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# DISTRIBUTION OF HEAVY METALS IN SOIL OF BEACH SAND ORIGIN IN NIGER DELTA AREA OF NIGERIA

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**Abstract:** The distribution of ten heavy metal ions (Pb. Cd. Ni, As, Se, Hg. Cr, Cu, Fe and Zn) in soil of beach sand origin in Akwa Ibom State, a humid tropical Niger Delta area was investigated. Soils were sampled in ten locations at predetermined depth intervals of 10 cm, 15 cm, 20cm and 25cm to represent top soil (0 - 15 cm) and sub soil (15 – 30cm. A general decreasing trend in metal ions concentration with soil depth was established. The mean concentration (μg/g) of the metals in the soil at 10 cm (surface soil) were 40.05 (Pb); 0.09 (Ni). 0.45 (Se); 0.04 (Hg), 0.60 (Cr), 126.25 (Cu), 6375.0 (Fe) and 254.50 (Zn), whereas at 25cm (sub soil) the concentration (μg/g) were 21.45 (Pb), 0.04 (Cd), 0.03 (Ni), 0.42 (Se), 0.02 (Hg), 0.56 (Cr), 79.55 (Cu), 3795.96 (Fe) and 130.25(Zn). The concentration values for Cu, Fe and Zn were high and adequate as soil nutrients both in the top soil and subsoil indicating sufficiency and intensity factor. The concentration of heavy metals of environmental concern, namely Pb, Ni, Se, Hg, Cr, and Cd in the soil were low and of minimal concern regarding pollution and toxicity to crops. However, continuous monitoring and proactive actions should be done to prevent buildup and persistence in the soil.

## INTRODUCTION

With increased exploitation of natural resources, industrialization and urbanization, most areas of the Niger Delta region of Nigeria are facing increasing ecological problems arising from the release of pollutants into both the aquatic and terrestrial environments. Heavy metals constitute a significant group of these pollutants(1). While many heavy metals are essential elements at low levels of concentration, they can exert toxic effects at concentrations higher than permitted in the environment (2). The soil serves as a sink for pollutants, and while acting as a buffer, it controls the movement of heavy metals to other components of the environment namely: surface water, ground water, plant and animal food chains. Most of the heavy metal pollution problems in soil are attributed to the accumulation of mercury, cadmium, lead, Arsenic, Nickel, Copper, Zinc, Chromium and Selenium. If these metal concentrations exceed the holding capacity of the soil, there is the danger of their seeping into ground water and flowing laterally into surface waters. Sources of heavy metals to the soil include pesticides and fertilizers (3), automobiles (4, 5 and 6), dumping of industrial and municipal wastes, etc.

In the present study, the content of some heavy metals in the dominant soil of beach sand origin in Akwa Ibom State in the Niger Delta region was examined with the aim of ascertaining the quality of the soils currently under intensive exploitation for oil, gas, agriculture, industries and dumping of wastes.

## MATERIALS AND METHODS

A total of 40 soil samples were taken using a sampling auger. The soil samples were taken from ten locations in Ibeno Local Government Area of Akwa Ibom State, Nigeria at depths of 10cm, 15cm, 20cm and 25cm respectively. Initially, three samples were taken from each location at the respective depths and later homogenized into composites. The samples were placed in labeled metal-free polythene bags and taken to the laboratory for processing and analysis.

In the laboratory, the samples were air-dried and later crushed with mortar and pestle, sieved through a 2.0mm sieve and stored for analyses. The samples were sub-sampled for chemical and physical analysis as well as for gravimetric moisture content determination. Samples meant for total metal determination were acidified with concentrated $HNO_3$[7].

Particle size analysis was carried out using the hydrometer method [10] while moisture content was determined by the gravimetric method. Soil pH was determined in the soil / water ratio of 1:1 using a glass electrode pH meter. Electrical conductivity (EC) was determined in the 1:1 soil to water ratio using conductivity meter. (Organic carbon was determined by the dichromate wet oxidation method [8].

Total Nitrogen was determined by the macro – Kjeldahl digestion and distillation method. Available phosphorus was extracted by Bray P-I method while P was determined in the extract by the blue colour method [9]. Exchangeable bases (Ca, Mg, Na, K) were determined by EDTA titration method while Na and K were determined by Flame Analyzer. Exchangeable Acidity (EA) was carried out by extraction with IN KCI solution while $H^+$ and $Al^{3+}$ were obtained by titration.

Effective Cation Exchange Capacity (ECEC) was obtained by Summation method [10]. The method was used for total metals after digesting 1g of soil sample with concentrated $HNO_3$ and Perchloric acid. Atomic absorption spectrophotometer (Pye Unicam 919 model) was used to assay metals element content in the soil samples.

## RESULTS AND DISCLISSION

The summary of the physical and chemical properties of the soil is given in Table I. The soils are mostly sandy loam to loamy sand on the surface and sandy loam in the subsurface. This texture allows for free drainage and ease of mobility of ions within the soil. Important parameters, namely: organic matter content appears very low with values averaging 2.9%, Effective Cation Exchange Capacity (ECEC) varied widely from 7.78 to 18.01 cmoh/kg, the pH ($H_2O$) values ranged from 4.46 to 5.46 while the exchangeable acidity (EA) showed a mean of 3.08 cmol/kg. Table 2 shows the distribution of nutrient elements and heavy metals in the soil. Soil texture and structure are key in exerting influence on soil physical and chemical properties notably: drainage, aeration, water holding capacity, nutrient retention and movement of contaminants within the soil profile. The mobility of elements, nutrients and metal ions depend on diffusion through porous medium and other variables such as soil porosity and moisture content.

Total pore space is significant in determining soil drainage and movement of nutrients and pollutants in the soil. In the soil under study, total pore space appears low but a large proportion of it is composed of large pores that are very efficient in the movement of water and air.

Organic matter content in the soil is generally low and conforms with previous studies within the zone [11 and 12]. Organic matter and its derivatives are important colloids involved in nutrient elements and metals retention. Soils with low organic matter and high content of low activity clay such as most soils in the zone allow free movement of ions to ground water and this is of importance to environmental quality. Soils high in organic matter could retain ions from various sources (organic, inorganic and air) thereby slowing down mobility of contaminants into various pools.

The range of Effective Cation Exchange Capacity is medium to high (7.78 – 18.01 cmol/kg) on the FAO (1979) rating of between 8 - 10 cmol/kg minimum values in the top 30 cm of fertile soils. The implication of the ECEC values is that the soil has strong affinity to hold nutrient elements and heavy metals in equilibrium between soil solution and soil colloidal complexes.

Table 1: Physicochemical characteristics of soil

| Location | pH | EC | Organic matter | Total N | Avail`. P. | Moisture content % | Ca | | Mg | Na | K | EA | ECEC | Base Saturation | Bulk Density | Total porosity | Sand | Silt | Clay |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Exchangeable Bases | | | | | | | | | Particle size Analyses | | | |
| | ($H_2O$) | ds/m | % | % | Mg/k | | | | Cmol/k | | | | | % | g/cm³ | % | % | % | % |
| 1 | 5.33 | 0.1940 | 3.86 | 0.91 | 21.66 | 20.00 | 9.60 | 4.82 | 0.10 | 0.25 | 2.72 | 17.49 | 84.44 | | 1.57 | 40.75 | 71.80 | 8.00 | 20.20 |
| 2 | 5.23 | 0.3680 | 3.26 | 0.16 | 10.66 | 13.60 | 4.80 | 2.40 | 0.29 | 0.32 | 2.74 | 10.55 | 74.03 | | 1.42 | 46.42 | 69.80 | 6.00 | 24.20 |
| 3 | 4.70 | 0.8260 | 2.61 | 0.13 | 9.33 | 21.70 | 10.32 | 4.20 | 0.23 | 0.30 | 2.96 | 18.01 | 83.56 | | 1.68 | 36.60 | 56.80 | 6.00 | 28.20 |
| 4 | 4.61 | 1.561 | 2.28 | 0.11 | 4.66 | 16.40 | 4.80 | 2.40 | 0.23 | 0.40 | 3.10 | 10.93 | 71.64 | | 1.36 | 48.68 | 67.80 | 6.00 | 26.20 |
| 5 | 4.46 | 0.600 | 4.52 | 0.23 | 2.49 | 17.00 | 2.88 | 1.92 | 0.27 | 0.27 | 2.44 | 7.78 | 68.63 | | 1.33 | 49.81 | 65.80 | 4.00 | 30.20 |
| 6 | 4.49 | 0.0159 | 3.00 | 0.15 | 5.46 | 14.40 | 4.80 | 2.88 | 0.30 | 0.26 | 3.96 | 12.20 | 67.54 | | 1.57 | 40.75 | 63.80 | 4.00 | 32.20 |
| 7 | 5.10 | 0.0195 | 1.62 | 0.10 | 2.83 | 12.90 | 4.80 | 2.50 | 0.22 | 0.29 | 3.72 | 11.53 | 67.74 | | 1.68 | 36.60 | 67.80 | 8.00 | 24.20 |
| 8 | 4.97 | 0.4630 | 2.61 | 0.12 | 1.66 | 20.40 | 4.80 | 2.16 | 0.21 | 0.29 | 2.93 | 9.16 | 68.01 | | 1.40 | 48.10 | 69.80 | 6.00 | 24.20 |
| 9 | 4.71 | 0.6880 | 3.53 | 0.18 | 4.36 | 18.20 | 3.60 | 1.92 | 0.35 | 0.30 | 2.70 | 8.91 | 69.69 | | 1.42 | 46.42 | 63.80 | 6.00 | 30.20 |
| 10 | 5.46 | 0.01530 | 1.75 | 0.11 | 4.36 | 13.10 | 2.40 | 1.68 | 0.16 | 0.31 | 3.60 | 8.15 | 55.83 | | 1.67 | 36.40 | 57.80 | 10.0 | 32.20 |
| Mean (x) | 4.90 | 0.4750 | 2.90 | 0.14 | 6.74 | 16.70 | 5.16 | 2.67 | 0.23 | 0.29 | 3.08 | 11.47 | 71.11 | | 1.51 | 43.05 | 66.4 | 6.40 | 27.20 |
| S.D. | 0.34 | 0.4564 | 0.871 | 0.0399 | 3.07 | 3.07 | 2.54 | 0.98 | 0.68 | 0.039 | 0.48 | 3.42 | 7.23 | | 0.13 | 5.13 | 4.78 | 1.74 | 3.82 |
| C.V (%) | 6.99 | 96.10 | 30.05 | 28.5 | 84.41 | 18.38 | 49.10 | 36 | 29.6 | 13.66 | 15.45 | 29.84 | 10.17 | | 8.73 | 11.92 | 7.19 | 27.24 | 14.04 |

Table 2: Variation of heavy metal concentration with soil depth

| Heavy Metal (μG/G) | Soil Depths | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 10cm | C.V. % | 15cm | C.V.% | 20cm | C.V% | 75cm | C.V.% | FEPA * |
| Pb | 40.05 ± 14.03 | 35.05 | 29.08 ± 13.30 | 45.58 | 24.69 ± 14.40 | 58.50 | 21.45 ± 16.17 | 75.36 | 100.0 |
| Cd | 0.00 ± 0.00 | - | 0.05 ± 0.16 | 320.00 | 0.04 ± 0.13 | 3.25 | 0.04 | - | 5.0 |
| Ni | 0.00 ± 0.00 | - | 0.06 ± 0.01 | 200.00 | 0.04 ± 0.13 | 3.25 | 0.025 ± 0.08 | 266.67 | 100.0 |
| Se | 0.445 ± 0.04 | 8.26 | 0.43 ± 0.03 | 9.30 | 0.43 ± 0.03 | 6.98 | 0.42 ± 0.03 | 7.14 | |
| Hg | 0.04 ± 0.12 | 3.15 | 0.04 ± 0.12 | 325.0 | 0.02 ± 0.06 | 300.0 | 0.02 ± 0.06 | 300.0 | |
| Cr | 0.0595 ± 0.12 | 4.71 | 0.61 ± 0.06 | 9.84 | 0.595 ± 0.04 | 6.67 | 0.555 ± 0.06 | 10.71 | 100.00 |
| Cu | 126.5 ± 0.03 | 3.11 | 107.75 ± 9.89 | 0.09 | 97.85 ± 15.81 | 15.87 | 79.55 ± 20.36 | 25.59 | 100.00 |
| Fe | 6375.0 ± 1646.79 | 25.83 | 5716.45 ± 1397.84 | 0.24 | 4770 ± 1769.91 | 37.11 | 3795.96 ± 2095.34 | 0.03 | |
| Zn | 254.5 ± 131.36 | 51.61 | 201.65 ± 97.65 | 0.48 | 143.3 ± 27.85 | 19.43 | 130.25 ± 21.70 | 16.66 | 300.00 |

The soils are generally acidic and acidity controls availability, mobidity and toxicity of heavy metal ions in the soils. Most metals tend to be less mobile in soils with high pH as they form insoluble complexes [(13)]. Generally, the concentrations of Fe, Zn and Cu in the soil are high and they decrease with depth, whereas the concentration of Cd. Ni, Pb, Hg and Cr are very low, indicating low potentials for contamination of the soil (Table 2). The results are within the range obtained by Aiyesanmi (2005)[(14)] and Awolala et al (2007)[(15)]. The concentrations of all the metals are below critical levels proposed by FEPA (1991) and NCC (1991) to constitute hazard. The solubility of Fe and resultant migration potential is influenced by the pH and redox equilibrium between $F^{2+}$ and $Fe^{3+}$.

Generally, the migration and solubility potential of the heavy metals within the various soil depths depend on the pH, redox potential. complexibility and ionic concentration of the metal [(16)]. The concentration of the metals showed inverse relationship with pH. Pb, Cu, Fe and Zn are transition metals and are capable of forming complexes. Complexation increases the potential mobility of metals because the complexed metal is effectively more soluble and the complex formed binds what would have otherwise been free metallic ions and thereby decreases the process of adsorption or precipitation as salts [(17)].

Lead often undergoes speciation to the more insoluble sulphate, sulphide oxides and phosphate salts and thereby has low mobility in soils coupled with the averagely low content (< 15ppm) in most soils [(18)]. Copper availability is also influenced by soil pH as availability of Cu decreases slowly with increasing pH, but the nature of the interaction is not well understood. Cu appears in the soil mainly as the divalent $Cu^{2+}$ ion adsorbed by clay colloids or associated with organic matter. Generally, organometallic substances are more soluble than either of the units making up the complexes. Hence $Cu^{2+}$ ion in an acid soil condition becomes soluble and available to plants in spite of the interaction with soil organic matter.

Although the most stable forms of chromium are $Cr^{6+}$ and $Cr^{3+}$, the former which is relatively mobile often reduces to $Cr^{3+}$ in acid medium. This often leads to the precipitation of Cr as Cr $(OH)_3$. However, in an acid soil condition, the precipitate dissolves making $Cr^{3+}$ mobile and available in the soil. The availability of Fe to plants is influenced mainly by soil pH and the redox equilibrium between ferrous ($Fe^{2+}$) and ferric ($Fe^{3+}$) forms, the solubility of both forms decreasing with increasing pH. Since the tendency for $Fe^{3+}$ ion to be reduced to the more stable $Fe^{2+}$ ion is much higher [19], it is not surprising to see the very high concentration levels of Fe in all the samples analyzed.

Zinc may exist as $Zn(N0_3)_2$, $ZnC1_2$ and $Zn(CH_3COO)_2$ or any soluble form in water and in the soil system. Cd exists in its most stable form in the soil as $Cd^{2+}$ ion [20]. Selenium exists in two major oxidation states namely; $Se^{6+}$ and $Se^{4+}$. $Se^{6+}$ is more mobile but less toxic and often reduces to $Se^{4+}$, a more toxic species, which is less mobile and often localized in the soil [28].

The contents of Ni and Hg in the soils studied appear in traces and highly restricted indicating possible point source deposition of materials containing low levels of Ni and Hg and subsequently migration over time to the subsoil.

## CONCLUSION

The contents of trace mineral elements and heavy metals ions have been assessed as a function of some physical and chemical properties of the soil. The availability of these metal ions and their mobility in the soil of beach sand origin is seen to be essentially influenced by the acidic nature of the soil, which aids in the speciation of the metals to more soluble mobile species. In view of the physical nature of the soil, being mostly sandy loam and loose, a build up of some of metals ( Cu, Fe, and Zn) from external sources namely industrial and municipal wastes may result in migration with percolating water into the ground water and lateral wash into surface water and create cycles of pollution. Routine monitoring of heavy metal content of these soils and methods of remediation of contaminated and polluted soils should be put in place for implementation in the ordinary day to day land use and environmental quality practices.

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