CONSEQUENCES OF EFFLUENT DISCHARGE AND SEAWATER INTRUSIONS ON SOILS' NUTRIENT POOLS AND BIOLOGICAL SPECTRA IN NIGER DELTA

Dennis I. Edem and Charles U. Udoinyang

Abstract: Terrestrial ecosystems are gradually becoming scarce for agricultural purposes due to population growth and rising food demands, infrastructural developments and their declining fertility status Wetlands with few exceptions are emphasized to supplement the terrestrial uplands because of favourable soil water balance, moderate to high fertility status and low soil erosion hazards. This study has investigated changes in wetland soils' nutrient pools and biological spectra along oil and gas flow line route in the coastal area of the Niger Delta, Nigeria, focusing on the recent changes in soil nutrients with the influences of seawater and effluent discharge from the crude oil exploration stations using spatial interpolation from observed point. We examined the statistical data at 115 sampling stations during low tide in the dry season. It was shown that discharge effluent and seawater intrusion was the major factor leading to differences in soil nutrients pool pattern in the region. The important physical advantage of this soil is its non-vulnerability to soil erosion particularly under aggressive rainfall condition. Also, the significant increase in PAH accounted for K immobilization (-0.932^{**}), where P increased on the surface soil, the population of HUB counts were negatively affected (-0.865^{**}). However, positive increase in Aliphatic hydrocarbon lead to corresponding increase in TPH (0.956^{**}) and sulfur (0.998^{**}) on the surface and subsurface soils respectively. Although low level of heavy metals occurrence in the soils is not of any environmental concern, the saline and organic nature of the soils places severe restriction on arable agricultural activities. Therefore, there are good reasons to control the level of effluent discharges into this unique soil environment.

Keywords: effluents, Niger Delta, oil and gas, salinity, seawater, soil pollution

Introduction:

Dennis I. Edem and
Charles U. Udoinyang:
Department of Soil Science and Land Resources Management
Faculty of Agriculture
University of Uyo, Uyo
P.M. B.1017
Akwa Ibom State, Nigeria
e-mail:
Dennis I. Edem:
dennis.edem@gmail.com
Charles U. Udoinyang:
Charles_udoinyang@yahoo.com

Soils are the heart of terrestrial ecosystems. An understanding of the soil system is therefore the key to success and environmental harmony of any human endeavor on the land (Brady and Weil 2013). Wetland ecosystems are sites of rapid biogeochemical cycling due to the interactions between the oxic soil surfaces and deeper anoxic soils (Weiss et al. 2003). Wetland soils are soils formed in a variety of parent materials that are commonly associated with saturated moisture conditions (Mitsch and Gosselink 2000). Saturated soils develop several unique morphological

characteristics as a result of several oxidation-reduction reactions influenced by the nature and content of organic matter, temperature, the nature and content of electron acceptors and pH.

Wetlands are heterogeneous environments which can exhibit substantial spatial and temporal variability in soil properties (Bruland and Richardson 2004). Wetland soils or hydric soils are soils with aquic soil moisture regime (Soil Survey Staff 1999). The occurrence of hydric soils is conditioned by hydrology, lithology, physiography, rainfall amount and distribution pattern (Ogban et al. 2011). Wetlands have multifarious potentials as seen in other parts of the world (Ojanuga, Okusami and Lekwa 1996). Izac, Swift and Andriesse (1990) and Ogban et al. (2011) reported that wetlands are reputable to produce over 90 % of crops grown on upland farms, suggesting that the, potentials of wetlands can be used for agricultural production on a sustainable basis.

Seawater intrusions caused by tidal fluctuations and effluent discharges from the crude oil activity is considered to be a major constraint to agricultural production in coastal area (Tuong 2003) of the Niger Delta. This is particularly the case in the Niger Delta regions with large lowland plains facing the sea. Here seawater and discharged effluent intrusions can reach deep into the soils through rivers and canal resulting in contamination of the soil environment. The extent of seawater and effluent intrusions varies widely with time and place; it is influenced by seasonal river flow (Sam 2006) and level of slurry discharges from the flow stations. Furthermore, there is concern that consequences of seawater and effluent intrusions on soil nutrient pools and biological spectra may be amplified by rising sea levels and changing rainfall patterns due to global climate change in the near future.

Canal and river water management for wetland soil protection has been changed with the conversion of wetland for oil exploration. As a consequence of recent hydrological developments and changes in coastal soil, it seems that the influence of seawater and effluent intrusions on soil has changed the soils' nutrient pools and biological spectra in this region. Several case studies (Bi et al. 2009; Cloquet et al. 2006; De Vleeschouwer et al. 2009) have shown that sewage or effluent discharged from production industries into the immediate environment (main waste disposal point) deposits varying degrees of metal and toxic organic concentrations which have been observed to exceed the threshold limit on vegetations and farmlands.

This anthropogenic activities, contribute significantly to high level of pollution. Also, since the sewage contains pathogenic disease carrying organism, it is extremely dangerous for health. Even though there have been extensive studies on wetland soils (Sahrawat and Narteh 2002; Bruland and Richardson 2004; Ogban et al. 2011) about sea water salinity effects on rice plants' physiology at the field level (Garcia 1997; Maas and Hoffman 2007), little or no recent information is available on interrelationships between seawater, oil and gas effluent discharges on soils' nutrient pools and biological spectra in coastal area of the Niger Delta.

Such information could be indispensible for planning agricultural policy and new research for developing methods that increase and stabilize agricultural development and a healthy standard of living among the coastal dwellers. This research is therefore describing the interrelationship between seawater and effluent intrusion on soils' nutrient pools and biological spectra along oil and gas flow line route in the coastal area and its commitment to a healthy, safe and sound environment.

Materials and methods:

Environment of the study sites

The field falls within the saline (mangrove swamp) zone of the Niger Delta, which is

straddled by the belt of beach-ridges seaward and the freshwater alluvial zone on the inland side of latitude 5°14' E and longitude 6°43' N. In addition, a network of rivers, creeks and inlets intersects the field, and mangrove swamps/forests abound. The major soil types in the Obieba (OB/OB) mangrove swamps consist of soft mud, Chikoko (Peaty Clays) and saline sands. However, soft mud constitutes about 90 % of the Soils. Most of the land is inundated by salt water during high tide. At Obieba field, the diurnal average for temperature is 29.6 °C, while maximum and minimum air temperatures were 35.5 °C and 24 °C, respectively. The diurnal average for relative humidity was 61.6 %. However, the relative humidity was maximum (84 %) and minimum (41 %) recorded at 04:00 GMT and 13:00 GMT, respectively. The average wind speed measurement was 2.10 m/s. A high percentage of the wind (45 %) was north and northwesterly, and this corresponds to the direction of the sea. The study area is a coastal region known to be affected by land and sea breezes. These breezes are products of local pressure differences resulting from the alternate warming of adjacent land and sea. The cloud measurements indicate a low mean of 3.00 Oktas. This was so because much of the sky was clear during the period of field measurements. However, the months of July and August have the highest mean cloudiness.

Sampling procedures

In the process of assessing the flow of effluent discharge along the flow-line, two simplified sampling procedures used were: lateral and vertical spreads. Laterally, assessment on the spreading of properties with surface displacements at 0-15, 15-30 and 30-60 cm depth exceed several meters to cover 115 sampling stations around the oil and gas facilities. Additionally, vertical stratified coring approach was adopted at two depths of 0-50 and 50-100 cm on the premise that downward ground movement of

effluent continue under gravity loads until a state of minimal potential energy (at 1 meter depth) was achieved. Soil samples were physically examined; analysed data were interpreted with statistical analysis of computer programme.

Laboratory analyses

Soil particles size distribution was analysed using Robinson pipette method on air dried soil sieved on 2 mm mesh sieve and following the procedure described by Mathieu and Pieltain (1998). Particles size distribution was measured after oxidation of the organic matter with hydrogen peroxide (H_2O_2) of a soil sample sieved through 2 mm mesh, followed by particles dispersion with a sodium hexametaphosphate solution $(NaPO_3)_6$ (Van Reeuwijk 1993).

Soil organic carbon was determined using the Walkley and Black method (1934). The total nitrogen was measured by dried combustion and by Kjeldahl method (Moral et al. 2005). All samples were dried in a forced-air oven at 60 °C and ground to 0.5 mm for analysis. Total organic carbon was determined by oxidation with $K_2Cr_2O_7$ in H_2SO_4, according to Yeomans and Bremner (1989).

NH_4^+-N was extracted with 2M KCl and determined calorimetrically by the phenol salt method (Honeycult et al. 1991).

NO_3^--N was determined by second-derivative spectroscopy in a 1:30 (w/v) water extract (Sempere et al. 1993). Total nitrogen (N_t) and organic nitrogen (N_{org}) were calculated as the sum of Kjeldahl -N and NO_3^--N and as the difference between N_t and the inorganic nitrogen (sum of NH_4^+-N and NO_3^--N), respectively.

Heavy metals in soil were determined by the perchloric acid digestion method as described by Udo (1986). Two grammes of air-dried soil which had been passed through a 2 mm sieve was weighed into a 150 ml beaker. To this was added 20 ml of concentrated HNO_3, followed by 15 ml of $HClO_4$ after it was allowed to stand for one hour. The mixture was then digested on a hot

plate till it turned white. The residue was dissolved in dilute HC1 and filtered. The filtrate was then used for the determination of Zn, Cd, Pb, Cr, V and Ni by atomic absorption spectrophotometry. Consideration was taken of the dilution factor in concentration calculations.

The total hydrocarbon content of soils was determined by the spectrophotometry method. Ten grammes of a representative soil sample were extracted with 20 ml of toluene. The absorbance of the toluene extract was then measured with the aid of a spectrophotometer at 420 nm wavelength. The spectrophotometer reading was then converted to parts per million by reference to a standard curve which was prepared using known concentrations of hydrocarbons in the extractor.

Microbiological Studies

Total Viable Bacterial Counts

The heterotrophic bacterial counts of the samples were determined by inoculating 0.1 ml aliquots of 10 soil dilution on to the surface of four (4) Nutrient Agar plates, spread by means of a sterile glass rod, and incubated at 28 ^{o}C for 48 hours. Suppression of fungal growth was ensured by incorporating fungi zone, 10 µg/ml (Walker and Colwel 1976) to the Nutrient Agar. Counting of colonies in plates with 30-300 colonies was done.

Enumeration of Fungal Populations

Potato Dextrose Agar containing penicillin (0.5 %) chloramphenicol (0.5 %) and streptomycin (0.25 %) (Raymond et al. 1976) was used. These antibiotics help to eliminate bacteria from the Agar plates. Aliquots (0.1) ml of 10^{-7} soil dilution was inoculated onto dry Agar plates. Incubation was at 28 ^{o}C for 72 hours and developing fungal colonies were counted.

Counts of Oil-Degrading Micro-organisms

The densities of oil-degrading bacteria and fungi in the samples were determined by inoculating 1.0 ml aliquots of 10^{-2} water dilution or 0.1 ml of 10^{-7} soil dilution on to oil Agar plates (at pH 7.6) to which were incorporated fungi zone, 10 µg/ml (Walker and Colwell 1976) for the isolation of bacteria. The incubation was done at a temperature of 37 ^{o}C for 72 hours. For the isolation of fungi, pH of the medium was adjusted to pH 4.0 and antibiotics (penicillin G, 0.5 %; chloramphenicol, 0.5 % and streptomycin, 0.25 %) were incorporated (Raymond et al. 1976) to suppress bacterial growth. The suspension was spread by means of a sterile bent rod and the plates were incubated at 28 ^{o}C for 72 hours until colonies appeared. Counting of colonies in plates with 30-300 colonies was done.

Statistical methods

The data were subjected to the analysis of variance according to the experimental design (linear model with interactions), by the analysis software SAS® (Statistical Analysis System Institute Inc., Cary, NC, USA). For the significant effects, the averages were compared using Student-Newman-Keuls method (Dagnelie 2003). To estimate the spatial distribution of the average contaminant concentration, we applied the spline interpolation method using ArcGIS 9.1 (ESRI Inc., CA) to the observation data points. The average area affected by total petroleum hydrocarbons (TPHs) were compared to show the level of effluent intrusion among the six strata in the coastal area.

Results and discussion:

Physical examination

Some important physical parameters examined in the field for this study are: texture, colour and odour.

The texture of the soil was judgmentally assessed by feeling with the hands. Textures

along the transects were observed to range from loamy sand to sandy loam.

The colour of the soils varied from its true colour to apparent colour. At the surface soil level (0-15 cm) and the sub surface levels (15-30 and 30-60 cm), most locations appeared dark brown, but in the areas with lush vegetation, the colour varied between dark brown to black, while areas with ponded effluent discharges changed the soil colour to dark yellow-grey-brown. This is accessioned during fermentation of gases and organic materials.

Odour measurement was by (smelling) physiological response of olfactory nerve to volatiles from organic matter and biological materials in the soil. The perceptile residual odour (threshold odour number) was pungent smell. This was common in locations with pH value < 5.0 and could be attributed to dissolved oxygen in the discharged water during anaerobic process in the soil environment.

A. Lateral assessment of soil properties

Soil pH (Redox reactions)

Soil reaction which is given in terms of pH value is a measure of the free hydrogen ion (H^+) concentration of soil solution. The value of the free H^+ concentration in a soil influences the availability of nutrient elements and biochemical reactions in the soil (Bohn and Connor 1984). In strongly acidic soils for instance basic cation uptake by plant roots is inhibited. Beneficial soil micro organisms are affected by soil reaction. Generally, the pH of OB/OB soil averaged very strongly acidic (4.9) in the three depths sampled. On the surface soil, it ranged from acidic value of 4.4 to slightly acidic value of 5.7 and from 4.3 to 5.2 at the sub surface level of 30 cm. At the depth of 60 cm, pH averaged 4.5. Acidity is generally associated with leached soils; however agricultural practices and industrial discharges do alter soil pH. Soil pH is often considered in terms of the soil capability and suitability to support plant growth. The pH

of 4.8 is set as the lower limit for optimum growth of plants, and conversely the pH greater than 7.5 is regarded as the extreme upper limit (alkalinity) at which some plants can still grow (Troeh and Thompson 1993). Thus, without any exception, the soils can support plant growth.

Electrical Conductivity

The electrical conductivity of a soil indicates the total ionic strength (anions and cations) of a soil. Low total ionic strength in a soil indicates low dissolved salt contents and vice versa. Consequently, Electrical conductivity increases with higher amount of soluble salts. Electrical conductivity values of soils on the surface soil ranged from 2.0 µs/cm (sample station 6) to 21.0 µS/cm (sample station 19), from 1.0 µS/cm (sample station 17) to 18.0 µs/cm (sample station 4) and from 7.0 (station 1) to 25.0 µS/cm (station 11) at the sub surface levels of 30 and 60 cm respectively. The electrical conductivity value of the soil at surface and sub surface levels is very low. These values are below the tolerance levels for exchange of plant nutrients for optimum growth (Akinrinde 2006) and it is an indication of nutrient inhibition due to low THBC and HUB (r = -0.462[**] and 0.437[**]).

Salinity

Salinity determined as chloride is a monovalent stable oxidation state of halogen in soils. It is essential for plant growth in trace amounts. Excessive amount of chloride in soils increase the osmotic pressure of the soil water thereby reducing the availability of water to plants (Isirimah et al. 2006). The concentration of chloride on surface soils (Tab. 1, Annexes) ranged from 17.00 mg/kg in station 6 to 455 mg/kg in station 18 and from 17.8 mg/kg to 530.0 mg/kg. However, EC values ranged from 9.33 mg/kg to 420.0 mg/kg at the subsurface soil levels of 30 and 60 cm respectively. The saline content of these soils was high both on surface soil and sub surface soil indicating that the greater

proportion of applied soluble salt is due to high nitrate concentration and from the discharge effluent from the oil and gas plant and seawater intrusion.

Phosphorus

This is a major nutrient require by plant in large quantity. Average P availability on the three depths is 2.35, 2.14, and 1.90 mg/kg respectively. That is the effect of the intrusions on Phosphorus was more on the 0-15 cm and reduced downward. Because of its low solubility in water, this nutrient particle accumulates in areas of slow-moving water and caused rapid increase in the population of photosynthetic algae which may exceed many times its normal density. Such a bloom turn the water bright green, prevent light from penetrating beneath surface layers and therefore often kill plant**s** living at the bottom (Massas et. al. 2009). Over time therefore, phosphorus enrichment of fresh water ecosystem leads to the destruction of aquatic life and their filling in with organic sediments.

Nitrate-N

As shown in (Tab. 1, Annexes), Nitrate-N content of soil gives an indication of the organic nitrogen present in the soil. Most of the Nitrogen in soils is in the organic form as only relatively small quantities occur in NH_4^+, and NH_3^+; the more available forms. The amount Nitrate-N in the soil is an indication of how suitable the conditions in the soils are and the content in this study sites could be classified as low to medium concentration. A value below 0.1% of nitrate N is considered low for soils (NPSP 2005). In the study area, the concentration on the surface soil (0-15 cm) ranged from 0.01 mg/kg to 10.0 mg/kg and from 0.017 mg/kg to 0.89 mg/kg at subsurface levels of 15-30 cm. However at depths of 30 cm - 60 cm, it varied from 0.01 to 0.79 mg/kg. Nitrate-N concentration level over the three depths averaged 1.045, 0.496 and 0.382 mg/kg respectively. These differences were

significantly at 5 % level. The highest concentration recorded on the surface was not surprising.

Total hydrocarbon (THC) content

The study area is at the proximity used for petroleum hydrocarbon production activities thus necessitating the need for evaluating the total hydrocarbon content of the soil. Results as presented in Tab. 1 (Annexes), revealed Total hydrocarbon (THC) concentrations ranged from 2.80 mg/kg to 33.6 mg/kg on the surface level (averaged 12.90 mg/kg), and from 0.80 mg/kg to 22.5 mg/kg averaged 8.15 mg/kg, and from 0.30 to 58.0 mg/kg (4.65 mg/kg) at the subsurface soil level of 30 and 60 cm. The ranges were higher at both surface levels. Although the THC result reveals that, the area therefore is contaminated by petroleum hydrocarbon. According to the findings of Rajvaida and Markande (1998), it is better to consider the toxicity of organic compound in groups on the basis of compound containing C=H, C=H=O, C=H=N and C=H=S=P, as these is capable of affecting the CNS. Therefore, in the analysis of petroleum slurry, the result suggests the contribuive effect of these toxic compounds to THC in this soil.

Total organic carbon (TOC)

Soil organic carbon usually mixes up with fine clay particles to form soil colloids. It is an important soil fraction due to its binding properties that enhance most physical and chemical activities in the soil. Thus, there is increased contact with other colloids and with soil solution. This results in the strong friction and cohesion bonds between particles and soil water. This is also a major reason why clay soil holds together better than sandy soil when wet. In some soil locations examined, the TOC was seen to be in small quantities, but its effects on soil function were profound. This ever-changing soil component exerts a dominant influence on the soil's physical, chemical and biological properties of OB/OB especially on

the surface horizon. The analytical result revealed that total organic carbon, ranged from 3.82 to 820 g/kg at the surface level (0-15 cm) and 195 to 780 g/kg, and from 105 to 600 g/kg at the sub surface levels of 15-30 and 30-60 cm, with average values of 568.74 g/kg, 503.35 and 418.75 g/kg in the respective soil levels. The ratio of carbon to nitrogen is generally lower for subsurface soils than the surface layer. Also, C/N ratio in the organic matter across the depth is > 500:1 and this is detrimental for cultivation of arable crops. Even-though the sites are very high in organic carbon, this level of concentration can be referred to as toxic in the present unsaturated form, and is capable of causing lungs and kidney discomfort including eye, lung and throat irritation.

Heavy metals

The mineral element originates from soil and is dissolved in water for plant root absorption. Those required in small quantity for optimum performance are regarded as trace elements. The concentration of these metals can however be increased to become potential pollutants if heavy metals – containing waste products from industrial or domestic activities **-** are introduced into the environment (Nunez-Delgado et al. 2002). Concern over the presence of heavy metals in an environment arises from the fact that they cannot be broken down into non toxic forms. Thus once aquatic ecosystems are contaminated by heavy metal**,** they remain a potential threat for many years (Isirimah et al. 2006).

Analyses of the soil samples showed that concentration of metals (Cadmium, lead and Mercury) were below detectable limits except for nickel and zinc at the two sampling stations. Ni concentrations were 0.168, 0.394 and 0.216 mg/kg at soil levels of 0-15, 15-30 and 30-60 cm respectively for the first station. And in the second station, the concentration at 0-15 cm was not detectable at 15-30 and 30-60 cm. Zn was detected at stations 5; -0.23 and 0.12 mg/kg, 6; -0.17 and 0.08 mg/kg, 7; -0.19 and 0.07

mg/kg and 8; -0.42 and 0.21 mg/kg for 0-15 and 15-30 cm depths respectively. The absence and minute concentrations of these substances at these stations indicated no metal pollution or toxicity in the study site due to the intrusions.

Biological studies

The soil environment is teeming with biological life and is one of the most abundant and diverse ecosystems on the earth (Brady 2002). The microbial community in soil is important because of its relationship with soil fertility and the biochemical cycling of elements. Hence the need to enumerate and isolate major and minor members of the microbial community in soils.

As shown in Tab. 1 (Annexes), the soil microbes consisting mainly of fungi and bacteria add substantially to the recycling of nutrients within the system and thus form a major part of the ecosystem. Total heterotrophic bacterial counts (THBC) in the site varied from nil to 15×10^3 cfu/g. The mean value for surface soil was found to be 7.95×10^3 cfu/g, sub surface layers (15-30 cm) found to range from nil to 13.0×10^3 cfu/ with an average value of 5.05×10^3 cfu/g. At the 60 cm depth the range of values recorded were nil to 3.0×10^3.

Similarly, THFC found on the surface soil range from zero to 12.0×10^2 cfu/g with a mean count of 2.35×10^2 cfu/g, at 15-30 cm layer, it varied from nil to 13×10^2 cfu/g in with an average value of 1.5×10^2 cfu/g. At a depth of 30 to 60 cm, the values ranged from nil to 1.0×10^2 cfu/g with an average of about 0.05×10^2 cfu/g.

Hydrocarbon utilizing bacteria (HUB) varied from zero to 4.0×10^1 cfu/g (average; 2.5×10^1 cfu/g) in surface soil and on the subsurface of 15-30 cm, it varied from zero to 3.0×10^1 cfu/g (average; 1.4×10^1 cfu/g) and none was found at 30-60 cm layer. On the other hand, Heterotrophic utilizing fungi (HUF) counts in the soil varied from 1.0 to 3.0×10^1 cfu/g (1.55×10^1 cfu/g) on the surface soil. But varied from zero to $2.0 \times$

10^1 cfu/g soil in 15-30 cm sub surface soil layers with mean values of 0.85 x 10^1 cfu/g and beyond this depth (30-60 cm), none was found. The presence of bacterial and fungal populations in the soil indicate that the soil have potential to biodegrade petroleum hydrocarbons when they are inadvertently released into the environment. From the results, the effect of microbes on soil properties in these soils is far-ranging, i.e. most of the stations sampled are polluted and lack microbes that could biodegrade the petroleum hydrocarbon discharged into this field.

Total Petroleum Hydrocarbon (TPH)

Petroleum hydrocarbons are hydrocarbons of petroleum origin. The study area being a petroleum hydrocarbon production based, thus necessitated the need for evaluating the total petroleum hydrocarbon (TPH) content of the soil. Total Petroleum Hydrocarbon concentrations of the soil along the flow-line ranged from 0.09 mg/kg to 13.80 mg/kg at the surface level, and at the 15-30 cm and 30-60 cm sub surface soil levels, it was found to array from 0.02 mg/kg to 8.60 mg/kg and 0.001 mg/kg to 2.12 mg/kg respectively. The average concentrations were 4.908 mg/kg, 2.934 mg/kg and 0.920 mg/kg for 0-15, 15-30 and 30-60 cm respectively. It is worthy to note that the surface horizons had values as high as: 13.80 mg/kg, 12.5 g/kg, 11.76 mg/kg and 10.55 mg/kg found to be enriched above 10 mg/kg thresh value limit.

Conversely to expectation, the spatial distribution of TPH was generally high (Fig. 1, Annexes) in all the sampling stations despite shutting down of production for about a year due to sabotage and militancy. The TPH contents distribution skewed towards high frequency of low discharge. It had a wide range of variation greater than 80 % among the sampling depths. The enrichment of TPH in the sub surface soil (> 30 cm) is considerably low, indicating depletion to minimal enrichment.

Polycyclic Aromatic Hydrocarbon Content (PAH)

The poly aromatic hydrocarbons are derivatives of petroleum hydrocarbon compounds. The presence of polycyclic aromatic hydrocarbon in the soil is an indication of carcinogenic, mutagenic and teratogenic properties of petroleum hydrocarbon production activities (ATSDR 1995). The PAH content of the soils of OB/OB oil and gas plant area at the surface level ranged from below detectable limit of the analytical equipment used to 6.12 mg/kg on the surface of 0-15 cm; 4.56 mg/kg at the 15-30 cm depth range and 1.36 mg/kg at the 30-60 cm sub surface soil levels. The average concentrations were 1.932 mg/kg, 1.248 mg/kg and 0.326 mg/kg at the subsurface soils layer. The concentrations of the polycyclic aromatic hydrocarbon in these soils receiving effluent are equally high. Hence, the TPH and PAH experienced strong synergistic effect with THC (0.567[**], and 0.715[**] respectively) for increasing contamination. Therefore, TPH and PAH concentrations increased considerably with increasing THC content and vice versa.

B. Stratified vertical assessment

In this procedure, we evaluated between 0-50 and 50-100 cm soil contents of chemical, organics, metals and biological groups developed on different strata based on physiognomy and where the contamination from anthropogenic sources was very likely. These conditions allowed us to relate the effluent and seawater concentrations to soil using simple indexes and to discuss the approach in establishing the natural background for contamination due to the oil and gas activities.

The total contents of chemical, organics, metal and biological groups' contents were highly variable, except pH, TPH, & PAHs in all soil horizons. As expected from the differences in discharges, and depositions of sewage in some cases, the extremely high contents which are typical of soils of

pollution (Tab. 2, Annexes), revealed that the lowest mean of 5.1 pH concentration was found in both depths, while the range for pH concentrations among stations were 4.1-5.1 (0-50 cm) and 4.2-5.2 (50-100 cm). The conductivity concentrations showed a different trend, with a wider range. The minimum values were as low as 6.00 µS/cm, and maximum 26.0 µS/cm (averaged 11 µS/cm) in 0-50 cm depth, and 0-100 cm depth was between 5.0 to 27.0 µS/cm with mean conductivity above 14.0 µS/cm.

The extractable salt in form of chloride (salinity) ranged on the average between 93.78 mg kg^{-1} and 43.06 mg kg^{-1} (strata 5,50 cm), and the highest variability of 188 %, which showed both the minimum of 18.20 and 12 mg kg^{-1} (strata 4 and 1) and the maximum concentration 530 and 182 mg kg^{-1} (strata 5).

Phosphorus was consistently very low, and the concentrations ranged from 0.3 to 3.5 mg kg^{-1} in strata 3,1 and from 0.13 to 2.70 mg kg^{-1} in strata 9,1 with mean concentrations of 1.59 and 1.10 mg kg^{-1} in the respective depths. The lowest nitrate concentration (0.14 mg kg^{-1}) was in strata 2, 4 and 5 (Tab. 2, Annexes), and highest amounts of 0.83 and 0.58 mg kg^{-1} was found in strata 8 at both depths. The estimated coefficients of variation (CV) were highly variable (48.7 and 53.8 %) even within the same 100 cm depth.

The topsoil samples up to 50 cm had TOC concentrations ranging from 330 mg kg^{-1} (stratum 7) to 782 mg kg^{-1} (stratum 2) with average concentration of 542.75 mg kg^{-1} and from 270 mg kg^{-1} (stratum 7 to 1665 mg kg^{-1} (stratum 7), averaged 583.99 mg kg^{-1} in the subsoil of 100 cm, and showed low CV of 25.9 % on the topsoil and high CV of 73.1 % in the 50-100 cm subsurface soil. Results revealed Total Hydrocarbon (THC) content ranged from 1.0 mg/kg (stratum 6) to 6.5 mg/kg (stratum 8) at the surface level of 50 cm (averaged 3.35 mg/kg), and from 0.30 mg/kg (stratum 2) to 2.0 mg/kg (sample station 8) averaged 1.08 mg/kg at the sub surface soil level of 100

cm. The ranges were higher at both surface levels.

Vertically down the profile, TPH reached mean values of 1.24 mg/kg, but ranged from 0.06 to 3.61 mg/kg at 0-50 cm depth. Beyond this depth, (> 50 cm), it varied from 0.02 mg/kg to 1.26 mg/kg with average concentrations of 0.34 mg/kg.

The aromatic hydrocarbon content of the soils, ranged from 0.01 to 1.62 mg/kg at the 0-50 cm depth. However, the values recorded at 50-100 cm depth, it ranged below the detection limit of the analytical equipment used to about 0.86 mg/kg, with an average concentration value of 0.10 mg/kg.

TPH and PAH were significantly correlated with THC contents (0.940** and 0.814** respectively). When the data set was divided according to the horizon type, the correlations were still valid. The concentration of TPH was higher than PAH in all cases. The percentage of variance explained by the regression was low at about 5 %. The trend was however evident and TPH concentrations above 2.0 mg kg^{-1} were present only at strata 3 and 8 (TPH; 2.69 and 3.61 respectively) and formed about 1.23% and 0.09 % of the contamination at 0 – 50 cm and 50-100 cm depths at both locations. This level of concentration is far below the threshold limit of toxic hydrocarbon (Richardson 1995).

The metal contents measured from the samples were below detection limit. For biological groups, the analytical results of the soil samples showed that the total heterotrophic bacteria counts (THBC) from the field varied moderately (CV = 31 %) on the surface of 0-50 cm, but in the subsurface of 50-100 cm, the variation was high (CV = 73 %). THBC ranged from 3.0 x 10^{3} cfu/g (stratum 5) to 11.0 x 10^{3} cfu/g (stratum 4) on the surface soil of 0-50 cm with mean counts of about 8.0 X 10^{3} cfu/g. But in the subsurface soil of 50-100 cm, THBC varied from nil (strata 6 and 9) to 3.0 x 10^{3} cfu/g (strata 4 and 5) with average counts of 1.56 x 10^{3} cfu/g. Conversely, no THFC was found in all the strata examined from the surface of 0-50 cm up to subsurface of 50-100 cm.

On the other hand, Hydrocarbon utilizing bacteria (HUB) varied from zero (strata 2 and 5) to 3.0×10^1 cfu/g (strata 1 and 6) with average counts of 1.63×10^1 cfu/g on surface soil, and was completely absent beyond this depth (50 cm). In a similar vein, there was no growth of heterotrophic utilizing fungi (HUF) in any of the locations examined. From these results, it was observed on the surface layer (0-50 cm) that the index of pollution exceeded the maximum value (> 1 %) which is an indication of recent pollution input into the environment. THBC correlated significantly high with pH, TOC and conductivity ($r = -0.455$, -0.270 and 0.821, respectively, $n = 9$, $p < 0.001$), whereas the proportion was lower and more variable for HUB (standard error $= 1.188$).

Conclusions:

As expected from the sampling strategies, the contents of chemical, organic, metal and biological concentrations in the uncontaminated adjacent soils were extremely low. The pH concentration however showed a more homogeneous distribution, with a smaller range than conductivity. Hence, their presence may justify the high correlation coefficient found between THBC and pH, TOC and EC. No correlation was in fact found between total hydrocarbon content and the THBC, HUB that are mostly of lithogenic origin as indicated.

Contamination of this environment is as a result of diesel, lubricants and lube oil which is utilized by associated machinery operating on the site, and also salinity with increased turbidity resulted from laying flow-lines at water crossings and loose soil carried in run-off from cleared and trenched area during high tide. The consequences of these include: degradation of water quality, reduced ecosystem productivity, expulsion of fish and other organisms from impacted areas. Impact from the operational phase resulted from hydrocarbon spills, due to corrosion leaks, equipment failure, sabotage

posed a threat to water quality and aquatic life. More so, these sites are very high in organic C, but this concentration is toxic in the present unsaturated form, and is capable of causing lungs and kidney discomfort including eye, lung and throat irritation.

In addition, heavy metals had the lowest concentrations down the depth, confirming that the differences are linked to the variability in the soil depth and stratification. As a consequence of the absence of redistribution of metals in the strata and profiles, the actual concentration in the soil from contaminated sites is linked only to the presence of TPH, THC and salinity. As indicated in Table 1, all the parameters, with exception to pH and conductivity, assumed a sinusoidal variation of lateral displacement with distance and depth. Hence, frequent monitoring will be helpful in dictating contamination particularly during and after rainfall periods.

Rezumat:

CONSECINȚELE SCURGERILOR DIN STAȚIILE DE EXPLORARE A ȚIȚEIULUI ȘI PĂTRUNDEREA APEI MARINE ASUPRA DEPOZITELOR DE NUTRIENȚI ȘI A SPECTRULUI BIOLOGIC AL SOLURILOR DIN DELTA NIGERULUI

Ecosistemele terestre se reduc gradual în scopuri agricole ca urmare a creșterii populației și cererii de hrană, a dezvoltărilor de infrastructură și a deteriorării statutului lor de fertilitate. Zonele umede, cu unele excepții, sunt în centrul atenției pentru a suplimenta zonele terestre înalte, datorită balanței favorabile a apei din sol, cu un statut de feritilate moderat până la înalt și cu un pericol scăzut de eroziune a solului. Acest studiu a investigat schimbările referitoare la depozitele de nutrienți și spectrul biologic din solurile zonelor umede aflate de-a lungul rutei de distribuire a petrolului și a gazului în zona de coastă a Deltei Nigerului (Nigeria), cu o atenție sporită pe schimbările recente în

nutrienții solului cauzate de apa marină și scurgerile provenite din stațiile de explorare a țițeiului folosind interpolarea spațială din punctul observat. Am examinat datele statistice din 115 stații pe timpul refluxului din anotimpul secetos. S-a demonstrat că scurgerile din stațiile de explorare a țițeiului și pătrunderea apei marine reprezintă principala cauză care determină diferențele în cadrul nutrienților solului din zonă. Cel mai important avantaj fizic al acestui sol este că nu este vulnerabil la eoziune mai ales în condițiile unor căderi abundente de ploaie. De asemenea, creșterea semnificativă a PAH determinată de imobilizarea K (-0.932[**]), valoarea crescută la suprafața solului a P și populația HUB au fost afectate în mod negativ (-0.865[**]). Totuși, o creștere pozitivă în hidrocarburile alifatice duce la o creștere corespunzătoare a TPH (0.956[**]) și a sulfului (0.998[**]) pe solurile de suprafață, respectiv de subsuprafață. Deși apariția metalelor grele la un nivel scăzut în sol nu reprezintă o problemă pentru mediu, natura sărată și organică a solurilor indică o restricție severă pentru activitățile arabile din agricultură. Astfel, există suficiente argumente pentru a controla nivelul scurgerilor în acest mediu de sol unic.

References:

AKINRINDE E.A. (2006), Issues of optimum nutrient supply for sustainable crop production in tropical developing countries. Pakistan journal of nutrition, 5 (4): 377-387.

BI X.Y., FENG X.B., YANG Y.G., LI X.D., SHIN G.P.Y., LI F.L., QIU G.L., LI G.H., LIU T.Z., FU Z.Y. (2009), Allocation and source attribution of lead and cadmium in maize (*Zea mays* L.) impacted by smelting emissions, Environ. Pollut., 157: 834-839.

BLASER P., ZIMMERMANN S., LUSTRE J., SHOTYK W. (2000), Critical examination of trace element enrichments and depletions in soils: As, Cr, Cu, Ni, Pb, and Zn in Swiss forest soils, Sci. Total Environ., 249: 257-280.

BRADY N., WEIL R. (2002), The nature and properties of soils, 13th Edition, prentice Hall. Upper Saddle River, New Jersey, 960 pp.

BRADY N., WEIL R. (2013), The nature and properties of soils, 14th Edition, prentice Hall. Upper Saddle River, New Jersey, 960 pp.

CLOQUET C., CARIGNAN J., LIBOUREL G., STERCKEMAN T. PEDRIX E. (2006), Tracing source pollution in soils using cadmium and lead isotopes, Environ. Sci. Technol., 40: 2525-2530.

DE VLEESCHOUWER F., FAGEL N., CHEBURKIN A., PAZDUR A., SIKORSKI J., MATTIELLI N., RENSON V., FIALKIEWICZ B., PIOTROWSKA N., LE ROUX G. (2009), Anthropogenic impacts in North Poland over the last 1300 years-a record of Pb, Zn, Cu, Ni and S in an ombrotrophic peat bog, Sci. Total Environ., 407: 5674-5684.

GARCIA A.B. (1997), Effects of osmoprotectants upon NaCl stress in rice, *Plant physiology*., 115: 159-169.

ISIRIMAH N.O, EFFIONG G.S., ESHIET U. (2006), Influence of liming on extractable P growth and yield evaluation of okra (*Abelmoscuhus esculentus* (L.) Moench), *NJAFE* , 3 (1&2): 131-134.

MAAS E.V., HOFFMAN G.J. (2007), Crop salt tolerance: current assessment, *Journal irrigation drainage*, 103: 115-134.

MASSAS I., EHALIOTIS C., GERONTIDIS S., SARRIS E. (2009), Elevated heavy metal concentrations in top soils of an Aegean island town (Greece): total and available forms, origin and distribution, *Environ. Monit. Assess*., 151: 105-116.

NATIONAL SPECIAL PROGRAMME FOR FOOD SECURITY (NPSP) (2005), Critical values for nutrient elements.

NUNEZ-DELGADO B., MORRISON L., GULSON L. (2002), Threshold of concern: a technique for evaluating environmental impact and amenity values, *Journal of forestry*, pp. 84-86.

ODU C.T. (2000), Rehabilitation of soils after oil spills, In: *Agronomy in Nigeria* (Akoroda M.O. editor), Department of Agronomy, University of Ibadan, Nigeria, pp. 223-227.

RAJVAIDA N., MARKANDE D.K. (1998), *Advances in Environmental Science*, Vol. 4 APH Publishers.

REIMANN C., FILZMOSER P., GARRETT R.G. (2005), Background and threshold: critical comparison of methods of

determination, *Sci. Total Environ.*, 346: 1-16.

RICHARDSON M. (1995), *Edn-Environmental toxicology assessment*, Taylor and Pranas publishers.

SAM L. (2006), *Xam nhap man o Dion Bang Song Cuu Long* (*Salinity intrusion in the Mekong Delta*), Nha Xuat Ban Nong Nghiep, Vietnam. pp. 387.

TROEH I.O., THOMPSON U.C. (1993), National soil survey manual.

TUONG T.P. (2003), Impact of seawater intrusion control on the environment, land use and household incomes in a coastal area, *Paddy water environ.*, 1: 65-73.

Annexes:

Figure no. 1   Spatial distribution of the average TPHs level along the flow-line due to effluent discharge and seawater intrusion
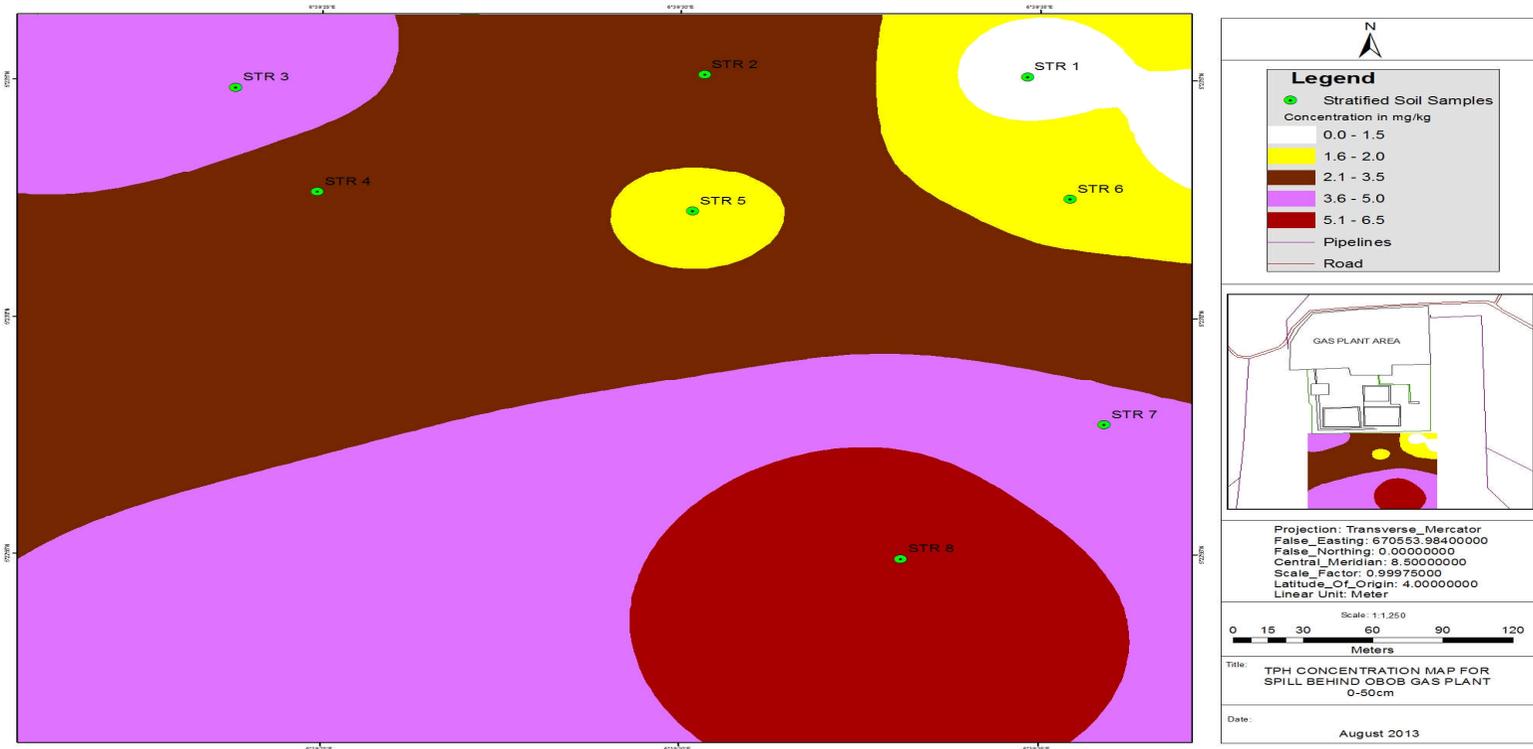
Table no. 1   Summary of soils' chemical, organic and biological characteristics at Obieba oil and gas plant.

	pH	Cond.	Salinity	Phosphorus	Nitrate	THC	TOC	TPH	PAH	THBC	THFC	HUB	HUF
		µS/cm	←			mg/kg			→	x 10^1 cfu/g			
0-15 cm													
Mean	4.942	8.550	68.030	2.347	1.045	12.895	568.741	4.908	1.932	7.950	2.350	2.500	1.550
SE	0.273	4.186	92.867	1.453	2.125	10.448	187.502	0.930	0.487	3.927	3.422	0.889	0.605
Minimum	4.440	4.000	17.000	0.820	0.010	2.800	3.820	0.090	0.000	0.000	0.000	0.000	1.000
Maximum	5.740	21.000	455.000	7.620	10.010	33.600	820.000	13.800	6.120	15.000	12.000	4.000	3.000
Skewness	0.894	1.319	4.193	2.690	4.365	0.787	-1.297	1.015	0.928	-0.498	2.119	-1.251	0.583
Kurtosis	3.090	2.650	18.260	9.296	19.344	-0.951	3.235	-0.080	-0.369	-0.088	3.447	2.285	-0.459
CV %	5.52	48.96	136.51	61.91	203.47	81.02	32.97	84.79	109.97	49.39	145.64	35.54	39.02
15-30 cm													
Mean	4.929	8.350	108.855	2.144	0.496	8.145	503.350	2.934	1.248	5.050	1.500	1.400	1.050
SE	0.207	3.815	176.681	1.327	0.244	6.502	150.549	0.556	0.318	3.913	2.705	0.995	0.759
Minimum	4.250	1.000	17.800	0.470	0.010	0.800	195.000	0.020	0.000	0.000	0.000	0.000	0.000
Maximum	5.200	18.000	530.000	6.900	0.890	22.500	780.000	8.600	4.560	13.000	10.000	3.000	2.000
Skewness	-1.919	0.705	2.093	2.537	-0.622	0.783	-0.035	0.580	0.806	0.257	2.332	0.485	-0.086
Kurtosis	5.532	1.400	2.734	8.795	-0.203	-0.239	0.054	-0.558	-0.433	-0.876	5.013	-0.707	-1.154
CV%	4.20	45.69	162.31	61.92	49.25	79.83	29.91	84.82	114.01	77.49	180.32	71.05	72.30
30-60 cm													
Mean	4.888	13.200	44.025	1.903	0.382	4.650	418.750	0.920	0.326	0.300	0.050	0.000	0.000
SE	0.193	5.327	89.585	1.319	0.202	12.698	119.910	0.183	0.111	0.923	0.224	0.000	0.000
Minimum	4.470	7.000	9.390	0.380	0.010	0.300	105.000	0.001	0.000	0.000	0.000	0.000	0.000
Maximum	5.200	25.000	420.000	6.680	0.790	58.000	600.000	2.120	1.360	3.000	1.000	0.000	0.000
Skewness	-0.882	1.023	4.296	2.583	-0.163	4.316	-0.803	0.228	1.249	2.888	4.472	0.000	0.000
Kurtosis	0.371	-0.131	18.883	9.214	-0.163	18.981	1.332	-1.559	-0.080	7.037	20.000	0.000	0.000
CV %	3.95	40.36	203.49	69.33	52.85	273.10	28.64	88.93	152.61	307.79	447.21		

Table no. 2   Stratified samples using coring method at 0-50 and 50-100 cm along Obieba oil and gas plant.

	pH	Cond.	Salinity	Phosphorus	Nitrate	THC	TPH	PAH	TOC
		μS/cm	◄—————————————————————————————————————				mg/kg		
0-50 cm									
Mean	4.786	11	93.775	1.585	0.481	3.35	1.42	0.50	542.75
SE	0.11	1.95	55.32	0.36	0.08	0.67	0.37	0.19	43.92
Mini	4.1	6.00	18.2	0.3	0.14	1	0.06	0.01	330
Max	5.09	26.00	530	3.5	0.83	6.5	3.61	1.62	782
Median	4.85	9.00	35.8	1.3	0.49	3.2	1.23	0.29	520
Skewness	-1.358	2.515	2.814	0.863	0.307	0.665	1.00	1.15	0.168
Kurtosis	1.99	6.767	7.941	0.489	-0.608	-0.83	0.50	0.26	0.157
CV%	6.90	56.70	188.20	65.20	48.70	64.40	0.79	1.13	25.90
100 cm									
Mean	4.96	14.556	43.056	1.098	0.324	1.089	0.34	0.10	583.889
SE	0.09	3.00	17.54	0.28	0.06	0.19	0.16	0.10	142.33
Mini	4.25	5.00	12	0.13	0.14	0.3	0.02	0.00	270
Maxi	5.2	27.00	182	2.7	0.58	2	1.26	0.86	1665
Median	5.01	11.00	29.2	1.08	0.32	1	0.09	0.00	430
Skewness	-2.551	0.539	2.884	0.76	0.44	0.381	1.53	3.00	2.484
Kurtosis	7.164	-1.639	8.5	0.341	-1.349	-0.509	0.86	8.98	6.57
CV %	5.60	61.80	122.20	75.60	53.80	53.40	1.38	2.85	73.10

(continuation)

Cr	Cd	Nickel	Zn	Pb	Mercury	THBC	THFC	HUB	HUF
						x 10^1 cfu/g			
0.001	0.001	0.001	0.001	0.001	0.001	8	0	1.625	0
0	0	0	0	0	0	0.79	0	0.37	0
0.001	0.001	0.001	0.001	0.001	0.001	3	0	0	0
0.001	0.001	0.001	0.001	0.001	0.001	11	0	3	0
0	0	0	0	0	0	8	0	2	0
0	0	0	0	0	0	-1.015	0	-0.394	0
0	0	0	0	0	0	1.521	0	-1.229	0
0.00	0.00	0.00	0.00	0.00	0.00	31.30		73.10	
0.001	0.001	0.001	0.001	0.001	0.001	1.556	0	0	0
0	0	0	0	0	0	0.38	0	0	0
0.001	0.001	0.001	0.001	0.001	0.001	0	0	0	0
0.001	0.001	0.001	0.001	0.001	0.001	3	0	0	0
0	0	0	0	0	0	2	0	0	0
0	0	0	0	0	0	-0.176	0	0	0
0	0	0	0	0	0	-1.171	0	0	0
0.00	0.00	0.00	0.00	0.00	0.00	72.70			