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Full Length Research Paper

Heavy metal concentrations in plants growing in crude oil contaminated soil in Akwa Ibom State, South-Eastern Nigeria

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A field study was conducted to assess heavy metal concentrations in plants grown on crude oil contaminated soil in Akwa Ibom State. Plant samples obtained from polluted and unpolluted (control) sites were digested and analysed for manganese (Mn), iron (Fe), lithium (Li), zinc (Zn), copper (Cu), cadmium (Cd), chromium (Cr), lead (Pb), cobalt (Co), vanadium (V), molybdenum (Mo), mercury (Hg) and selenium (Se). The selected plants were *Dissotis erecta* (DE), *Urena lobata* (UL), *Selaginella myosurus* (SM), *Diodia scandens* (DS) and *Pityrogramma calomelanos* (PC). Considerable amount of Mn and Fe were found to accumulate in all the plants grown on contaminated soil, while other elements assessed were obtained in trace amount. The order of bioacculation of trace metals were Mn > Fe > Zn > Li > Co > Pb > Mo > Cd > V = Hg > Cu = Se > Cr, while the plants accumulated the highest amount of trace metals were found to be in the order of: *Dissotis erecta* (DE) > *U. lobata* (UL) > *S. myosurus* (SM) > *D. scandens* (DS) > *P. calomelanos* (PC) indicating that DE and UL plants can be used for remediation of contaminated soils. The result of the correlation analysis showed positive relationships among the trace metals in both contaminated and uncontaminated soils. Results also imply that consuming plants growing in the vicinity of oil spills may pose a health risk to humans and animals.

Key words: Crude oil, contamination, heavy metal, phytoremediation, Nigeria.

INTRODUCTION

Anthropogenic activities have represented a growing environmental problem affecting food quality and human health in the Niger Delta region of Nigeria. Nigeria as a major producer and exporter of crude petroleum oil continues to experience oil spills and this exposes the environment to hazards and its attendant effects on agricultural lands as well as on plant growth and development (Agbogidi et al., 2005). Cases of oil pollution have been reported in the area and notable areas of oil pollution menace include community which the plants were sampled.

Heavy metals may have significant toxic and hazardous effects on human health, especially cadmium and lead which are contained in crude oil. Heavy metal contamination affects the bio-sphere in many places worldwide (Cunningham and Lee, 1997; Raskin and Ensley, 2000; Meagher, 2000). Certain plants do not only accumulate metals in the roots but also translocate from roots to the leaves or shoots (Baker et al., 2000). Toxic metal pollution of waters and soils is a major environmental problem and most conventional remediation approaches do not provide acceptable solutions (Salt et al., 1995). Medicinal plants are known to grow in various adverse environmental conditions including crude oil contaminated soils, hence the objectives of this study was to assess heavy metal contents in some plants species growing in crude oil contaminated soil.

MATERIALS AND METHODS

The study area

This study was carried out in Mbo Local Government Area, Akwa Ibom State. Mbo is bound to the North by Urueoffong Oruko and

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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 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 of the study area is humid tropical type. The climatic conditions of the area are influenced by the rain-bearing South-westerly wind from the Atlantic Ocean and by the dry North East Trade Winds from the Sahara desert (DHV Consultants, 1995; SLUS-AK, 1989). The area is therefore characterised by two main seasons; the wet or rainy season (April - October) and the dry season (November - March). The mean annual rainfall is 2,472 mm distributed throughout the year. The rainfall pattern is bimodal with two peak periods in July and October, and 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°C while the mean annual minimum is about 21°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 South Eastern 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 (Enwezor et al., 1981). 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 (Udo and Sobulo, 1981). The clay contents of the soil increase down the profiles while sand fraction decreases. The soils are generally very susceptible to accelerated erosion (SLUS-AK, 1989). The soil mapping unit as classified by USDA (1972) shows that the soils belong mainly to the ultisols order (Enwezor et al., 1990).

Vegetation and land use

The vegetation of the area falls within the tropical rainforest belt where Akwa Ibom State belongs.

Field studies

Plants sampling

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

Preparation of 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 were used. The samples were air dried to remove the residual moisture and then oven dried for 48 h at 80°C. The dried samples were ground using agate mortar and pestle and sieved to obtain and stored in an air tight container for analysis (Udo and Ogunwale, 1986).

Laboratory analysis

The leaves of each plant were analysed separately for heavy metal contents. 1 g of < 2 mm fraction of plant samples was weighed into porcelain crucibles and ignited in a muffle furnace for 6 h at a temperature between 45 - 500°C until a grey-white ash was obtained. The ash samples were allowed to cool and 10 ml 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 10 ml $2NHNO_3$ and filtered into 25 ml 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 analyse plant digests for each of the heavy metal studied (Table 1).

Statistical analysis

The data were analyzed for range, means and standard deviation. The Least Significant Difference (LSD) was used to compare differences in each heavy metal within treatments while student t-test was used to compare heavy 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:

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

$$\text{But } \bar{y}x = \sqrt{\frac{\Sigma(x - \bar{x})^2}{N - 1}}$$

$$ry = \sqrt{\frac{\Sigma(y - \bar{y})^2}{N - 1}}$$

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

Where:
t = Student t-value called t-calculation (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 analysis was used to examine inter-relationship existing among the heavy metal in respective group (polluted and unpolluted). The model was specified as follows:

Table 1. Heavy metal concentrations of plants growing in polluted and unpolluted soils.

Plant		Elements												
		Fe	Mn	Li	Zn	Cu	Cd	Cr	Pb	Co	V	Mo	Hg	Se
DE	P	95.84	208.35	8.05	16.85	0.16	0.32	0.08	0.65	1.72	0.21	0.32	0.20	0.11
	UP	73.41	166.23	9.49	20.98	0.12	0.29	0.07	0.61	2.63	0.19	0.17	0.12	0.07
UL	P	73.00	195.29	7.80	19.61	0.11	0.23	0.04	0.51	1.44	0.24	0.28	0.24	0.15
	UP	48.54	120.20	9.37	13.21	0.05	0.15	0.05	0.48	2.23	0.15	0.12	0.16	0.04
SN	P	64.96	155.83	7.61	9.82	0.07	0.12	0.01	0.28	1.37	0.09	0.23	0.11	0.08
	UP	39.82	106.21	8.51	8.39	0.05	0.11	0.01	0.25	1.12	0.11	0.07	0.05	0.01
DS	P	45.96	134.37	6.57	9.44	0.03	0.17	0.01	0.23	0.91	0.07	0.16	0.05	0.04
	UP	30.37	77.73	7.65	7.77	0.03	0.05	0.01	0.17	0.88	0.07	0.03	0.13	0.03
PC	P	17.37	117.73	5.63	6.24	0.03	0.081	0.01	0.15	0.71	0.03	0.08	0.03	0.01
	UP	28.30	71.16	7.61	5.93	0.01	0.02	0.01	0.08	0.64	0.04	0.03	0.03	0.01
Range	P	17.36 - 95.84	17.73 - 20.35	5.63 - 8.05	6.24 - 19.61	0.03 - 0.16	0.08 - 0.32	0.01 - 0.08	0.65 - 0.75	0.71 - 1.72	0.05 - 0.24	0.08 - 0.32	0.03 - 0.24	0.01- 0.15
	UP	28.30 - 73.41	01.16 - 66.23	7.61 - 9.49	5.95 - 20.98	0.01 - 0.12	0.03 - 0.29	0.01 ± 0.07	0.08 - 0.61	0.64 - 2.63	0.04 - 0.18	0.03 - 0.17	0.03 - 0.16	0.07-0.07
X ± SD	P	59.43 ± 29.54	162.31 ± 38.78	7.12 ± 1.02	12.39 ± 5.60	0.08 ± 0.06	0.18 ± 0.09	0.03 ± 0.03	0.36 ± 0.21	1.23 ± 0.41	0.13 ± 0.09	0.21 ± 0.10	0.13±0.09	0.08 ±0.05
	UP	44.09 ± 18.27	108.30 ± 38.13	8.53 ± 0.90	11.26 ± 6.06	0.053 ± 0.04	0.13 ± 0.10	0.03 ± 0.02	0.32 ± 0.22	1.50 ± 0.88	0.11 ± 0.06	0.08 ± 0.06	0.10±0.06	0.032 ±0.02

DE – *Dissotis erecta,* UL – *Urena lobata*, SM – *Selaginella myosurus*, DS – *Diodia scandens*, PC – *Pityrogramma calomelanos*. x±SD – Mean ±Standard Deviation, P – Pollu d, UP – Unpolluted.

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

Where

r = Correlation co-efficient
x, y and N are defined as in t-test model.

RESULTS AND DISCUSSION

Concentrations of heavy metals varied among the plant species as shown in Table 1. The data indicated that iron (Fe) and manganese (Mn) concentrations were higher in contaminated soils for *Dissotis erecta* with values of 95.84 and 208.35 $mgkg^{-1}$ than in UN soil, 73.41 and 166.23 $mgkg^{-1}$, for Fe and Mn, respectively. Iron and Mn contents in *Urena lobata* (UL) were 73.00 and 195.29 $mgkg^{-1}$ for polluted (P) soil and 48.54 and 120.20 $mgkg^{-1}$ for unpolluted (UP) soil. The values for *Selaginella myosurus* (SM) were 64.96 and 155.83 $mgkg^{-1}$ and 39.82 and 106.21 $mgkg^{-1}$ for P and UP soils, respectively. *Diodia scandens* (DS) and *Pityrogramma calomelonos* (PC) had Fe and Mn

Table 2. Comparison of heavy metal concentrations of plants growing on polluted and unpolluted soils.

Heavy metal (mg/kg)	Polluted	Unpolluted	t-value	Sig.
Fe	59.43	44.09	2.262	0.086*
Mn	162.31	108.30	9.351	0.001***
Li	7.12	8.53	-7.551	0.002***
Zn	12.39	11.26	0.673	0.538
Cu	0.078	0.053	2.483	0.068**
Cd	0.18	0.13	3.059	0.038**
Cr	0.03	0.03	1.000	0.374
Pb	0.36	0.32	5.510	0.005***
Co	1.23	1.50	-1.126	0.323
V	0.13	0.11	0.920	0.410
Mo	0.21	0.08	6.520	0.003***
Hg	0.13	0.10	0.881	0.428
Se	0.08	0.03	2.360	0.078*

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

values: 45.96, 134.97 and 30.37 and 77.73 $mgkg^{-1}$, 17.37, 117.73 and 28.30 and 71.16 $mgkg^{-1}$ for P and UP soils, respectively.

Lithium (Li) and Zn had much less concentrations in the various plant species than Fe and Mn (Table 1), with values ranging from 5.63 to 8.05 and 6.24 to 19.61 $mgkg^{-1}$ Li for P soil and 7.61 to 9.49 and 5.95 to 20.98 $mgkg^{-1}$ for UP soil, respectively. Copper, Cd, Cr, V, Mo, Hg and Se were very low in the various plant species. Lead content was relatively high in the plants. The mobility of trace metals in the plants studied in terms of abundance were in the order: Mn > Fe > Zn > Li > Co > Pb > Mo > Cd > V = Hg > Cu = Se > Cr. Table 2 presents the comparison of mean heavy metal contents of plants growing on polluted and unpolluted soils. The mean concentration of heavy metal in leaves of five plant species varies from species to species. The concentration of Fe, Mn, Li, Zn and Mo were high in *Dissotis erecta* and *Urena lobata*, respectively. However, heavy metals were lowest in *Pityrogramma calomelanos*. Comparing the heavy metals in the plants growing in the polluted sites and in unpolluted, a critical amount in Fe, Mn and existed in the leaves of *D. erecta* and *U. lobata* as reported by Kabata-Pendias and Pendias (1992).

Table 3 shows the relationship among the various trace metals obtained from different plants growing in the polluted soils. Iron correlated positively and significantly with Mn (r = 0.947*), Li (r = 0.968**), Cu (r = 0.917*), Pb (r = 0.924*), Co (r = 0.980**) and Mo (r = 0.990**). Manganese had the highest correlation relationship with other trace metals from plants in the polluted soil. Highly significant and positive relationship exists between Mn and Cu (r = 0.965**), Pb (r = 0.982**), V (r = 0.969**) and Hg (r = 0.961**). Lithium correlated significantly with Co and Mo while Zn was positively related to V (r = 0.995**), Hg (r = 0.983**), Se (r = 0.955*), Mo (r = 0.887*) and Pb (r = 0.909*). Other significant correlation relationships found were those of Cu and Cr, Pb, Co, V and Mo; Cd and Cr and Pb; Cr and Pb, Pb and Co, V, Mo and Hg; Co and Mo; V and Mo, Hg, Se; Mo and Se.

In unpolluted soil (Table 4), Fe had significant interrelationship with all trace metals studied except Hg and only Mo was positively related to Hg. Similarly, Mn, Li, Zn, Cd, Cr, Pb, Co and V did not have significant relationship with Hg. Apart from Hg, Cu did not have any significant relationship with V and Co.

In terms of plants that accumulate the highest quantity of trace metals in the soil, the order was as follows: *D. erecta* (DE), *U. lobata* (UL), *S. myosurus* (SM), *D. scandens* (DS) and *P. calomelanos* (PC). Tissue analysis of the five plant species growing in crude oil contaminated soil accumulate more heavy metals than those growing on uncontaminated soils.

This supports Baker et al. (1994) that certain plants not only accumulate metals in the plant roots but also translocate the accumulated metals from the root to the leaf or shoot. It is obvious from Table 1 that *D. erecta* can thrive in contaminated and uncontaminated soils based on the levels of Fe and Mn, implying that they can be potential materials for phytoremediation. The levels of Fe, Mn and Li were higher than the normal range in plants (Kabata-Pendias and Pendias, 2001). The leaf area, to some extent may determine the concentration of heavy metal in some plant species. For example, the larger the leaf area the higher the concentration of heavy metals extracted from them; as indicated by *U. lobata* and zinc accumulation.

The heavy metals present in the oil polluted soils when absorbed by plants are capable of making the plant leaves potentially toxic and harmful to man and livestock

Table 3. Interrelationship among concentrations of heavy metals in plant growing in polluted soils.

	Fe	Mn	Li	Zn	Cu	Cd	Cr	Pb	Co	V	Mo	Hg	Se
Fe	1												
Mn	*0.947	1											
Li	**0.968	*0.920	1										
Zn	0.824	*0.941	0.822	1									
Cu	*0.917	**0.965	0.854	0.841	1								
Cd	0.873	*0.894	0.745	0.833	0.888	1							
Cr	0.809	0.872	0.673	0.751	*0.947	*0.930	1						
Pb	*0.924	**0.982	0.853	*0.909	**0.981	*0.947	*0.945	1					
Co	**0.980	*0.950	**0.978	0.812	*0.937	0.801	0.794	*0.913	1				
V	0.860	**0.969	0.854	*0.995	*0.889	0.848	0.794	*0.939	0.860	1			
Mo	**0.990	**0.974	**0.980	*0.887	*0.923	0.860	0.775	*0.931	**0.981	*0.916	1		
Hg	0.853	**0.961	0.875	**0.983	0.877	0.787	0.748	*0.913	0.870	**0.992	*0.917	1	
Se	0.837	*0.918	*0.900	0.955	0.797	0.699	0.619	0.837	0.853	*0.958	*0.906	**0.980	1

Table 4. Interrelationship among concentrations of heavy metals in plant growing in unpolluted soils.

	Fe	Mn	Li	Zn	Cu	Cd	Cr	Pb	Co	V	Mo	Hg	Se
Fe	1												
Mn	**0.993	1											
Li	*0.890	*0.922	1										
Zn	**0.988	**0.970	0.870	1									
Cu	**0.982	**0.982	0.83	*0.957	1								
Cd	**0.988	**0.994	*0.885	**0.985	**0.990	1							
Cr	**0.965	*0.936	0.861	**0.986	*0.967	*0.953	1						
Pb	*0.954	**0.962	**0.964	**0.960	*0.910	*0.952	*0.945	1					
Co	*0.937	*0.941	**0.963	*0.951	0.875	*0.930	*0.953	**0.995	1				
V	*0.953	**0.976	0.970	*0.940	0.931	*0.957	*0.906	**0.989	**0.971	1			
Mo	**0.979	**0.983	**0.959	**0.969	*0.935	**0.972	**0.962	**0.985	**0.981	**0.979	1		
Hg	0.427	0.429	0.538	0.529	0.368	0.438	0.519	0.630	0.642	0.570	*0.493	1	
Se	*0.917	0.878	0.771	**0.967	0.872	*0.913	**0.966	*0.908	*0.910	0.859	*0.893	0.650	*1

if ingested or consumed as food (Ogri, 1998). Khan et al. (2008), also reported that accumulated of heavy metals in contaminated soils may pose health risks. This observation confirms the report by Benson and Ebong (2005) on vegetables where heavy metal accumulation in plants resulted in poor growth and in yield reduction. Similarly, Epstein (1972) reported that lead and cadmium prevent mineral uptake by either synergistic or antagonistic reactions. The high content of Mn in the plant tissues may result in Mn toxicity (Badoglio and Stumm, 1994, Cobb et al., 2000) with time.

Conclusions

The study has demonstrated that crude oil contamination can lead to gradual heavy metal build-up in plants growing in such soils. The plants studied were highly contaminated with Fe, Mn and Li, suggesting that the site poses potential hazards to grazing animals, humans and the food chain and there is, therefore, the urgent need for remediation strategies and management of the contaminated soils.

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