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Heavy metals assessment of leachate contaminated soils from selected dumpsites in Port Harcourt, Rivers state, South-South, Nigeria

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Abstract
The effects of leachate on heavy metals content of dumpsite soils were assessed using atomic absorption spectrophotometer (AAS). The results obtained showed that Iron (Fe) was the most abundant metal, with the highest concentration observed at the Rumuigbo dumpsite. The least concentrated metal in the dumpsites was vanadium (V) with the lowest value observed at the Slaughter dumpsite. The order of the metal concentrations in the dumpsites were Fe>Cu>Zn>Mn>Ni>Pb>Cr>Cd>V. All the metals except cadmium (Cd) were below the required permissible limit in soils by DPR, China and the world average value in shale. All the metals except cadmium (Cd) were below the permissible limits in soils. Contamination and pollution index models showed that the soils were within the uncontaminated – moderately contaminated in the various dumpsites for all the metals except Cu which was moderate – strong pollution and Cd which showed strong pollution in all the dumpsites. All the metals except Cd showed low contamination tendencies when tested against the geo-accumulation index. Interpretation of the data with ecological risk factor showed that all the metals except Cd had little or no Pollutional tendencies, but potential ecological risk assessment however, showed that the environment is at the risk of being polluted by these metals.

Keywords: Heavy metals assessment, leachate contaminated soils, Port Harcourt, spectrophotometer

Introduction
The pollution of the environment, whether aquatic or terrestrial constitute serious health challenges to both plants and animals which inhabit them. Different activities carried out by man lead to the introduction of heavy metals into the environment which at certain concentrations becomes dangerous to the end users which may be man, plant or animals [1]. Waste disposal problem is synonymous with urban development. Due to disposal issues most cities in Nigeria establish centres where wastes can be easily disposed and assessed for final evacuation at government approved dumpsites. However, at certain times delay in evacuating the waste from the dumpsites come into play.

However, when wastes are allowed standing without removal to approved dumpsites, the organic components which got decayed on contact with inorganic components and water in the dump flow as leachate which migrates through the soil strata and the surface of the soil, and contributes towards contamination of the ecosystem [2]. The leachate arising from solid waste within the municipality has some negative consequences which depend on the nature of the waste composition, volume, temperature, lifetime and soil characteristics [3]. The soil is known as the ultimate sink of waste. These freely disposed wastes, has the capacity to change both physical and chemical properties of the soil environment when it has interacted with it [4].

Dumpsites are provided for solid wastes which comprises of both organic and inorganic wastes. Waste production or generation is majorly due to rapid increase in production and consumption from industrial, agricultural and other human and animal activities within urban settlements. The non-useful components of these activities (production and consumption) are always discarded and considered as wastes. These, in effect, on the long or short run pose pollution problems to the environment [5]. The nature and composition of the wastes on dumpsites varies from one place to the other because of socio-economic conditions, location and season [6].

Heavy metals exhibit certain metallic properties which distinguish them from other metals [7]. They are known to be toxic when they reach or exceed certain concentrations in food, water, soil and air, although some of them are very important to humans, animals and plants at trace levels [8]. The presence of heavy metals in an environment alters the structure and functions of the ecosystem. This is due to the fact that their presence has effect or influence on the nature of the physical and chemical properties of the soil [9].

Indiscriminate discharge and delay in evacuation of wastes from dumpsites can constitute danger to the environment and can also lead to the introduction of new components which originally were not present. In view of this therefore, this study investigated the heavy metal contents of selected dumpsite soils that may have been contaminated by leachate in Port Harcourt, Rivers State.

Materials and Methods

Soil samples were collected randomly from five different points five metres apart within a dumpsite and mixed together to form an aggregate sample. The samples were collected between the months of November 2015 to May 2016 from ten (10) dumpsites within the Port Harcourt metropolis. The sampling was done on very dry days when the refuse (waste) has been evacuated. Soil auger was used to collect the soil samples from a depth of 0 – 20 *cm*.

The soil samples were transferred into black polythene bags and labeled accordingly. The samples were then transported to the Chemistry Laboratory of the Ignatius Ajuru University of Education, Rumuolumeni Port Harcourt. The samples were air-dried to constant weight for three weeks. The soil samples were macerated to powder and stones were removed without crushing them. The powdered samples were sieved with 2 *mm* mesh and then stored in a well cleaned and air-tight bottle and labeled accordingly.

About 2g weighed of each of the sieved samples was digested with acid mixture [10]. The digests were filtered with Whatman No. 1 filter paper and transferred into 250ml sample bottles after being cooled. The digest of filtrate was made-up to mark with de-ionized water in a 100 ml Erlenmeyer flask. The digest was then subjected to heavy metal analysis at the *Jaros Base* Scientific Laboratory using the Solar Thermo Elemental Atomic Absorption Spectrophotometer (AAS), flame model SE – 71096.The results obtained from the heavy metal analysis were expressed as mean ± SD. of the concentrations in mg/Kg.

The heavy metals results were further subjected to index models evaluation:

Contamination/Pollution Index

The contamination factor is expressed as:

Contamination Factor (C_f) = Cm/C_b

The Pollution Index (PI) is mathematically expressed as

Pollution Index (PI) = $n\sqrt{(C_f1xC_f2xC_f3x...x\ C_fn)}$

Where, C_f = contamination factor, n = number of metals, Cm = metal concentration in polluted sediments, Cb = background value of that metal.

Geo-accumulation index (I-geo)

Geo-accumulation index was calculated according to [11].

Mathematically, I-geo = log 2 (Cn / 1.5 Bn)

Where, Cn = Concentration of heavy metal in the sediment.

Bn = Geochemical background value in average shale of the metal.

The factor 1.5 is used for the possible variations of the background data due to lithological variations.

The classification of the I-geo shows that values < 1 are not polluted, while values > than 1 ranges from slight pollution to extreme pollution [11].

Ecological Risk Factor (E_f)/ Potential Ecological Risk (RI)

Ecological risk factor (E_f) was used to express the potential ecological risk of a given contaminant, while the potential ecological risk, assesses the effect of multiple metal pollutions in the sediments from the aquatic environment [12].

Mathematically, $E_f = Tr\ x\ C_f$ and

$RI = \sum E_f$

Where Tr = the toxic-response factor for a given element and C_f = the contamination factor of the element.

Results and Discussion

Heavy Metals

The values of chromium (Cr) ranged from 5.67±0.02 – 11.22 ± 2.04 mg/Kg in the sampled stations. The values of copper (Cu) differed between 69.84±5.32 – 98.64±7.12 mg/Kg in the stations. The observed values for Zinc (Zn) ranged from 41.80±2.21 – 94.61±5.13 mg/Kg. Nickel (Ni) concentrations from the sampled station were within the range of 7.81± 0.78 – 19.46±6.03 mg/Kg. Cadmium (Cd) concentrations were within the range of 4.44±0.31 – 8.71±2.15 mg/kg in the sampled station. Lead (Pb) values differed within the range of 6.17±0.77 – 18.74±2.96 mg/Kg concentrations in the stations. The concentrations of manganese from the soil leachate in the stations ranged from 32.32±1.65 – 71.32±5.87 mg/Kg. Those of iron (Fe) from the sampled sites ranged from 172.81±8.45 - 916.17±15.39 mg/Kg. The concentrations of vanadium (V) ranged from 0.153±0.00 -2.094±0.04 mg/Kg (Table 1).

A comparison of the concentrations of the heavy metals investigated showed that their concentrations in the dumpsite soils were all lower, except Cd than the recommended values by DPR, China and the World average value in shale (Table 2).

Table 1: Mean Concentrations (mg/Kg) of Heavy Metals in Selected Dumpsite Soils within Port Harcourt Metropolis (n =6)

Station	Heavy Metals								
	Cr	Cu	Zn	Ni	Cd	Pb	Mn	Fe	V
Mile 1	6.72±1.01	69.84±5.32	41.80±2.21	12.89±1.20	7.12±0.5	6.87±1.20	49.87±6.22	172.81±8.45	0.978±0.02
Mile 3	9.86±0.92	72.12±4.98	69.41±4.09	10.64±0.96	4.44±0.31	9.19±2.11	33.16±4.21	191.67±9.37	0.742±0.00
Town	7.52±0.85	89.30±6.33	81.81±7.23	14.90±2.29	6.87±2.11	14.63±2.34	63.70±4.98	206.37±10.22	0.502±0.00
Slaughter	11.01±1.30	95.41±5.48	78.61±7.80	13.49±1.03	8.14±1.34	8.44±0.45	71.32±5.87	240.17±10.67	0.153±0.00
Iwofe	8.71±0.33	71.73±5.23	51.90±4.33	8.71±0.06	6.60±0.56	6.17±0.77	46.33±2.76	189.30±6.54	0.925±0.01
Choba	5.67±0.02	98.64±7.12	48.10±2.11	18.29±3.00	8.71±2.15	8.43±1.22	41.99±2.13	198.82±5.98	0.789±0.00
Rumuigbo	8.96±1.32	76.21±8.01	94.61±5.13	16.04±2.15	3.45±0.02	9.74±0.98	32.32±1.65	916.17±15.39	1.427±0.03
Bundu	5.72±0.56	93.80±8.67	88.11±8.91	19.49±6.03	8.67±2.11	18.74±2.96	67.30±6.22	637.20±12.12	2.094±0.04
Eleme Junction	11.22±2.04	91.54±5.23	67.81±6.66	14.39±4.30	7.15±1.00	14.70±1.56	37.12±1.10	409.22±9.88	0.842±0.00
Aba Road	7.81±0.89	77.13±2.34	59.10±4.56	7.81±0.78	3.66±0.00	11.04±1.66	63.43±9.33	893.10±12.69	1.873±0.01
Mean	8.32	83.572	68.126	13.665	6.481	10.795	50.654	405.483	1.0325
STDEV	1.995	11.17	17.76	3.82	1.97	4.01	14.75	299.73	0.5998

Table 2: Comparison of the Concentrations of Heavy Metals (mg/Kg) in the Present Study to Some Known Standards

Metal	Present Study	DPR Intervention Value	World Average in Shale	China
Cr	8.32	380	90	-
Cu	83.572	190	45	35
Zn	68.123	720	95	150
Ni	13.665	210	68	-
Cd	6.641	17	0.3	0.5
Pb	10.795	530	20	60
Mn	50.654	850*	850	-
Fe	405	38000*	47000	-
V	0.325	120	130	-

*Target values

Contamination or pollution of heavy metals in the environment is of major concern because they are toxic and constitute threat to human life and the environment at certain concentration [13]. Increase in heavy metals contents of soils from dumpsite has been observed in many studies [9, 14, 15]. Increase in metal concentrations in soils from dumpsites could result from deposition of wastes which have high metal content [16]. The degradation of organic component of waste in dumpsites can also contribute to metal increase of the soils from the dumpsites. The oxidation state of metals and the redox potential of the system also contribute to increase in the metal content of any soil environment [17]. However, [15] observed other factors such as the nature of the waste, the time taken before the wastes were evacuated from the dumpsites and the non-stabilization or treatment of the waste before being discarded at the dumpsite are responsible for the increase in metals contents of dumpsite soils. The biodegradation of solid wastes in dumpsites lead to release of minerals (mineralization) and increase in the release of basic cations into the soil which cause increases in soil physicochemical properties [18].

The availability of heavy metals in any soil environment depends on the pH of that environment. This is due to the fact that solubility and mobility of metals is a pH dependent phenomenon. According to [19], heavy metals are found at moderate concentration levels in municipal landfills. Metals cause oxidative stress in organisms due to the formation of free radicals as a result of ion exchange and displacement reaction. They are known to interact with enzymatic activities and pigmentation and thus disrupt their normal functions in plants and animals [20] and so render such land where their concentrations are high unsuitable for agricultural purposes.

The concentrations of the heavy metals observed from the dumpsites in Port Harcourt in this study are far higher than those observed in other cities in Nigeria, such as Ibadan [21], Owerri [18] and Abuja [22], but either lower or higher than the values obtained from dumpsites in Akure, Ondo State [23], slightly higher (except in the case of cadmium) in an earlier study on dumpsites within Port Harcourt metropolis [24]. However, the observed values of the heavy metals from the dumpsite were quite lower than those observed in dumpsites within Lagos Metropolis [25]. The observed higher values of these heavy metals in Port Harcourt metropolis may be due to the presence of industries and the higher population density within the settlement area in Port Harcourt, which may have affected the nature of waste generated.

Contamination Factor/ Pollution Index

Contamination index values showed that Cr was lowest at the Choba sample station (0.063) and highest at the Eleme junction sample station (0.125). The values of Cu was least at the Mile 1 station (1.552) and highest at the Choba station (2.192). The value of Zn was lowest at the Mile 1 station (0.440) and highest at Rumuigbo station (0.996). The lowest contamination index value of Ni was observed at Mile 3 station (0.157) and highest at Bundu sample station (0.287). The value of contamination index for Cd was lowest at Rumuigbo station (11.493) and highest at Choba (29.037), while that of Pb was lowest at Iwofe station (0.309) and highest at the Bundu Station (0.937). Manganese had its lowest value at the Rumuigbo station (0.038) and highest at the Slaughter station (0.084). The contamination index of iron (Fe) ranged between 0.004 –1.078. The contamination index of Vanadium (V) ranged from 0.004 – 0.016. The pollution index (PI) of the sampled stations ranged from 0.169 - 0.459 (Table 2).

Table 3: Contamination Factor (C_f/) Pollution Index (PI) of Heavy Metals from Dumpsites in within Port Harcourt Metropolis, Rivers State.

Station	Contamination Factor of Heavy Metals									PI
	Cr	Cu	Zn	Ni	Cd	Pb	Mn	Fe	V	
Mile 1	0.075	1.552	0.440	0.190	23.727	0.344	0.059	0.004	0.008	0.174
Mile 3	0.110	1.603	0.731	0.157	14.793	0.460	0.039	0.004	0.006	0.172
Town	0.084	1.985	0.861	0.219	22.907	0.732	0.074	0.005	0.004	0.210
Slaughter	0.122	2.120	8.275	0.198	27.140	0.422	0.084	0.005	0.001	0.233
Iwofe	0.097	1.594	0.546	0.128	22.010	0.309	0.055	0.004	0.007	0.169
Choba	0.063	2.192	0.506	0.269	29.037	0.421	0.049	0.004	0.006	0.186
Rumuigbo	0.0996	1.694	0.996	0.236	11.493	0.487	0.038	1.078	0.011	0.359
Bundu	0.064	2.085	0.927	0.287	28.907	0.937	0.079	0.750	0.016	0.459
Eleme Junction	0.125	2.034	0.714	0.211	23.827	0.735	0.044	0.481	0.006	0.358
Aba Road	0.087	1.714	0.622	0.115	12.200	0.552	0.075	1.051	0.014	0.350

Considering the data obtained in Table 2, and comparing them to the intervals of contamination and pollution [26], it follows that all the sample stations were uncontaminated with Cr, V, Mn, Ni, Zn, Pb and Fe. However, Fe was moderately polluted at the Aba Road station. The stations were either at moderate pollution or between moderate-strong pollution with Cu. The contamination index for Cd was very strong due to the fact that it exceeded > 5 which is the category for very strong

pollution. The pollution index (PI) showed that all the stations fall into the > 0-1 category, which implies that they are uncontaminated-moderate contamination. These values were very low when juxtaposed with the values obtained from Olusosun landfill soil in Ojota Lagos [15], where the authors observed values of Pollution index range of 6.88-8.31, which showed very strong pollution of the environment with heavy metals.

Geo-accumulation Index

The geo-accumulation index for the various sample stations showed that Cr was lowest at Choba and highest at Mile 3, Cu was lowest at Mile 1 and highest at Choba. Zn was least at Mile 1 and highest at Rumuigbo, while Ni was lowest at Iwofe and highest at Choba. Cd was observed to be the metal with the highest geo-accumulation value of all the metals with the least value observed at the Rumuigbo station and the highest value at the Choba. The geo-accumulation values for Pb, Mn, Fe and V were very low (Table 4).

Table 4: Geo-accumulation Index (Igeo) of Heavy Metals from Dumpsites in within Port Harcourt Metropolis, Rivers State

Station	Heavy Metals								
	Cr	Cu	Zn	Ni	Cd	Pb	Mn	Fe	V
Mile 1	0.015	0.312	0.088	0.038	4.762	0.069	0.012	0.00	0.0015
Mile 3	0.022	0.322	0.147	0.031	2.971	0.092	0.0078	0.00	0.0011
Town	0.017	0.397	0.173	0.044	4.596	0.147	0.015	0.00	0.00
Slaughter	0.025	0.425	0.166	0.040	5.445	0.085	0.017	0.001	0.0023
Iwofe	0.006	0.320	0.110	0.026	4.415	0.062	0.011	0.00	0.0014
Choba	0.004	0.440	0.102	0.054	5.827	0.084	0.0099	0.00	0.0012
Rumuigbo	0.020	0.340	0.200	0.047	2.308	0.098	0.0075	0.0039	0.0022
Bundu	0.013	0.418	0.186	0.057	5.800	0.188	0.016	0.0027	0.0032
Eleme Junction	0.025	0.408	0.143	0.042	4.783	0.148	0.0087	0.0017	0.0013
Aba Road	0.017	0.344	0.125	0.023	2.448	0.111	0.015	0.0038	0.0029

The calculated I-geo data when compared to the Seven classes (ranging from 0-6) of the geo- accumulation index as proposed by [11], showed that the dumpsites are practically uncontaminated with Fe, V, Mn and Pb and Cr, but uncontaminated to moderately contaminated with Cu, Zn and Ni. However, Rumuigbo and Aba Road were moderately to heavily contaminated, Mile 1, Town, Iwofe and Eleme Junction were heavily to extremely contaminated while, Slaughter, Choba and Bundu were extremely contaminated with Cd.

Ecological Risk Factor and Potential Ecological Risk Assessment

The ecological risk factor for the metals showed that: Cr varied from 0.126 – 0.25, Cu varied from 7.76 – 10.96, Zn varied from 0.44 – 0.996, Ni varied from 0.575 – 1.435, Cd varied from 360.00 – 871.11, Pb varied from 1.72 – 4.685, and Mn values, from 0.039 – 0.084. The potential ecological risk index (RI) from the various stations varied from 372.78 – 886.20 (Table 4).

Table 5: Ecological Risk Factor (E_f) and Potential Ecological Risk Assessment (RI) of Heavy Metals from Dumpsites in within Port Harcourt Metropolis, Rivers State

Station	Ecological Risk Factor of Heavy Metals									RI
	Cr	Cu	Zn	Ni	Cd	Pb	Mn	Fe	V	
Mile 1	0.15	7.76	0.440	0.95	711.81	1.72	0.059	-	-	722.89
Mile 3	0.22	8.015	0.731	0.785	443.79	2.30	0.039	`-	-	455.09
Town	0.168	9.925	0.861	1.095	687.21	3.66	0.074	-	-	702.99
Slaughter	0.244	10.60	8.275	0.99	814.20	2.11	0.084	-	-	836.48
Iwofe	0.194	7.97	0.546	0.64	660.30	1.545	0.055	-	-	672.00
Choba	0.126	10.96	0.506	1.345	871.11	2.105	0.049	-	-	886.20
Rumuigbo	0.192	8.47	0.996	1.18	344.79	2.435	0.038	-	-	396.06
Bundu	0.128	10.425	0.927	1.435	867.21	4.685	0.079	-	-	884.89
Eleme Junction	0.25	10.17	0.714	1.055	714.81	3.675	0.044	-	-	730.72
Aba Road	0.174	8.57	0.622	0.575	360.00	2.76	0.075	-	-	372.78

Based on the terminologies for the interpretation of risk of heavy metal pollution of an environment as proposed by [12], all the metals in the various stations fall within the low potential ecological risk category (Er^i< 40), except Cd which had values that corresponded to very high ecological risk (Er^i> 320) at all the stations. The original purpose of the ecological risk was its use as a diagnostic tool for the control of water pollution. However, it has been used to determine or assess the quality of sediments and soils in environment contaminated by heavy metals in recent times [27].

Conclusion

Heavy metals concentrations in the different sampled stations were all (except cadmium) lower than the recommended or permissible concentrations by the relevant agencies (DPR, China and World average value in shale). The index models approach applied to the heavy metal concentrations values indicated that anthropogenic activities is a contributory factor in the total heavy metals content/ burden of the different dumpsite soils. Cadmium was observed to be the most noticeable metal in the soils amongst others in the dumpsites based on the model indices used. Therefore, efforts should be put in place to check the nature of refuse dumped at the different dumpsites and metal scraps be immediately removed for recycling to avoid heavy metal pollution of the soils and its health consequences on man and the environment in general.

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