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Source Analysis of Heavy Metals and Polycyclic Aromatic Hydrocarbons from a Popular Dumpsite, Lagos State, Nigeria

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Abstract: In this study, landfill leachates and plants from Olusosun landfill in Ojota area of Lagos State, Nigeria were investigated. Physicochemical parameters, concentrations of heavy metals (HMs – Pb, Cd, Cr, Ni, Mn and Zn) and polycyclic aromatic hydrocarbons (PAHs) were determined in leachates while HMs and PAHs were determined in plants. Nitric and Perchloric acid mixtures were used for digesting both leachates and plant samples before quantification by atomic absorption spectrometry. Cold extraction was used for extracting PAHs and was quantified using gas chromatography-mass spectrometry. The range of results on HMs analysis were: leachates (mg/L) - Pb: 0.60 - 1.10, Cd: 0.04 - 0.05, Cr: 0.30 - 0.40, Ni: 0.13 - 0.19, Mn:0.53 - 0.74 and Zn: 2.24 - 3.72; plants (mg/kg) – Pb: 1.0 – 6.0, Cd: 0.3 – 0.5, Cr: 0.0 – 4.0, Ni: 0.2 – 1.6, Mn: 10.1 – 41.2 and Zn: 0.0 – 13.2 respectively. For PAHs, the concentrations (mg/L) ranged from 0.10 - 0.24 and 0.09 - 0.31 mg/kg for leachates and plants respectively. Pearson correlation and principal component analysis identified the main sources of pollution in Olusosun landfill as anthropogenic. Proper management of the landfill is advised to prevent contamination of groundwater and surface waters.

Keywords: Landfill leachate, heavy metals, Olusosun, polycyclic aromatic hydrocarbons, plants.

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INTRODUCTION

Rapid urbanization and increasing population growth increase waste generation (1). Management of solid waste is an environmental challenge in many urbanized areas of the world (2). Landfilling is a standard method of waste disposal in several developing countries (3). However, the quality of many landfill sites is far from recommended standards mainly because the landfill systems are not correctly engineered and suited with the requisite leachate collection facilities and installation. These landfills thus serve as repositories for many toxic substances (4,5). The extent of the threats posed by these landfills depends on the depth of the water table, the direction of the groundwater flow, permeability of the geologic strata, the concentration and level of pollutants in the leachates, and municipal solid waste type (6).

Leachates are mixtures of dissolved inorganic and organic compounds as well as microbes generated via the percolation of water through disposed of

solid wastes in a landfill (5). Several factors are responsible for leachates composition, including the kind of waste deposited on the landfill, degree of compaction, particle size, the composition of the wastes, the age of the landfill, the climate, hydrology of the site and other various peculiar conditions such as landfill design and type of liner used (7). Leachates can thus contain substantial amounts of organic (polycyclic aromatic hydrocarbons (PAHs), persistent organic pollutants (POPs), polychlorinated biphenyls (PCBs)) and inorganic (heavy metals) pollutants (8,9). They can also serve as indicators of environmental pollution through their ability to leak, percolate, and contaminate groundwater (10).

There has been a growing interest regarding the possible harmful effects of PAHs released into the environment from anthropogenic sources as several PAHs have been reported to exhibit mutagenic and carcinogenic properties (3,11). Furthermore, uncontrolled inputs of heavy metals into the environment are unpleasant and undesirable due to non-biodegradability and bioaccumulation in soil, underground water, or plants; and the toxicity of several heavy metals is well documented in the literature. Leachate production via decayed solid waste materials mixed with precipitates of surface waters can bring about contamination of plants, surface and sub-surface water collection systems, and transportation of the contamination to the farther point of the ecosystem (12) while the volume of leachate generated in a landfill depends on the amount of solid waste deposited, water availability, condition of the landfill, and deposited refuse, as well as the soil condition (3). Leachate outflow and infiltration are reported to be the primary source of groundwater contamination from existing landfills (13).

In Lagos metropolis, three dumpsites – Olusosun, Solus, and Abule-Egba – are in use, with Olusosun being the most active in terms of quantity of waste generated daily (14). There are several reports on the state of different landfill sites in Lagos with particular interest on contamination of leachates and surrounding soils by heavy metals (10,15,16) and PAHs (17). However, the impact of heavy metals and PAHs from leachates on plants growing on the dumpsite is lacking. Therefore, in this study, the physicochemical properties, level of heavy metals and polycyclic aromatic hydrocarbons in leachates and plants from Olusosun dumpsite, were investigated

MATERIAL AND METHODS

Description of study area

Olusosun landfill is located in the Ojota area of Lagos State, Nigeria (Figure 1). It is known to be the largest landfill in Lagos State and ranked among the biggest in the world. It has been in existence since 1978 (18), occupies 42 hectares of land, and receives approximately 40% of the total waste deposit Lagosians (19). It lies between latitude 6°. 20' N and longitude 3°. 20' E. Various human activities take place around this vicinity, including automobile repairs, petrol fueling stations (18), and motor parks. The landfill does not have any protective bottom layer constructed to protect leachate plumes from migrating into groundwater.

Sample collection

Five Leachate samples were collected from each of the three leachate streams flowing out of the base of the landfill to make a composite (L1). Another five leachate samples (L2) were collected from the main pond located within the vicinity of the landfill. Each of the composite samples was placed in 1L pre-cleaned plastic bottles with the cap securely tightened, preserved in ice-chest, taken to the laboratory, and stored in a refrigerator at 4 oC pending analysis. Sample bottles were rinsed with the leachates before sample collection.

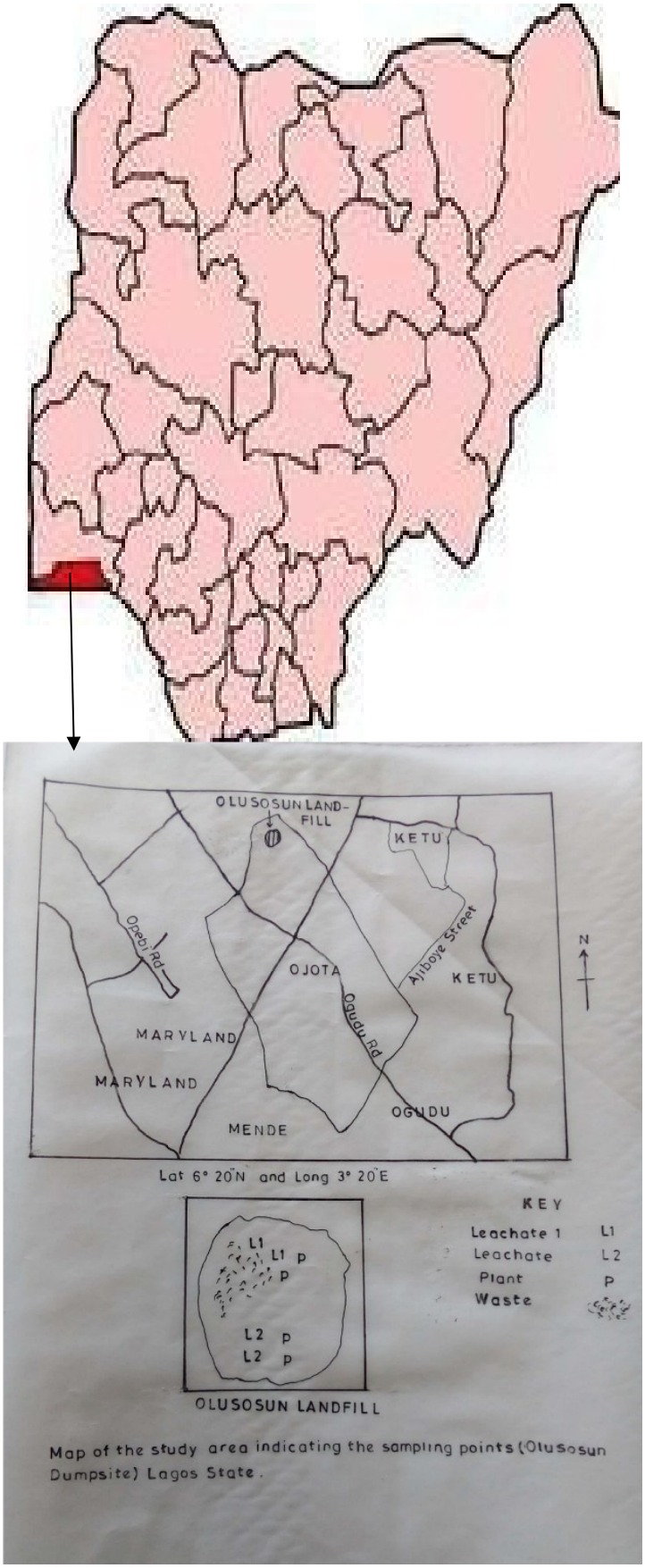

Figure 1: Map of the Study Area. (the red portion in the south-west quadrant).

The leaves of three different plants - pawpaw (*Carica papaya*, P_1), pepper (*Capsicum annum*, P_2) and banana (*Musa acuminata*, P_3) - were collected within the vicinity of L1 and L2. The collected plant leaves were placed in pre-cleaned polyethylene bags and transported to the laboratory. The plants were identified at the Department of Plant Biology, University of Ilorin, Nigeria. In the laboratory, the leaves were rinsed with tap water and distilled water and air-dried at room temperature. The dried samples were ground using an agate mortar and pestle and sieved using a 2 mm mesh size sieve.

Physico-chemical parameters

The pH of composite leachate samples was measured in-situ using a portable digital pH meter (pHep® Hanna, USA), which had been previously calibrated with buffer solutions of pH 4 and 7, respectively. The temperature was also determined in-situ using a thermometer. Electrical conductivity (EC) was measured with a conductivity meter calibrated with a potassium chloride solution. Colour was determined using colorimetry. Total dissolved solids (TDS) was determined gravimetrically by evaporating a known volume of leachate to dryness in a pre-weighed crucible on a steam bath. Total suspended solids (TSS) were also determined gravimetrically by evaporating a known volume of filtered leachate to dryness in a pre-weighed crucible on a steam bath. Biochemical oxygen demand (BOD), chemical oxygen demand (COD), chloride (Cl-), and hardness were determined titrimetrically. The concentration of sulfate (SO_4^{2-}) was determined turbidimetrically, phosphate (PO_4^{3-}) was determined via the colorimetric method, and nitrate (NO_3^-) was determined using the brucine method (20).

Analysis of heavy metals in leachates and plant samples

50 mL of each leachate samples were treated with 10 mL of concentrated HNO_3 and 5 mL of $HClO_4$. The entire mixture was heated in a digestion block at 125 °C until white fumes are observed to confirm the complete utilization of the acid, and the volume was reduced to about 25 mL. The mixture was removed from the block, cooled, filtered using a Whatman No. 40 filter paper, transferred to a 50 mL volumetric flask and made up to mark with distilled water (21). Atomic absorption spectrophotometer (Buck Scientific Model 210 VGP, USA) was then used for quantification of the following metals: Pb, Cd, Cr, Ni, Mn, and Zn. All samples were prepared in duplicate.

For plant samples, approximately 5.00 g of each of the powdered leaf samples was placed in a 25 mL conical flask. 10 mL of concentrated HNO_3 was added, followed by 5 mL of $HClO_4$. The contents of the flask were heated at 150 °C for 1 hour in a fuming hood and then cooled to room temperature. After that, 20 mL of distilled water was added, and the mixture was filtered using filter paper in a 50 mL volumetric flask (21). Atomic absorption spectrophotometer was also used for quantification of the following metals: Pb, Cd, Cr, Ni, Mn and Zn. All samples were prepared in duplicate.

Analysis of PAHs in leachate and plant leaves

For extraction and clean-up of PAHs in leachates, 100 mL of thoroughly mixed leachate sample was filtered using clean cotton wool to attain a clear solution without particles into a separating funnel. A 100 mL mixture of n-hexane and dichloromethane 1:1 (v/v) was added, and the separating funnel was left undisturbed on a retort stand for about 30 minutes. The separating funnel was then opened to drain the water phase while the organic phase was collected in a glass funnel containing 20 g of anhydrous sodium sulfate plugged with a ball of cotton wool. A second extraction was carried out on the organic phase and was re-extracted using a 50 mL mixture of dichloromethane and n-hexane 1:1 (v/v). The extract was concentrated to an absolute 20 mL prior to the determination of PAHs (22,23).

For plant leaves, a 2.00 g of each ground plant sample was weighed into a clean extraction container. 10 mL of dichloromethane was added and left for 20 minutes. Another 20 mL of dichloromethane was added again to the mixture and was then filtered into an extraction bottle. The extracted sample was concentrated to 3 mL for separation. The column was packed with 1 g of moderately packed cotton wool. 3 g of dried activated silica gel was then poured into the column, and 0.6 mL of sodium sulfate was added. The column was rinsed with 20 mL of dichloromethane to allow it to run through the silica gel. Pre-elution with dichloromethane (20 mL) was allowed to flow through the column for about 2 minutes, and 3 mL of the plant sample was poured immediately into the column. The stop-cork of the chromatographic column was opened, and the eluent was collected at intervals with a 10 mL graduated cylinder. Due to exposure of sodium sulfate to air, dichloromethane was added at intervals to the column in increments of 5 mL. The concentrated fractions were then transferred in a glass bottle with rubber crimps caps for GC-MS analysis (24). All samples were prepared in duplicate.

Extracts from leachates and plant leaves were analyzed for 16 PAHs by gas chromatography-mass spectrometry (GC-MS, Agilent 7890B GCMS, USA).

Data Analysis

All the experimental data were subjected to further statistical analyses such as Analysis of variance (ANOVA), Pearson correlation matrix, and principal component analysis to determine the source of pollution from the studied landfill (Olusosun) using Origin pro 2018.

RESULTS AND DISCUSSION

Physico-chemical properties of leachate

Physico-chemical properties of leachates obtained from Olusosun dumpsite are presented in Table 1. The pH values, ranging from 7.3 - 7.5, indicates slight alkalinity of the leachates. Leachate pH values are reported to increase with age and are usually greater than 7 (10,17,25). Values of pH greater than 7 may be attributed to high salinity, an increase in the utilization of unionized free volatile fatty acids by bacteria, and a decrease in short-chain fatty acids (26). The pH also serves as an indicator of the chemical state in which an environmental species will be present, and pH-dependent species such as heavy metals may become environmentally available at low pH (27). Hence, the metals' bioavailability might be low. Similarly, alkaline values have been reported for landfill leachates (10,16,17,26). The TDS values ranged from 5880 - 6500 mg/L. High TDS values imply the presence of a large concentration of soluble ions, leaching of the ions, and dissolved organic matter from the landfill caused by the hydrogeological, physical, and chemical conditions from the landfill, including chlorides, carbonates, phosphates, nitrates among others (27). The range of concentration values for TSS, BOD, COD, NO -, PO_4^{3-}, Cl^-, TH and $SO_4^{2-}$are: 1260-1805 mg/L, 640-658.2 mg/L, 2788-2866 mg/L, 18.4-21.2 mg/L, 9.0-9.8 mg/L, 3439-3471 mg/L, 7305-7670 mg/L and 107-150 mg/L, respectively. All but SO_4^{2-} exceeded their respective limits set by WHO (29) and NESREA (30). A high BOD level implies that the leachate cannot undergo self-purification, and therefore require some form of pre-treatment. Similarly, a BOD/COD ratio greater than 0.2 indicates that the leachate is old and relatively stable (17). For Cl-, no harmful level is reported in humans, but high concentrations exceeding the 250 mg/L permissible limit may be harmful to and cause damage to plants. The concentration of sulfate at high amounts in landfill leachate is reported to depend on depends on the following factors: landfill age, composition of waste, the biological, physical, and chemical composition (31). Nitrate level concentration values are important factors in determining the extent of pollution in leachates. Phosphate at high concentrations can lead to oxygen depletion of water bodies via eutrophication with a response to an increasing level of nutrients due to the presence of phosphates and nitrates (32). The color of the leachates was found to be very black, which is a result of the changes in the oxidation state of Fe^{2+} (ferrous ions) to Fe^{3+} (ferric ions). The ferric ion forms ferric hydroxide colloids and fulvic complexes contributing to the blackish color of the leachates (26).

Table 1: Physico-chemical properties of leachates

	Leachates			
Parameters	**L_1**	**L_2**	*	**
Color	Black	Black	Colorless	-
pH	7.5±0.10	7.3±0.10	6.0 - 9.0	6.5 - 9.5
EC (µS/cm)	724.0±0.40	740.0±0.90	_	1000.0
TDS (mg/L)	6500.0±0.90	6880.0±1.30	500.0	500.0
Temperature (°C)	17.0±0.90	18.7±0.10	40.0	_
BOD (mg/L)	640.0±0.51	658.2±0.90	50.0	_
COD (mg/L)	2788.0±0.20	2868.0±1.10	90.0	_
Cl^- (mg/L)	3439.0±0.80	3471.0±1.11	250.0	250.0
TH (mg/L)	7305.0±0.90	7670.0±0.71	_	180.0
TSS (mg/L)	1260.0±1.10	1505.0±0.92	25.0	_
SO_4^{2-} (mg/L)	107.0±0.30	150.0±0.90	250.0	250.0
NO_3^- (mg/L)	18.4±0.01	21.2±0.20	10.0	50.0
PO_4^{3-} (mg/L)	8.0±0.50	9.8±0.03	2.0.0	_

*NESREA, 2011

**WHO, 2007

Table 2: Pearson correlation matrix of the physicochemical parameters of leachate from Olusosun Landfill

	pH	**EC**	**TDS**	**Temp.**	**BOD**	**COD**	**Cl^-**	**TH**	**TSS**	**SO_4^{2-}**	**NO_3^-**	**PO_4^{3-}**
pH	1											
EC	-0.4096	1										
TDS	-0.8504	0.8283	1									
Temp.	-0.5903	0.9782	0.9267	1								
BOD	-0.8361	0.8429	0.9996	0.9363	1							
COD	-0.7219	0.9270	0.9780	0.9847	0.9832	1						
Cl-	-0.8072	0.8692	0.9970	0.9530	0.9987	0.9912	1					
TH	-0.7665	0.8999	0.9897	0.9709	0.9932	0.9978	0.9978	1				
TSS	-0.8085	0.8681	0.9972	0.9523	0.9988	0.9909	0.9965	0.9977	1			
SO_4^{2-}	-0.7672	0.8994	0.9899	0.9706	0.9933	0.9977	0.9979	0.9968	0.9978	1		
NO_3^-	-0.9209	0.7329	0.9883	0.8583	0.9838	0.9346	0.9735	0.9563	0.9740	0.9565	1	
PO_4^{3-}	-0.9226	0.7298	0.9876	0.8560	0.9830	0.9330	0.9724	0.9549	0.9729	0.9552	0.9999	1

Two-tailed significance is used.

The physicochemical parameters for all the leachates were analyzed with Origin pro 2018 using one-way ANOVA (Analysis of variance), which showed that all the physicochemical parameters analyzed were significantly different ($p > 0.05$ level). Also, Pearson correlation was used to analyze the physicochemical parameters, as shown in Table 2 above. The pH showed a negative correlation with EC ($p = 0.7313$), TDS ($p = 0.3527$), Temp. ($p = 0.5980$), BOD ($p = 0.3697$), COD ($p = 0.4865$), TH ($p = 0.4440$), TSS ($p = 0.4006$), Cl^- ($p = 0.4020$), SO_4^{2-} ($p = 0.4434$), NO_3^- ($p = 0.2550$), PO_4^{3-} (0.2521). There was a positive correlation among other physicochemical parameters with which includes EC vs. TDS, SO_4^{2-} vs. NO_3^- , TH vs. PO_4^{3-} BOD vs. Cl^-, Temp. vs. SO_4^{2-}, COD vs. TH, Cl^- vs. TH, TDS vs. Temp., TDS vs. BOD, Temp. vs. COD, EC vs. Temp., Cl^- vs. SO_4^{2-}, BOD vs. TSS, TDS vs. PO_4^{3-}, COD vs. SO_4^{2-} , TDS vs. TSS, BOD vs. COD, Temp. vs. TH, TSS vs. NO_3^-, BOD vs. TH, EC vs. NO_3^-, Cl^- vs. Temp., BOD vs. TSS, EC vs. TSS, TDS vs. NO_3^- TH vs. SO_4^{2-}, Temp. vs. PO_4^{3-}, TH vs. NO_3^- , TSS vs. SO_4^{2-}, EC vs. BOD, and NO_3^- vs. PO_4^{3-}. With the results from Pearson correlation, it can be deduced that the landfill is heavily polluted with diverse kinds of wastes dumped from the residents in this State.

Heavy metal concentrations in leachates and plant leaves

The concentrations of heavy metals (mg/L) in leachate samples were: 0.60 - 1.10 for Pb, 0.04 - 0.05 for Cd, 0.30 - 0.40 for Cr, 0.13 - 0.19 for Ni, 2.24 - 3.72 for Zn and 0.53 - 0.74 for Mn, respectively as shown from Figure 2 below. The increasing order of metals concentration metals in the leachate samples followed the order: Zn>Pb>Mn>Cr>Ni>Cd. These values are similar to the results obtained elsewhere (17) but slightly higher than those reported elsewhere (28). All analyzed metals in leachates samples exceeded their respective permissible limits set by WHO (29) and NESREA (30) except Cd, which was lower than the NESREA (30) permissible limit. The presence of heavy metals in both leachates can be attributed to the type of waste being deposited on the landfill site, which in turn is a function of the industrialized nature of the study areas.

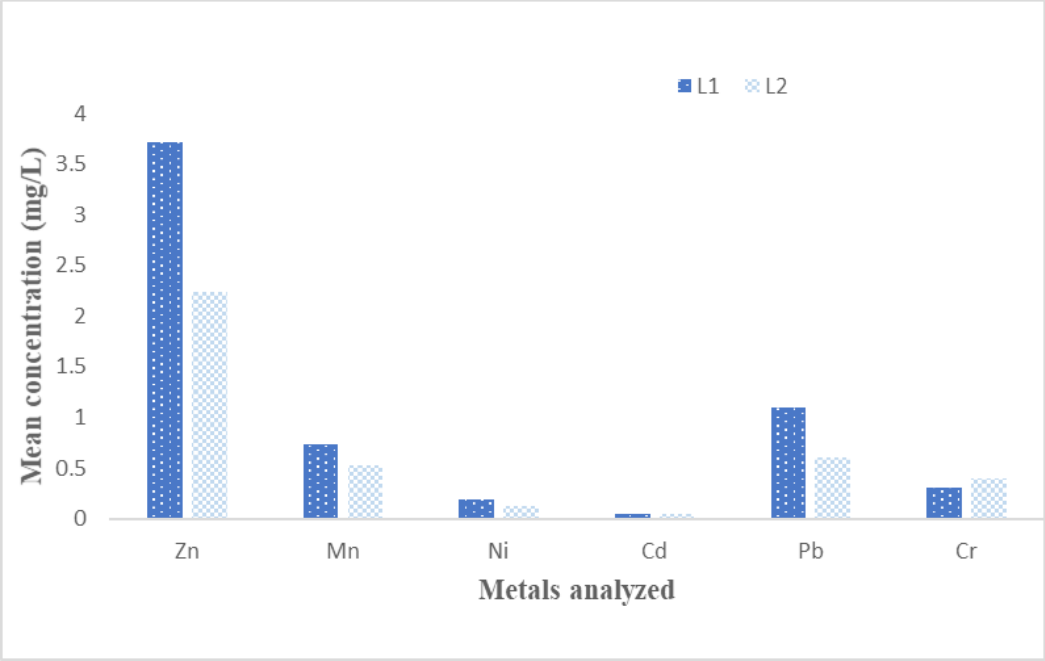

Figure 2: Metal concentrations in leachate samples.

The mean concentrations of heavy metals in plant samples analyzed are shown in Figure 3 below. The increasing order of metals concentration in plant samples followed the order: Mn>Zn>Pb>Cr>Ni>Cd. The concentration of heavy metals in all plant samples were all below their respective permissible limits set by WHO (33) (50 mg/kg for Zn, 10 mg/kg for Ni, 0.02 mg/kg for Cd, 2 mg/kg for Pb and 1.3 mg/kg for Cr).

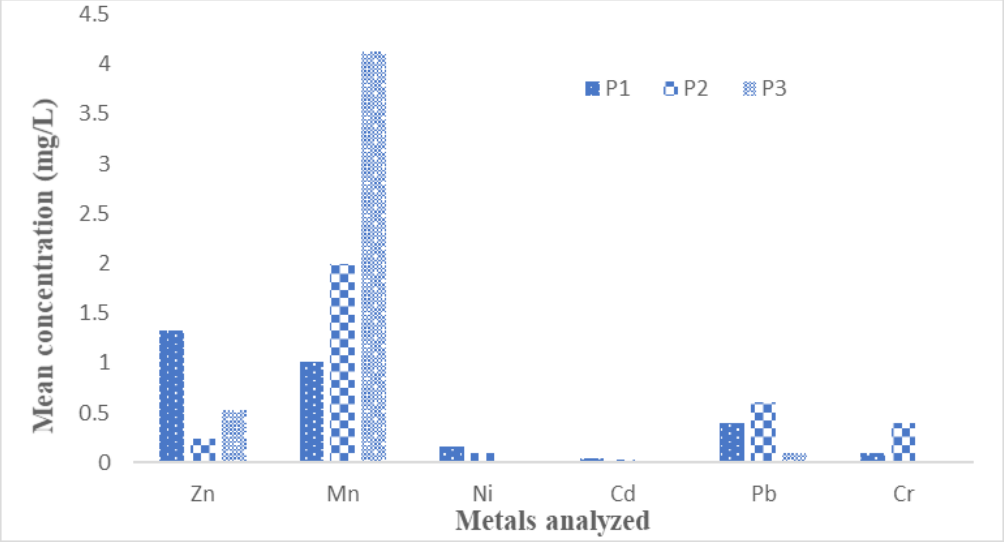

Figure 3: Metal concentrations in plant leaves.

Table 3: Pearson correlation matrix of heavy metals from leachates Samples in the Olusosun landfill.

	Zn	Mn	Ni	Cd	Pb	Cr
Zn	1					
Mn	0.9411	1				
Ni	0.7827	0.9471	1			
Cd	0.7278	0.4530	0.1429	1		
Pb	0.8967	0.9936	0.9774	0.3491	1	
Cr	0.1477	-0.1956	-0.5000	0.7857	-0.3054	1

Two tailed ($p > 0.05$ level)

Table 4: Pearson correlation matrix of heavy metals from the plant samples in the Olusosun landfill.

	Zn	**Mn**	**Ni**	**Cd**	**Pb**	**Cr**
Zn	1					
Mn	-0.5434	1				
Ni	0.7067	-0.9780	1			
Cd	0.7067	-0.9780	0.6215	1		
Pb	-0.1469	-0.7506	0.5960	0.5960	1	
Cr	-0.5171	-0.4376	0.2402	0.2402	0.9226	1

Two tailed ($p > 0.05$ level)

From Table 3 above, there is a strong positive correlation between Zn with other metals such as Mn ($p = 0.2197$), Ni ($p = 0.4277$), Cd ($p = 0.4811$), Pb ($p = 0.2919$) and Cr ($p = 0.9057$). Also, there is a positive correlation in Mn versus Ni ($p = 0.2080$), Mn versus Pb ($p = 0.0723$)), Ni versus Pb ($p = 0.1357$), and Cd versus Cr ($p = 0.4246$) and slight correlation between Ni versus Cd ($p = 0.9087$), Mn versus Cd ($p = 0.7007$) and Cd versus Pb ($p = 0.7730$). A negative correlation was identified between Mn versus Cr ($p = 0.8747$), Ni versus Cr ($p = 0.6667$) and Pb versus Cr ($p = 0.8024$). The Pearson correlation of the plant samples is shown in Table 4 above. A negative correlation was identified between Zn vs. Mn ($p = 0.6343$), Zn vs. Cr ($p = 0.6540$), Mn vs. Ni ($p = 0.1339$), Mn vs. Pb ($p = 0.4596$), Mn vs. Cr ($p = 0.7117$) and slight correlation exist between Ni vs. Pb ($p = 0.8456$) and very strong correlation exist between Zn vs. Ni and Zn vs. Cd having the same values ($p = 0.5004$), Ni vs. Cd, Cd vs. Pb are also having the same values ($p = 0.5935$). The correlation between the metals analyzed was from a similar source (34), and this confirmed that the landfill was contaminated with different composition of solid wastes dumped on this landfill, which percolated into soil and then contaminated the plants grown from this site. The relatively high concentrations recorded for Mn in plant leaves compared with leachate concentrations could be attributed to different degrees in bioaccumulation of Mn by the different plant laves studied.

The eigenvalues obtained from any data are used to determine components that are retained. A set of data having eigenvalues greater than unity indicates a component that is retrained, but when it is less than unity, the component is not retained (35, 36). The scree plot of heavy metals in leachates and plants were shown from Figure 4 below. There were

five components from each scree plot of leachates and plants. Components 1 and 2 are retained with eigenvalues of 4.00 and 1.97 respectively for both leachates and plants, while other components (3-6) are not retrained. However, components 1 and 2 are retrained for leachates and plants because the eigenvalues are greater than unity, as shown in Figure 5. It is similar to the previous research from the assessment of heavy metals from roadside dust in Ilorin (36). The two principal components analysis (PC 1 and PC 2) from heavy metals in leachate samples has a variance of 66.99 % and 33.01%, respectively, as shown from Figure 6 below.

In the plant samples, the PC 1 and 2 have 66.05% and 33.95% variance, respectively, as shown from Figure 6 below. PC 1 is strongly correlated with these metals (Zn, Mn, Ni, Cd, Pb) in leachates and negatively correlated with Cr while PC 2 is strongly correlated with Zn, Cd, and Cr, but negatively corrected with Mn, Ni, and Pb as shown from Table 5 below. Table 6 below indicates the PC 1 and PC2 of heavy metals in plant samples. PC 1 is strongly correlated with Zn, Ni, Cd, Pb, and Cr but negatively correlated with Mn. While PC 2 is strongly correlated with Mn, Pb, and Cr but negatively correlated with Zn, Ni, and Cd. With the statistical data from the principal component analysis, it can be deduced that the heavy metals from this landfill are heavily polluted by anthropogenic sources (17, 34, 37).

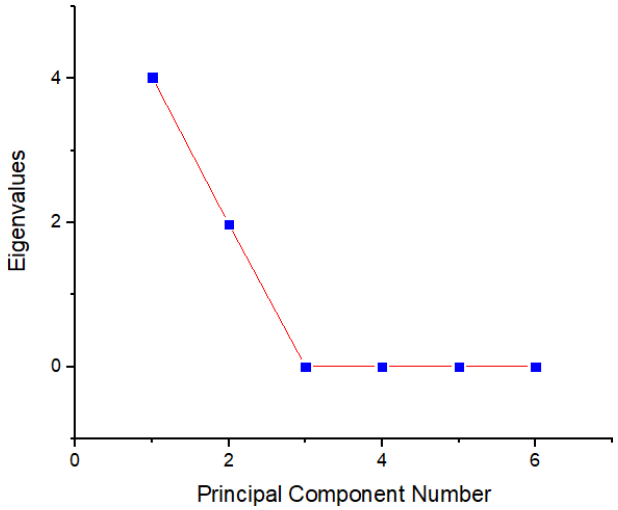

Figure 4: Screen plot of heavy metals in both plants and leachate samples.

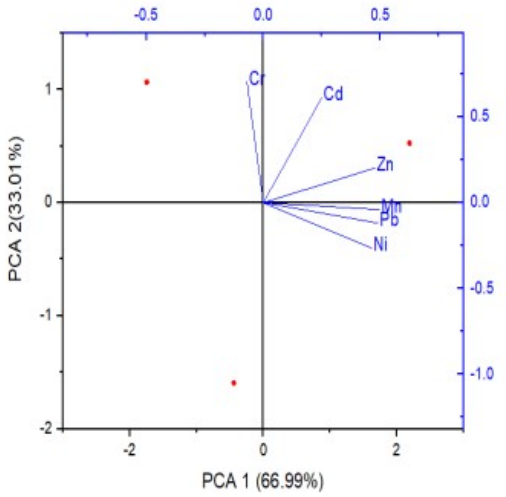

Figure 5: Bi-plot of heavy metals in plants leachates.

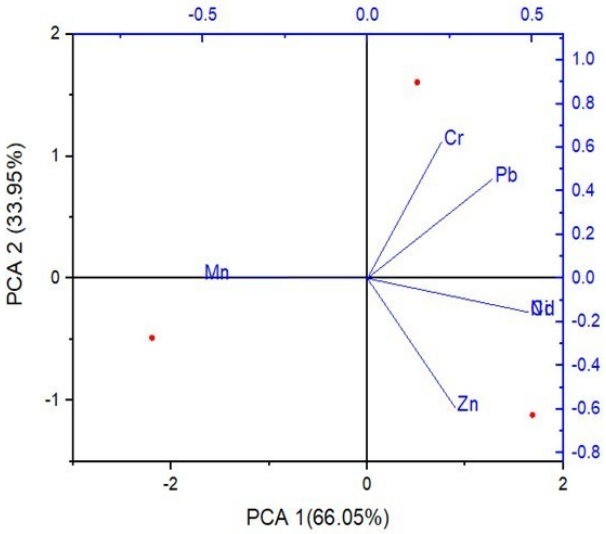

Figure 6: Bi-plot of heavy metals in leachates from Olusosun landfill.

Table 5: Extracted eigenvalues of the heavy metals in leachate samples.

	Coefficients of PC1	Coefficients of PC2
Zn	0.4781	0.2026
Mn	0.4980	-0.0397
Ni	0.4627	-0.2653
Cd	0.2504	0.6145
Pb	0.4916	-0.1198
Cr	-0.0701	0.7035

Table 6: Extracted eigenvalues of the heavy metals in leachate samples.

	Coefficients of PC1	Coefficients of PC2
Zn	0.2675	-0.5931
Mn	-0,5023	0.0091
Ni	0.4899	-0.1551
Cd	0.4899	-0.1551
Pb	0.3813	0.4562
Cr	0.2256	0.6260

Concentrations of PAHs in leachates and plant leaves

Table 7 shows the concentration of PAHs in leachate samples. Sixteen PAHs are recognized by the United States Environmental Protection Agency (EPA) and are classified as low molecular weight (LMW, petrogenic), medium molecular weight (MMW), and high molecular weight (HMW, pyrogenic). The following PAHs were detected in leachate and plant samples: HMW - chrysene, benzo(b)fluoranthene, and benzo(a)anthracene; MMW - pyrene and fluoranthene and LMW - phenanthrene. The concentration range (mg/L) for the detected PAHs in landfill leachates were: LMW: 0.17 - 0.22; MMW: 0.15 - 0.24 and HMW: 0.10 - 0.19 mg/L, respectively. The presence of LMW PAHs in the environment usually results from the emission of oil spills, noncombustible matter, and agricultural sources, while MMW and HMW PAHs are emitted mainly from sources like incomplete combustion/pyrolysis of organic matter and solid wastes, and incorporated into landfill leachate by rainwater (3). Municipal and waste discharge from industrial sites are part of the factors causing a high concentration of PAHs in leachates (38). The result of PAHs concentration in plant leaf samples is shown in Table 8. The concentration of PAHs in plant samples ranged between 0.09 - 0.31 mg/kg. Since P1 is far away and P2 and P3 are close, no PAHs were detected in P1, and some levels of PAH were found in P2 and P3.

Table 7: Concentration of polycyclic aromatic hydrocarbons found in leachates.

	Concentration (mg/L/)			**Concentration (mg/L/)**	
PAHs	**L1**	**L2**	**PAHs**	**L1**	**L2**
Anthracene	BDL	BDL	Pyrene	0.15	0.19
Acenaphthene	BDL	BDL	Perylene	BDL	BDL
Phenanthrene	0.22	0.17	Chrysene	0.10	0.13
Acenaphthylene	BDL	BDL	Benzo(b)fluoranthene	0.19	0.15
Naphthalene	BDL	BDL	Benzo(k)fluoranthene	BDL	BDL
Fluorene	BDL	BDL	Benzo(a)an thracene	0.14	0.16
Fluoranthene	0.21	0.24	Indeno(1,2,3-cd)pyrene	BDL	BDL
	Σ=1.01	Σ= 1.04			

Table 8: Concentration of PAHs in plant leaves.

	Concentration (mg/kg)		
PAHs	P1	P2	P3
Naphthalene	BDL	BDL	BDL
Acenaphthylene	BDL	BDL	BDL
Acenaphthene	BDL	BDL	BDL
Fluorene	BDL	BDL	BDL
Phenanthrene	BDL	0.31	0.19
Anthracene	BDL	BDL	BDL
Fluoranthene	BDL	0.16	0.14
Pyrene	BDL	0.24	0.11
Benz(a)anthracene	BDL	0.17	0.14
Chrysene	BDL	0.09	0.13
Benzo(b)fluoranthene	BDL	0.11	0.17
Benzo(k)fluoranthene	BDL	BDL	BDL
Benzo(a)pyrene	BDL	BDL	BDL
Indeno(1,2,3-cd)pyrene	BDL	BDL	BDL
Dibenzo(a,h)anthracene	BDL	BDL	BDL
Benzo (g,h,i) perylene	BDL	BDL	BDL
	Σ=0.0000	Σ= 1.08	Σ= 0.88

Table 9: Pearson correlation matrices of PAHs from leachate samples in the Olusosun landfill.

	Phe	Flu	Pyr	Chy	Benzo(b)F	Benzo(a)A
	1					
Phe	0.0576	1				
Flu	0.8572	0.5636	1			
Pyr	0.8934	0.5000	0.9972	1		
Chy	0.4018	-0.8910	-0.1273	-0.0524	1	
Benzo(b)F	-0.7825	0.5766	-0.3500	-0.4193	-0.8846	1
Benzo(a)A	0.7924	0.6547	0.9934	0.9820	-0.2402	-0.2402

Phe- Phenanthrane; Flu- Fluoranthene; Pyr- Pyrene; Chy- Chrysene; Benzo (b)- Benzo(b)fluoranthene; Benzo(a)A- Benzo(a)anthracene

Table 10: Pearson correlation matric of PAHs from plant samples in the Olusosun landfill.

	Phe	**Flu**	**Pyr**	**Chy**	**Benzo(b)F**	**Benzo(a)A**
Phe	1					
Flu	0.9477	1				
Pyr	0.7341	0.4790	1			
Chy	0.9995	0.9368	0.7559	1		
Benzo(b)F	-0.3192	3.61E-17	-0.8778	-0.3499	1	
Benzo(a)A	-0.4039	-0.0908	-0.9177	-0.4336	0.9959	1

The Pearson correlation of PAHs in leachates in shown from Table 9 above. A positive correlation exists between some PAHs found in leachates with significant difference >0.05 which includes: Pyr/Phe, Flu/Phe, Pyr/Flu, Chy/Phe, Benzo(a)A/flu, Benzo(b)F/ Flu, Benzo(a)A /Phe and a negative correlation exists between Benzo(b)F /Phe, Chy/Flu, Benzo(b)F/Phe, Benzo(b)/ Pyr, Benzo(a)A/ Benzo(b)F and Chy/Pyr. Also, a positive correlation exists between Phe/Flu, Chy/Phe, Flu/Pyr, Benzo(b)F/ Benzo(a)A Pyr/Phe, Chy/Flu, Phe/Chy, Pyr/Chy, and negative correlation occurred between Phe/ Benzo(b)F, Phe/ Benzo(a)A, Chy/ Benzo(b)F, Benzo(a)A, Chy, Benzo(a)A/Pyr with a significant difference >0.05 in plants as shown in Table 10 above. It indicates that the source of contamination in this study is a result of different anthropogenic activities that take place in the landfill.

Table 11: Extracted eigenvalues of the PAH in leachate samples.

	Coefficients of PC1	Coefficients of PC2
Phenanthrene	0.4812	-0.1872
Fluoranthene	0.4716	0.2317
Pyrene	0.4825	0.1806
Chrysene	0.1013	-0.6957
Benzo(b)fluoranthene	-0.3174	0.5481
Benzo(a)anthracene	0.4498	0.3072

Table 12: Extracted eigenvalues of the PAH in plant samples removed from the plants.

	Coefficients of PC1	Coefficients of PC2
Phenanthrene	0.4415	0.3221
Fluoranthene	0.3495	0.5156
Pyrene	0.4706	-0.2109
Benz(a)anthracene	0.4483	0.3004
Chrysene	-0.3454	0.5217
Benzo(b)fluoranthene	-0.3757	0.4727

The variance of PAHs in leachate and plant samples analyzed are 66.98 %, 33.02 %; 69.02%, 30.98% for PC1 and PC2, respectively, as shown from Figures 7 and 8 below. The scree plot of PAHs in plants and leachates proved the components that are retrained, as shown in Figure 8 below. Components 1 (4.34) and 2 (1.77) are retained because it is greater than unity (35, 36) while other components (3, 4 and 5) are not retained. There is a strong positive correlation between the PAHs in PC1 for leachate samples includes; Phenanthrene, Fluoranthene, Pyrene, Chrysene, and Benzo(a)anthracene but negative correlation occurred at Benzo(b)fluoranthene. While the positive correlation was seen between the PAHs in PC2 includes; Fluoranthene, pyrene, Benzo(b)fluoranthene and Benzo(a)anthracene but negative correlation exists in Phenanthrene and Chrysene as shown from Table 11 above. For plant samples, a positive correlation exists between Phenanthrene, Fluoranthene, pyrene, Benzo(a)anthracene, and a negative correlation exists between Chrysene and Benzo(b)fluoranthene for PC1. A positive correlation exists between these PAHs (Phenanthrene, Chrysene, Fluoranthene, Benzo(b)fluoranthene and Benzo(a)anthracene) and pyrene only had a negative correlation in PC2 as shown from Table 12 above. However, the statistical data from this study confirmed that the source of PAHs was through resistance to environmental degradation, surface run-off (17), and type of waste deposited on the landfill.

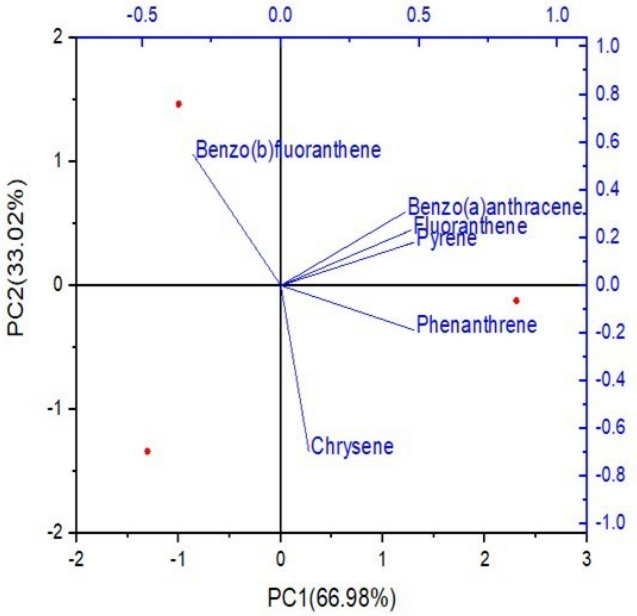

Figure 7: Biplot of the PAH in leachate samples.

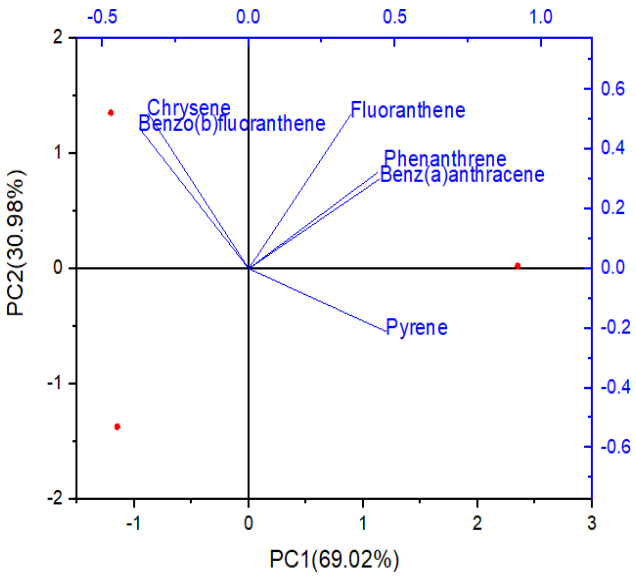

Figure 8: Bi-plot of PAH in plant samples.

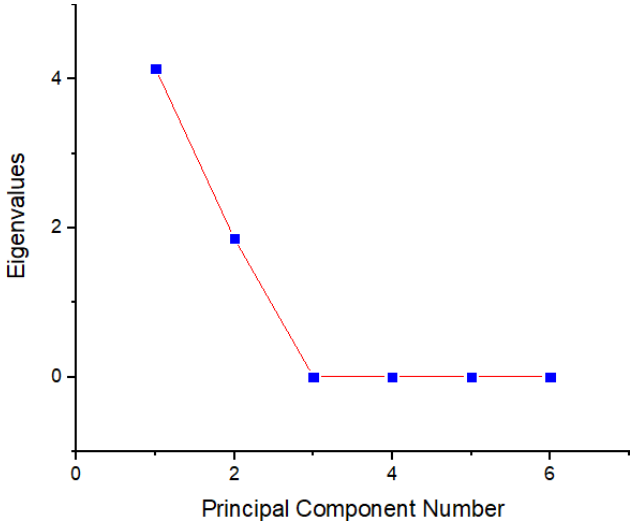

Figure 9: Screen plot of PAHs in plants.

CONCLUSION

Six (6) PAHs each were detected in both the plant and leachate samples analyzed, which includes the following: Chrysene, Benzo (b)fluoranthene, Benzo (a) anthracene, Phenanthrene, Pyrene, and Fluoranthene. Heavy metals such as Zinc (Zn), Lead Pb, Chromium (Cr), Manganese (Mn), Cadmium (Cd), and Nickel (Ni) were also detected. The majority of the physicochemical parameters analyzed were found to exceed their permissible limits set by WHO and NESREA. The source of pollution in this study is the same, and it is confirmed by the statistical analysis used. With the results obtained from this study, it could be deduced that the landfill is heavily polluted, and adequate management needs to be put in place by various agencies.

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CONFLICT OF INTEREST

All the authors declare no conflict of interest regarding this manuscript

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