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ROLES OF TOTAL METAL, pH AND ORGANIC MATTER CONTENT IN THE MOBILITY OF TOXIC METALS IN URBAN DUMPSITE SOILS WITHIN AKWA IBOM STATE, NIGERIA

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Abstract
Surface soil samples were collected from six (6) urban waste dumpsites within Akwa Ibom State, Niger Delta region of Nigeria during the dry and wet of the study area and examined their lead (Pb), cadmium (Cd) and arsenic (As) contents. Soil pH and organic matter (OM) contents were also analyzed for in these samples. Using Pearson Correlation, the roles of total metal content, pH and OM on the mobility of these metals in soils studied were investigated. Results obtained revealed Cd as the element with the highest mobility potential while As was the least mobile element in the area. It was also deduced from the study that, total lead in soil correlated negatively with its mobility in soil, the effect of total Cd in soil varied with season while total arsenic showed significant positive relationship with its mobility in soil irrespective of the season. Mobility of lead was strongly hindered by soil pH and OM notwithstanding the change in season experienced. However, soil pH and OM strongly promoted the mobility of cadmium and arsenic in the area during dry season but during the wet season these properties acted as impediments to their mobility in soil. This study has shown that the mobility and accessibility of these toxic elements could be controlled by the regulating soil pH and OM contents.

Keywords: Speciation, dumpsite soil, mobility factor, Pearson Correlation, pH and organic matter

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1. INTRODUCTION

Soil is the main medium which accumulates trace metals and transfers same into plants or leached into underground water but through whichever pathway these metals and their attendants' effects will eventually be felt by human. Recent studies have shown elevated metal enrichment of urban soils in Nigeria (Ebong et al., 2007; Olajire and Ayodele, 1997; Onianwa and Adogbe, 1997). Although trace elements are natural components of soil, the dumping of waste products on our terrestrial environment has been found to amplify their metal profile to toxic levels (Adeniyi et al., 1993; Adeniyi, 1996; Clarkson et al., 1983; Singh and Narwal, 1984). Eventually, this will enhance health hazards through exposure pathways particularly if edible plants which can absorb these metals are cultivated on such dumpsite soils and subsequently consumed (Alloway, 1990). Metals such as cadmium, lead, mercury and arsenic are known to be the most toxic (Park and Shin, 2006; Onweremadu and Duruigbo, 2007; Lokeshappa et al., 2012). Toxic metals have a potential hazardous effect not only on crop plants but also on human health (Das et al., 1997). However, the total metal content of the soil is commonly used to indicate the degree of contamination, but the concentration in solution mostly determines the actual environmental exposure or risk. The total metal concentration of a soil includes all fractions of a metal, from the readily available to the highly unavailable. According to Wolt (1994) total metal content provides the maximum pool of metal in the soil, other factors have a greater importance in determining how much of this soil pool will be available to plants. Metals within the soil solution are the only soil fraction directly available for plant uptake (Fageria et al., 1991; Lorenz et al., 1994; Marschner, 1995). The magnitude of this fraction is highly dependent on environmental conditions, and varies for different metals and specific organisms (Brezonik et al., 1991). Their uptake by plants from soil is also largely determined by their presence in the environment based on their chemical specification, soil particle and size, organic matter content, salinity, pH, etc. (Kock et al., 1989; Iwegbue et al., 2006; Gonzalez-Fernandez et al., 2008). It has been reported that different species of metals are more biologically available and mobile than others, thus there is a direct relationship between bioavailability and mobility, the higher the concentration of mobile metals in soil, the higher their mobility which increases the potential for plant uptake, and animal/human consumption (Nelson and Dunkin, 1985; Ratuzny et al., 2009). Hence, positive correlation between metal concentration and physicochemical parameters could imply a considerable effect on the amount of trace metals in the soil, since the mobility and bioavailability of metals present in soils depend on physicochemical properties of both the metal and the soil (McEldowney et al., 1993). The mobility and availability of heavy metals in soils depend on how the metals are associated with the components of the soil, and the measure of the mobility and availability of metals serves to predict the behaviour of heavy metals in the soil. It is therefore necessary to evaluate the bioavailability and mobility of heavy metals to establish environmental guidelines for potential toxic hazards and to understand chemical behaviour of heavy metal contaminations in soils (Davies, 1980).There are various fractions of metal in soil in terms of mobility: mobile fraction, mobilisable fraction, pseudo-total fraction and immobile fraction (Gupta et al., 1996).

Consequently, factors which affect the concentration and speciation of metals in the soil solution will affect the bioavailability of metals to plants. The most important factors affecting metal availability are: soil pH (Sanders et al., 1986; Anderson and Christensen, 1988), clay content (Herms and Brummer, 1984) and organic matter content (McGrath et al., 1988). Previous studies have shown that an accurate understanding of trace metals concentration and the forms in which they are found, their dependence on soil's physicochemical properties provide a basis for careful soil management, which will limit as far as possible, the negative impact of trace metals on the environment (Aydinalp and Marinova, 2003). Soil organic matter reduces availability of these trace metals by chelation (Ekundayo and Fagbami, 1996; Nyamangara and Mzezewa, 1999).

Studies have also shown that, the physicochemical properties of soil such as pH, organic matter, cation exchange capacity (CEC), salinity, clay content etc have a direct influence on the mobility, bioavailability and toxicity of trace metals in soil environment (Adamu et al., 1989; Song et al., 2009). It has also been reported that, environmental and health effects of trace metals in soils depend on their mobility and bioavailability, which are a function of their partitioning with soils (Lee et al., 2005). It has been reported that soil pH and organic matter content are the main soil properties controlling the mobility and bioavailability of metals in soil (Bozkurt et al., 1999; Iwegbue et al., 2006; Yobouet et al., 2010; Udom et al., 2004;). Research works on the effect of physicochemical properties of soils on the toxicity of metals to terrestrial invertebrates and plants have carried out. Correlations between metal toxicity and pH, organic matter content, clay content and cation exchange capacity (CEC) were identified and where possible integrated into predictive models (Lock and Janssen, 2001; Spurgeon and Hopkin, 1996; Crommentuijn et al., 1997; Van Gestel et al., 1995). This research was undertaken to ascertain the roles of total trace metal, soil pH and organic matter on metal mobility and bioavailability in some urban dumpsite soils within Akwa Ibom State, Nigeria. This study was undertaken in two regimes for substantial variations in total trace metals, pH and organic matter contents of areas studied to be recorded. A Control station was also incorporated into the study to understand the implications of lower levels of parameters studied on mobility of toxic elements in the location and compare with results recorded in dumpsite soils.

2. MATERIAL AND METHOD

Surface soil (0 – 15cm) samples were collected at six (6) waste dumpsite soils namely: Uyo, Ikono, Ikot Ekpene, Abak, Eket and Onna within Akwa Ibom State, Nigeria using auger (Aydinalp, 2009). At each location, samples were collected from the north, south, east and west and pooled together to form composite sample for that site (Anake *et al*., 2009). The collection of samples was done in two seasons (dry and wet), dry season samples were obtained between January and March while wet season samples were collected between June and August, 2011.

Control samples were also obtained for the two seasons in a forest within Etinan local government area of Akwa Ibom State. These samples were air dried for three (3) days and ground to pass through a 2mm mesh. Soil pH was measure in 1:2.5 (v/v) ratio of soil and water suspension (Van Reeuwijk, 1993). Soil organic matter (OM) was determined by wet oxidation methods of Walkley and Black illustrated by CEAEQ (2003). Total concentration of metals in soil was determined using Unicam 939/959 atomic absorption spectrophotometer (AAS) after digestion with Aqua-regia (Ogunfuwokan *et al.*, 2009). The optimized BCR sequential extraction procedures of Rauret *et al*. (1999) were applied for the speciation of trace metals. Mobility Factor (MF) of trace metals was calculated using the formular $F1 / F1 + F2 + F3 + F4 \times 100$ reported by Kabala and Singh (2001).Where F1 represents the acid extractable fraction; F2 is reducible fraction; F3 gives oxidisabe fraction while F4 indicates the residual fraction.

3. RESULTS AND DISCUSSION

3.1 Total concentration of toxic metals, pH and organic matter contents

Results recorded for the total concentration of the elements, pH and organic matter contents in soils studied during the dry and wet seasons are shown in Figs 1 and 2 respectively. The general results indicated a trend of Pb > Cd > As for total concentration of the elements in both seasons. However, concentrations of these elements obtained during the dry season were much higher than their wet season levels. This may be attributed to dilution and leaching effects by rainwater during the wet season. Soil pH indicated a more acidic nature during the wet season than in the dry season with higher dry season levels. The leaching basic elements into sub-soil by rainwater during wet season may be accredited to the acidic nature of soils studied during the period. Organic matter contents of soils were much higher in wet season than during the dry season. The possible reasons for this higher wet season levels could be higher rate of microbial activities and decomposition of biodegradable waste products during this season.

3.2 Mobility of toxic metals in soil.

Results in Tables 1-3 show ranges of mobility factors for lead, cadmium and arsenic as 20.22 – 32.85%, 42.34 – 64.46% and 16.67 – 23.43% respectively during the dry season. Whereas, the wet season results in Tables 4 – 6 indicate ranges for mobility factors of the elements as 22.86 – 27.59% Pb; 38.31– 44.28% Cd and 12.64–21.85% As respectively. Generally, mobility of toxic elements in soils studied followed the trend cadmium > lead > arsenic, demonstrating that, Cd was potentially more available in the area for plant uptake than Pb and As. The high mobility potential of Cd is attributed to its predominant existence in a weakly bound fraction (acid extractable) in soil whereas, Pb and As existed in a stronger bound phase (reducible) in the area.

The high mobility potential exhibited by cadmium in this study as also been reported by Oluwatosin *et al*. (2008) in their research works. The obtained results also revealed that, mobility factors of the elements in dry season were fairly higher than values recorded during the wet season. This may be attributed to the disparity in total metal contents and soil properties between the two seasons as illustrated below.

Table 1: **Concentration (mg/kg) of different fractions and mobility factors (%) of lead in dumpsite soils and Control during dry season**

Location	AEX	RED	OX	RES	SUM	MF (%)
S1	2.520	3.364	2.428	2.136	10.448	24.12
S2	2.571	3.150	2.022	1.853	9.596	26.79
S3	1.902	4.296	1.796	1.411	9.405	20.22
S4	2.153	3.541	1.932	1.766	9.392	22.92
S5	1.789	3.876	1.556	1.436	8.657	20.67
S6	1.919	3.302	1.658	1.441	8.32	23.07
S7	0.675	0.762	0.384	0.234	2.055	32.85

Table 2: Concentration (mg/kg) of different fractions and mobility factors (%) of cadmium in dumpsite soils and Control during dry season

Location	AEX	RED	OX	RES	SUM	MF (%)
S1	1.070	0.257	0.192	0.141	1.660	64.46
S2	0.881	0.356	0.228	0.174	1.639	53.75
S3	1.038	0.245	0.176	0.145	1.604	64.71
S4	0.949	0.292	0.160	0.122	1.523	62.31
S5	0.926	0.261	0.184	0.123	1.494	61.98
S6	0.760	0.484	0.126	0.089	1.459	52.09
S7	0.282	0.217	0.108	0.059	0.666	42.34

Table 3: **Concentration (mg/kg) of different fractions and mobility factors (%) of arsenic in dumpsite soils and Control during dry season**

Location	AEX	RED	OX	RES	SUM	MF (%)
S1	0.041	0.070	0.010	0.054	0.175	23.43
S2	0.036	0.061	0.008	0.049	0.154	23.38
S3	0.034	0.059	0.013	0.042	0.148	22.97
S4	0.024	0.055	0.009	0.045	0.133	18.05
S5	0.022	0.054	0.008	0.040	0.124	17.74
S6	0.021	0.050	0.007	0.032	0.110	19.09
S7	0.020	0.057	0.008	0.035	0.120	16.67

Table 4: **Concentration (mg/kg) of different fractions and mobility factors (%) of lead in dumpsite soils and Control during wet season**

Location	AEX	RED	OX	RES	SUM	MF (%)
S1	1.080	1.326	0.966	0.709	4.081	26.46
S2	0.998	1.297	0.897	0.693	3.885	25.69
S3	0.854	1.360	0.848	0.674	3.736	22.86
S4	0.898	1.022	0.807	0.534	3.261	27.54
S5	0.768	1.123	0.694	0.574	3.159	24.31
S6	0.381	0.667	0.356	0.248	1.652	23.06
S7	0.242	0.391	0.147	0.097	0.877	27.59

Table 5: **Concentration (mg/kg) of different fractions and mobility factors (%) of cadmium in dumpsite soils and Control during wet season**

Location	AEX	RED	OX	RES	SUM	MF (%)
S1	0.369	0.267	0.191	0.088	0.915	40.33
S2	0.349	0.249	0.181	0.090	0.869	40.16
S3	0.321	0.263	0.162	0.092	0.838	38.31
S4	0.364	0.211	0.139	0.108	0.822	44.28
S5	0.349	0.237	0.161	0.072	0.819	42.61
S6	0.301	0.222	0.140	0.066	0.729	41.29
S7	0.277	0.187	0.154	0.050	0.668	41.47

Table 6: Concentration (mg/kg) of different fractions and mobility factors (%) of arsenic in dumpsite soils and Control during wet season

Location	AEX	RED	OX	RES	SUM	MF (%)
S1	0.026	0.05	0.006	0.037	0.119	21.85
S2	0.024	0.042	0.008	0.036	0.110	21.82
S3	0.021	0.049	0.009	0.029	0.108	19.44
S4	0.011	0.044	0.006	0.026	0.087	12.64
S5	0.011	0.046	0.006	0.024	0.087	12.64
S6	0.013	0.043	0.007	0.028	0.091	14.29
S7	0.01	0.038	0.008	0.020	0.076	13.16

3.3 Correlation between total concentration of toxic metals and their mobility (MF) in soil

Total lead content indicated a strong negative relationship with its mobility in soil during the dry season ($r = –0.794$ at $P < 0.1$). The obtained results indicated that mobility of lead in soil was inversely proportional to the total lead concentration. This is in agreement with the negative relationship reported between total Pb and its mobility in soil by Oluwatosin *et al*. (2008). However, the negative association recorded between total Pb and MF-Pb during the wet season was a weak one with $r = –0.107$ at $P < 0.1$. The r value obtained during the wet season confirmed that a higher total Pb concentration in soil may hinder its mobility in significantly. The negative correlation between total Pb and its mobility recorded in this study was a justification that, the metal existed mostly in strongly bound form. This negative association between total Pb and its mobility in soil may have led to the high mobility factors recorded in the Control site with low total Pb during the dry and wet seasons. Mobility of cadmium (MF-Cd) recorded a significant positive relationship with its total concentration during the dry season $r = 0.829$ at $P< 0.1$. This was an indication that despite the higher total concentration of Cd obtained in dry season; there was consistency with its mobility and bioavailability in the area. The obtained result confirmed that, Cd existed mostly in weakly bound forms in the area as confirmed by the highest mobility factor recorded by the metal in dry season. Mobility factor recorded at the Control site during dry season also correlated positively with the low total Cd recorded at the site during the period, substantiating the strong positive relationship of total Cd with its mobility during the period. Conversely, total Cd showed a weak negative relationship with its mobility during the wet season ($r = –0.110$ at $P< 0.1$). This is consistent with the negative relationship reported by Oluwatosin *et al*. (2008). Result acquired during wet season revealed that, the lower levels of Cd recorded during the period may not have supported its mobility positively. Generally, it could be deduced from this study that, a higher concentration of total Cd in soil can elevate the mobility and bio availability of the element in the area. Thus a reduction in total Cd level in soil can decrease correspondingly (a) the bioavailability of the metal for plant uptake and (b) the quantity of Cd leached into surface and underground water. Mobility of arsenic in soil showed significant positive relationship with its total concentration during dry and wet seasons with $r = 0.844$ and 0.920 respectively at $P < 0.1$. It could be deduced from the positive correlation exhibited by As in both seasons that, total content of As in soil may not have any influence on its mobility as the considerable variations in the total As between seasons is not noticed in its mobility. This is consistent with reports by Zhang *et al*. (2013) that, the mobility and bioavailability of As in soil are dependent upon arsenic fraction not on the total content in soil. Arsenic in this study was found mainly in the reducible fraction in both seasons, this corresponds with the report by Khan *et al*. (2010) that arsenic in the soil is mainly bound to iron ox hydroxides. Despite the considerable difference in total As content recorded at Control site between dry and wet seasons, mobility factors obtained in both seasons did not show significant distinction.

Consequently, validating the nonexistence of significant relationship between total As content and its mobility in soil within the study area.

3.4 Relations between toxic metals and soil properties:

Results obtained during the dry season indicated that mobility of lead in dumpsite soils demonstrated a significant negative relationship with soil pH ($r = –0.761$ at $P < 0.1$). This indicates that during the dry season with a higher pH range (5.65 – 7.43), the mobility and bio-availability of Pb reduced considerably. A negative relationship though a weak one was also recorded during the wet season between mobility of Pb and soil pH ($r = –0.207$ at $P < 0.1$). Thus a lower pH range (5.96 –7.34) obtained during the wet season might have hindered the mobility of the metal in the area but not as significant as noticed in the dry season. Generally, the obtained result has shown that mobility of lead in the study area was inversely proportional to soil pH. Consequently, if the pH of the soil environment is elevated, the mobility and bioavailability of lead in the area will be drastically diminished. This is consistent with the findings by Kashem *et al*. (2011) and Rieuwerts *et al.* (1998). This observation was further confirmed as the Control site with the lowest pH level recorded the highest mobility factor for Pb in both seasons. Mobility of lead showed a strong negative association with organic matter (OM) during the dry season with $r = –0.677$ at $P<0.1$. During the wet season too a moderately weak negative relationship was established between Pb mobility and organic matter ($r = –0.438$ at $P< 0.1$). This is in agreement with reports by Kashem *et al*. (2011). It could be inferred from the result that Pb might have formed stable complexes with organic ligands in soil thereby reducing its mobility and bioavailability. This may have contributed to a lower range of mobility factor reported during the wet season with a higher range of organic matter. The obtained result has also shown that a higher proportion of organic matter in soil may hinder the availability of Pb in the area significantly so it can serve as a technique for the remediation process. The reported negative relationship between organic matter and mobility of Pb in the area was authenticated by a higher mobility factor of Pb at Control site with a lower organic matter content during the dry season.

Mobility of cadmium (MF-Cd) demonstrated a strong positive relationship with soil pH during the dry season of the study area ($r = 0.813$ at $P< 0.1$). The positive association recorded in this work between MF-Cd and pH is consistent with the report by Oluwatosin *et al*. (2008). This implies that mobility and bioavailability of Cd in the area was directly proportional to the level of soil pH recorded during that period. In other words, the higher pH range recorded during dry season supported positively the mobility of Cd in soil as exhibited in a higher range of mobility acquired during this period. Nevertheless, during the wet season a weak negative relationship was shown between MF-Cd and soil pH with $r = –0.266$ at $P< 0.1$. Indicating that during the wet season a lower range of soil pH obtained may have hindered the mobility of Cd in soil though not significantly. The relationship between mobility of Cd and soil pH was validated by the near similar mobility factors recorded at the Control site with acidic nature of soil pH obtained in both seasons. Accordingly, this study has shown that a drastic reduction in soil pH may reduce the availability of Cd for plant uptake in area under investigation. Organic matter showed a strong positive correlation with the mobility of Cd during the dry season of the study area with $r = 0.691$ at $P< 0.1$. Nevertheless, a weak positive correlation was recorded between OM and mobility of Cd during the wet season($r = 0.323$ at $P< 0.1$). This is similar to the positive association reported by Oluwatosin *et al.* (2008) between Cd mobility and soil organic matter. Studies have shown that, cadmium forms soluble complexes with organic matter and this enhances its mobility in soil (Dunnivant *et al.*, 1992; Neal and Sposito, 1986). The high mobility factors recorded by Cd at all the locations and seasons may be attributed to its high potential in the formation of soluble complexes with organic matter. However, a higher range of MF-Cd was reported in dry than in wet season. This may be accredited to a higher OM contents recorded in wet season, since it has been reported that as the amount of OM increases, there is a tendency for more Cd to be adsorbed on the soil complex and hence reduces their mobility potentials in soils (Kashem *et al*., 2011). Soil pH exhibited a strong though insignificant positive relationship with mobility of As in soil during the dry season with r = 0.635 at P< 0.1. On the other hand, mobility of As recorded a significant positive correlation with soil pH during the wet season. (r = 0.682 at P< 0.1). Generally, results obtained in both seasons revealed that variations in soil pH may not affect the mobility of arsenic in soil substantially. Mobility factors at Control site during the dry and wet seasons corroborated this finding since the difference in soil pH did show significant variation in MF values obtained. This may be accredited to the fact that, in oxidizing conditions As (V) is the major specie in soil whereas in reducing conditions As (III) predominates (Woolson, 1977). Despite the fact that, both As (III) and (V) occur together even in oxidizing conditions since the oxidation of As (III) to (V) is a kinetically slow process (Sadiq, 1997). Arsenic mobility in soil indicated a very weak negative relationship with soil organic matter during the dry and wet seasons at P < 0.1 with r = –0.135 and –0.094 respectively. These r values show that, the amount of organic matter obtained in both seasons were negatively though slightly correlated with mobility and bioavailability of As in the area. The higher organic matter content in soil recorded during the wet season might have contributed to a lower range of mobility factor obtained in that season. Studies have shown that organic matter in soil is inversely proportional to the mobility of As in soil (Lombi *et al*., 2000; Wang and Mulligan, 2006). Results recorded at the Control site affirmed this observations as the higher OM content recorded at the site during wet season resulted in a lower MF of As. This study has also revealed that the application of high organic content in soil can reduce considerably the quantity of arsenic available for plant uptake in the area studied. Consequently, reducing the amount of As available to pollute water and accessible to human.

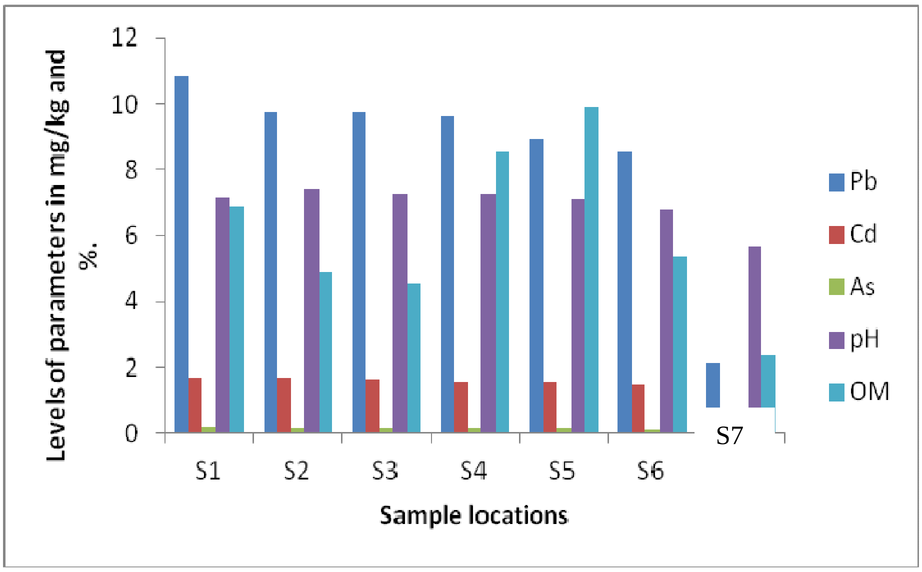

Fig.1: Mean levels of total trace metals, soil pH and Organic matter (OM) during dry season.

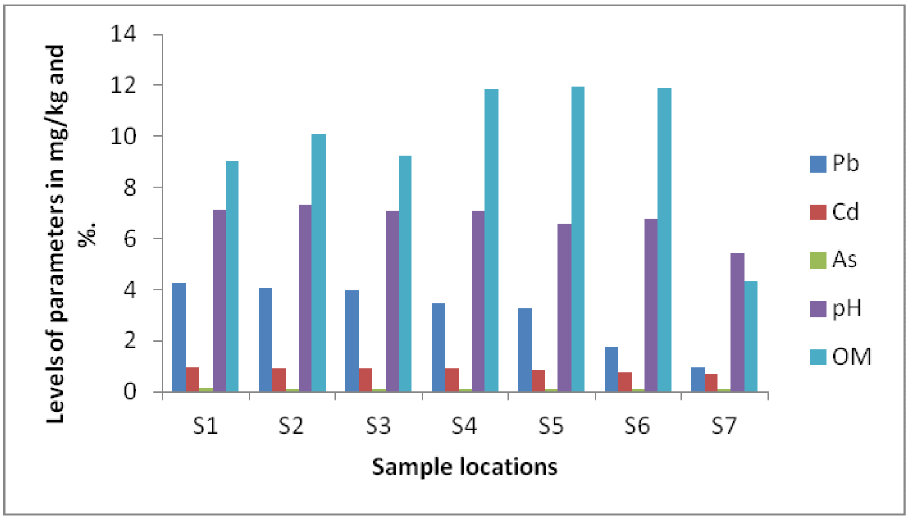

Fig.2: Mean levels of total trace metals, soil pH and Organic matter (OM) during wet season.
Key: S1 =Uyo; S2 = Abak; S3 = Eket; S4 = Onna; S5 = Ikono; S6 = Ikot Ekpene and S7 = Etinan (Control)

4. CONCLUSIONS

It could be concluded from results obtained in this study that, the bioavailability, accessibility and toxicity of toxic metals could be controlled in soil by monitoring the physicochemical properties of such environment. It has also been noticed that cadmium is a very mobile metal thereby can its availability should be periodically examined to for forestall the attendants health implications on human. However, this work has shown that some soil properties varied with season and at the same time their influence on the availability of toxic metals in soil fluctuated with season.

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