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Archives of Applied Science Research, 2011, 3 (1):9-16

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ISSN 0975-508X
CODEN (USA) AASRC9

Trace metal Contents in Medicinal Plants Growing in Crude Oil Polluted Soil in Akwa Ibom State, Southeastern Nigeria

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ABSTRACT

Samples of Anthocleista djalonensis (AD), Costus afer (CA) Anthocleista vogelii (AV), Raphia hookeri (RH) and Alstonia boonei (AB) plants to growing in oil polluted soil were analysed for their trace metal contents. Iron (Fe), manganese (Mn), lithium (Li), zinc (Zn), copper (Cu), cadmium (Cd), chromium (Cr), lead (Pb), cobalt (Co), vanadium (V), molybdenum (Cd), mercury (Hg) and selenium (Se) were analysed using absorption spectrophotometer (AAS). Results indicate the order of mobility of trace metal to be: Mn > Fe > Zn > Li > Pb > Co > Cu > Mo > Cd > Hg > V > Se > Cr. Trace metal contents were systematically higher in oil polluted than in unpolluted soils except Li and Co. Plants that adsorbed the greatest quantity of trace metal from the soil in increasing order were: AD > and CA > AV > RH and AB. Results also show that AD and CA plants can be used for phytoremedication of polluted soils of trace metals. Using these plants for consumption by man and animals may pose a serious health risk.

Keywords: Trace metal contents, medicinal plants, oil polluted soil, phytoremediation, Nigeria.

INTRODUCTION

Trace metal pollution in soil has become a serious problem for agriculture as well as human health because these metals may be taken up by plants in toxic levels and transferred to man through the food chain. These metals have been found to exhibit damaging effects on man and animals. Above certain concentrations and over a narrow range, the heavy metals turn into toxins [1, 2]. Mercury is particularly a toxic heavy metal even at low level and has led to the greatest death toll in the world [3, 4]. Several workers who have conducted research on heavy metal contamination in plants [5-8] have also made similar observations.

The aim of the present work was to investigate the accumulation of trace metals by leaves of plants growing in soils contaminated with crude oil and to assess the interrelationship among these metals in plants.

MATERIALS AND METHOD

Study Area

The study was carried out in 'Mbo Local Government Area; Akwa Ibom State where oil pollution was reported in October 2008. Mbo is bound to the North by Urueoffong Oruko and Udung Uko Local Government Areas to the East by Cross River State while sharing the west boundary with Esit Eket and Ibeno Local Government Areas. The area is surrounded by the tributary of Atlantic Ocean and the Qua Iboe River, which flows from Mbo to some parts of Ikot Abasi Local Government Area in Akwa Ibom State. The area lies between latitudes 4 15′ and 5 00′ N and Longitudes 7 05′ and 8 00′.

Climate of the Area

The climate is humid tropical type. The climate conditions of the area are influenced by the rain-bearing South-Westerly wind blowing over the Atlantic Ocean and by the dry North East Trade Winds from the Sahara desert. The area is characterized by two main seasons; the wet or rainy season (April – October) and the dry season (November – March). The mean annual rainfall is 2,472mm distributed throughout the year. The rainfall pattern is bimodal with two peak periods in July and October, 2 – 3 weeks of moisture stress period in August, popularly known as "August break". Temperatures are high and change only slightly during the year. The mean annual maximum temperature is about 29^{o}C while the mean annual minimum is about 21^{0}C. Temperature is lower in the raining months than in the dry months. Relative humidity is high especially in the wet season than in the dry season; usually with no month less than 60%.

Geology of the Area

The area lies entirely on the coastal plain sands of Southeastern Nigeria where sediments are supplied by the Cross River, the Qua Iboe River, Imo River and the Gulf of Guinea. The underlying parent materials consist of coastal plain sands [9]. The area generally has an undulating topography which breaks at river and stream valleys. The soils are derived from sand deposits and shales, sandy parent materials which are highly weathered and are dominated by low activity clay [10]. The clay contents of the soil increase down the profiles while sand fraction decreases. The soil increases down the profiles while sand fraction decreases. The soils are generally very susceptible to accelerated erosion [11]. The soil mapping unit as classified by [12] shows that the soils belong mainly to the ultisols order [13].

Vegetation and Land Use

The vegetation of the area falls within the tropical rainforest belt where Akwa Ibom State belongs. Lands are used for subsistence agriculture. Major produce include cassava, cocoyam, okra and other vegetables.

Field Studies

Five representative plant samples were collected randomly from crude oil polluted soil and 100m away from the polluted soil, respectively. The choice of plants was based on their general growth pattern on the contaminated soil and the availability and significance at the study area. For each plant, depending on the blomass, two to six replicate were collected from each location within an area of 4m^2. The samples were mixed to form a composite of the particular plant and transported in properly labeled brown envelopes to the laboratory for analysis. Plants sample were identified by a taxonomist in the Department of Botany and Ecological Studies, University of Uyo, Nigeria.

Preparation of Plant Samples for Analysis

Plant samples were gently washed under running tap water to remove adhered soil particles and then rinsed with distilled water before separating into roots and shoots out of which only the leaves used for analysis. The samples were air dried to remove the residual moisture and then oven dried for 48 hours at 80^0C to constant mass. The dried samples were ground using agate mortar and pestle and sieved to obtained particles less than 2mm and stored in an air tight container for analysis.

Laboratory Analysis

The leaves off each plant were analysed separately for trace metal contents (manganese (Mn), Iron (Fe), zinc (Zn), lithium (Li), copper (Cu), cadmium (Cd), chromium (Cr), lead (Pd), cobalt (Co), vanadium (V), molybdenum (Mo), mercury (Hg) and selenium (Se). 1g of <2mm fraction of plant samples was weighed into porcelain crucibles and ignited in a muffle furnace for 6 hours at a temperature between 45 – 500^0C until a grey-white ash was obtained. The ash samples were allowed to cool and 10ml of $2MHNO_3$ was added to each sample. The solution was evaporated to near dryness on a hot plate and the cooled residues were re-dissolved in 10ml $2NHNO_3$ and filtered in 25ml volumetric flasks. Both the crucible and the filter paper were washed into the flasks; made up to mark with deionized water and then stored in polyethylene tubes for instrumental analysis. Atomic absorption spectrophotometer (Buck Scientific Zoo) was used to analysis plant digests for each of the trace metal studied.

Statistical Analysis

The data were analysed for range, means and standard deviation. The student t-test was used to compare trace metal concentration in polluted (P) and unpolluted (UP) plant samples. Range was calculated as the difference between the highest and the lowest value. The t-test was computed as follows:

$$x = \frac{\bar{x} - \bar{y}}{\sqrt{\frac{rx^2}{Nx} + \frac{n^2}{Ny}}}$$

$$\text{But } ry = \sqrt{\frac{?\,(x - \bar{x})^2}{N - 1}}$$

$$\text{But } ry = \sqrt{\frac{?\,(y - \bar{y})^2}{N - 1}}$$

and df = Nx + Ny – 2 = (5+5) – 2 = 10 – 2 = 8.

Where:

t	=	Student t-value called t-calculated (t-cal)
$\bar{x}$	=	Mean of group one observation (x); polluted plant sample.
$\bar{y}$	=	Mean of group two observation (T); unpolluted plant samples.
N	=	Number of observation in each group.

Also, correlation coefficients were used to examine inter-relationship existing among the heavy metals in polluted and unpolluted soil. The model was specified as follows:

$$y = \frac{N?\,xy - ?\,xy}{\sqrt{N?\,xy^2 - (?\,x)^2}\sqrt{N?\,y^2 - (?\,y)^2}}$$

Where: r = Correlation co-efficient

x, y and N are defined as in t-test model.

Table 1: Heavy Contents of Plants Growing in Polluted and Unpolluted Soils

PLANT		ELEMENTS Fe (mg/kg)	Mn (mg/kg)	Li (mg/kg)	Zn (mg/kg)	Cu (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Co (mg/kg)	V (mg/kg)	Mo (mg/kg)	Hg (mg/kg)	Se (mg/kg)
AD	P	110.9	179.69	2.77	29.14	1.09	0.29	0.05	1.21	1.03	0.24	0.33	0.19	0.11
	UP	73.45	165.16	4.89	16.86	0.15	0.25	0.11	0.71	1.48	0.21	0.29	0.11	0.12
CA	P	83.97	138.10	2.37	21.80	0.15	0.25	0.03	0.97	0.81	0.15	0.28	0.16	0.17
	UP	58.29	131.26	4.79	13.88	0.11	0.23	0.07	0.55	1.15	0.16	0.23	0.15	0.09
AV	P	61.49	120.02	1.35	11.48	0.12	0.28	0.01	0.72	0.51	0.12	0.21	0.08	0.08
	UP	47.12	117.78	3.48	7.37	0.07	0.16	0.03	0.44	0.99	0.08	0.19	0.08	0.05
RH	P	28.99	106.00	0.60	10.68	0.08	0.11	0.01	0.43	0.29	0.05	0.19	0.12	0.05
	UP	34.70	106.89	3.20	4.67	0.04	0.11	0.01	0.19	0.76	0.06	0.11	0.04	0.03
AB	P	21.74	86.53	0.31	7.99	0.03	0.08	0.02	0.21	0.24	0.01	0.11	0.08	0.01
	UP	24.21	87.75	3.13	3.11	0.01	0.05	0.01	0.11	0.39	0.01	0.08	0.01	0.05
Range	P	21.74-110.09	86.53-179.69	0.31-2.77	7.99-29.14	0.03-1.09	0.08-0.29	0.01-0.05	0.21-1.21	0.24-1.03	0.01-0.24	0.11-0.33	0.08-0.19	0.01-0.11
	UP	24.21-73.45	87.75-165.16	3.13-4.89	3.11-16.86	0.01-0.15	0.05-0.25	0.01-0.11	0.11-0.71	0.38-1.48	0.01-0.21	0.08-0.29	0.01-0.10	0.05-0.12
$\bar{X}$+SD	P	61.26±37.09	126±35.44	1.48±1.08	16.215±8.93	0.29±0.45	0.20±0.10	0.02±0.02	0.71±0.40	0.58±0.34	0.12±0.09	0.22±0.09	0.13±0.05	0.09±0.04
	UP	47.55±19.34	121.77±29.01	3.90±0.87	9.18±5.75	0.08±0.05	0.16±0.08	0.05±0.04	0.40±0.25	0.95±0.41	0.10±0.08	0.18±0.09	0.08±0.05	0.07±0.04

AD – Anthocleista djalonensis, CA – Costus afer, AV – Anthocleista vogelii, RH – Raphia hookeri, AB – Alstonia boonei
$\bar{x}$ + SD – Mean ± Standard Deviation, P – Polluted, UP – Unpolluted.

RESULTS AND DISCUSSION

The results of the trace metal concentrations determined in plant tissue are presented in Table 1. The concentration of metals in plants varied widely in different plants studied. The highest concentrations were observed for Fe and Mn in *Anthocleista djalonensis* with values of 110.09 and 179. 09mgkg for P and UP soils (73.42 and 165.16mgkg^{-1}). The values for *Anthocleista vogelii* were 61.49 and 120.02 and 47.12 and 117.78mgkg^{-1} for P and UP soils, respectively. *Costus afer* (CA) had values of 83.97 and 138.10 and 58.29 and 131.26 mg/kg for Fe and Mn, respectively.

Raphia hookeri and *Alstonia boonei* had Fe and Mn levels of 29.00, 106.00 and 34.70, 106.90mgkg^{1}, 21.74, 86.53 and 24.21 and 87.75mgkg^{-1} for P and UP soils, respectively copper was relatively low in *Anthocleista djalonensis* and *Alstonia boonei* while Cd, Cr,V,Mo, Hg and Se were very low in the various plants. Leads content was relatively high in the plants. Zinc was the third most abundant trace metal in both P and UP soils. The mobility of trace metals in the plants studied in terms of abundance were in the order Mn > Fe > Zn > Li > Pb > Co > MO > Cd > V > Cu > Hg > Se > Cr.

Table 2 presents the comparison of mean heavy metal contents of plants growing on polluted and unpolluted soils. The mean concentrations in the leaves of the five plants varied from plant to plant. The concentration of Fe, Mn, Li,Zn and Mo were high in *Anthocleistat djalonensis* and *Costus afer*, respectively. Heavy metals were lowest *Alstonia boonei*. Comparing the heavy metals in the plants growing in the polluted and unpolluted sites, a substantial amount of Fe and Mn existed in the leaves of *Anthocleista djalenensis* and *Costus afer*. Kabata Pendias and Pendias [14] had made similar observation. Concentration of Cd, Cr V and Se were lower both in polluted and unpolluted plants than the normal range. Fe, Zn, Co and Mo were significant at 1% probability level. Four trace metals, Mn, Li, Pb and Hg were significant at 5% probability level.

Table 2: Comparison of Heavy Metal Contents of Plants Growing on Polluted and Unpolluted

Heavy Metal (mg/kg)	Polluted	Unpolluted	t-value	Sig.
Fe	61.26	47.55	-11.49	0.000***
Mn	126.07	121.77	7.88	0.001**
Li	1.48	3.89	-3.53	0.24**
Zn	16.23	9.18	4.83	0.008***
Cu	0.29	0.07	1.20	0.296
Cd	0.20	0.16	2.09	0.105*
Cr	0.24	0.05	-1.98	0.119*
Pb	0.71	0.39	4.42	0.12**
Co	0.58	0.95	-5.97	0.004***
V	0.11	0.10	1.10	0.332
Mo	0.22	0.18	-12.91	0.000***
Hg	0.13	0.08	2.79	0.050**
Se	0.09	0.69	0.79	0.476

****Significant at 1%; **Significant at 5%; *Significant at 10%.*

Table 3 shows the relationship among the various trace metals obtained from different plants growing in the unpolluted soils. Iron correlated positively and significantly with Mn (r = 0.970**), Li (r = 0.990**), Zn (r = 0.951**), Cd (r = 0.901*), Cr (r = 0.897*), Pb (r = 0.992**), Co (r = 0.993**), V (r = 0.987**) and Mo (r = 0.963**). Fe had the highest correlation relationship with other trace metals from plants in the polluted soil. Highly significant and positive relationship exists between Mn and Zn (r = 0.968**), Pb (r = 0.970**), V (r = 0.990**), Mo (r = 0.971**).

Li correlated significantly with Pb (r = 0.986**), Co (r = 0.994**), V (r = 0.961**), Mo (r = 0.968**) while Zn was positively related to Co (r = 0.978**), Pb related significantly with Mo (r = 986**) and V (r = 0.985**). Other significant correlation relationships found were for V and Mo.

Table 3: Interrelationship among Concentration of Heavy Metals in Plants Growing on Unpolluted Soils

	Fe	Mn	Li	Zn	Cu	Cd	Cr	Pb	Co	V	Mo	Hg	Se
Fe	1												
Mn	0.986**	1											
Li	0.926*	0.878*	1										
Zn	0.977**	0.954*	0.984**	1									
Cu	0.977**	0.985**	0.946*	0.988**	1								
Cd	0.985**	0.947*	0.941*	0.974**	0.983**	1							
Cr	0.950*	0.955*	0.952*	0.976**	0.966**	0.910*	1						
Pb	0.990**	0.957*	0.913*	0.963**	0.981**	0.982**	0.924*	1					
Co	0.989**	0.980**	0.875**	0.942*	0.980**	0.977**	0.902*	0.973**	1				
V	0.987**	0.976**	0.966**	0.995**	0.996**	0.978**	0.914*	0.964**	0.964**	1			
Mo	0.994**	0.970**	0.920*	0.971**	0.988**	0.979**	0.943*	0.998**	0.976**	0.974**	1		
Hg	0.851	0.760	0.896*	0.878	0.853	0.927*	0.757	0.874	0.835	0.858	0.854	1	
Se	0.875	0.857	0.937*	0.933*	0.894*	0.842	0.965**	0.874	0.794	0.906*	0.890*	0.732	1

In polluted soil (Table 4), Fe had significant interrelationship with all trace metals studied except Hg and Se. Similarly, Se had no significant relationship with any of the heavy metals studied. Manganese (Mn), zinc (Zn), Copper (Cu), chromium (Cr), lead (Pb), cobalt (Co), vanadium (V) and molybdenum (Mo) did not have significant relationship with Hg, likewise lithium (Li) with cobalt (Co) and so also was mercury (Hg) and selenium (Se).

The highest quantity of trace metal accumulation by plants were as follows AD > CA> Av> RH > AB. It can be noticed that metal contents in the five plants were more in the polluted than in unpolluted soils and this agrees with the works of Baker *et al.* [15], that certain plants not only accumulate metals in the plant roots trasnslocate the accumulated metals from the root to the leaf or shoot. *Anthocleista djalonensis* plant can thrive in polluted and unpolluted soils based on the levels of Fe and Mn in its leaves, implying that these plants can be used for phytoremediation. The concentrations of Mn, Zn, Cu, Cd, Pb, Hg, Se and V exceeded the normal range in plants as reported by Kabata- Pendias and Pendias [16].

Table 4: Interrelationship among Concentration of Heavy Metals in Plants Growing in Oil Polluted Soils

	Fe	Mn	Li	Zn	Cu	Cd	Cr	Pb	Co	V	Mo	Hg	Se
Fe	1												
Mn	0.970**	1											
Li	0.990**	0.950*	1										
Zn	0.951*	0.968**	0.958*	1									
Cu	0.797	0.895*	0.737	0.854	1								
Cd	0.901*	0.820	0.872	0.726	0.576	1							
Cr	0.879*	0.937*	0.856	0.957*	0.957*	0.614	1						
Pb	0.992**	0.970**	0.986**	0.943*	0.776	0.905*	0.850	1					
Co	0.993**	0.968**	0.994**	0.978**	0.802	0.846	0.907*	0.907*	1				
V	0.986**	0.990**	0.961**	0.940*	0.853	0.893*	0.893*	0.985**	0.971**	1			
Mo	0.963**	0.971**	0.968**	0.948*	0.768	0.846	0.850	0.986**	0.961**	0.968**	1		
Hg	0.811	0.870	0.848	0.941*	0.760	0.511	0.885*	0.827	0.864	0.806	0.882*	1	
Se	0.779	0.676	0.851	0.730	0.292	0.737	0.502	0.815	0.792	0.703	0.813	0.702	1

This implies that oil pollution increases the concentration of heavy metals in plants [17]. This also supports Treshow [18] research that some plants, especially vegetables may have some health implications as they are bio-indicators of heavy metals. Ogri [19] and Bakirdere and Yaman [20] reported that heavy metals in oil polluted soils if present in high amount in plants are capable of making the plants leaves toxic and harmful to man and livestock if ingested or consumed as food.

CONCLUSIONS

Our study proves that the five plants studied (AD, CA, AV, RH and AB) accumulate metals in their leaves in large amount, particularly Mn, Fe, Zn and Li and thus can be recommended for phytoremediation in oil polluted sites especially *Anthocleista djaloneensis*. The contents of metals in the examined plants were higher than permitted concentrations for Mn, Zn, Cd, Pb, Hg, Se and may probably be toxic to man as well as animals grazing on them, thereby leading to health hazards and ultimately death. There is therefore the urgent need to bioremediate such soils.

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