

Preliminary assessment of heavy metals levels of soils of an oil field in the Niger Delta, Nigeria

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ABSTRACT: This communication presents the results of preliminary investigation of the characteristic levels of heavy metals in surface soils of an oilfield in the Niger Delta. The results indicate higher concentration of the following metals: Cd, Pb, Cu; Ni, Zn, Cr, Mn and Hg in soils around the gas plant than the pipeline areas. There is a significant temporal and spatial variation in the concentrations of the heavy metals. Samples collected during the wet season showed lower concentrations of heavy metals. The distribution pattern of heavy metals follows the following order Fe > Mn > Zn > V > Cr > Pb > Cu > Ni > Cd > Hg > As. The soils around the oilfield could be considered unpolluted since the concentrations of the metals fit into background levels and concentrations found in natural and agricultural soils. Since metal build up is a gradual process, farmland, fishing ponds and water bodies closer to these facilities will be at risk of heavy metal pollution over time.

Key words: Heavy metals, soil, oil field, Niger Delta

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INTRODUCTION

Contamination of heavy metals in the environment is of major concern because of their toxicity and threat to human life and the environment (Purves, 1995; Ma and Rao, 1997). Metal interaction in soil vary considerably with the nature of soil types. The phytoavailability of metals is determined by the nature of the metal species, their interaction with soil colloids, the soil characteristics and duration of contact with surface binding (Naidu *et al.*, 2003). Soil characteristics (e.g. soil pH, clay, organic matter content and types, and moisture content) also determine availability to plants by controlling the speciation of the elements, temporary binding by particles surface (adsorption-desorption processes), precipitation reaction and availability in soil solution and the amount of moisture present in the soil (Fotovat *et al.*, 1997; Naidu *et al.*, 2003). Much research has been conducted on heavy metals contamination in soils from various anthropogenic sources such as industrial waste (Haine and Pocock, 1980; Parry *et al.*, 1981; Culbard *et al.*, 1983; Gibson and Farmer, 1983), automobile emission (Largerwerff and Specht, 1970; Furgusson *et al.*, 1980

and Garcia-Miragaya, 1980), minning and smelting activities (Davies and Ginnever, 1979; Culbard and Johnson, 1984; Ma and Rao, 1997 and Kabala and Singh, 2001), agricultural practice (Culbard and Johnson, 1984), and urbanization (Lavado *et al.*, 1998). From the foregoing, it is evident that considerable works have been done on the contamination of soil by anthropogenic sources in most developed countries. There is paucity of information from developing countries like Nigeria, and more so, relatively few studies have been reported on the heavy metals status of soils of some oilfield in the Niger Delta. The primary objectives of the present study were to investigate the characteristic levels of heavy metals and some physicochemical properties of soils from an oilfield in the Niger Delta.

MATERIALS AND METHODS

The study area lies between longitude 6° 20' to 6° 50' E and latitude 5° 20' to 5° 40' N. The area is located at the Northern part of the Niger Delta. This area is characterized with multiple oil wells, criss-crossing of

surface and subsurface pipelines and multiple gas flare points. The area also houses three major gas plants and gas compression stations. Apart from peasant farming, the major industrial activity in this area is that of oil and gas exploration and exploitation.

Sampling and analysis

Soil samples were collected within 2 km x 2 km quadrant around the gas plant and within 20 m radius at designated interval along the existing oil pipelines. The quadrant was subdivided into 16 cells (125 m x 125 m) with each denoting a sampling station. A composite sample consisting of at least six random samples were collected in each cell. A total of 32 sampling sites were examined. The soil samples were collected at 0 – 20 cm depths using a hand auger. All samples were air dried and ground to pass through 2 mm mesh. The samples were collected in two regimes (1) January – February, 2005 for dry season samples and June and July, 2005 for rainy season samples. The particle size distribution was determined by the hydrometer method for silt and clay and by dry sieving for sand fraction (Reeuwijk, 1995). Soil pH was measure in 1':2.5 (v/v) ratio of soil and water suspension (Reeuwijk, 1995). Cations exchange capacity was determined as a sum of basic cation extracted with neutral IM NH₄OAc and the extractable acidity (Reeuwijk, 1995). Total organic carbon was determined by the wet dichromate method of Walkley and Black (Nelson and Sommer, 1985). Total trace metal content contents (Cd, Cr, Cu, Pb, Ni, Fe, and Zn) were determined as aqua-*ragia*/HF extracted amount using air-acetylene flame atomic absorption spectrophotometer (AAS) (Perkin Elmer A3100). For analysis of vanadium, a nitrous-oxide flame was used. Mercury and arsenic was determined by cold vapour and hydride generation atomic absorption respectively after a specific destruction (Cottenie *et al.*, 1982). The atomic absorption spectrophotometer was fitted with D₂ background correction devices. Sample was analyzed in triplicate. Uncertainty is expressed as a percentage calculation on the basis of maximum standard deviation. The coefficients variation obtained were less than 5% for all metals.

RESULTS

Table 1 reports the particle size distribution and some general characteristics namely pH, percentage organic carbon, cation exchange capacity (CEC),

conductivity and moisture content of the examined soils. The pH is acid with mean pH values of 4.63 (3.51-6.83) and 5.00 (4.29-7.33) for wet season and dry season respectively. Analysis of variance ($p > 0.05$) showed no significant spatial and temporal variation in the pH levels of the examined soils. The mean levels total organic carbon (TOC) were 1.83% with range of 0.89 to 2.5% for wet season and 1.53% with range of 0.89 to 2.3%. The cation capacity of soils ranged from 5.46 to 23.5 meq/100g with mean value of 13.31 and 0.39 to 9.2 meq/100 g with mean value of 3.99 meq/100 g for wet and dry season respectively. Also the moisture contents of examined soil ranged from 13.6 to 52.7% and 0.9% to 29.3% for wet and dry seasons respectively. Analysis of variance ($p < 0.05$) showed significant spatial and temporal variations in the levels of total organic carbon, cation exchange capacity and moisture content of the examined soils. Sand fraction forms the predominant fraction in terms of particle size distribution. It ranged from 30% - 100% in the soils. Whereas silt and clay fractions ranged from 0.00-45.8 and 0.00 – 30.0%. Like other soil general characteristics there is significant spatial variation in the particle size distribution. Table 2 presents the mean concentrations, range of heavy metals in the investigated soils. The mean concentrations of cadmium were 0.68 mg/kg (0.22-1.73 mg/kg) and 0.76 mg/kg (0.02-1.60 mg/kg) for wet season and dry seasons respectively. At $p < 0.05$ the concentrations of cadmium showed significant spatial variations. The concentrations of lead in all sites ranged from 2.00 to 15.00 mg/kg with mean levels of 6.53 mg/kg and 3.00 mg/kg with mean levels 10.2 mg/kg for wet and dry seasons respectively. Like cadmium and lead, other metals showed significant spatial and temporal variations in the concentrations of these metals except for arsenic. Iron showed the highest concentration in all sites compared with other metals. Table 3 presents the mean concentrations, coefficient of variation and ranges of heavy metals in soil samples collected within the gas plant areas and those collected along the pipeline areas. Paired t-test ($p < 0.05$) was used to compare the concentrations of heavy metals in soils from gas plant areas and pipeline area. The results revealed that gas plant areas have significant ($p < 0.05$) higher concentrations of heavy metals compared to pipelines areas in for both wet and dry seasons.

Table 1: Some physicochemical properties of soils of an oilfield in the Niger Delta

Parameter	Mean \pm S.D.	Wet season range	CV (%)	Mean \pm S.D.	Dry season range	CV (%)
Sand (%)	63.78 \pm 26.16	30.0 – 100	41.0	-	-	-
Silt (%)	24.59 \pm 16.58	0.00– 45.8	67.4	-	-	-
Clay (%)	11.67 \pm 10.71	0.00 – 30.0	91.8	-	-	-
pH	4.63 \pm 0.78	3.51 – 6.83	16.8	5.00 \pm 0.85	4.29 – 7.33	17.0
Conductivity μ S/cm	75.89 \pm 66.20	28.7 - 309	87.2	83.76 \pm 54.10	31.0 – 276	64.5
TOC(%)	1.83 \pm 0.89	0.89 – 2.5	486	1.53 \pm 0.74	0.89 – 2.30	48.4
CEC (Meq/100g)	13.31 \pm 5.16	5.46 – 23.5	38.8	3.99 \pm 3.44	0.39 – 9.20	86.2
Moisture (%)	26.82 \pm 9.17	13.6 – 52.7	34.2	12.87 \pm 8.38	0.90 – 29.3	65.1

TOC = Total organic carbon; CEC = cation exchange capacity; SD= standard deviation; CV = coefficient of variation

Table 2: Total metals concentration of soils of an oilfield in the Niger Delta, typical range and most common values, average abundance in the earth crust (values in mg/kg unless otherwise stated)

Metal	Mean \pm S.D.	Wet season range	CV (%)	Mean \pm S.D.	Dry season range	CV (%)	Typical range	Common value
Cd	0.68 \pm 0.51	0.02 – 1.73	75	0.76 \pm 0.43	0.02 – 1.60	56.7	0.01 – 2.0	0.1 – 1
Pb	6.53 \pm 3.53	2.00 – 15.00	54.1	10.2 \pm 10.6	3.0 – 58.0	103.9	2 – 300	10 – 30
Cu	6.33 \pm 4.38	0.05 – 19.00	69.2	7.09 \pm 4.58	1.00 – 97.5	67.7	2 – 250	20 – 30
Cr	15.74 \pm 7.50	4.00 – 35.00	47.6	11.70 \pm 11.30	1.00 – 62.0	76.9	3 – 1500	70 – 100
Ni	4.43 \pm 3.26	0.10 – 12.00	73.6	5.73 \pm 2.38	1.50 – 10.0	41.5	2 – 750	50
Fe	55595.97 \pm 33410.92	36186– 108,054	60.0	15109.16 \pm 11081.83	481 – 46,431	73.3	7000– 42,000	-
Mn	183.61 \pm 113.30	13.0 – 364	61.7	247.38 \pm 158.57	7.00 – 623.0	64.1	20 – 10,000	1000
Zn	32.41 \pm 19.41	4.00 – 73.0	59.9	21.41 \pm 15.98	4.00 – 61.0	74.6	1 – 90	50
V	24.05 \pm 17.27	0.20 – 58.0	74.2	21.35 \pm 14.91	<0.20 – 55.0	69.8	-	-
**As	0.0005 \pm 0.000	0.0005 - <0.001	0.0	-	-	-	-	-
**Hg	0.38 \pm 0.32	0.02 – 2.55	84.2	-	-	-	-	-

DISCUSSION AND CONCLUSION

In general, the soils have a low clay content and organic matter, so they tend to be permeable. The soils have also low CEC. The CEC found in this study is similar values reported for Rivers State swamp soil (Isirimah, 1987). The pH of the soils of the oilfield is acidic, such acidic characteristics is typical of the Niger Delta soils (Isirimah, 1987 and Odu *et al.*, 1985). Several studies have shown that increased availability of many of these metals with decreasing pH (Itanna, 1998). The pH values of the soil examined also indicate a generally high tendency of high availability of these metals. Hence, this is a favorable natural mechanism increasing risk of at least plant uptake. The effect of pH value < 6 in increasing metal ion activities in soil can be attributed to the decrease in pH-dependent surface charge on oxides Fe, Al and Mn, chelation by organics of metal hydroxide (Adriano *et al.*, 2002). Table 2 presents the mean concentrations, range of heavy metals in the investigated soils and, for comparism, their typical concentration ranges in soils (Alloway, 1990). The

examined soils can be considered unpolluted, since the concentrations of metals fit into typical range and concentrations found in agricultural soils (Kabata-Pendias and Pendias, 1992) with exception of cadmium and lead in some sites. This suggests that heavy metal contents in the soils of the oilfield are not largely affected by human activities. The examined soils showed spatial variation in the concentrations of metals in the examined soils. The spatial variation is probably due to differences in moisture content, clay content, cation exchange capacity, organic matter content and pH of the different sites. Arsenic showed no significant spatial and temporal variation in concentration. The concentration of arsenic in all soils examined was less than 0.005 μ g/g. The results indicate that concentrations of these metals were higher in the dry season except for chromium, zinc, and vanadium. The seasonal variations in the concentrations of the metals could be attributed to differences in individual metal solubility, pH and leaching by acidic rain during the wet season.

Table 3: Mean concentration of heavy metals (mg/kg), range of soils around the Gas plant and pipeline Areas Gas plant Area

Metal	Mean \pm S.D.	Wet season Range	CV. (%)	Mean \pm S.D.	Dry season Range	CV (%)
Cd	0.84 \pm 0.61	0.05 – 1.73	51%	0.96 \pm 0.47	0.41 – 1.60	48
Pb	7.44 \pm 2.94	4.00 – 13.0	39.5	13.30 \pm 13.80	4.00 – 58.0	103.8
Cu	7.78 \pm 4.02	3.00 – 17.0	51.7	8.00 \pm 3.90	3.00 – 16.0	48.8
Cr	17.78 \pm 6.06	11.0 – 35.0	34.1	19.00 \pm 12.90	7.00 – 62.0	67.9
Ni	4.81 \pm 2.20	2.0 – 10.0	45.7	6.13 \pm 2.28	3.00 – 10.0	37.2
Fe	61625.88 \pm 12447.82	36,186 – 108,059	31.6	15653.88 \pm 10613.24	1385.0 – 37,480	67.8
Mn	199.56 \pm 115.36	50.0 – 506.0	57.8	237.19 \pm 160.07	52.0 – 623	67.5
Zn	38.13 \pm 17.30	19.0 – 73.0	45.4	23.06 \pm 13.67	10.0 – 56.0	59.3
V	28.19 \pm 14.16	11.0 – 69.0	50.2	25.08 \pm 15.00	0.20 – 49.0	59.8
As **	0.0005 \pm 0.000	0.0015 – 0.001	-	-	-	-
Hg *	0.32 \pm 0.08	0.06 – 0.41	25.8	-	-	-
Along pipelines						
Cd	0.52 \pm 0.48	0.02 – 0.88	92.3	0.61 \pm 0.39	0.02 – 0.97	63.9
Pb	5.67 \pm 3.91	1.00 – 15.0	69.0	7.13 \pm 4.54	3.00 – 20.0	63.4
Cu	4.88 \pm 4.36	0.05 – 13.0	89.3	6.63 \pm 7.00	1.00 – 29.0	105.6
Cr	13.69 \pm 8.40	4.00 – 27.0	61.4	9.76 \pm 7.20	1.00 – 23.0	73.8
Ni	404 \pm 410	0.10 – 12.0	101.5	5.34 \pm 2.49	1.50 – 9.00	46.6
Fe	49566.06 \pm 33556.17	8,862 – 115,229	67.7	13380.00 \pm 12322.41	481.0 – 46,430	92.1
Mn	167.66 \pm 112.61	31.0 – 357.0	67.2	257.56 \pm 161.61	7.00 – 544.0	62.7
Zn	26.69 \pm 20.94	4.00 – 57.0	78.5	19.75 \pm 18.30	4.00 – 61.0	92.7
V	19.91 \pm 19.48	0.20 – 58.0	97.8	18.95 \pm 14.54	0.20 – 55.0	76.7
As	0.02 \pm 0.06	<0.0001 – 0.21	0.0	-	-	-
Hg *	0.43 \pm 0.57	0.02 – 2.55	134.5	-	-	-

* $\mu\text{g/kg}$

**mean computed based on half of detection limit

Table 3 Soils around the gas plant showed significantly higher mean levels of these metals in all seasons compared to those collected along the pipeline areas. The high concentrations of metals in the around the gas plant area reflect an anthropogenic input, since exogenous metals are usually more weakly bound to the soil matrix, therefore are more readily released (Li *et al.*, 1995 and Abollino *et al.*, 2002). There is more build up of metals in the gas plant area than along existing pipelines, obviously because the heavy metal build up is a gradual process and hence farmlands and fish ponds closer to these facilities will be also risk of heavy metal pollution overtime. The following metals V, Ni, Cr, Fe, Pb, Cu and Zn showed significant positive correlation with cation exchange capacity. This correlation suggested that non-specific adsorption process controls metal adsorption and the adsorption capacity of the soil is dictated by the cation exchange capacity. However, in many soils the amount of metals sorbed exceeds the cation exchange capacity of the soils. This infers that in addition to non-specific adsorption/other processes such as specific adsorption, precipitation and complex formation also contribute to the retention of metals (Adraino *et al.*, 2002). The correlation between

the following metals Pb, Cu, Cr, Ni, Fe, Mn, Zn, and V cannot be explained in terms of chemical properties, origin or biological function. While clay cation exchange capacity and organic carbon content may be the major factors in determining the retention of trace metal that mainly occur in cationic forms (eg Zn, Cu, Pb etc.), the more complex environmental chemistry of Hg implies that several mechanism may significantly control Hg retention. For example, the retention of Hg in soil is not only cause by valence-type adsorption by organic and inorganic materials. It may be retained by formation of covalent bonds with organic compounds or by precipitation as highly insoluble carbonates, phosphates and sulphides (Adraino, 1986; Yaron *et al.*, 1996 and Tack *et al.*, 1997). Mercury is present naturally in soils at concentration from a few $\mu\text{g/kg}$ to several hundred $\mu\text{g/kg}$ (Adraino, 1986). While concentration and median values were in order of 100 $\mu\text{g/kg}$, value up to 2.26 $\mu\text{g/kg}$ were considered representative for current Hg in common Flemish soils (Tack *et al.*, 1997). The concentration of mercury we found in our study is lower than this range. Will and Suter (1995) derived a benchmark Cu concentration of 100mg/kg for the protection of terrestrial plants,

incidence of phytotoxicity has been recorded at concentrations in the order of 100 mg/kg in the Australian environment. Olzowy *et al.*, (1993) observed maximum Cu concentration of 466 mg/kg soil with 95th percentile of 122 mg/kg in Australian urban soils but found no incidence of phytotoxicity at these site. Similarly, Merry *et al.*, (1983) reported Cu concentrations in Australian orchard soils of 11-320 with an average value exceeding 100 mg/kg. The concentration of copper found in this study was far below levels reported by these researchers. The concentration of Pb, Cr, Cd, Cu, Ni and Zn we found in our study were far below levels reported for agricultural soils from Piedmont, Italy (Abillono *et al.*, 2002), contaminated sites in U.S.A (Ma and Rao, 1997) and soils from Baia Mare region, North West side of Romania (Mihaly-Cozmuta *et al.*, 2005). However the concentrations of the metals recorded in this study fit into the range reported by Tack *et al.*, (1997). Osuji and Onojake (2004) reported mean levels ranging from 12.6 mg/kg – 12.8 mg/kg Ni, 4.1 mg/kg – 5.2 mg/kg Cu, 10.0 – 10.8 mg/kg Pb, <0.2 mg/kg V and <0.2 mg/kg Cd for subsoil to topsoil respectively for soil samples collected 6 months after the Ebocha – 8 oil spillage in the Niger Delta, Nigeria. The levels we found in our study are comparable to the levels reported by these authors except for vanadium and cadmium. Arsenic is widely distributed in soils and with average concentrations in the range of 1-40/mg, with a mean value of approximately 5 mg/kg (Yan Chu, 1994). Arsenic content range between < 5 and 175 mg/kg with a median value of 8 mg/kg have reported for Swedish tills. Tack *et al.*, (1997) reported as concentrations in the range of 0.82 – 95 mg/kg with a median value of 7.0 mg/kg in Flemish rural soil. Bhattacharya *et al.*, (2002) reported high concentration of arsenic varying between 10 mg/kg and as high as 1067 mg/kg in mineral soils of contaminated sites at Konsterund, Kristinehamn Community, Central Sweden. The concentration of as we found in this study were far below those range. The concentration of Arsenic all sites were below the limits of analytical detection except for two sites that have arsenic concentrations of 0.14 mg/kg and 0.21 mg/kg. Since characteristic levels of heavy metals recorded in our study fitted into concentrations found in natural and unpolluted soils. The soils collected around these facilities are considered unpolluted and are not largely influenced by human activities. However, it is evident that there is a gradual build up of heavy metals in the

soil around the gas plant area compared to soil collection along the transport pipelines. This reflect intense anthropogenic activities around the gas plant areas. The distribution pattern of these heavy metals were in the following order Fe > Mn > Zn > V > Cr > Pb > Cu > Ni > Cd > Hg > As. Non specific adsorption process form the major control mechanism for metal adsorption in these soil and the adsorption capacity of the soil is controlled by cation exchange capacity. Metal build up is gradual process, constant monitoring of the levels of these metals is required to safeguard farmlands, fish pound and water bodies around these facilities.

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