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Research Article

CHEMICAL COMPOSITION ANALYSIS OF SOIL FROM SELECTED OIL PRODUCING COMMUNITIES IN THE NIGER DELTA REGION OF NIGERIA

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ABSTRACT
The level of heavy metals and pH in surface soils of some non- oil and oilfield in Eleme, Eket and Egbema in Niger Delta region and Keffi, Nigeria were determined. The results of pH varied considerably with the sampling sites. The results of heavy metals obtained in all the soil samples showed significant concentrations of metals within the tolerance limit while calcium and magnesium were exceptionally high. The percentage concentration of heavy metals obtained at Eleme was higher than those obtained from Eket, Egbema and Keffi with the trend: Eleme>Eket>Egbema>Keffi. The average abundance of metals in all the soil samples put together were of the order; Fe> Ca> Mg> Na> Pb> Cd> Zn> As> Co> Cu> Al> K while the ions were Cl^-> SO_4^{2-}.The studies did not indicate severe pollution, however there is a gradual built up of these metals in the soil while the sulphate content in the sampling sites have the tendency of plugging the pores of reservoirs leading to reservoir formation damage.

Key Words: *Chemical Composition, Niger Delta, Soil, Nigeria, Analysis*

INTRODUCTION
Niger Delta region of Nigeria is greatly endowed with abundant natural resources giving rise to increased industrial activities. Refining and petrochemical companies account for about 70-75% of industrial activities in the region (Odjurwederhie *et al.,* 2006). Human activities do modify considerably the chemical composition of soils, crops and water (Ogunyemi *et al.,* 2003).The environmental degradation of the oil rich Niger-Delta region has led to wanton destruction of the ecosystem resulting into negative effect of both social and economic well-being of its people. Petroleum refineries operations produce a wide variety of air, soil and water pollutants and hazardous solid wastes. According to annual reports, Department of Petroleum Resources (DPR) (1997); over 6000 spills had been recorded in the 40 years of oil exploration in the Country with an average of 150 spills per annum. In the period between 1976 and1996 over 647 accidents occurred resulting in the spillage of 2,369,407.04 barrels of crude oil with only 549,060.38 barrel recovered, 1820,410.50 barrels of oil were lost to the ecosystem (Gideon and Josephine, 2008).Spills in populated area often spread out over a wide area, destroying crops and aquacultures through contamination of the groundwater and soils. The consumption of dissolved oxygen by bacterial feeding on the spilled and hydrocarbon also contributes to the death of fishes and other aquatic animals. In agricultural communities, often a year's supply of food can be destroyed instantaneously because of the careless nature of oil operations in the Niger Delta (Osuji and Anojake, 2004).When oil spill occur close to and within the drainage basin, the hydrologic force of both the river and tides forces spilled petroleum to move up to vegetation area. The effects of petroleum spills on mangrove are known to acidity the soils, halt cellular respiration, and starve roots of vital oxygen. An area of mangroves that has been destroyed by petroleum may be susceptible to other problems. These areas may not be suitable for any native plant growth until bacteria and microorganism can remediate the conditions (Stumm, 1981). The indiscriminate disposal and use of urban and industrial wastes on agricultural lands pollutes the soil with heavy metal elements that may lead to health hazards (Alloway, 1990 and Sposito, 1989).According to Atolaiye *et al.* (2006) contamination of heavy metals in the

environment has adverse effect on soil chemical composition; this has been a major concern because of their toxicity and threat to human life and the environment (Purves, 1995). The most important factor in controlling the partitioning of a metal to soil is the solution pH; heavy metal adsorption is governed by soil characteristics such as pH and organic matter content (Evans, 1989). Often trace metals are present in the solid phase as a result of adsorption to components of the soil (Kuo and Baker, 1980). Thus, high levels of heavy metals in the soil for instance do not always indicate similar high concentration in plantbut could often lead to lower and loss of certain land use capacities (Mihaly *et al.*, 2005). In Nigeria, a study of metal concentration near Warri refinery found three to seven times elevated level of various heavy metals in the soil (Ndiokwere *et al.*, 2000). The major pollutants from industrial discharge have been shown to be lead, mercury, nickel, arsenic, zinc and copper. Heavy metals like iron, tin, copper, manganese, vanadium and chromium occur naturally in the environment and could serve as plant nutrients depending on their concentrations (Bonati *et al.*, 1993). Although the petroleum industry is by far the largest industrial sector in the Niger Delta area, at least six of the eight most polluting industrial sub sectors in Nigeria: steel works, metal fabrication, food processing, textiles, refineries and manufacturing operate in the area. Researchesinto activities arising from these processes are known to affect soil chemical composition (Culbard and Johnson, 1984; Largerwerff and Specht, 1970; Fergusson *et al.*, 1980; Duffus, 2002; Culband and Johnson, 1984 and Kabata and Sigh, 2001).The land and amount of solid phase metal in contaminated soil may influence the bio-availability of the metals; it is often assumed that thermodynamic solubility of compounds correlated with solid-phase dissolution rates (Adriano, 1986).The aqueous concentration of an inorganic contaminant in contact with soil can be predicted from appropriate thermodynamic measurement (Evans,1989). The increasing industrialization particularly due to oil exploration and exploitation in the Niger Delta region of Nigeria has created a lot of damages to the environment (Asia *et al.*, 1998).Considerable work have been done on the contamination of soil by anthropogenic source 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 some oilfield in the Niger Delta.

MATERIALS AND METHODS

Study Area

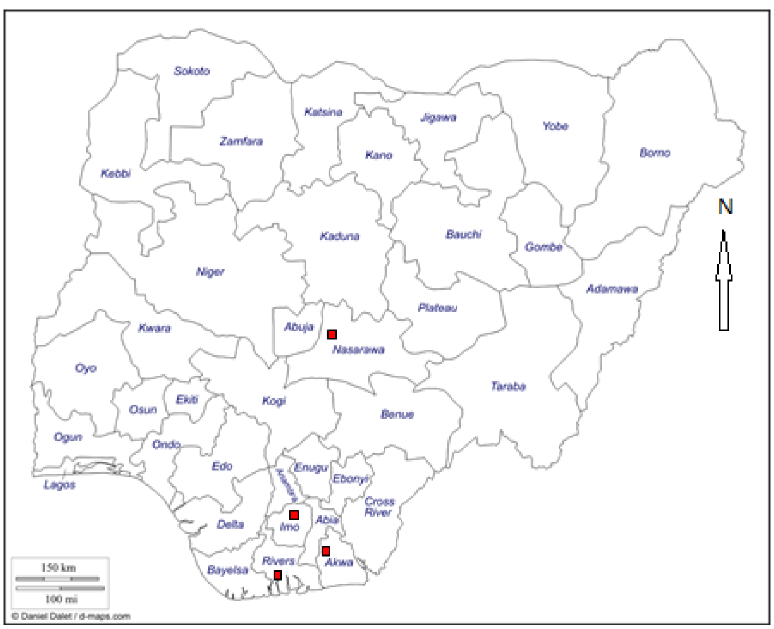

Figure 1: Map of Nigeria Showing the Studied Areas (Not to Scale)

Eleme (River State), Eket (Akwa Ibom State) and Egbema (Imo State) are the main study areas located in the Niger Delta Region of Nigeria. The region is an intricate, interconnected body of river, which drains from Central and Northern Nigeria through a landmass into the Atlantic Ocean. It consists of a huge deltaic wetland of about 70,000 square kilometers (Osuji and Anojake). The area which extends from the coast to about 150km inland, shares similar climatic characteristics as the equatorial region. It has two seasons, the wet season March to October and dry season November to March. Rainfall is between 1500 and 3000mm per annum with an annual mean of 400mm along the coast decreasing to about 2000mm in the interior with temperature of 25.50^{0}C in the rainy season and 30 ^{0}C in dry season. Daily relative humidity values ranges from 55.5 % in dry season to 96 % in the rainy season(Anonymous, 1995). It is the largest wetland and maintains the third largest drainage basin in Africa. Nasarawa State University, Keffi is the control area located in the North Central part of the Country, its 58km from Abuja; the Federal Capital Territory .The town is located on latitude 8^{0}50' north of the equator and longitude 7^{0}50 east,850m above sea level (Makut and Olaoye, 2008). The justification for this choice was that it does not have history of petroleum occurrence or facilities (Fig.1).

Sample Collection

Three soil samples were collected some kilometers away from oil producing companies and the fourth from non-oil community. The sampling sites were carefully selected for this study in order to reflect the different activities within them and level of heavy metals pollution and some chemicals present in the soils. At each site the samples were taken with hand trowel. The soil was scooped to 5-10cm depth as described by Awofolu *et al.,* (2005). The collected samples were kept in an appropriate labeled polythene bags ready for analysis.

Sample Preparation

A small quantity of each of the representative soil samples were properly air-dried for four days in the laboratory environment at room temperature and unwanted objects discarded. Each of the air-dried samples was then crushed using mortar and pestleinto fine powder to pass through a sieve of 2 mm steel wired meshes. These were packed in a polythene bags ready for digestion (Reenwijk, 1995).

Digestion of Soil Samples

2.0g of the sieved soil samples were accurately weighed with an analytical weighing balance and transferred into a crucible; 100ml of aqua regia in the ratio 3:1 of concentrated $HN0_3$ and concentrated HCl was added to the soil samples. The samples were allowed to stand for 20min; it was then heated thereafter for about 3h at the temperature of 110^{0}C with adequate stirring at regular intervals. On cooling, the digested soil samples were then filtered into 100ml volumetric flask and made up to the mark with distilled water (Oluyemi *et al.,* 2008).Themetals were determined using Atomic Absorption Spectrophotometer (AAS) model VGP 210 system while the pH was determined using an Orion research digital pH meter model 407A after prior calibration with standard pH buffer solutions at Abubakar Tafawa Balewa University of Technology, Bauchi, Nigeria (Anderson and Ingram, 1989).

RESULTS AND DISCUSSION

The results obtained for the soil composition in this research varied when compared with the one obtained by Lavado *et al*., (1998) for heavy metals in Argentina, Merry *et al.,(*1983) for Canada and Onianwa, (2001) for Pb concentration in some soil in Ibadan, Nigeria. These variation in the results may be due to the differences in soil composition, texture and locations with respect to the activities been carried out (Oluyemi *et al.*, 2008).

As shown in (Table 2), pH values obtained ranged between 4.89-6.34$\pm$0.39. The highest pH value was in the soil sample from Keffi with a value of 6.34 indicating weakly acid to alkaline soil while the lowest valuewas in the soil sample from Eleme indicating strong acidic soils. This soil property is a typical characteristic of soil in the region. The pH values above compared well with the results obtained previously by Gideon and Josephine, (2008) for soils in other parts of the Niger Delta region. Leaching processes which removes bases from these soils may be responsible for the lowering of the pH (Fato *et* *al.*, 1997). Acidic properties of soils has great effect on soil composition, it is a well-known fact that pH is an important soil property having great effect on solute concentration and sorption/adsorption of contaminant in soil (Isirimah, 1987). High pH values might reduce the mobility of some metals species down the soil strata while low pH value usually enhances metals distribution and transport in soil. As the pH decreases, the concentration of soluble metal increases (Kuo and Baker, 1980).The level of Fe were very high in all the soil samples analyzed with ranged values of 12044.36-48663.45 (mg/kg) with standard deviation of ±18784.35 and coefficient of variation 67.25% (Table 1).

Table 1: Result of Heavy Metals from Egbema, Eket, Eleme and Keffi, Nigeria (mg/kg)

Parameters	Keffi (control)	Egbema	Eket	Eleme	Mean	S.D	CV%
Fe	6.39	12044.36	23084.99	48663.45	27930.93	± 8784.35	67.25
Cu	0.27	4.87	8.36	11.45	8.23	± 339	39.25
Cd	0.008	29.53	36.79	43.81	36.71	± 7.41	19.45
Zn	1.38	18.72	21.33	29.67	22.24	± 11.08	47.66
Pb	0.001	63.41	72.22	81.16	72.26	± 8.88	12.38
As	0.66	12.86	ND	13.96	13.41	± 0.78	5.80
Co	0.58	8.45	9.57	11.59	9.87	± 1.83	14.01
Ca	29437.10	19034.10	14112.35	11422.90	14856.45	± 3859.77	25.98
Mg	6842.34	4366.88	3428.11	3110.08	3635.02	±653.45	17.98
Al	0.08	2.15	2.90	3.45	2.83	± 0.65	22.97
Na	2104.11	2311.09	2717.53	3016.44	2561.69	± 383.33	14.96
K	0.08	2.13	2.82	3.02	2.66	± 0.46	17.25

ND=Not Detected, SD=Standard Deviation, CV%=Coefficient of variation percent

The highest concentration was from Eleme while the least from Egbema. The high concentration of Fe is an indication of its abundance in all the sampling areas, this observation may not be unconnected with the already established fact that iron is a major component of the earth crust (Giwa *et al.*, 2009). Though iron being relatively abundant in nature has no contamination/pollution index C/P value as the lists of standards formulated by Directorate for Petroleum Resources in Nigeria also excludes iron (DPR, 1991). However, discussion of iron toxicity in this regards to environmental exposure does not exclude iron as a heavy metals of great concern (Anonymous, 1995). Ingesting dietary iron supplements may acutely poison young children. The adverse effect of iron may cause conjunctivitis and retinitis if in contact and remain in the tissues. Fe deficiency may leads to anemia (Lenntech, 2005).Next in abundance to iron was Ca followed by Mg, Na and Pb. Calcium had ranged values of 11422.90-19034.10 with standard deviation of ±3859.77mg/kg and coefficient of variation 25.98% (Table 1). Egbema soil samples have high concentration of calcium among the studied area followed by Eket and Eleme. Ca is one of the metals that are essentials for plant growth. The ranged value for Mg was 3110.08-4266.88 with standard deviations of ±653.45mg/kg and the coefficient of variation of 17.98% (Table 1). The highest concentration of Mg determined was in the sample from Egbema while Eleme was found to have the least. Sodium has ranged values of 2311.09-3016.44 with standard deviation of 383.33 (mg/kg) and coefficient of variation 14.98% (Table 1), the soil that contain high level of sodium can develop salinity problems and also affect soil pH (Kuo and Baker, 1980). Lead values obtained ranged 63.41-81.16 and standard deviation of ±8.88 mg/kg with coefficient of variation 12.38% (Table 1).

Table 2: Result of Sulphates, Chloride ions (mg/kg) and pH Concentrations in the Soil Samples

Sampling Locations	**SO_4^{2-}**	**Cl^-**	**pH**
Control	0.19	0.18	6.34
Egbema	1.87	1.59	5.64
Eket	2.37	2.75	5.12
Eleme	2.84	3.13	4.89
Mean	2.36	2.49	5.22
S.D	± 0.49	± 0.80	± 0.39
CV %	20.55	32.13	7.39

ND=Not Detected, SD= Standard Deviation, CV % =Coefficient of Variation percent

Table 3: Concentrations of Heavy Metals in Soils (mg/kg)

Parameters	Normal range	Critical total concentrations
Cd	0.01 – 2.0	3.0 – 8.0
Co	0.5 - 65	25 – 50
As	0.1 – 40	20 – 50
Cr	5.0 – 1500	75 – 100
Cu	2.0 – 250	60 – 125
Mn	20 – 1000	1500 – 3000
Ni	2.0 – 750	0.0 – 1000
Pb	2.0 – 300	100 – 400
Zn	1.0 – 900	70 – 400

Source: Kabata Pendias and Pendias (1984, 1995 and 2001)

Eleme soils have high concentration when compared to the rest location, though these values indicated significant concentration of this metal but within the standard ranges in soil (Table 3). However, these values may become high above this standard if strict regulations are not put in place. It was reported that lead has the highest compositions of heavy metals in waste oil (Anonymous, 1995). Lead is a common industrial metal that has become widely spread in air, soil, food and water. Inhalation of lead fumes or dust causes abdominal pains and vomiting. The significant concentration of lead in this study may be due to the presence of discarded waste from the industries within the sampling area and its high usage in the form of tetraethyl lead as an anti-knocking agent in the petroleum industry. Cadmium has ranged values of 29.54-43.81 with standard deviation of ±7.14mg/kg and coefficient of variation 19.45% (Table 1), the least concentration was in the soil from Egbema and the highest from Eleme. The irregularities in distribution of cadmium may be attributed to either human activities in these different areas or the soil composition. Metals such as Cd, As and Hg are known to be extremely poisonous. Ayodele and Gaya (1994) reported a high concentration of these metals in municipal dust in Kano, northern Nigeria implying, people in the area may be affected by epidemic associated with these metals pollution, and these could also be said of the sampling areas based on the values obtained for the metals. The concentrations of Cu, Zn, As, Co,Al and K were considered to be low when compared to rest metals with ranged values of between 4.87-11.45 and standard deviation of ±3.39 (mg/kg) for Cu; 18.72-29.67 and standard deviation of 11.08 (mg/kg) for Zn; 12.87-13.96 and SD±0.76 (mg/kg) for As; 8.45-11.59 with

SD ±1.38 (mg/kg) for Co; 2.15-3.45 with SD ±0.65 (mg/kg) for aluminum and 2.13-3.02 with SD ±0.46 (mg/kg) K respectively, (Table 1). For these metals which showed low values, the lower concentrations may be attributed to the average pH values of the soils. Soils with high pH values> 6.6 are known to tie relatively large quantities of these metals and hence their availability (Kuo and Baker, 1980). Values obtained indicated that virtually all the soils are mildly acidic. Olzowy *et al.*, (1993) observed maximum Cu concentration of 460mg/kg with percentile of 122mg/kg in Australian urban soils but found no incidence of toxicity at the site. Similarly, Merry *et al.*, (1983) reported lower Cu concentrations in Australian orchard soil with an average value exceeding 100mg/kg. The concentration of Cu found in this study was far below levels reported by these workers. The concentration of Fe, Cd, Pb, Zn, Co and Cu found in this studies were also far below the one reported by Giwa *et al.*, (2009) for industrial soils from Ibadan, south western, Nigeria implying a gradual accumulation of these metals. Comparisons of the values obtained from Niger Delta region with the control site showed that the control site has lower concentration of heavy metals investigated but ranked high in Ca and Mg content. The difference in the abundance of these metals between control site and the other sites was due to the differences in industrial, human and oil related activities. The examined soils showed spatial variation in the concentrations of these metals in them. The spatial variation in the three oil producing communities is probably due to differences in the amount/rate of oil spills and soil composition and level of industrialization, particularly oil exploration and refining. However, a comparison of the values of metals obtained in this study with the values reported by Kabata Pendias and Pendias, (1984) and Murrman and Koutz, (1972) indicated that the examined soils can be considered unpolluted since the concentration of these metals fit into the typical ranges acceptable with the exception of Ca and Fe. Metals such as Ca, Mg and K that were detected in high concentrations are said to be metals which are essentials for plants growth whereas Na and Al are metals that can affect soil pH and not essential to plants growth. Cd is considered a metal of great concern due to its high toxicity (Giwa *et al.,* 2007). Excessive level of Fe can seriously affect flora and fauna in water bodies (Oluyemi *et al.*, 2008), high ingestion of Zn through the food chain may cause anemia, damage the pancreas, dizziness and neutropenia (Dambo, 2000). Results of sulphates and chlorides in the soil samples indicated high concentration in the soil (Table 2). The high sulphate values were from Eleme and the least from Egbema. Similarly, high chloride content was obtained in Eleme than the rest location. These values compares well with the ones obtained by Paul *et al.,* (2001) for eastern, Nigeria. However, the control site showed the least concentration of ions (Table 2). The presence of sulphate and chloride in the studied area indicated the high level of ions. In tropics, much highly weathered soil can have an anion exchange capacity (Davidson, 2000). This means that the soil will attract and retain anions rather than cations. At high concentration of metals ,cationic metals will form insoluble hydroxides, carbonates or sulphide precipitate (Sposoti, 1989).The solubility is a function of the concentration of the metal and precipitant, the solution pH and the concentration of other interacting metal ions and ligands (Harter, 1983). High concentration of sulphates has the tendency of plugging the pores of reservoirs, thereby reducing fluid flow in the reservoir and sustained injection pressure of solution which can lead to reservoir formation damage during oil exploration while the chloride ion have the tendency of bonding with some metal ions leading to high salinity problems in the area (Gogoi, 2003). The reaction of metal ions with solid phase has a dependency on pH resulting from the surface chemistry of soil material (Harter, 1983).

Conclusion

The result obtained from this study showed variation in pH values for all the soil samples. The acidities of the soilsindicated high tendency of the availability of heavy metals. The higher values obtained for heavy metals in the Niger Delta may be as a result of increasing industrialization and oil exploration activities in the area and the soil composition. In general, the concentration of the metals in the studied sites does not indicate pollution except for Pb and Cd. These metals may exceed their limits overtime when proper measures are not put in place.

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