CONCENTRATIONS OF SEVEN HEAVY METALS IN THE LEAVES OF OIL PALM TREE (*ELAEIS GUINEENSIS)* AND ALMOND TREE (*PRUNUS DULCIS)* IN STEEL PRODUCTION AREAS OF DELTA STATE, NIGERIA

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ABSTRACT
Samples of leaves of two species of plant: oil palm tree (*Elaeisis guineensis*) and almond tree (*Prunus dulcis*) were collected from seven sampling stations in the steel production areas of Ovwian and Aladja Towns in Delta State, Nigeria each season (dry and rainy) for two years and analyzed for heavy metals by methods of mixed acid digestion and flame AAS. Results shows that average concentrations of heavy metals in oil palm are: Cu (49±18 mg/kg), Pb (114±91 mg/kg), Ni (21.9±5.6 mg/kg), Cd (6.8±2.0 mg/kg), Zn (250±120 mg/kg), Fe (1020±240 mg/kg), and Mn (430±220 mg/kg), and in almond leaves are: Cu (212±83 mg/kg), Pb (190±120 mg/kg), Ni (24.9±8.0 mg/kg), Cd (8.3±3.1 mg/kg), Zn (680±440 mg/kg), Fe (1230±590 mg/kg) and Mn (1000±640 mg/kg). Concentrations of heavy metals in the study area are significantly higher than the concentrations of corresponding metals in control area.

Keywords: Steel production; heavy metals; rainy season; dry season; environment.

INTRODUCTION

Certain human activities contribute high proportions of heavy metals into any environment. Among these are the mining and smelting of metals, steel production, atmospheric fall outs brought about by exhaust of motor vehicles (e.g. use of leaded gasoline), combustion of fossil fuels, disposal of urban and industrial waste and waste from use of inorganic fertilizers in agriculture (Forstner and Wittman, 1983). Mining and smelting of metals contribute the highest proportion of heavy metal pollutants to any environment. Effects of individual heavy metals on man and animal health and on plants are well documented (Ayleit, 1979; Nriagu and Pocyna, 1988; Langston, 1990; Bryan, 1971; Forstner and Wittman, 1983; Sharma and Agrawal, 2000).

Various studies on the determination of heavy metals in plant have been carried out with results which shows that high concentrations of heavy metals are often found in plants which grow close to industries producing metals or related products such as batteries or metal containing substances are used in the process of manufacturing (Yusuf *et al.,* 2003; Oleveira, and Autia, 1984; Gbaruku and Friday, 2007; Levy *et al.,* 1991; Denton *et al.*, 1980). Yusuf *et al.* (2003) found concentration ranges of Cu (25.1 – 56.8 mg/kg) Ni (1.33 – 2.06 mg/kg) and Cd (1.13 – 1.67) mg/kg) in *Talium triangulare*, *Celisa trigna* and *Ceralus olitarus* plants in industrial areas of Lagos. Levy *et al.* (1992) found concentrations of Cu (11.2 mg/kg), Pb (52.0 mg/kg) Cd (7.27 mg/kg) and Zn (517 mg/kg) in *Achillia lanulosa* plants in the mining areas of Arkansas River (Leadville Colorado), USA. Steel production has been taking place in Ovwian – Aladja areas of Delta State, Nigeria, since later part of the 1980s. The extents to which this activity has affected the area have not been well studied.

Therefore the objectives of this study was to assess the pollution effect of the activities of steel production in Ovwian and Aladja areas of Delta State, especially on the vegetation by the determination of selected heavy metals in two species of plant i.e. the leaves of oil palm tree (*Elaeis guineensis*) and the almond tree (*Prunus dulcis*) and to investigate the source of the metals if the areas are found to be heavy metal polluted. The heavy metals determined include Cu, Pb, Zn, Fe, Mn, Cd and Ni. Most of the metals are toxic and most are associated with steel.

MATERIALS AND METHOD

Description of study area

The Area under study is given in Fig. 1 (Map of study area), it is located between longitudes $5^0\,42^1$ East and $5^0\,48^1$ East and between Latitudes $5^0\,29^1$ North and $5^0\,33^1$ North. The sampling stations are designated as A, B, C, D, E, F and G with sampling station A very near to the Delta Steel Company (DSC) and sampling station G is furthest from DSC along the Udu River. Each sampling station is separated from the next successive sampling station by 1 km distance.

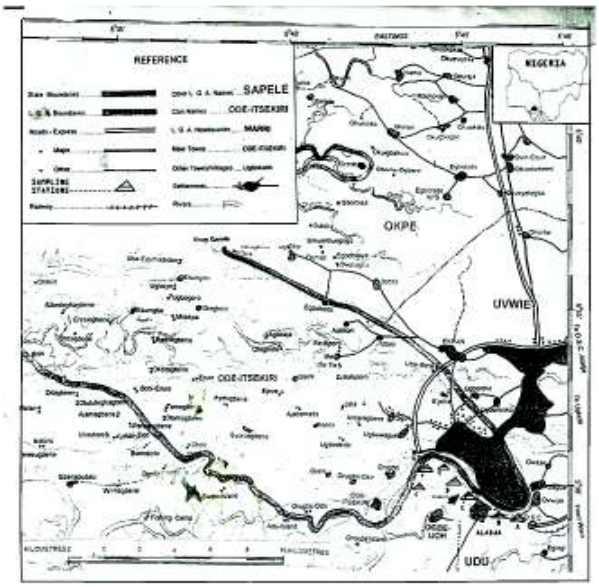

FIG 1: MAP OF STUDY AREA
***SOURCE**: Directorate Of Land and Survey, Governor's Office, Delta State, Nigeria*

Design of Study, Sample Collection/ preparation and preservation

Samples were collected twice every season for two years (i.e. dry and rainy seasons) starting from January 2007 to September 2008. The heavy metals determined in the leaves of the two plant species are Cu, Pb, Ni, Cd, Zn, Fe and Mn. Samples were also collected from two points around Ovwuvwe River at Abraka Inland (Otorho) in Ethiope East Local Government Area of Delta State, Nigeria these served as control samples. Fresh shoots of leaves were collected using sharp plastic knives and these were transferred to the laboratory in polythene bags inside coolers containing iced blocks where, they were oven dried at 60 ^{0}C for 24 hrs.

Analytical Procedures

Digestion of Leave Samples: To 0.5g of dried and well ground leave samples in a kjedhahl flask was added 5 ml of concentrated nitric acid, 1 ml of 60% perchloric acid and finally 0.5 ml of concentrated sulphuric acid, details as described in manual by Allens (1989).

AAS Analysis of Digest Solution: The digest solution was aspirated into an atomi absorption spectrophotometer (AAS) that has already been calibrated with standard solutions of the metals being determined as described by Allens (1989).

Quality Assurance Programme

A quality assurance programme which included observation of general laboratory precautions and cleanliness, establishment of a good representative sampling programme, determination of blanks and analysis of duplicates was put in place. In addition to these the percentage recoveries of each metal was determined from samples of both oil palm and almond tree as follow: Two grammes of well ground leave sample was spiked with a known concentration of metal standard solution and oven dried. It was then homogenized using a glass rod. This spiked and homogenized sample (0.5g) was analyzed using the same procedure as described above for the samples. The concentration obtained in this case is the concentration of the re-analysis of the same sample after it has been spiked with the metal standards. Results of percentage recoveries of the metals from oil palm leave samples are 93.4%, 91.5%, 97.2%, 92.8%, 101%, 99%, and 103% for Cu, Pb, Mi, Cd, Zn, Fe and Mn respectively. The percentage recoveries of metals from almond tree leaves are 94%, 96.7%, 93.3%, 91.8%, 101%, 95% and 99% for Cu, Pb, Ni, Cd, Zn, Fe and Mn respectively. The percentage recoveries for all the metals are within the acceptable range of 90 – 110 %.

Statistical Analysis: Analysis of Variance (ANOVA-single factor) from Microsoft Excel (2007 version) was used to compare the means of the concentrations of the heavy metals in each of the plants in the four seasons (two dry seasons and two rainy seasons). T-

test (two sample, assuming equal variance) from Microsoft Excel (2007 version) was used to compare the means of the concentrations of heavy metals in each plant of study area with that of control. The concentrations of heavy metals in each plants were also correlated with each other using the Pearson (2-tailed) correlation from the Statistical package of the Social Sciences (SPSS) (version 17).

RESULTS AND DISCUSSION

The results are given in Tables 1 - 6. The concentrations of the metals in oil palm leaves (Table 1) and almond tree leaves (Table 2) for the four seasons studied are not statistically significantly different from one another when compared using analysis of variance (ANOVA – single factor). Table 3 shows a comparison of concentrations of the seven heavy metals in oil palm leaves of study area with those of control area and Table 4 shows a comparison of the concentration of the seven heavy metal in almond leaves of study area with those of control area. With the exception Cd in almonds leaves, the concentrations of all heavy metals in leaves of both oil palm and almonds in the study area are statistically significantly higher than their corresponding concentrations in the control area when compared using T - test (two sample, assuming equal variance). This shows that the study area is polluted with respect to these heavy metals. The concentrations of heavy metals in the study area were also correlated with each other (Table 5).

Table 1: Average concentration of the metals in leaves of oil palm (*Elaeis guineensis*) in each season

Table 2: Average concentration of the heavy metals in leaves of almond tree (*Prunus dulcis*) in each of the seasons.

Heavy Metals	First dry season	First rainy season	Second dry season	Second rainy season
Cu (mg/kg)	46 ± 18	47 ± 20	46 ± 18	46 ± 20
Pb (mg/kg)	142 ± 110	145 ± 110	141 ± 110	145 ± 110
Cd (mg/kg)	6.4 ± 2.6	6.5 ± 2.6	6.5 ± 2.6	6.5 ± 2.5
Ni (mg/kg)	21.0 ± 4.2	21.0 ± 4.2	20.8 ± 4.1	21.5 ± 4.4
Fe (mg/kg)	1050 ± 190	1060 ± 200	1040 ± 190	1060 ± 200
Mn (mg/kg)	350 ± 180	356 ± 180	356 ± 190	357 ± 180
Zn (mg/kg)	230 ± 120	236 ± 120	232 ± 120	233 ± 120

Heavy Metals	First dry season	First rainy season	Second dry season	Second rainy season
Cu (mg/kg)	211 ± 68	216 ± 200	219 ± 71	229 ± 64
Pb (mg/kg)	184 ± 120	188 ± 130	187 ± 120	182 ± 130
Cd (mg/kg)	7.9 ± 3.3	8.1 ± 2.9	8.0 ± 2.7	8.5 ± 3.0
Zn (mg/kg)	611 ± 420	623 ± 430	633 ± 420	643 ± 430
Ni (mg/kg)	24.9 ± 6.7	26.0 ± 6.7	25.1 ± 7.6	27.4 ± 6.6
Fe (mg/kg)	1240 ± 570	1250 ± 570	1280 ± 570	1300 ± 590
Mn (mg/kg)	910 ± 720	931 ± 740	921 ± 690	921 ±740

Table 3: Concentrations of heavy metals in oil palm leaves in the study and control areas.

Heavy metals	Study area	Control area
Cu (mg/kg)	49 ± 18	16.1 ± 3.0
Pb (mg/kg)	114 ± 91	11.6 ± 1.7
Ni (mg/kg)	21.9 ± 5.6	7.2 ± 1.1
Cd (mg/kg)	6.8 ± 2.0	1.8 ± 0.1
Zn (mg/kg)	250 ± 120	20.3 ± 3.5
Fe (mg/kg)	1020 ± 240	26.8 ± 4.6
Mn (mg/kg)	430 ± 220	21.4 ± 2.0

Table 4: Concentrations of heavy metals in almond tree leaves in the study and control areas

Heavy metals	Study area	Control area
Cu (mg/kg)	212 ± 83	15.2 ± 1.2
Pb (mg/kg)	190 ± 120	13.6 ± 0.5
Ni (mg/kg)	24.9 ± 8.0	14.6 ± 0.7
Cd (mg/kg)	8.3 ± 3.1	6.20 ± 0.60
Zn (mg/kg)	680 ± 440	21.1 ± 1.4
Fe (mg/kg)	1230 ± 590	23.1 ± 4.8
Mn (mg/kg)	1000 ± 640	17.0 ± 2.5

Table 5: Pearson (2-tailed) correlation of heavy metals in leaves of oil palm (*Elaeis guineensis*)

	Cu	Pb	Ni	Cd	Zn	Fe
Cu						
Pb	0.587**					
Ni	0.896**	0.685**				
Cd	0.84**	0.602**	0.780**			
Zn	0.965**	0.649**	0.847**	0.881**		
Fe	0.884**	0.621**	0.827**	0.927**	0.902**	
Mn	0.828**	0.432**	0.687**	0.824**	0.799**	0.850**

*** Coefficient of correlation significant (∞= 0.01)*
** Coefficient of correlation significant (∞= 0.05)*

The results show that the seven heavy metals are correlated very strongly with each other, the coefficient of correlation in each case being significant at 99% confidence level. Pb and Cu (0.587), Ni and Cu (0.896), Ni and Pb (0.685), Cd and Cu (0.840). Cd and Pb (0.602), Cd and Ni (0.780), Zn and Cu (0.965), Zn and Pb (0.649), Zn and Ni (0.847), Zn and Cd (0.881), Fe and Cu (0.884), Fe and Pb (0.621), Fe and Ni (0.827), Fe and Cd (0.927), Fe and Zn (0.902), Mn and Cu

(0.828), Mn and Pb (0.432), Mn and Ni (0.687), Mn and Cd (0.827), Mn and Zn (0.799), and Mn and Fe (0.850). This indicates that all the heavy metals have identical sources. The source of the metal is most likely the iron and steel industry located in the area since there are no other notable industries or activities that can result in the release of all these heavy metals to the environment at such concentrations.

Table 6 shows a comparison of results of determination of heavy metals in plant from studies elsewhere with the results obtained from the present study. From the table, it is evident that the results obtained for this work are comparable with results obtained for other plants species elsewhere. The average concentration for Cu in Elaeis guineensis (49 ± 18 mg/kg) and prunus dulcis (212 ± 83 mg/kg) in the study area are comparable to the range of concentrations obtained for T*alium triangulare*, *Celisia trigna* and *Carclus oliterus* (25.1 – 56.8 mg/kg) from the industrial area of Lagos, *Agropyron spp* (8.10 mg/kg) in mining area of Arkansas river, Heliphica spp (9.00 mg/kg) in the sea Port of Cape York, Australia and *Achilla lanulosa* (11.2 mg/kg) of the mining area of Arkansas River in Leadville, Colorado. The average concentrations of Cu in the two species in the study area are higher than the concentration ranges normally encountered in plants (2.50 – 25.0 mg/kg) (Table 6) (Allens, 1989). This shows an enhancement in the concentration of Cu in the study area. This means that there has been anthropogenic input of Cu into the environment of the study area, i.e. the area is polluted with respect to Cu. The average concentration of Pb in *E. guineensis* (114 ± 91 mg/kg) in the study area is comparable with those obtained for *Achillia lanulosa* (52.0 mg/kg) in Arkansas River mining area, *Iris missouriensis* (23.4 mg/kg) of the same area *Hibiscus esculenta* (root) (0.50 ± 0.03 mg/kg), in Niger Delta oil prospecting area, *Hibiscus esculenta* (stem) (0.41 ± 0.02 mg/kg) *Hibiscus esculenta* (leaves) (0.37 ± 0.01 mg/kg) and *Hibiscus esculenta* (fruit) (0.22 ± 0.03 mg/kg) of the same area and in the same study. The average concentrations of Pb in the two species studied are also very much higher than the concentration ranges normally encountered in plant (0.05 – 3.00 mg/kg) (Table 6) thus showing that the area is polluted with respect to this metal. The average concentration of Ni in *E. guineensis* (21.9 ± 5.6 mg/kg) and *P. dulcis* (24.9 ± 8.0 mg/kg) are comparable with the range of concentrations found in three species: *Talium triagulare*, *Celisa trigna* and *Carclus oliterus* (1.33 – 2.06 mg/kg) and *Helophica spp* (1.70 mg/kg) of the mining area around Arkansas River, Leadville Colorado, USA. The average concentrations of Ni in both species also exceeds the concentration ranges normally encountered in plants (0.50 – 5.00 mg/kg) (Table 6) showing that the area is polluted with respect to Ni.

Table 6: Results of determinants of heavy metals in plant from studies elsewhere compared with result for perfect study and re-concentration ranges normally encountered in plants.

Country	Location	Major activities in area	Species of plant	Cu (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	Zn (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	References
Nigeria	Lagos	Industrial	(i) Talim triangulare (ii) Celisa trigna (iii) Carclus olitarus	25.1 – 56.8		1.33 – 2.06	1.13 -1.67				Yusuf et al., 2003
Nigeria	Niger Delta	Oil prospecting	(i) Hibiscus esculenta (root)	0.20 ± 0.03	0.50 ± 0.03	0.16 ± 0.04	-	1.83 ± 0.05			Gbaruka and Friday, 2007
			(ii) Hibiscus esculenta (stem)	0.16 ± 0.01	0.41 ± 0.02	0.41 ± 0.01		1.10 ± 0.00			
			(iii) Hibiscus esculenta (leaf)	0.16 ± 0.01	0.37 ± 0.01	0.13 ± 0.01		0.88 ± 0.02			
			(iii) Hibiscus esculenta (fruit)	0.12 ±0.030	0.22 ± 0.03	0.08 ± 0.01		0.65 ± 0.03			
USA	Arkansas River, Leadville Colorado	Mining	Agropyron spp	8.10	1.06		0.27	61.0			Levy et al., 1992
Austria	Cape York	Sea Port	Helophila spp	9.00	1.00	1.70	0.50	67.0			Denton et al, 1980
USA	Arkansas River, Leadville Colorado	Mining	Achilia Lanulosa	11.2	52.0		7.27	517			Levy et al., 1992
USA	Arkansas River, Leadville Colorado	Mining	Iris missouriensis	4.70	23.4		21.0	40.3			Levy et al., 1992
Nigeria	Udu River (Aladja/Ovwian)	Steel manufacturing	Eleais guineensis	49 ± 180	114 ± 91	21.9 ± 5.6	6.8 ± 2.0	250 ± 120	1020 ± 240	430 ± 220	Present study
Nigeria	Udu River (Aladja/Ovwian)	Steel manufacturing	Prumis dulcis	212 ± 83	190 ± 120	241 ± 8.0	8.3 ± 3.1	680 ± 440	1230 ± 590	1000 ± 640	Present study
Concentration ranges normally encountered in plant				2.50 – 25.0	0.05 – 3.00	0.50 – 5.00	0.01 –0.30	15.0 – 100	40 – 500	50 – 1000	Allens 1989

The average concentrations of Cd in *E. guineensis* (6.8 ± 2.0 mg/kg) and *P. dulcis* (8.3 ±3.1 mg/kg) are comparable to concentration ranges obtained for three species: *Talium triangulare*, *Celisia trigna* and *Carclus oliterus* (1.13 – 1.67 mg/kg), *Achillia lanulosa* (7.27 mg/kg) and *Iris missouriensis* (21.0 mg/kg). The average concentrations of Cd in the two species of plants in the study area also exceed the concentration range normally encountered in plant materials (0.01 – 0.30 mg/kg) (Table 6). This also indicates that the area may be polluted with respect to Cd. The average concentration of Fe in *E. guineensis* (1020 ± 240 mg/kg) and *P. dulcis* (1230 ± 590 mg/kg) by far exceeds the normal concentration range of Fe encountered in plant materials (40.0 – 500 mg/kg) (Table 6) which also indicates that the area is polluted with respect to Fe. The average concentrations of Mn in *E. guineensis* (430 ± 220 mg/kg) and P. dulcis (1000 ± 640 mg/kg) appears to fall within the concentration ranges normally encountered in plant materials (50 – 1000 mg/kg). Concentration of Mn in *P. dulcis* (1000 ± 640 mg/kg) appears to be in the high side of this range, thus indicating the increasing input of Mn to the environment.

CONCLUSION

Concentrations of heavy metals were determined in the leaves of oil palm tree (*E. guineensis*) and almond tree (*P. dulcis*). The concentrations found in the study area were statistically significantly higher than concentrations of heavy metals in the control area for each of the heavy metals. The average concentration of the heavy metals in the leaves of these two plant species were comparable to results obtained elsewhere i.e. areas which could be said to be polluted. The average concentration of the seven heavy metals in the leaves of the two plants were also higher than ranges of concentrations of the corresponding heavy metals normally encountered in plant material. These also go to show that the area is polluted with respect to the seven heavy metals. Anthropogenic input of the metals has also been established.

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