



Environmental Pollution Induced By an Aluminium Smelting Plant in Nigeria

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Abstract - The extent of pollution of Imo, Utaewa Rivers and Essene Creek being sources of drinking water were assessed due to the smelting activities of the Aluminium Smelter at Ikot Abasi City, Nigeria. Soil and plants samples in the field near the water bodies were equally assessed. The physicochemical parameters investigated on all sampled water bodies were within the WHO and USEPA limits for drinking water with the exception of salinity, turbidity, TDS and few heavy metals (Mn, Fe, Al, Pb). The overall average levels of these parameters were 7.6 ± 2.8 % (salinity), 16 ± 12 FTU (Turbidity), 793 ± 250 mg/L (TDS), 2.59 ± 0.48 mg/L (Mn), 0.49 ± 0.27 mg/L (Al) and 0.85 ± 0.43 mg/L (Pb). Principal component biplot revealed strong and positive metal loadings whose ranges were (1.284–1.687), (0.499–0.515) and (0.959–1.630) for Essene Creek, Imo River and Utaewa River respectively. Similarly, cluster analysis showed that elemental compositions of soil and plants in the vicinity of aluminium smelter were traceable to the smelting activities. Also, accumulation of airborne particle by vegetation and surface soil was resulted from the activities in the smelting site. Al (1830–2170 $\mu\text{g/g}$) and Zn (141–147 $\mu\text{g/g}$) were more abundant at 0–5 cm soil depth than other metals (Cd, Mn, Ni, Fe, Pb, Co). Bioaccumulation results revealed increased metal uptake by *Vernonia amygdalia* (Bitter leaves), *Manihot esculenta* (Cassava) and *Carica papaya* (Paw-paw) at the sites closest to the industry, hence can be used as good biomarkers for soil pollution.

Keywords : *Pollution, Heavy metal, Bioaccumulation, Multivariate analysis.*

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Abstract - The extent of pollution of Imo, Utaewa Rivers and Essene Creek being sources of drinking water were assessed due to the smelting activities of the Aluminium Smelter at Ikot Abasi City, Nigeria. Soil and plants samples in the field near the water bodies were equally assessed. The physicochemical parameters investigated on all sampled water bodies were within the WHO and USEPA limits for drinking water with the exception of salinity, turbidity, TDS and few heavy metals (Mn, Fe, Al, Pb). The overall average levels of these parameters were 7.6 ± 2.8 % (salinity), 16 ± 12 FTU (Turbidity), 793 ± 250 mg/L (TDS), 2.59 ± 0.48 mg/L (Mn), 0.49 ± 0.27 mg/L (Al) and 0.85 ± 0.43 mg/L (Pb). Principal component biplot revealed strong and positive metal loadings whose ranges were (1.284–1.687), (0.499–0.515) and (0.959–1.630) for Essene Creek, Imo River and Utaewa River respectively. Similarly, cluster analysis showed that elemental compositions of soil and plants in the vicinity of aluminium smelter were traceable to the smelting activities. Also, accumulation of airborne particle by vegetation and surface soil was resulted from the activities in the smelting site. Al (1832 ± 170 $\mu\text{g/g}$) and Zn (141 – 147 $\mu\text{g/g}$) were more abundant at 0-5 cm soil depth than other metals (Cd, Mn, Ni, Fe, Pb, Co). Bioaccumulation results revealed increased metal uptake by *Vernonia amygdalia* (Bitter leaves), *Manihot esculenta* (Cassava) and *Carica papaya* (Paw-paw) at the sites closest to the industry, hence can be used as good biomarkers for soil pollution.

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I. INTRODUCTION

Smelting of aluminium does not come without its environmental problems. There have been a number of recent studies investigating the emissions of various pollutants during the aluminum smelting process. Some of the studies were laboratory-scale investigations which quantitatively determined the species present in flue gases (Wei, 1996). Other investigation concentrated on the emissions from aluminium smelters. The pollutants identified in the studies were chlorinated organic compounds (Laue et al., 1994; Westberg and Selden, 1997), organic compounds containing chlorine and sulphur (Sinkkonen et al., 1994), polycyclic aromatic hydrocarbons (PAHs) (Aittola et al., 1993; Westberg and Selden, 1997; Healy et al., 2001), heavy metals (Kozanoglou and Catsiki,

1997). PAHs in general are mutagenic and/or carcinogenic in nature. Also, heavy metal load from smelting activities near water bodies has been proved to result in contamination of river and has various implications on the ecosystem (Ellis, 1987, Vucadin and Odzak, 1991, Malea and Haritonidis, 1995; Kozanoglou and Catsiki, 1997). These toxic pollutants may eventually reach human bodies through the food chains and inhalation of polluted air. In addition, the dumping of smelting by-products in aluminium smelter inhabited areas brings up crucial questions about the degree of metal contamination and the effects on human life. Regions near such activities need to be under investigation in order to avoid gross pollution.

It was for this reason that this investigation was conducted on the aluminium smelter in Ikot Abasi city, Nigeria. The surrounding vegetation has turned yellowish and some of the agricultural plants around the vicinity of the factory have been observed for poor growth and yield. Consequent upon this, there is possibility that the vicinity of the company is susceptible to pollution arising from the smelting activities. The parameters mentioned in this study were metals, salinity, dissolved cations and anions. The aims of the study were to investigate the surface water quality of water bodies in the vicinity of aluminium smelter, and distribution of heavy metals in soil and plants. This study provides background information on the environmental status of the vicinity of aluminium smelter in the tropical area of south-south region of Nigeria.

II. MATERIALS AND METHODS

a) Sampling area

The Aluminium smelter at Ikot Abasi city is in the southern part of Nigeria where aluminium smelting activities have been on-going for more than a decade. It is the second largest producer of primary aluminium in the world (BNW News, 2004; World Bank, 2009). The smelting site is located at latitude $4^{\circ}34' \text{N}$ and longitude $7^{\circ}54' \text{E}$ and bordered by water bodies namely Imo River that opens-up to Atlantic Ocean, Utaewa River and Essene Creek. The area belongs to the southern rain forest climate and is relatively populated. A control site was located at about 3km upstream of Essene Creek. Figure 1 shows the Aluminium smelter company and the sampling locations. The description of locations, sample codes and the type of samples collected are highlighted in Table 1.

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b) *Sample Collection and preservation*

Water samples were collected monthly between September 2009 and December 2009 from Imo River (IR), Utaewa River (UT) and Essene Creek (EC) at eight locations each. Eight water samples were equally collected from Jaja Creek (JC) situated at the control site with thoroughly cleaned polyethylene bottles without disturbing the water. Water samples collected for metal analyses were acidified with HNO_3 .

Soil and plant samples were collected from three locations [Pot Room (PR), Jetty (J), and Cast House (CH)] on the fields near the company as well as from the field near Jaja Creek situated at the control site. Leaves of Cassava (*Manihot esculenta*), Paw-paw (*Carica papaya*) and Bitter leaves (*Vernonia amygdalia*) were collected and thoroughly washed with distilled water. The vegetation samples were dried in an oven at 60 °C, and ground with agate mortar and pestle. The samples were then sieved with 0.5mm mesh size and kept in polythene bags. The air-dried soil samples were pulverized with agate mortar and pestle to a fine powder and then sieved through a 100 - mesh screen sieve to obtain homogenous particles.

c) *Sample preparation and analysis*

Five grams of soil samples was digested with 50mL of aqua regia (HCl and HNO_3 - 3:1 v/v) in a beaker placed on hot plate in a fume hood for 1 hour. The filtered extract was used for metal analysis. The vegetation samples were equally weighed into vitreous crucibles and nitric acid was added as an ashing aid just before the commencement of ashing. The vegetation samples were dry-ashed in a muffle furnace at 500 °C. The ash was dissolved with hot 2M HNO_3 and was filtered where necessary. Extract of the soil and vegetation samples were analysed for cadmium, manganese, zinc, nickel, iron, aluminium, lead and cobalt using atomic absorption spectrophotometer (UNICAM 939/59). Quality control of metal measurements in soil, vegetation and water was verified by including blanks and carrying out recovery study by spiking. All recoveries were within the range of 92.3-98.7%. A blank sample was incorporated for every ten soil and vegetation extracts analysed. The acid solutions used for extraction were made from Analar grade stock acids, while the distilled water was doubled deionised. Standards for the atomic absorption analysis were obtained as the commercial BDH stock metal standards from which working standards were prepared by appropriate dilution. For other water quality parameters, the analytical data quality was ensured through careful standardization, procedural blank measurements and duplicate samples.

Conductivity and salinity were recorded with a HACH conductivity/salinity meter model CO150, dissolved oxygen was determined by the alkali-azide modification of Winkler's technique, alkalinity was determined titrimetrically while nitrate was determined

colorimetrically using phenoldisulphonic acid method. Phosphate and sulphate were determined colorimetrically using ascorbic acid and turbidimetric methods respectively according to the standard method (APHA –AWWA, 1998).

d) *Data treatment and multivariate statistical methods*

Duncan multiple range test of variable at $p < 0.05$ was used to ascertain statistical significance in the soil quality data. Multivariate analysis of the data was performed through Cluster Analysis (CA) and Principal Component Analysis (PCA). The distributions of metals within soil profile were represented by means of Box and Whisker Plots (Winderlin et al., 2001). All mathematical and statistical computations were made using Excel 2003 (Microsoft, 2003) and STATISTICA 6.0 (StatSoft, Inc., USA, 2001).

III. RESULTS AND DISCUSSION

The results of the physicochemical parameters conducted on the water samples from the Imo, Utaewa Rivers, Essene Creek and Jaja Creek are summarized in Tables 2 and 3. Table 4 specifically gives the averages and ranges for parameters used to assess the suitability of these water bodies (Imo, Utaewa Rivers and Essene creek) around the smelting company for beneficial purposes such as drinking and industrial use. In all the sampled water bodies, the physicochemical parameters as shown in Table 4 were generally within the WHO and USEPA guidelines for drinking water with the exception of salinity, turbidity, TDS and few heavy metals (Mn, Fe, Al, and Pb).

The pH values of water from the Imo River, Utaewa River, Essene and Jaja Creeks were within the range of 6.1 and 7.2. Water from the rivers and creeks could be considered acidic since their average pH values were below 7.0. Water pH of 6.3 ± 0.2 and 6.5 ± 1.1 for Essene and Utaewa were the least and highest averages values (Table 2) and were significantly different from the average water pH of Jaja Creek at the control site. Acidification of water samples could have led to the release of loosely bonded ions present on the surface of suspended particle matter; thereby increasing the metal concentration in water samples. Essene Creek and Utaewa River revealed turbidity levels of 25.3 ± 2.1 FTU and 25.0 ± 2.5 FTU respectively, which were significantly higher than the WHO limit of 5 FTU (Table 2). The TDS constituent of Imo River, when compared to the same constituent of Essene Creek and Utaewa Rivers, was indeed higher by factors 3.99 and 3.19 respectively. Correspondingly, sulphate was higher by factors of 0.34 and 0.52 respectively. The average levels of TDS and sulphate for the Imo River water were 1370 ± 21 mg/L and 547 ± 71 mg/L respectively (Table 2). High level of TDS is traceable to the impact of navigation on the river.

The average salinity for the Imo River was $13.0 \pm 1.1\%$ while $3.2 \pm 0.4\%$ and $4.8 \pm 0.7\%$ were

obtained for the Essene Creek and Utaewa River. These salinity levels were observed to exceed the limit of 0.5%, thus making the water toxic to sensitive freshwater life and not portable for human consumption. High salinity level indicates an increase in the concentration of total dissolved solids in water and can often be detected by an increase in the chloride, an important anion of many dissolved salts. A positive correlation coefficient (0.526) between TDS and salinity was observed. Increases in salinity up to 0.1 % (1,000mg/L) can have lethal and sub lethal effects on aquatic plants and invertebrates (Hart *et al.*, 1991). The observed salinity levels for the Essene Creek, Imo and Utaewa Rivers are high enough to induce a variety of other effects within both aquatic and terrestrial ecosystems. These effects include acidification of the water bodies (Lofgren, 2001), mobilization of toxic metals through non-exchange (Norrstron and Bergstedt, 2001), changes in mortality and reproduction of aquatic plants and animals (Strayer and Smith, 1992; James *et al.*, 2003; Eaton *et al.*, 1999), altered community composition of plants (Eaton *et al.*, 1999; Richburg *et al.*, 2001; Elshahed *et al.*, 2004). At relatively low concentration of salinity, salt has been shown to inhibit denitrification (Cunningham, *et al.*, 2009, 2010; Kaushal, *et al.*, 2005) a process critical for removing nitrate and maintaining water quality in surface waters. Increased salinity is an important ecological variable in explaining the extremely low abundance and diversity of freshwater life observed in the Imo and Utaewa Rivers.

The water quality monitoring data (Table 2) found its application in the classification of rivers into utility classes based on quality indices. Some water quality indices have been reported in different part of the world (Pesce and Wunderlin, 2000; Simeonov *et al.*, 2000). There is no water classification index established for Nigerian rivers and streams yet. However, the well utilized water index of Prati *et al.* (1971) was applied to the data of this study using the parameters pH, turbidity, suspended solids, DO, BOD, and COD. The categories of classification ranged from Utility Class I to V which corresponds to excellent for drinking, irrigation and industrial use without treatment (Class I), suitable for drinking (Class II), slightly polluted (Class III), polluted (Class IV) and heavily polluted water which is not fit for any of these beneficial purposes (Class V). Based on the Prati scale, Imo River, Essene Creek and Utaewa River are categorized under Class III (Table 3) which is indicative of water not suitable for beneficial purposes such as drinking, irrigation and industrial use, but may be rigorously treated for use by private consumers. The classification showed that Jaja creek at the control site fell into Class II reflecting that its water sample is suitable as sources of municipal water supply.

The overall average concentrations of Mn, Fe, Al and Pb (Table 4) in surface waters studied were higher than the WHO and USEPA limits and hence the waters portability are impaired for drinking. The only exception

was the zinc with concentration lower than the USEPA limit of 5.0 mg/L. The Imo River contained Mn, Fe and Al levels of 2.52 ± 0.71 mg/L, 0.37 ± 0.10 mg/L and 0.77 ± 0.13 mg/L respectively. The respective corresponding concentrations in Essene Creek were 2.62 ± 0.42 mg/L, 0.59 ± 0.41 mg/L and 0.52 ± 0.08 mg/L while Utaewa River contained 2.70 ± 0.30 mg/L, 0.49 ± 0.05 mg/L and 0.15 ± 0.03 mg/L respectively. These metal concentrations that were above the limits may be attributed to deposits resulting from the company's smelting activity. The Imo River (IR) and Essene Creek (EC) serve as water channels to ships bringing the raw materials for the company and other commercial activities. The discharge from exhausts of ships and speed boats using leaded fuels explains the high lead levels of 0.90 ± 0.17 mg/L and 0.84 ± 0.50 mg/L in waters from the Imo River and Essene Creek. The high concentrations of aluminium with ranges of 0.67–0.91 mg/L and 0.50–0.60 mg/L for Imo River and Essene Creek (Table 3) are not unexpected as alumina (Al_2O_3) being the major raw material used in the company splits into water bodies occasionally during off-loading to the conveyor belt.

Principal Components (PC) analysis was performed on the standardized data matrix (Table 5) of metal concentrations in surface water samples. This is necessary to explain the structure of the underlying data set. The experimental data was standardized in order to avoid mis-calculation due to wide differences in data dimensionality (Liu *et al.*, 2003). Standardization tends to increase the influence of small variance and reduce of large ones. Furthermore, the standardization procedure eliminates the influence of different units of measurement and renders the data dimensionless (Benza-Deano *et al.*, 2008). Liu *et al.* (2003) classified the factor loading as "strong", "moderate", and "weak" corresponding to absolute loading values of >0.75 , 0.75-0.50 and 0.50-0.30 respectively. The first component (PC1) explained 62.2% of total variance (Table 5) and has strong and moderate positive metal loadings for water from Essene Creek (1.284- 1.687) and Imo River (0.499-0.515). Principal component biplot in Figure 2 indicates that Al, Pb, Co and Fe are associated with the strong and metal loadings in PC1. Essene Creek (EC) and Imo River (IR) sampling points that lie to the right of the origin on the first component axis and closer to the metal (Al, Pb, Co, and Fe) vectors have the highest metal concentrations. The control sampling points (Jaja creek) that lie to the left of the origin and far from the metal vectors have the lowest metal concentrations. It was revealed in Figure 2 that Zn and Mn accounted for 18.1 % (as indicated by PC2) of total metal load of Utaewa River. The metal loading was strong with a range of 0.959- 1.630 (Table 5) and was an indication of water pollution arising from the fall out of scrap iron and aluminium bars during navigation.

Table 6 shows that pH, total organic carbon (TOC), total organic matter (TOM), sand, silt and clay

compositions of soil samples from Jetty, Cast House and Pot Room sampling points are not significantly different from the corresponding compositions of soil from the control site. Soil sample from the cast house where the smelted aluminium is processed into bars contains the highest aluminium level of $24500 \pm 3300 \mu\text{g/g}$. The highest concentrations of Cd ($2.17 \pm 0.55 \mu\text{g/g}$), Zn ($132 \pm 160 \mu\text{g/g}$), Pb ($144 \pm 48 \mu\text{g/g}$) in the soil were above the corresponding levels of $0.125 \mu\text{g/g}$ (Cd), $59.8 \mu\text{g/g}$ (Zn), $8.62 \mu\text{g/g}$ (Pb) in smelting waste contaminated soil from Sierra Almagrera in Spain (Navarro *et al.*, 2008). On the other hand, the highest concentrations of Ni ($15.2 \pm 3.7 \mu\text{g/g}$) and Co ($3.5 \pm 3.4 \mu\text{g/g}$) were far below levels of $119 \mu\text{g/g}$ (Ni) and $16.8 \mu\text{g/g}$ (Co) reported by Navarro *et al.* (2008).

Box and Whisker plots in Figures 3 and 4 shows the distribution of Fe, Pb, Al, Co, Cd, Mn, Zn and Ni at various depths. The results indicate that Al and Zn are more abundant at 0-5cm soil depth than other metals suggesting that Al and Zn will be more readily available in soil for uptake by crops. The values for Cd, Mn, Fe and Co are highest at 10-15cm soil depth while Pb concentrations are nearly constant. The soil quality data was further subjected to cluster analysis to explore their temporal trend. A dendrogram shown in Figure 5 grouped all the sampling points for soil samples into two main clusters (A and B). Cluster A includes majorly soil samples with the highest average aluminium concentration obtained from the Cast house, where bars are being packaged for export. The second cluster B includes the rest of the analyzed soil (samples from Jaja Creek, Pot Room and Jetty sites). The cluster was further divided into two sub-clusters (b_1 and b_2). Sub-cluster b_1 includes the samples from Jaja Creek (control site) while sub-cluster b_2 includes samples from the Pot room and Jetty sites. The sites in sub-cluster b_2 have similar characteristics and natural sources types. This implies that the elemental composition of soil from the control site differs significantly from what obtained for Cast House, Pot Room and Jetty soil samples. Therefore, elevated metals concentrations in soil from Cast House, Pot Room and Jetty sites indicate soil contamination resulting from smelting activity around the sites.

Concentrations of metals investigated in crops and leaf samples are shown in Table 7. Crop samples contained lower metal concentrations than soil samples. Bitter leaf, a vegetable for common people, had the highest accumulation factors of 11.4 (Cd), 3.59 (Zn), 4.71 (Mn), 12.6 (Ni), 8.82 (Fe), 52.7 (Al). The highest accumulation factor of 14.3 for Pb was observed in cassava leaves. These accumulation factors reflect the generally high levels of metals and their degrees of contamination in the crops. Also, it is interesting to infer that bitter and cassava leaves can be used successfully as biomarkers for heavy metal pollution in soil. High aluminium concentration on the leaves is attributed to the atmospheric particulate deposition occurring around

the smelting area. Cluster analysis as shown in Figure 6 was able to distinguish between metal concentrations in crops from the contaminated sites and that from the control site. The classification indicates the aluminium smelter as the anthropogenic source of metal contamination for crops.

IV. CONCLUSION

These findings revealed that smelting activities were the dominant source of contamination of Essene Creek, Imo and Utaewa Rivers which are major sources of drinking water for the community at a far distance downstream. There was an increasing evidence of metal pollution in Ikot Abasi soil and edible crops planted on it. Further research on air quality assessment of the area is necessary in drawing a better conclusion on the overall effect of the aluminium smelting on environments of Ikot Abasi.

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Table 1 : Description of sampling locations, sample code and type of sample collected

Sampling location	Sample code	Location description	Sample collected
Pot Room	PR	Located North-East (NE) of the company with respect to the main gate. It covers a wide expanse of land up to 6 hectares. The location (PR) shares the same fence with the facility where the alumina is smelted in pots. Hence the name 'pot room'.	Soil and plant
Jetty	J	This is the North of the company with respect to the gate. It is mid-point far from the PR and Cast House.	Soil and plants
Cast House	CH	Located North-West of the company with respect to the main gate. The cast house is where the smelted aluminium is cast into ingots (bars) ready for export. The sampling site shares the same fence with the Cast House.	Soil and plants
Imo River	IR	This is located south of the company with respect to the gate. It is the water that host the harbour where raw material arrives and finished product leaves.	Water
Essene Creek	EC	It is a major tributary of IR that borders the company at the far south-west. It is closer to the CH than any other facility of the company.	Water
Utaewa River	UT	The river borders the company at the far South-east (SE). It is closer to the PR and the power plant of the company than any other facility of the company.	Water
Jaja Creek (Control site)	JC	It was the reference site situated at 1 km upstream of Essene Creek. It is a drainage stream located North of the company	Water, soil and plants

Table 2 : Average values and ranges of physicochemical characteristics of the water from Imo river (IR), Essene creek(EC), Utaewa river (UR) and Jaja creek (JC)

Sampling location	pH	Temp. (°C)	Cond. (µS/cm)	Turbidity FTU	TS (mgL ⁻¹)	TDS (mgL ⁻¹)	TSS (mgL ⁻¹)	Hardness (mgL ⁻¹)	SO ₄ ²⁻ (mgL ⁻¹)	PO ₄ ³⁻ (mgL ⁻¹)	NO ₃ (mgL ⁻¹)	DO (mgL ⁻¹)	COD (mgL ⁻¹)	Salinity (%)	Utility class
IR	6.4±0.1	24.0±0.2	21.9±0.2	3.3±0.6	1380±25	1370±21	18.7±1.5	170±2	549±71	1.14±0.11	11.1±0.2	4.8±0.2	38.7±0.6	13.0±1.1	III
	6.2-6.7	23.9-24.2	21.7-22.0	3.0-4.0	1360-1410	1350-1390	17-20	168-172	480-622	1.03-1.21	9.8-12.8	4.0-6.2	35.0-40.2	12.0-14.2	
EC	6.3±0.2	25.0±1.1	5.9±0.2	25.3±2.1	355±15	343±17	12.3±2.5	161±2	113±11	3.4±0.2	10.3±0.1	4.4±0.1	39.8±1.1	3.2±0.4	III
	6.1-6.5	24.0-26.1	5.8-6.1	23.0-27.0	342-372	327-360	10-15	160-162	101-121	3.25-3.61	8.91-10.5	3.9-5.5	36.6-41.0	2.8-3.6	
UR	6.5±1.1	26.0±0.4	6.3±0.1	25.0±2.5	452±17	430±14	22.7±1.2	165±5	120±8	2.19±0.2	11.8±0.1	4.5±0.2	44.4±0.6	4.8±0.7	III
	6.2-7.2	24.1-26.5	5.5-6.2	22.5-27.3	412-473	401-495	19.6-23.8	153-180	101-146	1.82-2.40	10.5-12.5	4.1-5.2	40.1-49.4	4.32-5.01	
JC	7.1±0.1	25.0±0.2	5.3±0.1	1.54±0.27	186±11	178±9	8.42±0.73	70.6±5.3	4.2±1.1	0.08±0.01	0.74±0.1	6.8±0.2	17.2±3.0	0.93±0.21	II
	7.0-7.2	24.0-25.6	4.8-5.7	1.10-1.93	152-195	162-201	7.56-10.4	521-84.3	3.62-5.71	0.05-0.09	0.52-1.01	6.01-7.21	15.1-22.6	0.75-1.14	

Table 3 : Average values and ranges of metal concentrations (mgL⁻¹) in water from Imo River (IR), Essene Creek(EC), Utaewa River (UR) and Jaja Creek (JC)

	Cd	Zn	Mn	Ni	Fe	Al	Pb	Co
IR	Mean±SD	0.08±0.03	2.52±0.71	< 0.001	0.37±0.10	0.77±0.13	0.9±0.17	0.05±0.01
	Range	0.07-0.12	1.82-3.23		0.28-0.48	0.67-0.91	0.71-1.02	0.05-0.06
EC	Mean±SD	0.12±0.02	2.62±0.42	< 0.001	0.59±0.41	0.52±0.08	0.84±0.50	0.03±0.01
	Range	0.11-0.14	2.14-2.92		0.46-1.05	0.50-0.60	0.80-1.90	0.01-0.06
UR	Mean±SD	0.15±0.02	2.70±0.30	< 0.001	0.49±0.05	0.15±0.03	0.81±0.05	0.04±0.01
	Range	0.13-0.17	2.41-3.01		0.51-0.53	0.12-0.18	0.75-0.99	0.03-0.04
JC	Mean±SD	0.02±0.01	0.42±0.10	< 0.001	0.10±0.03	0.04±0.01	0.49±0.03	0.02±0.01
	Range	0.01-0.04	0.32-0.52		0.07-0.13	0.04-0.05	0.39-0.59	0.01-0.03

Table 4 : Water quality standards compared with the overall water quality of rivers and creeks in the vicinity of aluminium smelting company.

Parameter	*Mean±SD	Range	Water Quality Standard		
			^a WHO	^b USEPA	^c New Zealand
Temperature (°C)	24.7±0.9	23.9-26.5	27 – 28	-	-
Conductivity (µS/cm)	12.8±2.5	5.5-22	1000	-	-
pH	6.4±0.3	6.1-7.2	6.5 - 9.2	6.5 – 8.5	-
Turbidity (NTU)	16±12	3.0 – 27.3	5	-	-
TDS (mg/L)	793±250	327-1390	1000	500	-
TSS (mg/L)	16.4±4.4	10 – 23.8	-	-	-
TS (mg/L)	809±540	342-1410	-	-	-
Total hardness (mg/L)	166±5	160-172	500	-	-
DO (mg/L)	4.67±0.3	3.9-6.2	6	-	-
Salinity (%)	7.6±2.8	2.8-14.2	0.5	-	-
COD (mg/L)	40.3±0.9	35.0-49.4	-	-	-
SO ₄ ²⁻ (mg/L)	300±230	101-622	400	250	-
PO ₄ ³⁻ (mg/L)	2.25±1.1	1.03-3.61	0.51 - 3.50	-	-
NO ₃ ⁻ (mg/L)	9.11±0.6	8.91-12.8	50	10	50
Cd (mg/L)	-	<0.001	0.003	0.005	0.004
Zn (mg/L)	0.11±0.03	0.06-0.14	5	5.0	-
Mn (mg/L)	2.59±0.48	1.82-3.23	0.4	0.05	0.4
Ni (mg/L)	-	<0.001	0.07	-	0.08
Fe (mg/L)	0.49±0.27	0.28-1.05	0.05 - 0.36	0.3	-
Al (mg/L)	0.57±0.25	0.12-0.91	0.2	0.05 – 0.2	0.1
Pb (mg/L)	0.85±0.43	0.71-1.90	0.01	0.015	0.01
Co (mg/L)	0.04±0.02	0.01-0.06	-	-	-

WHO= WHO Drinking water guidelines, USEPA= US Environmental Protection Agency. ^aSource= WHO (2006), ^bSource= USEPA (1999), ^cSource= New Zealand (2005), * = Overall mean of water quality of Imo river, Essene creek and Utaewa river(This study)

Table 5 : Principal components analysis scores (loadings) of metal concentrations on the first six rotated principal components (PCs) for various sampling locations.

Sampling location	PC1	PC2	PC3	PC4	PC5	PC6
IR-1	0.499	-0.758	-0.976	-0.589	0.460	0.002
IR-2	0.515	-1.083	-1.095	0.181	-0.051	-0.002
IR-3	0.512	-0.039	-0.770	0.877	-0.431	0.002
EC-1	1.775	-0.203	0.503	-0.392	-0.330	-0.008
EC-2	1.284	-0.530	0.536	-0.848	-0.330	0.005
EC-3	1.687	-0.868	1.137	0.926	0.353	0.001
UR-1	0.509	0.959	0.210	-0.166	0.303	0.003
UR-2	0.287	1.297	-0.191	0.108	-0.086	-0.003
UR-3	0.882	1.630	-0.246	0.018	0.148	0.001
JC-1	-2.412	0.091	0.326	0.028	-0.304	0.005
JC-2	-2.502	-0.349	0.416	-0.117	0.060	0.00001
JC-3	-2.638	-0.147	0.152	-0.026	0.207	-0.007
% Variance	62.2	18.1	11.0	6.45	2.21	0.0004
%Total Variance	62.2	80.3	91.3	97.8	100	100
Eigenvalue	2.57	0.75	0.456	0.27	0.09	0.00002

Table 6 : Average levels and range of physicochemical properties of soil samples from sampling locations – Jetty, Cast House, Pot Room and Jaja Creek

	Jetty (J)		Cast House (CH)		Pot Room (PR)		Jaja Creek – Control site (JC)	
	Mean±SD	Range	Mean±SD	Range	Mean±SD	Range	Mean±SD	Range
pH	6.4±2.4 ^a	4.2-9.0	8.0±2.4 ^a	5.5-10.3	7.4±4.5 ^a	3.0-7-1	7.1±0.4 ^a	6.8-7.5
TOC (%)	0.88±0.70 ^a	0.09-1.39	0.66±0.04 ^a	0.61-0.68	0.49±0.33 ^a	0.29-0.87	0.78±0.15 ^a	0.62-0.91
TOM (%)	0.15±0.12 ^a	0.02-0.24	0.11±0.01 ^a	0.10-0.12	0.08±0.06 ^a	0.05-0.15	0.10±0.01 ^a	0.10-0.11
Sand (%)	59.2±2.4 ^c	56.4-60.8	42.5±2.0 ^a	40.4-44.4	51.1±2.3 ^b	48.4-52.4	60.9±3.0 ^c	58.2-64.2
Silt (%)	5.2±5.5 ^a	0.40-11.2	3.2±1.6 ^b	1.6-4.8	8.9±3.9 ^a	5.6-13.2	7.0±1.6 ^b	8.4-7.4
Clay (%)	35.7±3.4 ^a	32.4-39.2	54.3±0.5 ^b	54.0-54.8	40.0±5.8 ^a	34.4-46.0	32.1±4.6 ^a	27.4-36.5
Cd (mg/kg)	1.9±0.7 ^b	1.20-2.60	2.17±0.55 ^b	1.60-2.70	1.43±0.57 ^b	0.80-3.20	0.14±0.15 ^a	0.06-0.32
Zn (mg/kg)	39±42 ^a	8.50-87.7	127±170 ^a	18.7-319	132±160 ^a	29.6-41.8	14.0±5.8 ^a	9.65-20.5
Mn (mg/kg)	21.9±8.2 ^a	13.4-29.8	88±19 ^{ab}	76.6-109	164±130 ^b	104-311	11.0±2.1 ^a	8.94-13.2
Ni (mg/kg)	13.2±4.7 ^{ab}	8.5-17.8	15.2±3.7 ^b	12.9-19.5	12.6±1.3 ^{ab}	11.1-13.5	7.7±1.7 ^a	7.68-9.3
Fe (mg/kg)	1690±200 ^b	1490-1890	2250±23 ^c	2220-2260	2230±79 ^c	2140-2290	1240±210 ^a	1067-1478
Al (mg/kg)	9680±540 ^a	9320-10300	24500±3300 ^{bc}	21000-27500	17700±6600 ^b	12300-15800	5440±1200 ^a	4562-6780
Pb (mg/kg)	27.4±3.9 ^a	24.8-32.0	111±43 ^b	83.0-161	144±48 ^b	163-184	23.9±3.6 ^a	20.8-27.9
Co (mg/kg)	0.27±0.30 ^a	<0.001-0.6	1.60±0.45 ^a	1.1-2.0	3.5±3.4 ^a	1.9-7.5	0.02±0.01 ^a	0.01-0.03

Mean values with different superscripts in a row are significantly different at p=0.05; Total Organic Carbon (TOC), Total Organic Matter (TOM)

Table 7 : Average metal concentrations (µg/g) and the accumulation factors (AF) in plants from the vicinity of aluminium smelting company and control site.

Plant type	Sample code	Cd, µg/g (AF)	Zn, µg/g (AF)	Mn, µg/g (AF)	Ni, µg/g (AF)	Fe, µg/g (AF)	Al, µg/g (AF)	Pb, µg/g (AF)	Co, µg/g (AF)
*Bitter leave	BL	0.8(11.4)	141(3.59)	27.3(4.71)	4.8(12.6)	179(8.82)	1830(52.7)	18.3(5.34)	<0.001(NA)
*Cassava leave	CL	0.5(2.38)	142(2.53)	1.48(3.73)	5.7(2.71)	112(2.96)	2170(38.3)	38.7(14.3)	<0.001(NA)
*Paw-paw	PL	0.9(15.0)	147(1.94)	15.0(3.88)	8.3(2.87)	68.4(5.56)	1830(37.4)	16.4(6.83)	<0.001(NA)
**Bitter leave (from control site)	PLC	0.07	39.3	5.8	0.38	20.3	347	0.34	<0.001
**Cassava leave (from control site)	CLC	0.21	56.2	39.7	2.1	37.9	567	0.27	<0.001
**Paw-paw (from control site)	PLC	0.06	75.9	3.87	2.89	12.3	489	0.24	<0.001

(*) = Each value in the row is an overall average concentration of nine determinations and

(**) = Each value in the row is an overall average concentration of triplicate determinations

NA = Not applicable

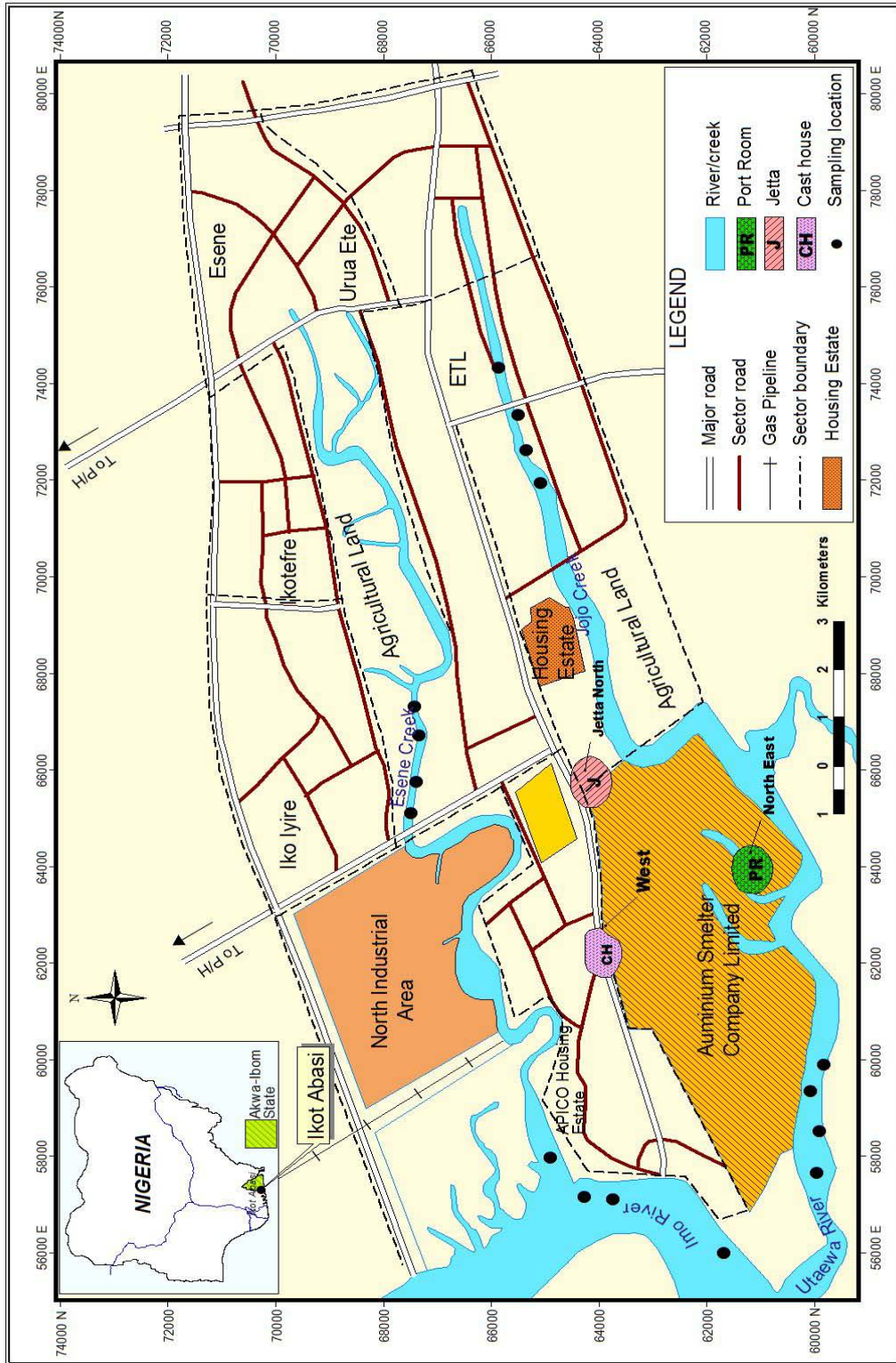


Figure 1 : Map of the study area showing the various sampling locations

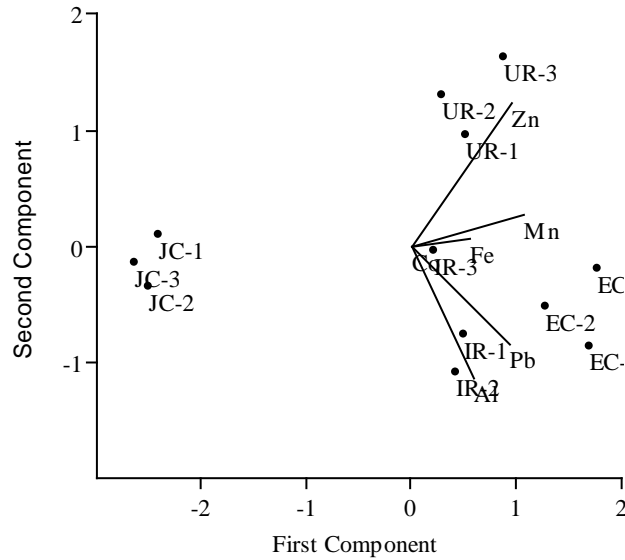


Figure 2 : Principal component biplot of heavy metal concentrations in Imo River (IR), Utaewa River (UR), Essene Creek(EC) and Jaja Creek (JC).

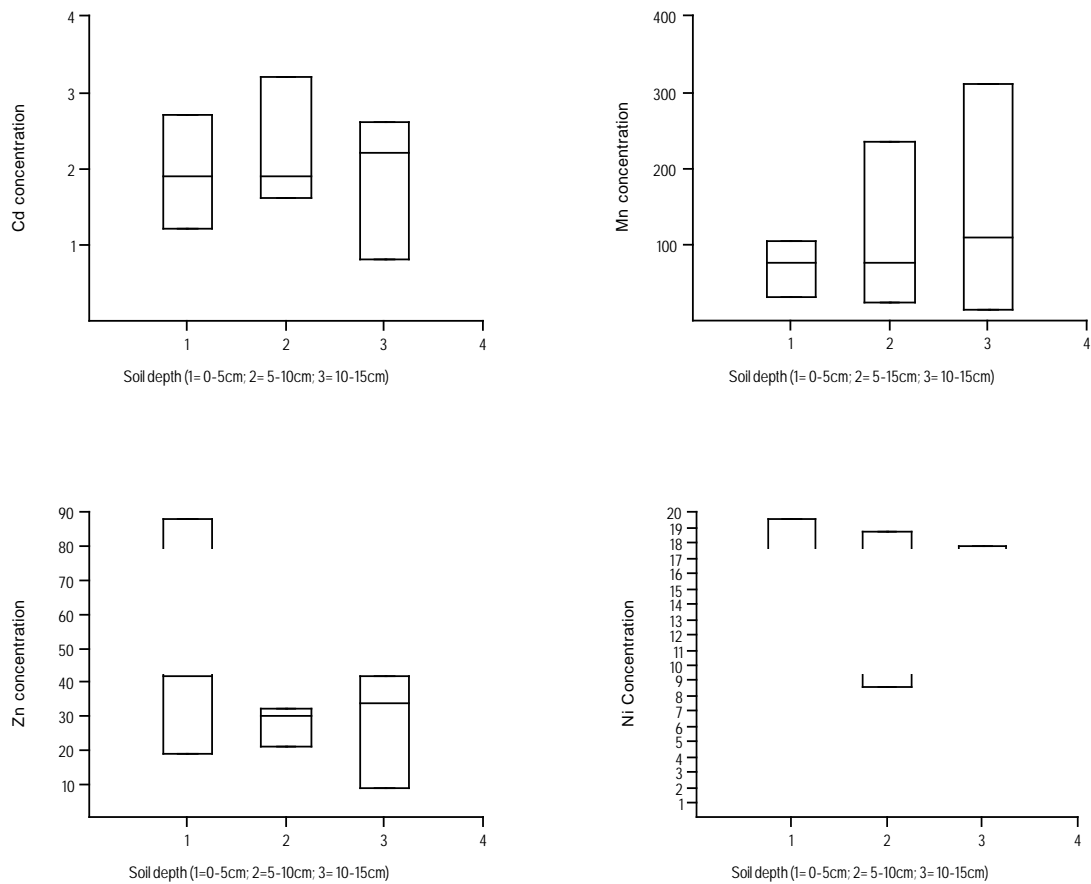


Figure 3 : Distribution of Cd, Mn, Zn and Ni concentrations ($\mu\text{g/g}$) within the soil profile.

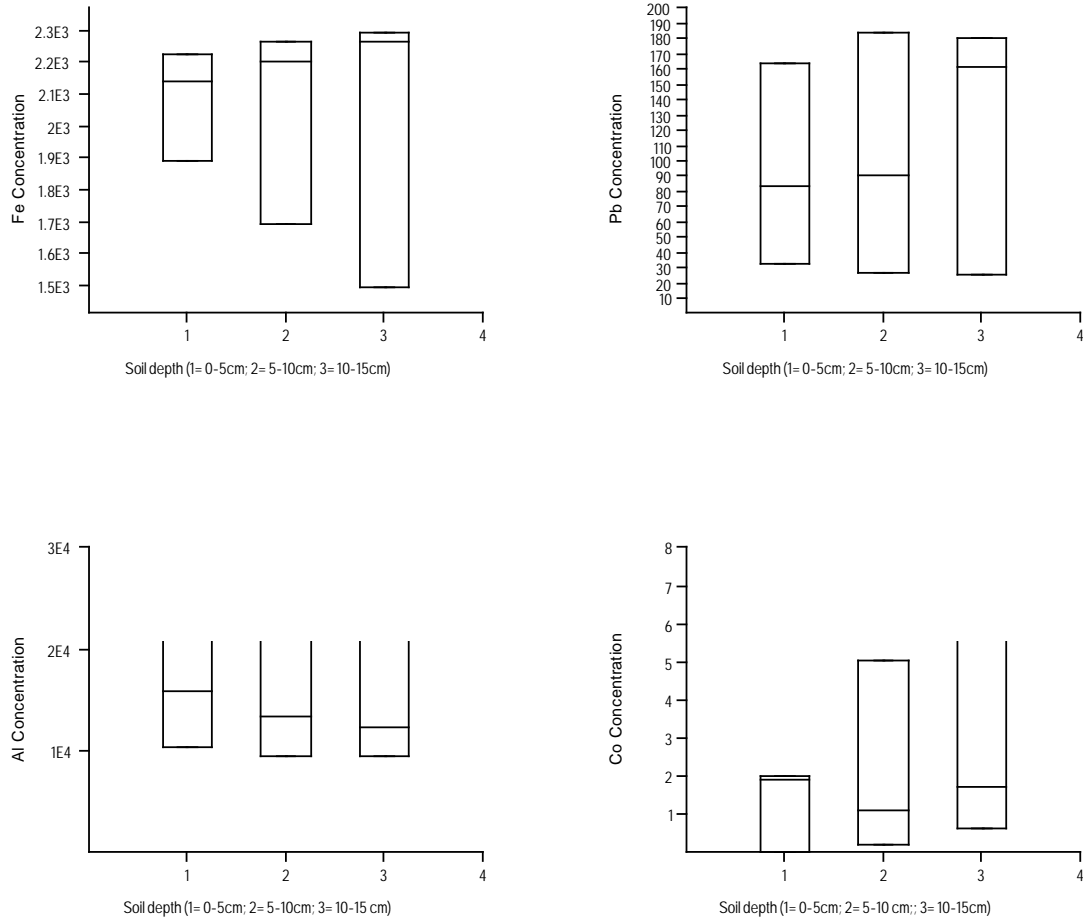


Figure 4 : Distribution of Fe, Pb, Al and Co concentrations (μg/g) within the soil profile.

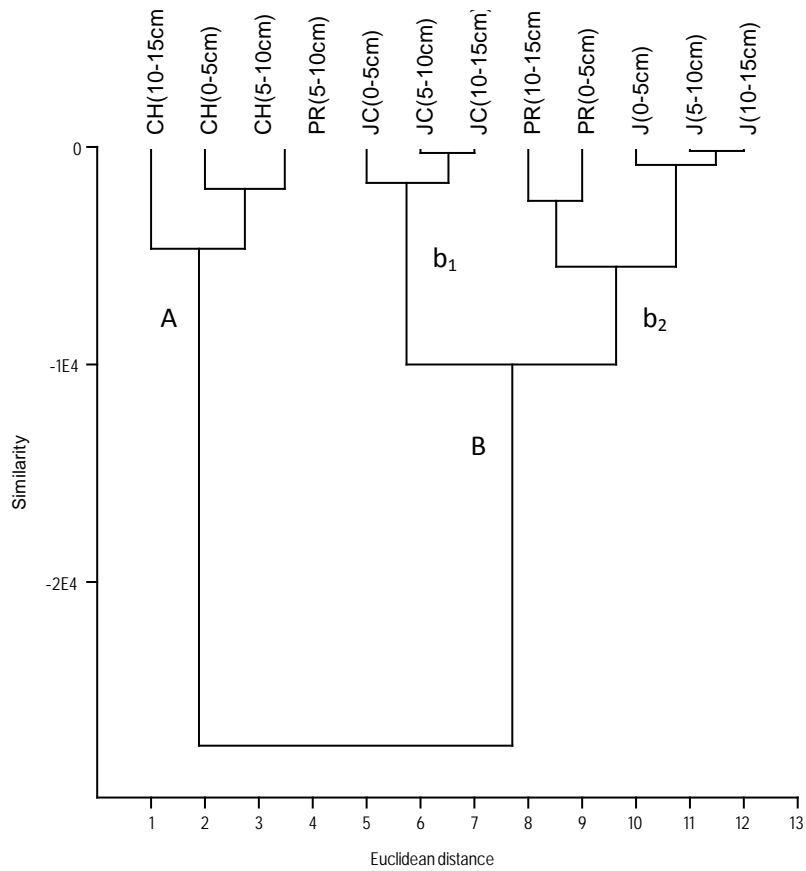


Figure 5 : Dendrogram showing clustering of sampling on soil from various locations (Pot room=PR; Jetty= J; Cast House= CH, Jaja Creek= JC).

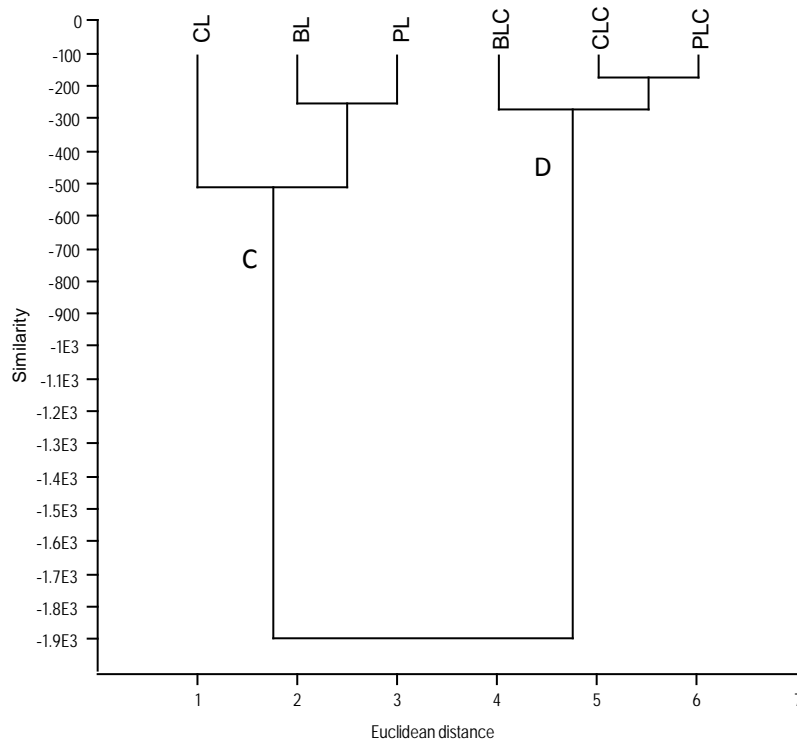


Figure 6 : Dendrogram showing classification of metals concentrations in plants (Cassava leave= CL; Bitter leave=BL; Paw-paw=PL) from sampling sites and control site (Cassava leave= CLC; Bitter leave=BLC; Paw-paw=PLC).

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