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SPREAD AND BIO AVAILABILITY OF HEAVY METALS IN TOPSOIL AND GROUNDNUT *(ARACHIS HYPOGAEAL*) IN CRUDE OIL POLLUTED AREA OF DELTA STATE

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ABSTRACT

A green house study was carried out to examine the spread and bioavailability of heavy metals in topsoil and ground-nut (Arachis hypogeal) at various distance from the site of crude oil pollution in Uzere community, Delta State. The heavy metals considered in the study were Nikel (Ni), Zinc (Zn), Iron (Fe), cadmium (Cd), and Lead (pb). It was observed that these heavy metals were more concentrated at distance closer to the point of pollution. More so, iron and cadmium concentrations have contaminated the topsoil as stipulated by United Nation Environmental protection (UNEP). In addition, the heavy metals studied have higher concentration in the root than in stem of groundnut. The concentration of cadmium and lead in both the root and stem of groundnut have exceeded the permissible level for human and animal consumption as recommended by FAO and WHO. Therefore, the polluted environment should be treated

Keyword: *Spread, bioavailability, heavy metals, groundnut, green house.*

INTRODUCTION

Environmental pollution has become very extensive and dangerous problem as a consequence of industrial and human activities. Widespread low to high pollution of large area of agricultural land is a particular problem from indiscriminate sludge discharge from industries, crude oil pollution and wastes. Heavy metals are among the most common environmental pollutants and their occurrence in soils indicates the presence of natural or anthropogenic sources (Yoon et al; 2001). The anthropogenic heavy metals believed to be easily accumulated in the topsoil (Nelson and Sommers, 1982), causing potential problems such as toxicity to plant and animals (Verner and Ramsey, 1996), accumulation in food chain, perturbation of the ecosystem and adverse health effects (Voutsa, et al, 1996). The concentration of heavy metals in the soil solution plays a critical role in controlling the availability of ions to plants (Lorenz et al, 1994). The solubility and therefore, the bioavailability of heavy metal ions vary widely because many factors including soil pH, clay content, organic matter content (Lee et al,1997), distance from source of pollution (Shiler and Babrikov, 2005) amongst others, influence their concentrations in soil solution. Since food chain contamination is one of the major routes for entry of metals into animal system, monitoring the bio available pools of metals in contaminated soils has generated a lot of interest (Tarakoioglu et al; 2006, Henning et al; 2001; Dai, et al, 2004, Antanaitis and Antanaitis, 2004). Vegetables constitute an important part of the human and animal diet by contributing protein, vitamins, calcium and other nutrient which are usually in short supply. Vegetables also act as buffering agents for acidic substances obtained during digestion process. However, these plants may contain toxic elements (heavy metals) at a wide range of concentrations (Maleki and Zarasvand, 2008). Heavy metals such as Cranium (Cr), Cadmium (Cd), Lead (Pb), Nikel (Ni), Arsenic (As) and Mercury (Hg) are often cited as primary contaminants of concern, and the possibility of synergistic effects of two or more of these metals may be of considerable importance at some sites contaminated with heavy metals (Nan et al, 2002). These metals can be transferred and concentrated into plant tissue from the soil and bring about toxic effect which is largely connected to their extremely high concentration in cells (Aqthar and Ahmad, 2002; Gondek and Filipek-Mazur, 2003). Different plant parts exercise differentially in accumulating metals in their tissues (Behbahaninia and Mirbagher, 2008). Plant roots participate primarily in the heavy metal cation uptake because of its complete contact with soil solution. However, the above ground tissues-stem, leaves, grains, fruits etc accumulate heavy metals by the amount translocated by the roots (Lasat,2002). Mohammed et al; (2003) comparing Cadmium (Cd), cobalt (Co), Copper (Cu), Manganese (Mn), Nikel (Ni), Lead (Pb) and Zinc (Zn) concentration in vegetable plants of family solanaceae found that eggplant had the highest level of Mn, Pb and Zn, potatoes had the highest levels of Cd and Co and tomatoes had the highest level of Cu and Ni. Abdullahi et al; (2008) investigated some trace metals level in onion leaves from irrigated farmland on the bank of river Challawa, Nigeria. They found the levels of the studied metals to be in order of Ni>Cu>Zn>Mn for the onion leaves and were above the FAO/WHO and WHO/EU allowed limits. Awode et al, (2008) also found levels of Zn>Ni>Cd in pepper grown on the soil irrigated with contaminated water.

While the levels of Cd and Zn were above the FAO/WHO allowed limits, Ni concentration was lower than the recommended maximum limits for vegetables. Several studies have been done on heavy metal concentrations in polluted soils (Yoon et al, 2007, Nelson and Sommera, 1982; Ogboi,2012) and their levels in some crops (Lasat, 2002, Mohammed et al; 2008). However, limited researches have been done on variation in concentration of heavy metals in crude oil contaminated soils in relation to the distance from the point of pollution and their photo toxic effect on full grown crops. Therefore, this work was initiated in order to examine the spread in the concentration of some heavy metals (Nikel, Zinc, Iron, Cadmium and lead) in top soil and parts of groundnut in relation to the site of pollution in crude oil polluted areas of Delta State.

Materials and Methods

The work was done in a crude oil polluted site in Uzere community in Isoko south local Government Area of Delta State. Uzere is one of the crude oil producing communities in Delta State that is subjected to crude oil pollution. It lies between Latitude 5^0 $45^{''N}$ and 5^0 $53^{''N}$ of the Equator and longitude 6^0 $05^{''}$ and 6^0 $15^{''E}$ of the Greenwich Meridian. The area experiences a humid tropical climate with distinct wet and dry sea of 8 and 4 months respectively (Offune, 1993). Mean annual rainfall is 3200mm and the mean annual temperature is 32^0C. Uzere is an agerian community that arable crops majorly cultivates groundnut, pepper, plantain, sweet potatoes, cassava, vegetables

Soil Sampling and Preparation for Analysis

Four transects were selected and designated as UZ1, UZ2, UZ3 and UZ4 representing 100, 200, 300 and 400m respectively from the source of crude oil pollution. Bulk soil samples of field moist weight were collected from 0-25cm depth at each sampling point using a soil auger. The samples were air dried, grind and sieved with 2mm mess sieve and divided into two parts for analysis of soil properties and extraction of heavy metals.

Determination of Soil Properties

Soil pH was determined in 1:2.5 soil water suspension by pH meter (Peech, 1965); Organic matter was determined by walkey black method (Nelson and Sommers, 1982); total nitrogen was determined by Kjedahi disgestion while phosphorous and potassium were determined as phosphorous (v) oxide (P_2O_5) and potassium oxide (K_2O) after extraction with 0.4mol/1 acetic acid and 0.1mol/1 ammonium lactate. The particle size distribution was determined by the hydrometer method (Gee and Bauder, 1979)

Determination of Total and Available Heavy Metals

The other part of the soil samples were dried again at 110^0C for one day. Samples were then sieved with sets of soil sieve. Weighted samples were transferred into acid baths. The acids volumes used were 15ml Hydrochloric acid (Hcl) and 5ml Hydrogen trioxonitrate (v) (HNO_3) for each sample. On a hot plate, the samples were heated at 120^0C. After observing reddish gas exit from the heated samples and making sure that the prepared samples are almost dry, the samples were removed from the plate. A 10ml Hydrochloric acid (Hcl) and Hydrogen trioxonitrate (v) (HNO_3) mixture (both 1% v/v) was added to each sample. Whatman paper was used to filter the prepared samples into test tubes. The heavy metals of concern (Ni, Zn, Fe, Cd and Pb) were then analyzed using a Perkin Elmer 2280 model Atomic Absorption spectrophotometer with flame or graphite (26). The available metal contents were determined by extraction of the soils with 0.005MDTPA (pH =7.3). Twenty (20)ml of DTPA solution were added to the 10g of soil samples placed in polypropylene bottles. The bottles were shaken on a rotating shaker for 2 hours and were centrifuged for 10minutes at 3000rpm (Lindsay and Norvell, 1978). The concentration of total available metals in the supernatant liquid were measured with a Flame Atomic Absorption Spectrometry (Perkin Elmer, 2280 model). All soil samples were treated in duplicate. In all cases, standards, (Stock standard solution of 100mg/1 concentration) and blank were treated in the same way as the real samples to minimize matrix interferences during analysis.

Green House Study

Bulk soil samples were collected from the designated distance and transported to the Delta State polytechnic, Ozoro research and teaching farm for a green house experiment during 2012 cropping season. Twenty (20) specially prepared polythene bags of 120 x 120 x120cm in dimension and with provision of drainage were used for the experiment. Twenty (20) kg of the soil samples were put into each of the polythene bag and 3 seeds of groundnut (*Arachis hypogaeal*) were sowed into each polythene bag and watered regularly. Weeds were removed manually throughout the growth period. At 12 weeks after sowing (12 WAS), three plants per polythene bag were used for analysis of heavy metals, uptake preparation of plant samples and extraction of heavy metals. The selected plants were separated into roots and above ground materials (stem and leaves). Each component was then raised with deionized water 'dried in an oven at 65^0C for two days and grounded thoroughly with an agate mill. The contents of studied heavy metals in the plant tissues were determined after simple mineralization in a muffle furnace at 500^0C for 5 hours and dissolved the ashes in HNO_3 (1:2). The contents of the studied heavy metals (Cd, Ni, Pb, Fe and Zn) were assessed by Atomic Absorption Spectrometry (AAS) in a Perkin Elmer 2880 model Spectrophotometer.

Statistical Analysis

Statistical analysis was done using the statistical package for social sciences (SPSS, version 10.0) programme and t- values were calculated for all possible pairs at $P<0.05$.

RESULTS AND DISCUSSION

Physico-chemical properties of the study site

Some physico-chemical properties of the studied top soil at different distances from the source of pollution are presented on Table 1. The texture of the soil in all the sample area was loamy sand. Sand, clay and silt contents wwere 70-79, 10-15 and 12-17% respectively. Soil pH was acidic and ranged from 4.2 -6.5. Total nitrogen was low and ranged between 0.05 and 0.45% with UZ1 and UZ4 having the least and highest values respectively. Organic matter content was generally low (ranged between 0.45 - 0.70%) and increased as the distance from pollution source increased. Pollution causes loss of organic matter because the waste and debris are characterized by high chemical oxygen demand (COD) and high Biochemical Oxygen Demand (BOD) as reported by Osinowo (2003). Phosphorus and Potasium values ranged between 135.1-155.2mg/kg and 553.3 – 603.5 mg/kg respectively
The same trend was also obtained as regards variation with distance from source of contamination.

Table 1: Descriptive Statistics on Selected soil physical and chemical properties.

Soil property	Range*	Arithmetic mean
pH	4.2 - 6.5	5.35
Sand %	70 - 79	74.50
Clay %	10 – 15	12.50
Silt %	12-17	14.50
Total Nitrogen %	0.05 -0.45	0.25
Organic Matter %	045 – 0.70	0.57
Phosphorus oxide (P_2O_5) (mg/kg)	135.1-155.2	145.15
Potasium Oxide (k_20) (mg/kg)	553.3-603.5	578.4

Source : Field 2012

* Range values correspond to decrease in distance from source of contamination.

Table 2: Heavy metal concentration (Mg/kg) in the soil samples.

Parameters	Different locations from pollution source (m)				
	UZ1 100m	UZ2 200m	UZ3 300m	UZ4 400m	Av.*.
Lead (Pb)	2.40	2.16	1.45	1.36	75
Iron (Fe)	688	621	548	523	10
Nikel (Ni)	2.06	1.60	1.20	1.01	10
Cadmium (Cd)	1.60	1.32	1.24	106	1
Zinc (Zn)	4.11	3.99	2.41	1.56	100

Source: Field work, 2012 * UNEP and BMPT (1983) N/B Action Value (AV)

Table 3: Bioavailable content as a percentage of total metal content.

Element	**Range***	**Arithmetic Mean**
Nikel (Ni)	13.2-11.1	12.15
Zinc (Zn)	20.6-18.3	19.55
Iron (Fe)	19.3-17.9	18.60
Cadmium (Cd)	14.6-13.3	13.95
Lead (Pb)	17.4-14.6	16.00

Source: Field work, 2012.

* Range values correspond to decrease in distance from pollution source.

Table 4: Toxic heavy metal concentrations in groundnut plant (mg/kg dry weight).

	Uz1	Uz2	Uz3	Uz4
Nickel (Ni)				
Roots Stems & Leaves t-test	1.96 1.42 1.02^{ns}	1.91 1.36 1.06^{ns}	1.84 1.22 1.86^{ns}	1.72 1.19 1.73
Cadmium (Cd)				
Roots Stems & Leaves T-test	3.54 2.36 2.03^{ns}	3.01 2.59 1.35^{ns}	2.87 2.08 0.93^{ns}	2.03 1.87 0.83^{ns}
Iron (Fe)				
Roots Stems & Leaves t-test	0.93 0.54 1.25^{ns}	0.86 0.45 1.03^{ns}	0.73 0.40 0.95^{ns}	0.68 0.32 0.84^{ns}
Zinc (Zn)				
Roots Stems & Leaves t-test	0.83 0.71 1.62^{ns}	0.74 0.62 1.37^{ns}	0.65 0.51 1.03^{ns}	0.53 0.32 1.21^{ns}
Lead (Pb)				
Roots Stems & Leaves t-test	1.73 1.32 2.05^{ns}	1.54 1.03 1.97^{ns}	1.32 0.92 1.43^{ns}	0.93 0.56 1.02^{ns}

NS = Not Significant

Level of Heavy Metal Contents in Soils

The data on the heavy metal concentrations of the soils are presented on Table 2. The average concentration of heavy metal in the soils ranged from 1.36 to 2.40 mg/kg for lead, 523 to 688 mg/kg for Iron, 1.01 to 2.06 mg/kg for Nikel, 1.06 to 1.60 mg/kg for cadmium and 1.56 and 4.11 mg/kg for zinc respectively with the concentration of Iron higher than the rest of the elements. There was a reduction in the values of the metals as the distance from the point of contamination increases, indicating a relative pollution of the soil by these heavy metals. The implication is the higher amount of each of these heavy metals are very close to the point of pollution (Shilev and Babrikov, 2005). This finding agrees with Loggins (1983) who reported that metal's concentration is highest near road sides and dump sites and decreases with increasing distance from the road and dumping sites. The concentration of Iron and Cadmium were above the action values for heavy metals in cultivated soils with regards to the health of plants, livestock's and Man (UNEP and BMFT, 1983). On the other hand, the concentration of Lead, Nikel and Zinc were below the action values.

Bioavailable Heavy Metal Concentrations

Bioavailable heavy metal's concentrations of the studies area are as shown on Table 3. It reveals that Nikel bioavaiblable content range between 11.1 and 13.2% Zinc ranges from 18.3 to 20.6%, Iron, ranges from 17.9%, cadmium ranges between 13.3 and 13.6% while lead ranges from 14.6 to 17.4%. The determination of total heavy metal contents in soil was considered an indication of potential environmental risk posed by these metals, but do not always reveal metals' labile fraction available for plant use uptake (Gastparatos and Haidouti, 2001). The severity of pollution depends not only on total metal content of the soil, but also on the proportion of their mobile and bioavailable forms, which are generally controlled by the texture and other physicochemical properties of soils (Imperatoe el al; 2003).

Consequently, element availability is very important when assessing the effect of soil contamination on plant metal uptake and related phototoxic effects. The percentage of the total metals extract with DTPA is regarded as a good indicator of the quantity of metal available for plants and could reflect their comparative mobility (Papafilippata et al 2007) (Table 3). According to Ullrich et al; (1999), the metals are not potentially available for plant uptake, if the bioavailability percentage is below 10% and potentially available if the bioavailability percentage exceeds 10%. The bioavailability percentage of the studies metals in the top soils were above 10%, indicating the availability of the metals for plant uptake. The potential availability to those maybe due to low retention capacity of the soils as a result of the acidic nature soil. A the Bansal et al; (1992) reported that low pH value decreases the absorptive capacity of soils, increases the bioavailability (range values) and the mobility of the metals. The relative and consequently the comparative mobility of the studies metals followed the order of Zinc (Zn) > Iron (Fe) > Lead (Pb) > Cadmium (Cd) > Nikel (Ni). Organic matter plays a significant role in the availability and mobility of heavy metals in soils as it is involved in the formation of soluble complexes especially with Zn and Fe which during organic mineralization, become more available for plants (Leita et al; 1999). This explain higher availability of Zinc and Iron in the soils relatively to other elements. This agrees with the findings of Wild (1996) that among the heavy metals, Zn is present in largest amounts in sludge commonly followed by Iron. Cadmium, a toxic heavy metal is also mobile and bioavailable (Alloway, 1995). On the other hand, Nikel (another toxic metal) was less abundant and relatively retained to the soil.

Heavy Metal Concentrations In Groundnut Plant Tissue

Heavy Metal concentrations in different parts of groundnut plant are presented on Table 4. A gradual decrease was obtained in heavy metal contents in the tissues of groundnut as the distance from the source of anthropogenic contamination decreases. In all cases, higher concentrations of studies toxic heavy metals were found in the roots compared to the above ground stems and leaves. Kabata Pendias and Pendias (2001) and Inouhe et al; (1994) reported that an increased uptake of heavy metal mostly accumulates in the roots. Table reveals that Nikel (Ni) concentrations in groundnut plant ranged from 1.72-1.96 mg/kg; 1.19-1.42 mg/kg for the roots and stems/leaves respectively. Cadmium contents varied from 2.03 to 3.54 mg/kg for the roots and 1.87 to 2.36 mg/kg for the stems and leaves. Iron content ranged between 0.68 and 0.93 mg/kg for the roots and 0.32 and 0.54 mg/kg for the stems & leaves. Zinc content varies from 0.53 to 0.83 mg/kg in the roots and 0.32 to 0.71 mg/kg for the stems and leaves. Lead content ranged from 0.93 to 1.73 mg/kg and 0.56 to 1.32 mg/kg for the roots, stems and leaves respectively. In all, there were no significant difference, of the these heavy metals content in the root and the stem systems.

The accumulation of the heavy metals followed the order of Cd > Ni >Pb > Fe > Zn. The highest concentrations of cadmium in roots, stems and leaves of groundnut is consistence with the results on the total heavy metal concentrations in soils, relatively high mobility and bioavailability for plant uptake. This confirms the findings of Alloway (1993) who submitted that Cadmium is a very mobile and bioavailabie metal which may accumulate in crops and humans. Comparing the level of the toxic heavy metal accumulation with set standards for threshold values of heavy metals in vegetables for human and animal consumption, Cadmium and Lead concentions in all parts of the plant were above the maximum allowed limit of 0.2 and 0.3mg/kg respectively for vegetables (FAO/WHO,2003) while, Nikel, Iron and Zinc levels were lower than the recommended maximum limit for vegetables (Weigert, 1991).

CONCLUSION AND RECOMMENDATION

This study investigated the spread of heavy metals (Ni, Fe, Cd, Pd and Zn) in surface soil and groundnut at various distances from crude oil polluted site in uzere community. The total heavy metal concentrations indicated that the soils are contaminated by iron and cadmium, and uncontaminated by Lead, Nikel and Zinc. The bioavilable concentrations of the studied metals were high which may be due to the acidic nature of the soil, PH and low organic matter content and they followed the order of Zinc, Iron, Lead, Cadmium and Nikel. Higher concentrations of studied heavy metals were ground in the roots compared to the above found stems and leaves. The concentration of heavy metals in groundnut were in the order of Cadmium > Nikel >Lead > Iron > Zinc. Based on the result, it is recommended that the polluted environment should be treated and put in place appropriate checks and balances to preserve the health of the communities within the area of pollution as the effects of heavy metals are bioaccumulative and pose great dangers to the health of humans, animals and plants.

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