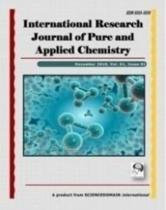

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Pollution Indices of Trace Metals in Urban Dumpsite Soils within Akwa Ibom State, Nigeria

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Authors' contributions

This work was carried out with the collaboration of all the authors. Author OEO designed the study while author GAE performed the modeling and collation of results for the production of first draft of the manuscript with assistance from author OEO. All the authors read and approved the final manuscript.

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ABSTRACT

Surface soil samples were obtained from six (6) urban dumpsite soils namely: Uyo, Abak, Eket, Onna, Ikono and Ikot Ekpene within Akwa Ibom State, Nigeria. Control samples were also collected from a forest in Etinan local government area of the same State. Samples collected were treated and analyzed based on standard techniques to ascertain the pollution status of Pb; Cd; Ni; Cr and Fe at each dumpsite soil and Control using geoaccumulation index (Igeo) and Contamination factor (CF) analysis. The source of metals to dumpsite soils and Control was identified using enrichment factor model. Pollution status of each dumpsite soil was also established using degree of contamination (Cdeg). Igeo results showed that, Pb, Ni and Cr moderately polluted dumpsite soils studied, Cd varied between unpolluted to moderately polluted status. However, Fe indicated very low Igeo values indicating the low availability of the metal in the study area. Enrichment factor analysis showed that Pb and Cr were primarily from anthropogenic sources; Ni and Fe were mostly from natural source while Cd source varied between anthropogenic and natural at the different dumpsite soils but the source of all the metals at Control site was natural. Contamination factor analysis disclosed that Cd, Ni, Cr and Fe moderately

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contaminated dumpsite soils evaluated while Pb showed a considerable level of soil contamination. The Cdeg indicated that Uyo dumpsite soil recorded the highest degree of soil contamination while the lowest level of contamination was at Ikot Ekpene dumpsite soil. Cd recorded highest mobility potential in both dumpsite soils and Control while Cr was the least mobile element. Speciation results indicated that, Pb existed mostly in reducible fraction, Cd in acid extractable while Ni, Cr and Fe occurred mainly in the residual fraction.

Keywords: Contamination factor; degree of contamination; mobility factor; speciation; geoaccumulation index; enrichment factor.

1. INTRODUCTION

Trace metals contamination of soil is a far more serious problem than either air or water pollution because they are usually tightly bound by the soil and may persists for centuries depending on the conditions. Thus the environmental problem of soil pollution by trace metals has received increasing attention in the last decades in both developing and developed countries of the world [1]. Metal toxicity though dependent on their chemical forms, can cause several diseases affecting almost all the vital organs and functions of the human body [2,3]. However, trace metals, such as Zn, Cu, Cr, Fe and Mn, are required by the body in small amount, but can be toxic in larger quantities [4]. It has been reported that, the determination of total trace metal content in soil cannot indicate the comprehensive pollution status of that environment but metal speciation can indentify the bioavailability, mobility and toxicity of trace metal in soils [5, 6]. Unlike the single extraction technique, sequential extraction gives information about both mobile and stabile fractions of metals in soil, which evaluates the actual potential mobility of metals and according to Bashir et al. [7] the understanding of metal bio-availability and mobility in soil is important for evaluating its potential environmental and health effects. Environmental reports have also shown that, pollution of soil environment is ascertained by calculating the enrichment factor, the contamination factor/degree of contamination and Index of geoaccumulation [8,9].However, previous studies in dumpsite soils within the area concentrated on the determination of total metal contents without assessing the pollution status of each dumpsite and metal. This study aimed at using the above mention procedures and models to identify the forms, mobility, bio-availability, toxicity and sources of trace metals in dumpsite soils. It also aimed at establishing the pollution status of each dumpsite soil studied and compare results obtained at Control site with that of dumpsite soil thereby stressing the possible factor for any variation observed.

2. MATERIALS AND METHODS

2.1. Study Area

This research work was carried out in some local government areas of Akwa Ibom State, Niger Delta region of Nigeria. Akwa Ibom is a state in Nigeria named after Qua Iboe River. It is located in the coastal South- South part of the country, lying between latitudes 4º 32' and 5º 33' North and longitudes 7º 25' and 8º 25' East. (See Fig. 1). The state has basically two distinct seasons namely the wet and dry. The wet season lasts between 8 to 9 months starting from mid-March till the end of November. The dry season has a short duration of between the last week of November or early December and last till early March. This study was undertaken in the dry season of the area and surface soil samples were obtained from the following urban dumpsites: Uyo (007. 56 E and 0.502 N); Abak (007.59 E and 04.59 N); Eket (007.55 E and 04.38 N); Onna (007.51 E and 04.37 N); Ikono (007.06 E and 05.06 N); Ikot Ekpene (007.42 E and 05.11 N). Samples were also obtained from a Control site in Etinan local government Area of the same State with coordinates 007.50 E and 04.52 N (Fig. 1).

2.1.1. Sample collection and treatment

Top 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 [10]. At each location, samples were collected from the north, south, east and west and pooled together to form composite sample for that site [11]. A total of four (4) samples were obtained at each location thus, one hundred and twelve sub-samples (112) and twenty eight (28) composite samples were collected for this study. These samples were collected for a period of four (4) months December, 2010 to March, 2011. This research was conducted during the dry season so that rainwater may not dilute or leach concentrations of metals analyzed for. All samples were air dried for three (3) days and ground to pass through a 2mm mesh. While trace metals speciation was done using the procedures of modified BCR (Community Bureau of Reference of the European Commission) to quantify trace metals in the four (4) different phases namely: acid extractable (F1), reducible (F2), oxidisable (F3) and residual (F4) fractions [12]. Mobility factors were calculated using equation (I) below according to the methods of Adaikpoh [13]; Kabala and Singh [14]. Degree of contamination was calculated using the formula in equation (II) where contamination factors of all the elements are taken into account. Contamination factor of each element was calculated using the formula in equation (III) below. In this study geo-accumulation index of trace metals in dumpsite soils and Control was determined using equation (IV) where the measured concentration of trace metal in dumpsite soil and the background concentration of trace metal in Control site are considered [15].

The method of Rubio et al. [16] was applied for the determination of Enrichment factor (See equation V below). In this study, Fe was used as the reference metal because it was the most abundant element with low occurrence variability in the area signifying that its occurrence within the study area is natural. Several authors have previously used Fe as the reference metal in their studies [17,18].

$$\text{Mobility factor} = F1/F1 + F2 + F3 + F4 \times 100 \qquad (I)$$

Where F1, F2, F3 and F4 are Acid extraction, reducible, oxidisable and residual fractions of metals respectively.

$$C_{deg} = \Sigma C^{i}_{f} \qquad (II)$$

Where C^{i}_{f} is the contamination factor for all the elements involved.

$$C^{i}_{f} = C^{i}_{0\text{-}1}/C^{i}_{n} \qquad (III)$$

Where C_F is the contamination factor, $C_{0\ -1}$ is the mean content of metals from dumpsite soils and C_n is the concentration of individual metal in Control site.

$$I_{geo} = \text{Log}_{2}\ (C_n/1.5B_n) \qquad (IV)$$

Where Cn is the measured concentration of trace metal in dumpsite soil and B_n is the background concentration of trace metal in Control site

$$EF = (M/Fe)_{\text{Dumpsite}} / (M/Fe)_{\text{Control.}} \qquad (V)$$

Where $(M/Fe)_{\text{Dumpsite}}$ is the ratio of metals and iron concentration in dumpsite soil and $(M/Fe)_{\text{Control}}$ is the ratio of metals and iron concentration in Control site.

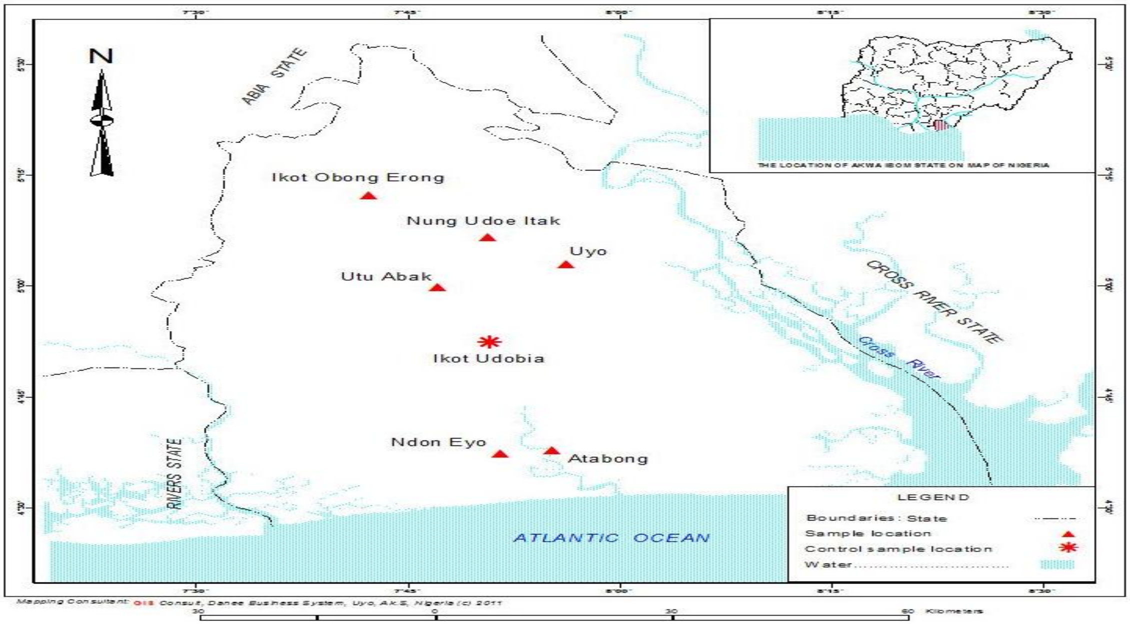

Fig. 1. Map of Akwa Ibom State showing sample locations

3. RESULTS AND DISCUSSION

Results obtained in this study for Contamination factor/Degree of contamination; Enrichment factor and Geoaccumulation Index are shown in Tables 1–3 respectively. However, results recorded for the Mobility factors of the metals are shown in Fig. 2 while results for the speciation of trace metals are exhibited in Figs. 3-7.

3.1 Contamination Factor (CF) and Degree of Contamination (C_{DEG})

Table 1 gives results for the contamination factors and degree of contamination of each dumpsite soil studied. Results obtained showed the following mean CF values for the trace metal: (4.43) Pb; (2.61) Cd; (1.49) Ni; (2.58) Cr and (1.25) Fe. The obtained results indicated that based on classes of CF proposed by Hakanson [19], Cd, Ni, Cr and Fe moderately contaminated dumpsite soils evaluated whereas Pb showed a considerable contamination level. The contamination factor for all the metals at Control site was 1.00 indicating low contamination levels of these metals at this location. Results obtained for these metals at the Control site correlated positively with the low Igeo and EF values recorded thereby validating the choice of the location. Results for the degree of contamination of each dumpsite soil by these trace metals indicated the following: (14.17) Uyo; (13.32) Abak; (12.74) Eket; (12.15) Onna; (11.10) Ikono and (10.70) Ikot Ekpene. The degree of contamination of the dumpsite soils studied followed the following trend: Uyo > Abak > Eket > Onna > Ikono >Ikot Ekpene. The obtained trend for C_{deg} showed that Uyo dumpsite soil though within the range of moderate degree of contamination was the highest contaminated area while Ikot Ekpene dumpsite soil was the lowest contamination site. This may be attributed to the difference in age, size and location of these dumpsites as reported by Ebong et al. [20]. The Control site indicated a C_{deg} of 5.00 which revealed a very low level of soil contamination by the trace metals. This may be accredited to the absence of human activity in the area that would have introduced some level of these trace metals into the environment.

3.1.1 Enrichment factor (EF)

Results obtained for enrichment factors in dumpsite soils and Control is given in Table 2. This model identified the source of trace metals to the terrestrial environment is it natural or anthropogenic. According to Hernandez et al. [21] EF values ranging between 0.5 and 2 indicate that the occurrence of the metal is due to natural processes, whereas ratios greater than 2 are considered as enrichment mainly from anthropogenic inputs. Results for EF of trace metals in dumpsite soils indicated the following ranges: 3.29 - 3.87 Pb; 1.82 – 2.35 Cd; 1.08 – 1.24 Ni and 2.01- 2.18 Cr while the EF values for Fe at all the locations was 1.00. These results indicated Pb and Cr as metals from anthropogenic sources while Ni and Fe may have existed mainly from natural source. Cadmium levels recorded at Uyo (S1) and Abak (S2) were mostly from the geochemical processes whereas at other dumpsite soils assessed, Cd was from anthropogenic sources. The Control site showed an EF value of 1.00 for all the metals showing that the source of these metals to that environment was predominantly natural.

3.1.1 Geoaccumulation index (Igeo) of trace metals

Igeo indices of trace metals in dumpsite soils are shown in Table 3, results obtained indicated the following ranges in dumpsite soils: 1.41 to 1.73 Pb; 0.69 – 0.89 Cd; – 0.41 – 0.27 Ni; 0.03–1.03 Cr; – 0.53 – 0.02 Fe. These results revealed that, Pb, Cd, Ni and Cr concentrations varied between unpolluted and moderately polluted. While Fe levels at the locations remained unpolluted. The low Igeo values together with the existence in residual fraction and low mobility factors substantiated the non-availability of Fe in the area. Generally, it was observed that Uyo dumpsite soil (S1) was the oldest and largest indicated the highest Igeo value for all the metals whereas, a newly established and smallest Ikot Ekpene dumpsite soil (S6) recorded the Igeo values for all the metals. This revealed that, the age and size of a dumpsite is directly proportional to the concentration of trace metals in the underlying soil as reported by Odukoya et al. [22].

3.1.2 Mobility factor (MF)

Mobility factor of a metal is one of the factor determining its bioavailability and toxicity. Results for mobility factors of trace metals in dumpsite soils and Control are depicted in Fig. 2. Results recorded indicated mean MF (%) for the trace metals in dumpsite soils as follows: Pb (22.65); Cd (60.06); Ni (11.70); Cr (8.70) and Fe (18.58). However, the Control site showed MF

(%) values of 35.21; 49.41; 13.06; 8.37 and 19.25 for Pb; Cd; Ni; Cr and Fe respectively. This revealed that the mobility of trace metals was higher in the Control site than in dumpsite soils except for cadmium and chromium. This may be attributed to the relationship between individual metal and soil pH. It was inferred from the results too that, an increase in soil pH favoured the mobility and bioavailability of Pb, Ni and Fe while the mobility of Cd and Cr was highly supported by low soil pH. Mobility of metals followed the order: Cd> Pb> Fe > Ni > Cr indicating that, Cd exhibited the highest metal mobility in the area under investigation as reported by Okunola *et al*. [23] and Beesley [24] in their respective studies. The high mobility potential of Cd obtained in this work justified its existence predominantly in the readily available fraction (Acid extractable). This indicated that Cd was highly available for plant consumption and this was a serious threat to human since the metal in not known for any beneficial role to either plant or human.

Table 1. Contamination factor/degree of contamination of trace metals in dumpsite soils and Control

Location	Lead	Cadmium	Nickel	Chromium	Iron	Degree of contamination
S1	4.99	2.77	1.81	3.08	1.52	14.17
S2	4.53	2.72	1.70	2.99	1.38	13.32
S3	4.52	2.70	1.61	2.62	1.29	12.74
S4	4.45	2.57	1.38	2.55	1.20	12.15
S5	4.11	2.49	1.31	2.13	1.06	11.10
S6	3.98	2.43	1.13	2.12	1.04	10.70
S7	1.00	1.00	1.00	1.00	1.00	5.00

Table 2. Enrichment factors (EF) of trace metals in dumpsite soils and Control

Location	Lead	Cadmium	Nickel	Chromium	Iron
S1	3.27	1.82	1.18	2.03	1.00
S2	3.29	1.98	1.23	2.18	1.00
S3	3.50	2.09	1.24	2.03	1.00
S4	3.70	2.13	1.14	2.12	1.00
S5	3.87	2.35	1.23	2.01	1.00
S6	3.83	2.33	1.08	2.05	1.00
S7	1.00	1.00	1.00	1.00	1.00

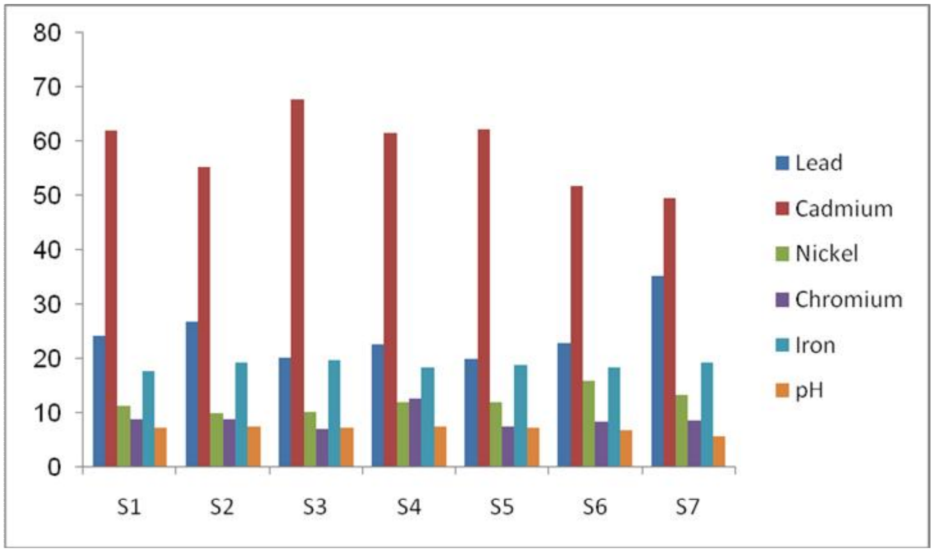

Fig. 2. Mean mobility factors (%) of trace metals and pH in dumpsite soils and Control

Table 3. Geoaccumulation indices (Igeo) of trace metals in dumpsite soils and control

Location	Lead	Cadmium	Nickel	Chromium	Iron
S1	1.73	0.89	0.27	1.03	0.02
S2	1.60	0.86	0.18	0.99	-0.13
S3	1.59	0.85	0.10	0.80	-0.22
S4	1.57	0.78	-0.12	0.76	-0.32
S5	1.45	0.73	-0.20	0.51	-0.50
S6	1.41	0.69	-0.41	0.50	-0.53
S7	-0.58	-0.59	-0.58	-0.58	-0.58

3.1.2.1 Correlation between pH and trace metal mobility in soil

The results acquired in this study showed a strong negative correlation between mobility of lead and soil pH with $r = -0.787$ at $P < 0.1$. This revealed that as the soil pH was increasing, mobility and bioavailability of Pb may have been decreasing and vice versa. This explained why the higher mean pH in dumpsite soils may have resulted in a lower mobility factor for Pb when compared with the Control site. This observation confirmed that the solubility of lead increases in acidic soils as previously reported by Baranowski et al. [25]. The mobility of cadmium indicated a strong positive relationship with soil pH ($r = 0.714$ at $P < 0.1$). Consequently, a higher soil pH may result in a corresponding increase in cadmium mobility in soil. Thus, the lower mobility factor of Cd recorded at the Control site may be attributed to a lower pH level recorded at the location. Nickel showed a moderate negative relationship with soil pH with $r = -0.572$ at $P < 0.1$. This disclosed that, mobility of Ni in area studied was indirectly proportional to the soil pH; this is similar to the report by Prasanth et al. [12]. The r value obtained correlated positively with a higher mobility factor recorded at the Control site with a lower pH level. The relationship between pH and mobility of chromium in soil was a very weak positive one ($r = 0.151$ at $P< 0.1$). This showed that an increase in soil pH may not accelerate significantly the mobility of Cr in the area. This of course may be the reason behind the non-significant difference in mobility factors of Cr obtained in dumpsite soils and Control notwithstanding the significant variation in pH levels of between the two sites. The study has shown that, although the relationship between soil pH and mobility of Ni and Cr may not have been very strong their compounds may have been more soluble in alkaline soil condition. Mobility of iron exhibited a very weak negative association with soil pH ($r = -0.188$ at $P< 0.1$). This disclosed that, mobility of Cr in the area was inversely proportional to the soil pH. The observed relationship between soil pH and mobility of Cr validated the higher mobility factor recorded for Cr in Control site with a lower pH level than in dumpsite soils. Iron indicated a very weak negative correlation with soil pH with $r = -0.188$ at $P < 0.1$. This indicated that soil pH may have affected the mobility of Fe in soils studied negatively though insignificantly.

3.1.2.2 Speciation of trace metals in dumpsite soils and Control

Results obtained for the speciation of trace metals in dumpsite soils and Control are shown in Figs. 3 – 7. Lead existed principally in the reducible fraction in dumpsite soils whereas, the highest proportion of the metal at Control site was found in acid extractable fraction. This may be attributed to the lower pH level recorded at the Control site which may have mobilized Pb from the mobilizable fractions into the mobile fraction. This substantiated the higher mobility factor of Pb obtained at the Control site. The trends obtained for the speciation of Pb in dumpsite soils and Control was Reducible > Acid extractable > Oxidisable > Residual and Acid extractable > reducible > oxidisable > Residual respectively. This is very risky to the environment under study since at both locations, Pb existed more in the mobilizable fractions than in immobilization fraction. Thus a minor adjustment in the soil chemistry can elevate the proportion of the readily available fraction of the metal thereby exposing the human to Pb toxicity and its attendant's health implications. However, this consistent with reports by Ajiboso et al. [26] and Umoren et al. [27] who also obtained Pb principally in a similar form. The obtained results indicated that, lead in the area was predominantly from anthropogenic sources as proposed by Enrichment factor since reports have shown that high proportion of trace metal associated with oxide phases is indicative of anthropogenic pollution [28]. Cadmium existed more in the acid extractable fraction in both dumpsite soils and Control. This is consistent with the findings by Osakwe [29] and Kashem et al. [30] in Nigeria and Japan respectively. Speciation of Cd in dumpsite soils and Control is Acid extractable > Reducible > Oxidizable > Residual, thus Cd was more available in the mobilizable than immobilizable fractions. This confirmed the high mobility potentials exhibited by Cd in both dumpsite soils and Control. The principal form of Ni acquired in this study in both locations was the residual fraction; this is similar to the reports by Ajiboso et al. [26] and Prasanth et al. [12] in their studies within Nigeria and India. Speciation of Ni followed the trend: Residual > Reducible > Acid extractable > Oxidizable, this substantiated the low mobility factors recorded for Ni. According to Abeh et al. [31] the residual fraction is considered the most stable, less reactive and less bioavailable. Speciation of Cr showed that, the metal existed principally in residual fraction in both dumpsite soils and Control. This is in agreement with the findings by Iwegbue [32] and Kotoky et al. [33]. The obtained trend for the different fractions of Cr in both dumpsite soils and Control indicated the following: Residual > Oxidizable > Reducible > Acid extractable. Thus, Cr existed more in the immobile than mobile fractions and this authenticated the low mobility factor recorded for Cr. Iron existed predominantly in the residual fraction in both dumpsite soils and Control. This is consistent with the reports by Fagbote and Olanipakan [34] and Segarra et al. [35]. At both locations speciation of Fe followed the trend: Residual > Reducible > Oxidizable > Acid extractable showing the less availability of the essential element in the area studied. The residual fraction can be taken as a guide to the degree of pollution of the soil. The smaller the quantities of the metal present in this fraction, the greater the pollution of the area [36]. However, the high proportion of iron found in residual fraction is an important repository of iron in the soil. This corroborated the negative Igeo values recorded for Fe at dumpsite soils.

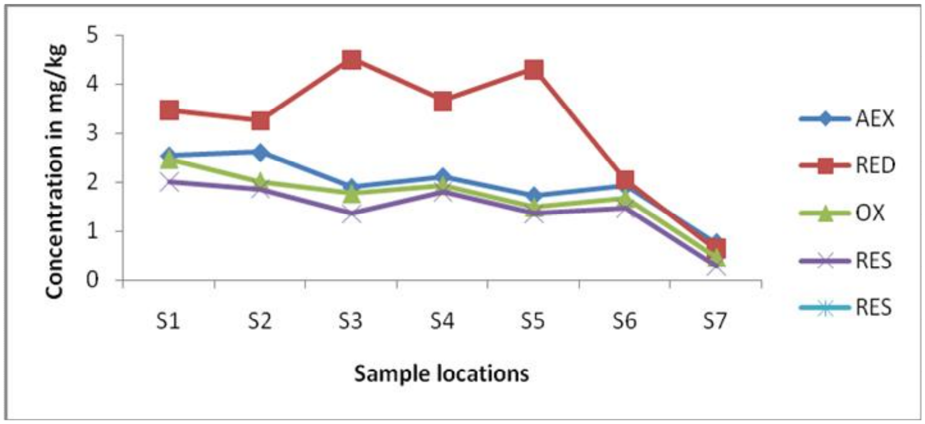

Fig. 3. Mean concentrations of different species of lead in dumpsite soils and control

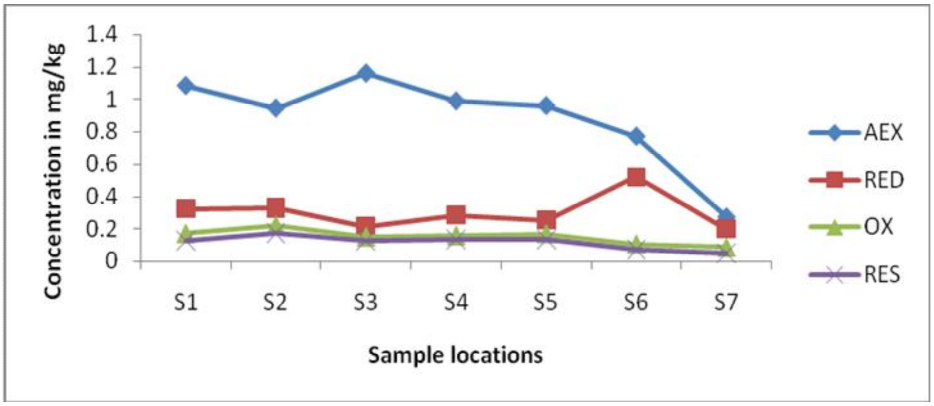

Fig. 4. Mean concentrations of different species of cadmium in dumpsite soils and control

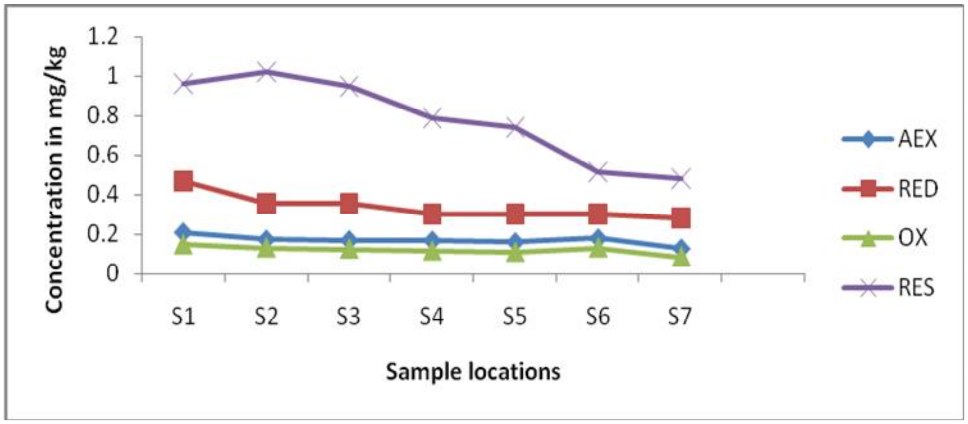

Fig. 5. Mean concentrations of different species of nickel in dumpsite soils and control

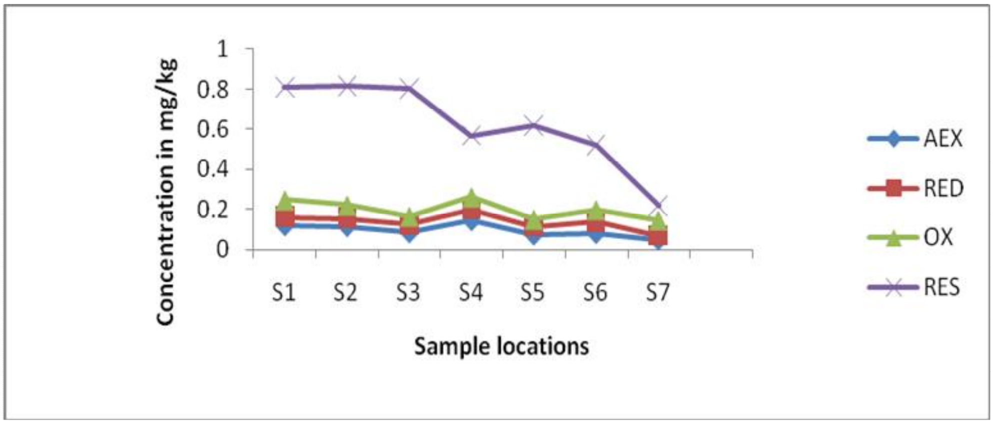

Fig. 6. Mean concentrations of different species of chromium in dumpsite soils and control

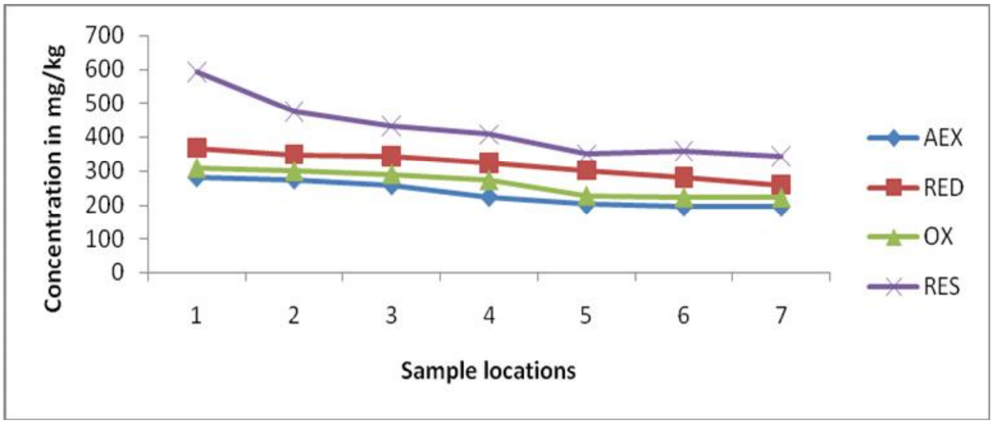

Fig. 7. Mean concentrations of different species of iron in dumpsite soils and control
S1 =Uyo; S2 = Abak; S3 = Eket; S4 = Onna; S5 = Ikono; S6 = Ikot Ekpene and S7 = Etinan (control)

4. CONCLUSION

This study has shown that, the use of environmental equations for evaluating the pollution status of any location proposed to be polluted is highly necessary. The pollution category of trace metals, dumpsite soils and Control site studied has been established and the sources of these metals to dumpsite soils and Control have been identified. The high mobility of cadmium recorded has shown that both terrestrial and aquatic environments may be threatened by the metal. It has also been noticed that the influence of soil pH on metal mobility varied between metals.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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