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Assessment of heavy metals contamination in leachate under waste dumpsites and automobile workshops in Calabar, Nigeria

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Abstract

The concentration of eight (8) heavy metals (Cd, Cr, Co, Fe, Mn, Ni, Pb, Zn) were measured for one year in Calabar Municipality dumpsite, a mechanic workshop and University of Calabar (Unical) at two depths (0.5 m and 1.0 m). Results comparison with World Health Organization (WHO) and Nigerian Industrial Standard (NIS) guide values showed high values for Cadmium, chromium, iron and lead in all locations while copper, manganese (except in the dumpsite), nickel and zinc showed concentration within the specified standard limits. The contamination level was summarized as Calabar Municipality dumpsite > Mechanic workshop > University of Calabar (Unical) with 1.0 m depth (except for Zn, Pb and Cu) showing a higher contamination level than the 0.5 m depth.

Keywords: Heavy metal; Contaminant; Leachate; Waste; Dumpsite

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1. Introduction

1.1. Overview

Soil pollution can be hazardous to human health because of the tendency of the pollutants to penetrate and contaminate crops and ground water. This is possible because soils generally act as filters by permitting the passage and allowing retention of these toxic substances (Harrison, 1999) and any place where surface water makes its way into the groundwater, organic chemicals and pathogens potentially can enter. Inorganic chemicals that occur naturally in soils, sediments and rocks can also degrade the quality of groundwater. Water percolating through soils picks up naturally occurring minerals, salts and organic compounds. This leads to a process known as mineralization, where there is a marked increase in the concentration of minerals and salts.

Heavy metals are generally a dangerous group of soil contaminants (Smejkalova et al., 2003). The contamination by heavy metals causes a serious problem because they are practically irreversible and cannot be naturally degraded like some organic pollutants hence, accumulate in different parts of the food chain. The buildup of heavy metals in soil from anthropogenic sources has been reported to be harmful to crops and human health (Smith et al., 1996). Consequently, higher soil heavy metal concentration can result in higher levels of uptake by plants (John et al., 1972). However, Juste and Mench (1992), kabata-Pendias and Pendias (1984), Amusan *et al.* (2005), and Moreno *et al.* (2005) independently concluded that the rate at which plants accumulate heavy metals is dependent on the metal species involved, plants species involved, age of the plant and plant parts. Sources of these heavy metals range from industrially and municipally generated (Alloway, 1996; Olajire and Ayodele, 1998; Cobb et al., 2000; Udosen et al., 2006; Ebong et al., 2008), automobile emission (Olajire et al., 2003), agricultural and land practices (Shi et al., 2014).

Studies in landfills have shown that leachate is of particular interest because it contains potentially toxic heavy metals (Dosumu et al., 2003; Olajire et al., 2003; Elaigwu et al., 2007; Abdus-Salam, 2009) and the current trend in municipal waste disposal and management practices may increase the heavy metal burden of soils and underground water (Albores et al., 2000; Okoronkwo et al., 2006).

Typical exposure to heavy metals is normally chronic (exposure over a longer period of time) due to food chain transfer while there are rare cases of acute poisoning, which may be possible through direct ingestion or contact to skin. A few examples of the chronic effects linked to heavy metal exposures have been highlighted in literature (Oliver, 1997; Baldwin and Marshall, 1999; Gil et al., 2006; Navarro et al., 2008; Brevik and Burgess, 2013; Morgan, 2013): Cadmium (affects kidney, liver, and gastrointestinal tract), Chromium (associated with allergic dermatitis in humans), Copper (causes gastrointestinal disorder), Iron (has no effect), Manganese (associated with neurological disorder), Nickel (carcinogenic), Lead (Cancer, interference with Vitamin D metabolism, affects mental development in infants, toxic to the central and peripheral nervous systems) and zinc (toxic and carcinogenic effects).

This study aims to assess the level of soil contamination with heavy metals (cadmium, chromium, copper, iron, manganese, nickel, lead, and zinc) from dumpsites and mechanic workshops in Calabar, Nigeria.

1.2. The study areas

The selected study areas are two different points (Dumpsite A and Dumpsite B) in Calabar Municipality dumpsite (5°2ˈ 3"N, 8°21ˈ 46"E), a mechanic workshop in Etta-Agbor (4°57ˈ 30"N, 8°20ˈ 41"E), and UNICAL (4°57ˈ 1"N, 8°21ˈ 3"E) all within Calabar Metropolis, Cross River state, Nigeria. The two main climatic conditions in the study areas are dry season which begins in October and ends in March and wet season from April to September with a peak in June and July. The area is characterized by high annual rainfall in the range of 350-400 mm and run-off estimated to reach 90% (Ekpo et al., 2000). Data from the Department of Geography in the University of Calabar and Calabar International Airport show the mean temperature to be in the range of 24.0°C to 28.5°C.

2. Materials and methods

2.1. Leachate sampling procedure and analysis

PVC pipes were cut into two categories (1m and 0.5m length). The base end of each pipe was permanently sealed with a pipe cover and an adhesive while the top ends were firmly fitted with pipe covers. The pipes (both 1m and 0.5m lengths) were perforated evenly at considerable distances from their base ends to allow for water percolation and collection. The whole pipe lengths were then inserted into the ground in each sampling station with small allowances at the top for access to top ends (which were only temporarily sealed).

Leachate was sampled using a pipette, a 1 Liter plastic container and a suction pipe. The sampling apparatus were washed with distilled water before use. The suction pipe was fitted to a pipette and inserted into the PVC pipe through the top end until contact was made with the percolated liquid at the base of the pipe. Suction pressure was applied by the pipette pump until the liquid sample was adequately drained from the pipe into the 1 Liter plastic container which was immediately transferred into an ice container. The heavy metals such as Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were analyzed using Atomic Absorption Spectrophotometer (AAS) by standard analytical methods as specified by APHA, 1998. Sampling and analyses were carried out quarterly for one year duration.

3. Results and discussion

3.1. Leachate analysis

3.1.1. Cadmium

As shown in table 1 and figure 1a, results from each location and depth for all the quarters show very high contamination level of cadmium as compared with standard regulation limits of WHO (World Health Organization) and NIS (Nigerian Industrial Standard). Furthermore, FIG 1 shows that the contamination is higher in the dumpsite than other locations and the trend generally depicts a greater level in the 1.0 m depth than 0.5 m depth. The high Cadmium level in the mechanic workshop could be from lubricating oil spent oil, and nickel-cadmium car batteries (Atayese et al., 2009) while the contamination source for the dumpsite may be from vehicles.

3.1.2. Chromium

As shown in table 2 and figure 1b, the levels of chromium at all locations are comparable for both depths and results for UNICAL and mechanic workshop are either on or slightly higher than the WHO and NIS standard guide value of 0.05 mg/L. The dumpsite shows very high contamination level. Just as with lead and cadmium, the explanation for high chromium concentrations is the nearness to major roads and the very high commercial activity around both the mechanic workshop and the Calabar Municipality dumpsite and the possibility of deposition from the different fuels as well as aerial deposition from motor vehicle emission (Miroslav and Vladimir, 1999).

3.1.3. Copper

Compared to the guide value, all locations showed no contamination level and the concentration levels were almost the same through all quarters with low standard deviation as shown in table 3 and figure 1c. The highest concentration was found at the dumpsite. This may be due to the use of copper as electrical wiring, communication equipment and electromagnetic waste found in the location. Brake wear emissions from traffic in the study locations may also be a significant source of copper as about 50% of the total copper emissions from road transport was reported to be the result of car wear (Ven der Gon et al., 2007).

3.1.4. Iron

High iron concentrations were recorded in the study locations all above the guide values of WHO and NIS as shown in table 4 and figure 1d. Depth variation does not show any conclusive trend in the deposition levels.

3.1.5. Manganese

High manganese concentrations were recorded in the dumpsite while other locations recorded values within the guide values as shown in table 5 and figure 1e. The high concentration in the dumpsite is associated with its use in electroplating of some parts of motor vehicles which form a substantial part of the refuse.

3.1.6. Nickel

Table 6 and figure 1f show very low nickel concentration levels for all locations and depths which are well within the guide values. The deposition is almost the same for all the sites showing low and comparable standard deviations. Its deposition in the dumpsite and mechanic workshop could be due to its use in various items such as industrial machinery, automobiles automobile batteries and electronic equipment and also emissions from mechanical wear of vehicles and oil (Shi et al., 2014).

3.1.7. Lead

Loska *et al.* (2004) highlighted the dangerous impacts of Pb pollution to the environment in that several vital organs in the body (especially kidneys and liver) are reported to be potential targets.

Though the locations have concentration values above the guide value, Unical shows a constant trend and lower values than the other locations as shown in table 7 and figure 1g. There is also no noticeable relationship between the depth and concentration. Traffic is one of the major sources for Pb pollution (Cai et al., 2013). This is possible due to the introduction of Pb into the atmosphere from fuel combustion as Pb is widely used as an intermediate for antiknock additives. The released Pb subsequently accumulates in the topsoil of exposed areas making them highly vulnerable (Kayhanian, 2012; He et al., 2013).

3.1.8. Zinc

There is a growing concern about zinc being one of the most readily mobile elements and the fact that high doses of zinc will cause toxic and carcinogenic effects (Yaylali-Abanuz, 2011). Table 8 and figure 1h show that the zinc concentrations for all locations are within the guide values but the depth-concentration relationship does not indicate a conclusive trend. However, the dumpsite recorded higher values than all other locations.

Table 1. Cadmium concentration values for Unical, Calabar Municipality dumpsite and mechanic workshop

QUARTER	Cd/(mg/l)							
	UNICAL		DUMPSITE A		DUMPSITE B		MECHANIC WORKSHOP	
	0.5 m	1 m	0.5 m	1 m	0.5 m	1 m	0.5 m	1 m
1st	0.024	0.015	0.183	0.265	0.242	0.275	0.053	0.037
2nd	0.029	0.021	0.011	0.043	0.026	0.033	0.059	0.108
3rd	0.070	0.125	0.105	0.099	0.121	0.114	0.063	0.081
4th	0.018	0.012	0.122	0.196	0.212	0.255	0.061	0.040
Mean	**0.035**	**0.043**	**0.105**	**0.151**	**0.150**	**0.169**	**0.059**	**0.067**
Stdev	**0.024**	**0.055**	**0.071**	**0.099**	**0.098**	**0.116**	**0.004**	**0.034**
WHO	0.005							
NIS	0.003							

Table 2. Chromium concentration values for Unical, Calabar Municipality dumpsite and mechanic workshop

QUARTER	Cr/(mg/l)							
	UNICAL		DUMPSITE A		DUMPSITE B		MECHANIC WORKSHOP	
	0.5 m	1 m	0.5 m	1 m	0.5 m	1 m	0.5 m	1 m
1st	0.03	0.05	0.26	0.21	0.27	0.23	0.04	0.03
2nd	0.02	0.18	0.02	0.10	0.07	0.08	0.11	0.08
3rd	0.13	0.10	0.22	0.21	0.18	0.19	0.07	0.07
4th	0.02	0.04	0.10	0.11	0.18	0.18	0.04	0.03
Mean	**0.05**	**0.09**	**0.15**	**0.16**	**0.18**	**0.17**	**0.06**	**0.05**
Stdev	**0.05**	**0.06**	**0.11**	**0.06**	**0.08**	**0.06**	**0.03**	**0.03**
WHO	0.05							
NIS	0.05							

Table 3. Copper concentration values for Unical, Calabar Municipality dumpsite and mechanic workshop

QUARTER	Cu/(mg/l)							
	UNICAL		DUMPSITE A		DUMPSITE B		MECHANIC WORKSHOP	
	0.5 m	1 m	0.5 m	1 m	0.5 m	1 m	0.5 m	1 m
1st	0.15	0.19	0.35	0.31	0.37	0.34	0.09	0.07
2nd	0.15	0.03	0.32	0.29	0.23	0.39	0.03	0.03
3rd	0.05	0.04	0.17	0.11	0.12	0.12	0.08	0.06
4th	0.09	0.11	0.30	0.31	0.32	0.34	0.07	0.06
Mean	**0.11**	**0.09**	**0.29**	**0.25**	**0.26**	**0.30**	**0.07**	**0.06**
Stdev	**0.05**	**0.07**	**0.08**	**0.10**	**0.11**	**0.12**	**0.03**	**0.02**
WHO	1.0							
NIS	1.0							

Table 4. Iron concentration values for Unical, Calabar Municipality dumpsite and mechanic workshop

QUARTER	Fe/(mg/l)							
	UNICAL		DUMPSITE A		DUMPSITE B		MECHANIC WORKSHOP	
	0.5 m	1 m	0.5 m	1 m	0.5 m	1 m	0.5 m	1 m
1st	0.41	0.61	0.90	0.72	0.90	0.91	0.69	0.65
2nd	3.25	4.03	1.94	2.18	1.51	1.75	3.56	3.01
3rd	0.46	0.21	0.77	0.76	0.69	0.81	0.57	0.59
4th	0.51	0.59	0.80	0.81	0.73	0.82	0.71	0.67
Mean	**1.16**	**1.36**	**1.10**	**1.12**	**0.96**	**1.07**	**1.38**	**1.23**
Stdev	**1.40**	**1.79**	**0.56**	**0.71**	**0.38**	**0.46**	**1.45**	**1.19**
WHO	0.3							
NIS	0.3							

Table 5. Manganese concentration values for Unical, Calabar Municipality dumpsite and mechanic workshop

QUARTER	Mn/(mg/l)							
	UNICAL		DUMPSITE A		DUMPSITE B		MECHANIC WORKSHOP	
	0.5 m	1 m	0.5 m	1 m	0.5 m	1 m	0.5 m	1 m
1st	0.09	0.09	0.13	0.11	0.15	0.13	0.10	0.09
2nd	0.13	0.11	0.10	1.12	1.00	1.06	0.09	0.09
3rd	0.09	0.18	0.14	0.13	0.12	0.12	0.08	0.08
4th	0.08	0.08	0.10	0.10	0.11	0.11	0.10	0.09
Mean	**0.10**	**0.11**	**0.12**	**0.36**	**0.35**	**0.36**	**0.10**	**0.09**
Stdev	**0.02**	**0.04**	**0.02**	**0.50**	**0.44**	**0.47**	**0.01**	**0.01**
WHO	0.20							
NIS	0.20							

Table 6. Nickel concentration values for Unical, Calabar Municipality dumpsite and mechanic workshop

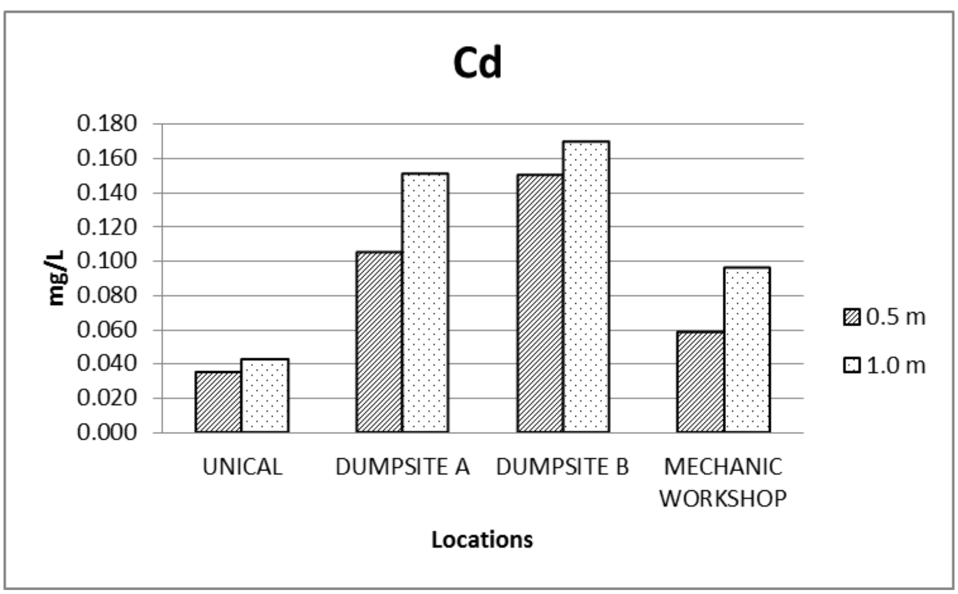
QUARTER	Ni/(mg/l)							
	UNICAL		DUMPSITE A		DUMPSITE B		MECHANIC WORKSHOP	
	0.5 m	1 m	0.5 m	1 m	0.5 m	1 m	0.5 m	1 m
1st	0.013	0.015	0.017	0.016	0.016	0.015	0.015	0.011
2nd	0.021	0.010	0.011	0.021	0.014	0.019	0.008	0.009
3rd	0.016	0.019	0.010	0.014	0.011	0.013	0.009	0.014
4th	0.012	0.014	0.015	0.015	0.017	0.015	0.016	0.012
Mean	**0.016**	**0.015**	**0.013**	**0.017**	**0.015**	**0.016**	**0.012**	**0.012**
Stdev	**0.004**	**0.004**	**0.003**	**0.003**	**0.003**	**0.003**	**0.004**	**0.002**
WHO	0.020							
NIS	0.020							

Table 7. Lead concentration values for Unical, Calabar Municipality dumpsite and mechanic workshop

QUARTER	Pb/(mg/l)							
	UNICAL		DUMPSITE A		DUMPSITE B		MECHANIC WORKSHOP	
	0.5 m	1 m	0.5 m	1 m	0.5 m	1 m	0.5 m	1 m
1st	0.03	0.02	0.15	0.13	0.14	0.14	0.08	0.06
2nd	0.04	0.03	0.07	0.08	0.09	0.09	0.08	0.07
3rd	0.04	0.04	0.11	0.12	0.18	0.13	0.10	0.12
4th	0.04	0.03	0.15	0.10	0.12	0.10	0.09	0.07
Mean	**0.04**	**0.03**	**0.12**	**0.11**	**0.13**	**0.11**	**0.09**	**0.08**
Stdev	**0.00**	**0.00**	**0.04**	**0.02**	**0.04**	**0.03**	**0.01**	**0.03**
WHO	0.01							
NIS	0.01							

Table 8. Zinc concentration values for Unical, Calabar Municipality dumpsite and mechanic workshop

QUARTER	Zn/(mg/l)							
	UNICAL		DUMPSITE A		DUMPSITE B		MECHANIC WORKSHOP	
	0.5 m	1 m	0.5 m	1 m	0.5 m	1 m	0.5 m	1 m
1st	0.26	0.36	1.15	0.91	1.16	1.03	0.67	0.58
2nd	0.31	0.40	0.92	0.89	1.00	0.72	0.54	0.62
3rd	0.16	1.64	0.72	1.14	1.11	0.95	0.06	0.08
4th	0.31	0.42	0.97	0.92	1.01	0.93	0.71	0.58
Mean	**0.26**	**0.71**	**0.94**	**0.96**	**1.07**	**0.91**	**0.49**	**0.46**
Stdev	**0.07**	**0.62**	**0.18**	**0.12**	**0.08**	**0.13**	**0.30**	**0.26**
WHO	5.0							
NIS	3.0							



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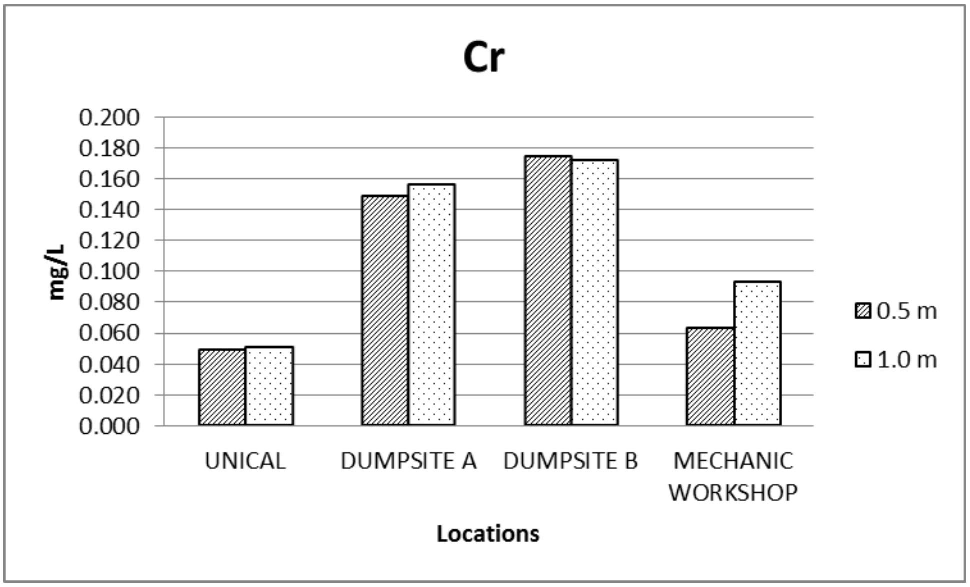
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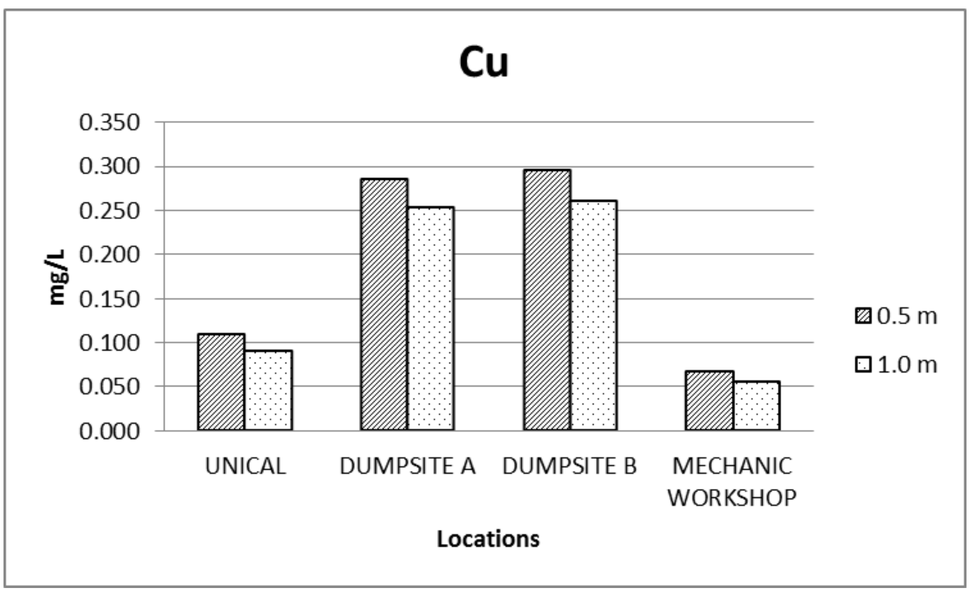
mg/L
UNICAL
DUMPSITE A
DUMPSITE B
MECHANIC WORKSHOP
Locations
0.5 m
1.0 m

(b)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MECHANIC WORKSHOP
Locations
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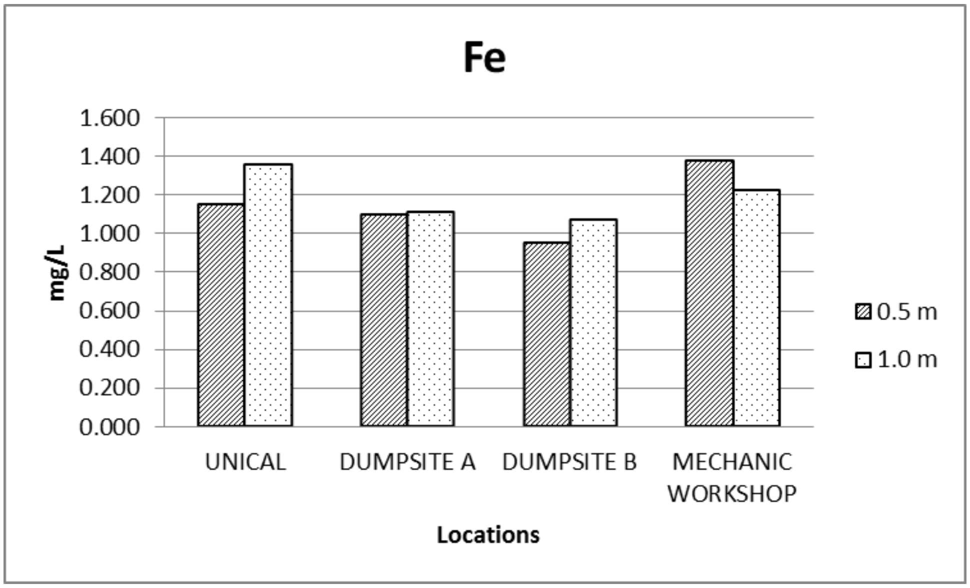
(c)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DUMPSITE B
MECHANIC WORKSHOP
Locations
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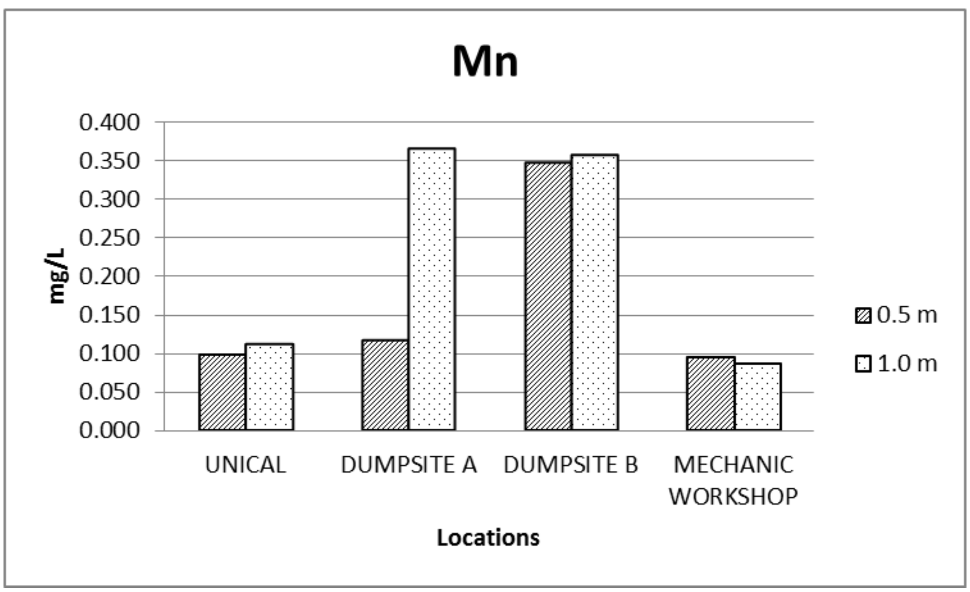
(d)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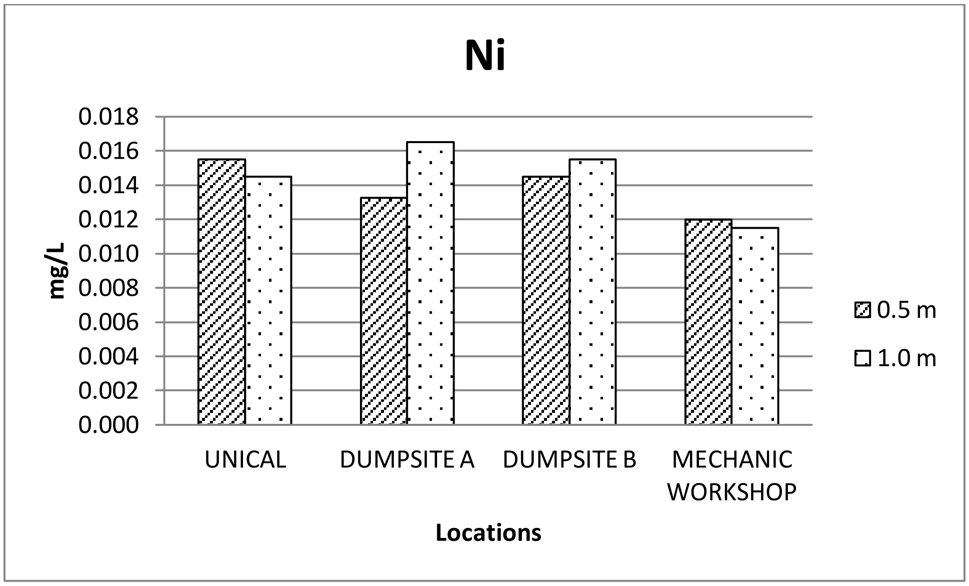
DUMPSITE B
MECHANIC WORKSHOP
Locations
0.5 m
1.0 m

(e)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DUMPSITE B
MECHANIC WORKSHOP
Locations
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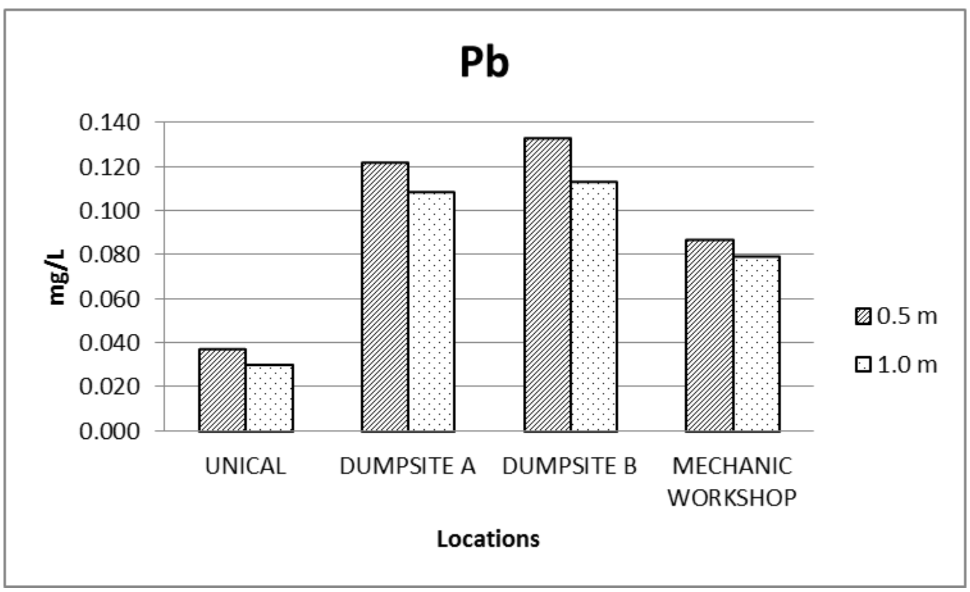
1.0 m

(f)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Locations
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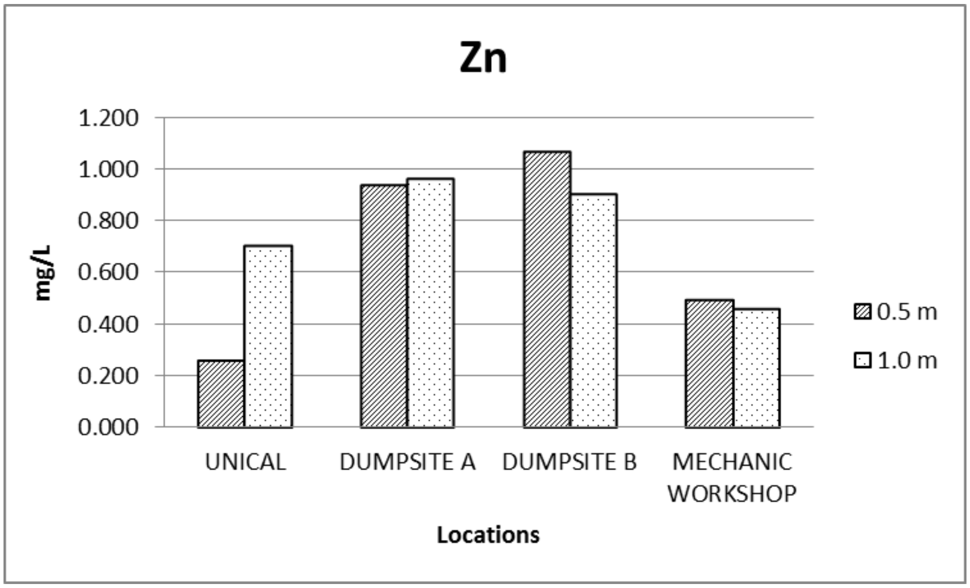
(g)



(h)

Figure 1. Concentration levels of (a) cadmium (b) chromium (c) copper (d) iron (e) manganese (f) nickel (g) lead (h) zinc for Unical, Calabar Municipality dumpsite and mechanic workshop for one-year duration at 0.5 m and 1.0 m depths

3.2. Statistical analysis

Table 9. Correlation between the different heavy metals in 0.5 m depth

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Cd	1.00							
Cr	**0.97**	1.00						
Cu	0.83	0.94	1.00					
Fe	-0.74	-0.78	-0.82	1.00				
Mn	0.86	0.75	0.56	-0.77	1.00			
Ni	-0.01	-0.01	0.10	-0.62	0.35	1.00		
Pb	0.93	0.92	0.78	-0.48	0.64	-0.37	1.00	
Zn	**0.97**	**0.99**	0.89	-0.67	0.72	-0.16	**0.97**	1.00

The correlation matrix applied on the experimental data showed that there were a few strong correlations between groups of elements. Parameter pairs having significant trends were selected based on a confidence level of 95%. From table 9a for 0.5 m depth, zinc showed a greater correlation than all other metals. The highest correlation of 0.64 was obtained for the couple Zn-Cr (r = 0.99 where r = Pearson correlation coefficient), followed by Zn-Cd and Zn-Pb (r = 0.97). For 1.0 m depth (table 9b), the metals showed more relationships (both positive and negative correlations) with Cu-Cr couple being the highest for the positive relationship (r = 0.99) while pb-Fe couple has the highest negative relationship (r = -0.99). Significant correlation among the variables indicates that there are linear relationships between them.

Table 10. Correlation between the different heavy metals in 1.0 m depth

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Cd	1.00							
Cr	0.91	1.00						
Cu	**0.96**	**0.99**	1.00					
Fe	**-0.96**	-0.76	-0.85	1.00				
Mn	**0.96**	0.97	**0.98**	-0.87	1.00			
Ni	0.67	0.90	0.83	-0.46	0.84	1.00		
Pb	0.92	0.67	0.77	**-0.99**	0.81	0.37	1.00	
Zn	0.80	**0.96**	0.92	-0.61	**0.92**	**0.98**	0.52	1.00

4. Conclusions

The study provides important information about the distribution of heavy metals in soils (dumpsites and mechanic workshops) around Calabar, Nigeria, bearing in mind that the pollution of soils can be dangerous for human health because the toxic substances can enter crops and ground water. For all locations, Cadmium, chromium, iron and lead showed values above the guide values by the standard of World Health Organization (World Health Organisation, 1996) and Nigerian Industrial Standard (Standards Organisation of Nigeria, 2007) for drinking water while only the dumpsite recorded value above the recommended limit for manganese. Generally, the Calabar Municipality dumpsite showed higher heavy metals concentration levels while University of Calabar (Unical) showed the least. Except for copper, lead and zinc, some metals showed higher concentrations in the 1.0 m depth than the 0.5 m depth suggesting the risk of groundwater contamination as the contaminants are washed down the soil profile. The correlation matrix was applied to identify and quantify the relationship between couple of investigated heavy metals. The results revealed that there is significant correlation between the metals. Regular monitoring of heavy metals in soils, groundwater, leachates and crops should be encouraged since the detrimental effects of heavy metal pollution manifest many years after exposure.

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