thousands of millions of world inhabitants suffer health problems related to industry and atmospheric pollutants. Worldwide increasing levels of industrialization and urbanization have led to environmental pollution (Filazi *et al*, 2003). Industries have been responsible for discharging effluent containing heavy metals such as zinc, copper, manganese, cadmium, mercury, arsenic, barium, nickel, lead, vanadium chromium, etc. into our environment (Chen and Chen, 2001). Plants take up metals by absorbing them from contaminated soils as well as from deposits on different parts of the plants exposed to the air from polluted environment (Zurera *et al*, 1987). Soils, whether in urban or rural areas represent a major sink for metal released into the environment from a variety of anthropogenic activities. Once in soils, some of these metals will persist because of their fairly immobile nature, others however, will be more mobile in migrating to either groundwater aquifer or plants (Nwajei and Iwegbue, 2007). The mobility and availability of metals in a flood plain soil can be significantly reduced by the formation of metal sulphide precipitates under anoxic conditions (Dulaing *et al*, 2009). Atmospheric deposition can contribute to contamination of floodplains with trace elements (Kowalik *et al*; 2003; Forstner *et al*; 2004). The consequences of chronic exposure to metallic elements are potentially dangerous for children and women of childbearing age (Koller *et al*; 2004; Fonturbel *et al*; 2011). Saad, (2003) reported that the current configuration of Nile Delta Lakes is changing rapidly, due to man's activities and natural processes. Most of their water supply comes from polluted agricultural drains. Several problems affect the conservation of the Nile Delta Lakes mainly pollution, land reclamation, intensive aquatic vegetation, over fishing and coastal erosion (Abdo and El-Nasharty, 2010). The contamination of soil, sediment, water resource and biota by heavy metals is one of the major concern especially in many industrialized countries because of their toxicity persistence and bioaccumulation (Iken *et al*; 2003). Metal particles present in dust will not self-degrade or naturally diminish in the environment, residing for a long time (Stigliani *et al*; 1991). Consequently they will accumulate as long as dust is not removed (Nwajei, and Iwegbue, 2007). The capacity of each soil to retain metals depends on the soil properties (Alloway, 1995; Ross, 19944).

Plants species and varieties vary in their capacity for heavy metal accumulation. Increase in concentrations of heavy metals in soil increases the crops uptake depending on the specie. Today, heavy metals are well recognized as potentially toxic to plants and other living organisms (Zurera *et al*, 1987). Heavy metals produce toxicity by forming complexes or

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legends with organic compounds (Wilspenyer, 1994). Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissue (Nwajei and Iwegbue, 2007). The heavy metals that most commonly cause problems in human are lead, mercury, cadmium, arsenic, nickel and aluminum. These metals tend to accumulate in the brain, kidneys and immune system where they can severely disrupt normal function (Passwater and Cranton, 1993; Gerstner and Huff, 1997, Dibofori-Orji and Edori 2013). The availability of lead in plant is dependent upon the level of contamination, of soil condition and the response of the root to lead in the soil water (Andrews *et al*, 1989; Nwajei *et al*; 2012). Municipal solid waste heaps have become land marks in several major cities in Nigeria, thereby blocking vehicles ways and threatening to cause disease epidemics and flooding (Iwegbue *et al*; 2006). Wastes are constantly dumped in discriminately on every available space such as highway, undeveloped plots and streets. The categories of urban waste include; lubricating oil films, junked cars, anthropogenic wastes household rubbish etc. These indiscriminate dumping of wastes have become unbearable hence it became necessary for this study. The objectives of this study therefore are to determine the heavy metals content in soil and vegetations grown around waste dumps in selected urban areas; and to provide information on the adverse impact of heavy metals as a result of these waste dumps.

MATERIALS AND METHODS

Description of study area: Agbor, Sapele and Warri are three major towns mapped out for this study. The aforementioned towns are located in Delta State. Commercial and industrial activities in these areas have contributed very high rate of generation wastes. These towns have lands that are interlocked by tributaries of River Niger flowing across. They have high population density and numerous streams that interconnect into intricate web of rivers, lagoons, swamps and wetlands. The natural resources found in the study areas are oil palm, plantain, yam, maize, rubber products, cassava, paw-paw, pineapple, etc. Industries located in these study areas include petroleum and petrochemicals company, paint industry, timber industry, steel industry, Etenit company and Warri Sea Port. There are numerous waste dumpsites within Delta State but Warri, Agbor and Sapele were the major towns selected for this study. Geographically, Agbor lies between Latitude 6.15^0N and Longitude 6.12^0E; Sapele lies between Latitude 5.54^0N and Lonitude 5.40^0E and Warri lies between 9.45^0N and Longitude 8.53^0E respectively.

Sample Collection

Soil and vegetation samples were collected from dumpsites for the period of eight months (December – August, 2012). Four composite soil surface (0 – 15cm) samples were collected with a stainless steel soil ring 10cm in diameter driven into the soil approximately 24m to 46m away from the north, east, and west sides of the waste dumpsites (ASTM 1990; Fresquez, 1996). At each site, samples of soil were collected from the centre and corners of a square area 10m preside; the five sub-sample were combined and mixed thoroughly in a plastic reseal able bag to form a composite sample. Vegetation samples were collected from plants as close as possible to the soil sampling locations. The plant samples were placed in a separate clean plastic resealable bag and labeled (Fresquez *et al*; 1996), before transport to the Laboratory. The botanical names of the two plants in this study were Brachiaria deflexa and Amaranthus Spinosus.

Sample Digestion

1.0g of the sieved air dried soil sample was weighed into 250ml Tetcon beaker. Thereafter, 20ml HNO_3, 5ml HCl and 2ml HF were added. The mixture was placed on hot plate with constant stiring for few minutes and later transferred into the fumehood for overnight digestion. On cooling the digest was filtered into 100ml volumetric flask and made up to 100ml. The resultant solutions from the respective digestions were kept in the refrigerator prior to metal analysis. The blank was also prepared following the same procedure above. (Oniawa *et al.*, 2001; Lv et al., 2006). 1.0g of each dried and crushed vegetation sample was weighed (for wet digestion) into Teflon beaker. Then 20ml HNO_3 and 5ml $HClO_4$ were added and stirred vigorously. The mixture was transferred to a hot plate for few minutes. The mixture was further transferred into the fumehood for overnight digestion (Zurera *et al*; 1992). On cooling, the mixture was filtered and the filtrate was made up to mark in a 100ml volumetric flask with deionized water. The resultant solutions from the different digestions were also stored in the refrigerator prior to metal analysis. The blank was also prepared by following the same procedure. The atomic absorption spectrophotometer used for the metal determination is model GBC-Scientific A6358, Austria.

Quality Control

Analytically, quality control measures and recovery study ranging from 92 – 99% were carried out. All glass wares for metal analysis were previously soaked in 14% HNO_3 for 24 hours. All reagents used were of analytical analar grade.

Soil – Plant Transfer of the Metals

This is a convenient method of expressing the relative ease with which trace elements in soils are taken up above ground tissues. This can be calculated using the expression adopted by Oyedele *et al.* (1995). Soil – plant transfer factor is written as:

$$\text{Transfer Factor} = \frac{\text{Metal Concentration in Plant}}{\text{Metal Concentration in Soil}}$$

Contamination/Pollution Index (C/P)

The contamination/pollution index values greater than unity indicates a pollution range whereas when the value is lower than unity, it indicates contamination range. The standard employed for the interpretation of the contamination/pollution index values was adopted by Lacatusu (2000).

Mathematically, contamination/pollution can be Mathematically, contamination/pollution can be computed thus:

$$C/P = \frac{\text{Concentration of Metal in Soil}}{\text{Target Value from Reference Table}}$$

Table 1. shows the significance of intervals of contamination/ pollution index values

C/P	Significance
<0.1	Very slight contamination
0.10 – 0.25	Slight contamination
0.26 – 0.50	Moderate contamination
0.51 – 0.75	Severe contamination
0.76 – 1.00	Very severe contamination
1.10 – 2.00	Slight pollution
2.10 – 4.00	Moderate pollution
4.10 – 8.00	Severe pollution
8.10 – 16.00	Very severe pollution
>16.00	Excessive pollution

Source: Lacatusu (2000)

Table 2. Shows target and intervention values for metals in soil as formulated by the Department of Petroleum Resources (DPR) in Nigeria

Metals in mg/kg	Target Value	Intervention value
Barium	200.00	5000
Cadmium	0.80	17
Chromium	100.00	380
Copper	36.00	190
Mercury	0.30	10
Lead	85.00	530
Nickel	35.00	210
Zinc	140.00	720
Cobalt	20.00	240

Source: DPR (2002).

RESULTS AND DISCUSSION

Table 3 presents the results for total heavy metal concentrations in surface soils from waste dumpsites in Agbor, Sapelee and Warri. The results indicate significant metal variations with respect to sites. All metals analysed were also detected. The levels of metals found in Agbor, Sapele and Warri were below the target and intervention values of heavy metals in soils in Nigeria except for Cadmium. On the other hand mean lead content in soil from Agbor was also above the target value (DPR, 2002). The levels of heavy metals in the examined sites from the three towns were in the following order: Pb > Ni > Cu > Ba > Cd > Cr > V. The concentration of Pb was very high in all the sites measured, indicating that Pb constitute contamination hazards at the three sites. Table 4 and 5 also presents the results of heavy metals in Amaranthus spinosus and Brachiria deflexa collected from waste dumpsites in Agbor, Sapele and Warri. A close look at the results revealed that Ba and V were below detection limits for both plant species, except for Agbor dumpsite where low levels were recorded (0.02± 0.01 for Ba and 0.60± 0.32 mg/kg dry weight). The levels of Ni and Cd found in Amaranthus spinosus were higher than those levels in Brachiria deflexa whereas Pb contents in were higher in Brachiria deflexa. A further look also showed that dumpsites in Sapele had highest metal levels in both Amaranthus spinosus and Brachiria deflexa than Agbor and Warri but this was not the case for soils samples. This is an indication that the rate of metal absorption from the soil was high in Sapele. Heavy metals levels in soil exceeded those of vegetation, indicating that soil is the reservoir of pollution load. The soil – plant transfer factor values recorded in this study shows that Amaranthus spinosus and Brachiria deflexa have the ability to accumulate Ni, Cu, Cr and Cd and Pb. However, high transfer factor were recorded for Ni, Cr and Cd (Table 6) except for Warri dumpsite where Cu was high for both plant species. These high transfer factor may be due to mobile nature of metals in soils. The rate of Cd and Cr transfer from soil to plants could pose threat to food chain through consumption of the vegetables.

Table 3 Mean ± SD and Range of Heavy metal concentration (mg/kg dry weight) in soil from waste dumpsites in Agbor, Sapele and Warri Towns.

Metals (mg/kg dry wt)	Mean± SD and Range	Agbor	Sapele	Warri
Ni	Mean± SD	23.93± 13.08	40.50± 21.41	9.61± 7.73
	Range	4.44 – 36.50	8.64 – 52.91	0.62 – 18.77
Cu	Mean± SD	25.78± 15.07	21.38± 19.91	0.52± 0.37
	Range	9.19 – 43.16	2.39 – 40.99	0.22 – 1.06
V	Mean± SD	1.01± 0.87	1.50± 0.70	1.75± 1.22
	Range	0.42 – 2.31	0.82 – 2.34	0.22 – 3.84
Cr	Mean± SD	1.13± 0.45	1.23± 1.20	2.94± 2.62
	Range	0.73 – 1.70	0.25 – 3.20	0.40 – 6.40
Cd	Mean± SD	3.83± 0.43	2.00± 1.03	3.29± 2.39
	Range	0.98 – 8.80	0.69 – 3.15	0.56 – 6.40
Pb	Mean± SD	89.62± 23.09	76.02± 30.07	44.33± 42.55
	Range	64.62 – 113.56	45.10 – 115.30	9.92 – 97.70
Ba	Mean± SD	22.77± 3.51	0.81± 0.55	3.90± 0.20
	Range	0.46 – 66.01	0.40 – 1.61	3.64 – 4.06

Nickel (Ni)

The concentrations of nickel in soil of these study sites ranged between 9.61 and 40.50 mg/kg dry weight. In Armaranthus spinosus the range was between 10.35 and 13.64 mg/kg dry weight whereas for Brachiria deflexa the range was between 3.92 and 10.30 mg/kg dry weight. The highest levels of nickel were observed in waste dumpsite at Sapele for both soil and vegetation samples. This may be due to activities in hydroelectric power plant and Eternit company located in Sapele, since nickel could be released into air by power plants which may eventually fall down after reactions with precipitation. The levels of nickel in waste dumpsites of Sapele and Agbor were higher than 11.30 mg/kg reported by Iwegbue *et al*, (2013) and 5.00 mg/kg obtained in surface soil of scrap sites in Warri metropolis (Iwegbue *et al*, 2009). The mean levels of nickel in soil and vegetations in this study exceeded those levels in soils and vegetations in the vicinity of Shell Petroleum Development Company operating area in Ughelli Delta State of Nigeria (Nwajei, 2009). In terms of contamination index, the soil of Warri is slightly

Table 4. Mean± SD and Range of Heavy Metal Concentrations (mg/kg dry weight) in Amaranthus Spinosus from Waste Dumpsites in Agbor, Sapeele and Warri

Metals (mg/kg dry wt)	Mean± SD and Range	Agbor	Sapele	Warri
Ni	Mean± SD	10.78± 5.13	13.64± 10.12	10.35± 5.70
	Range	0.22 – 20.94	1.66 – 22.12	0.14 – 21.22
Cu	Mean± SD	0.36± 0.25	3.19± 2.42	0.39± 0.30
	Range	0.22 – 20.94	0.36 – 0.25	0.14 – 0.94
V	Mean± SD	<0.01	<0.01	<0.01
	Range	–	–	–
Cr	Mean± SD	0.58± 0.29	1.37± 1.19	<0.01
	Range	0.00 – 1.16	0.00 – 2.86	–
Cd	Mean± SD	0.98± 0.81	0.93± 0.66	0.91± 0.78
	Range	0.00 – 1.16	0.00 – 1.40	0.00 – 1.58
Pb	Mean± SD	1.86± 1.73	10.58± 9.37	1.00± 0.80
	Range	0.00 – 4.24	0.26 – 22.80	0.00 – 2.20
Ba	Mean± SD	<0.01	<0.01	<0.01
	Range	–	–	–

Table 5. Mean± SD and Range of Heavy Metal Concentrations (mg/kg dry weight) in Brachiria Deflexa from Waste Dumpsites in Agbor, Sapeele and Warri

Metals (mg/kg dry wt)	Mean± SD and Range	Agbor	Sapele	Warri
Ni	Mean± SD	5.00± 3.20	10.30± 6.20	3.92± 2.90
	Range	0.20 – 6.80	1.00 – 13.60	0.00 – 8.20
Cu	Mean± SD	0.54± 0.39	0.63± 0.27	0.63± 0.45
	Range	0.04 – 1.20	0.24 – 0.84	0.12 – 1.40
V	Mean± SD	0.60± 0.32	<0.01	<0.01
	Range	0.00 – 1.22	–	–
Cr	Mean± SD	0.59± 0.33	1.50± 0.99	<0.01
	Range	0.00 – 1.20	0.08 – 3.20	–
Cd	Mean± SD	0.53± 0.29	0.60± 0.34	0.55± 0.32
	Range	0.10 – 0.70	0.06 – 0.78	0.06 – 0.72
Pb	Mean± SD	7.10± 4.76	8.60± 2.73	5.27± 3.23
	Range	4.20 – 14.2	6.60 – 12.60	2.20 – 9.00
Ba	Mean± SD	0.02± 0.01	<0.01	<0.01
	Range	0.00 – 0.04	–	–

Table 6. Shows Values of Soil-Plant (Amaranthus Spinosus and Brachiria Deflexa) Transfer Factors of Metals

Metals	Amaranthus Spinosus			Brachiria Deflexa		
	Agbor	Sampele	Warri	Agbor	Sampele	Warri
Ni	0.45	0.34	1.08	0.21	0.25	0.41
Cu	0.02	0.15	0.75	0.02	0.03	1.20
V	0.00	0.00	0.00	0.52	1.22	0.00
Cr	0.51	1.11	0.00	0.52	1.22	0.00
Cd	0.26	0.47	0.28	0.14	0.30	0.17
Pb	0.02	0.14	0.02	0.08	0.11	0.12
Ba	0.00	0.00	0.00	0.001	0.00	0.00

Table 7. Contamination/Pollution index Heavy Metals in Soils from Waste Dumpsites Agbor, Sapelee and Warri Towns

Metals	Agbor	Sapele	Warri
Ni	0.68	1.16	0.28
Cu	0.72	0.59	0.01
V	NA	NA	NA
Cr	0.01	0.01	0.03
Cd	4.79	2.50	4.11
Pb	1.05	0.89	0.52
Ba	0.11	0.004 (<0.001)	0.02

contaminated; that of Agbor could be ranked as highly contaminated and soil of Sapele could be ranked as polluted. Copper concentrations in soil ranged between 0.52 and 25.78mg/kg dry weight whereas in vegetations the range was between 0.39 and 0.63mg/kg dry weight. Highest mean levels of copper were observed in soils from waste dumpsites in Agbor and Sapele whereas highest level of copper was recorded in Amaranthus spinosus from waste dumpsites of Agbor and Sapele in this study exceeded the selected average (13 – 24mg/kg) reorted by Alloway (1995) for soil except Warri waste dumpsite. The levels reported by Iwegbuee *et al*; (2009). With respect to contamination index, the soils can be ranked as slightly contaminated to very severe contamination.

Vanadum (V)

Vanadum levels in vegetations were below detection limit except for Agbor waste dumpsite (0.60mg/kg dry weight) in Brachiria deflexa sample. On the other hand, vanadium levels were detected in soils from waste dumpsites of Agbor, Sapele and Warri. The highest vanadium level was observed in soil from Warri waste dumpsite, followed by Sapele waste dumpsite. This may be due to the fact that vanadium is an abundant element in crude oils. Warri and Sapele towns are around the crude oil wells locations in Delta State.

Chromium (Cr)

Chromium levels in soils recorded in three sites (Agbor, Sapele and Warri) ranged between 1.13 and 2.94mg/kg dry weight. For Amaranthus spinosus, the range was between 0.36 and 3.19mg/kg dry weight whereas in Brachiria deflexa, the range was between <0.01 and 1.50mg/kg dry weight. Highest level Chromium was observed in soil in waste dumpsite of Warri whereas highest levels of Chromium in Amaranthus spinosus and Brachiria deflexa were observed in Sapele dumpsites. These levels of chromium in soil and vegetations may be attributed to activities of rubber industries in Sapele and other materials such as anthropogenic wastes. Chromium levels in both soils and vegetations in this study were lower than those reported by Nwajei (2009). The levels of chromium found in soils in this study exceeded the levels reported in soils around cassava processing mills (Iwegbue *et al*; 2013). Similar levels of chromium have been observed in soils of selected waste dumpsites in Warri and Effurun in Delta State (Nwajei, 2007).

Cadmium (Cd)

Cadmium was detected in all samples and the trend of the levels are in the following order: Soil > Amaranthus Spiinosus > Brachiria deflexa. Cadmium levels in both soils and vegetations are considered elevated in this study. Anthropogenic wastes and other materials such as batteries, dumped refrigerators, dumped rechargeable, lantern, electric appliances wastes, cadmium coated vessels, vehicles scraps and tyres and paints could account for high levels of cadmium in this study. The levels of Cadmium observed in sol in this study were higher the levels previously reported by Iwegbue *et al*, (2013) and Nwajei, (2007). The levels of Cadmium in soil in this study also were similar to levels reported for soils of Uwelu motor spare part market in Benin City, Nigeria (Nwajei and Iwegbue, 2007). The levels of Cadmium in soils and vegetations in this study were lower than the levels reported for soils and vegetations in the vicinity of Shell Petroleum Development Company operating area in Ughelli, Delta State (Nwajei, 2009). The concentration of Cadmium in the three examined sites ranged between 2.00 and 3.83mg/kg dry weight. These levels exceeded the Department of Petroleum Resources target maximum allowed value of Cadmium in soils. The calculated contamination/pollution index showed that Cadmium value in soils for the three examined sites were above unity, (Table 7), indicating that soils from the three sites were polluted with Cadmium.

Lead (Pb)

The concentrations of lead in soils ranged between 44.33 and 89.62mg/kg dry weight. Fro amaranthus spinosus, lead levels ranged between ranged 1.00 and 10.58mg/kg dry weight while lead levels in Brachiria deflexa ranged between 5.27 and 8.60mg/kg dry weight. Lead levels in soils in this study exceeded the level of lead in toxicological soil criteria (40.00mg/kg dry weight) for soil (Danish EPA 2000) and those levels reported for soils from a Gold mining area in Ghana (Faanu et al; 2011). Lead concentration in soil from Agbor waste dumpsite was higher than the Department of Petroleum Resources target maximum allowed value of lead in soil (Table 2). The calculated contamination/pollution index of lead ranged from 0.52 to 1.05 (Table 7). Therefore, the soils could be ranked as moderately contaminated, very severely contaminated and slightly polluted with lead. Waste batteries and petrol additives may account for the levels of lead.

Barium (Ba)

Low levels of barium were generally observed in soils in all waste dumpsites. Secondly, barium was below detection limits in Amaranthus spinosus and Brachiria deflexa sample examined. Lead levels in soils of Agbor and Warri waste dumpsites were higher than those reported by Nwajei and Iwegbue (2007) in soils of Uwelu motor spare part market, Benin city.

Conclusion

Contamination levels assessment of potential toxic metals in soils and vegetations around the waste dumpsites in three urban towns (Agbor, Sapele and Warri) in Delta State were carried out. The results show that in general, the concentrations Ni, Cu, V, Cr, Cd, Pb and Ba in soils were higher than their values in Amaranthus spinosus and Brachiria deflexa. In soil-plant transfer factors of metals, Ni, Cu, Cr, Cd and Pb show positive responses, which is one of the key components of human exposure to metals through the food chain. The levels of Cd in soils in all waste dumpsites were greater than the DPR target values. Also Ni level in soil of Sapele and Pb in Agbor waste dumpsites recorded greater values than the DPR target values. The contamination/ pollution index of heavy metals calculated for soil revealed that the three sites were polluted with Cd. Secondly Ni was polluted in Sapele site whereas Pb was also polluted in Agbor site. Barium and Vandadium were below detection limits in both Amaranthus spinosus and Braciria deflexa except Agbor site where barium level was recorded. Anthropogenic wastes and urbanization could account for the high levels of potential toxic metals observed in this study.

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