EVALUATION OF ORGANIC MATTER CONTENTS FROM DEEP WELL SAMPLES WITHIN THE UMUTU OIL FIELD, SOUTHWEST NIGERIA.

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ABSTRACT

Deep well samples from the Umutu oil well-2 were analyzed for the purpose of determining their organic matter contents within the zone. Thirty ditch cuttings from the borehole were subjected to analysis of their organic contents (TOC), total hydrocarbon (THC), nitrogen and phosphorus contents. Evaluation of the stratigraphy indicated ten lithostratigraphic units (Z_o-S_2) composed of sandstone, sandy shale and shale within the studied field which were demarcated. The lithologic units were grouped as fair – good and good – excellent source rocks with potentials for gas and oil, and oil respectively. C/N ratio varied from 14.77-18.53 (mean=17.00) indicating that the organic matter was derived from plant remains. C/P ratios varied with depth and lower than 3900values for laminated shales.

Keywords: *Oil well, Niger Delta, Deep section, Organic matter.*

INTRODUCTION

Organic matter in sediments consists of carbon and nutrients in the form of carbohydrates, proteins, fats and nucleic acids. Sediment organic matter is derived from plant and animal detritus, bacteria or plankton form in situ, or derived from natural and anthropogenic sources in catchment. Bacteria quickly eat the less resistant molecules, such as the nucleic acids and many of the proteins. Total Organic Carbon (TOC) defines the amount of organic matter preserved within sediment. Sediment nutrients are assessed as Total Nitrogen (TN) and Total Phosphorus (TP) concentrations, and have inorganic as well as organic sources. The amount of organic matter found in sediment is a function of the amount of various sources reaching the sediment surface and the rates at which different types of organic matter are degraded by microbial processes during burial. Organic matter breakdown (mineralisation) reduces sediment carbon and nutrient concentrations and the dissolved nutrients are in turn released from the sediment to the water column. Carbon is released as CO_2 gas and as dissolved organic carbon (DOC) (Froelich *et al.,* 1979). Mineralisation rates are faster when dissolved oxygen is present than under anoxic conditions (Kristensen *et al.*, 1995). Low pH can also reduce mineralisation rates and contribute to organic matter accumulation.

Total phosphorus is exchanged between sediment and water to maintain water column phosphorus concentrations at near constant levels. Surface sediments can become enriched in phosphorus if phosphorus is released by sulfate reduction at depth in sediment and then trapped by iron oxyhydroxides in the surface oxygenated layer. Enhanced sediment transport caused by erosion (gully and streambank erosion and sheetwash) in catchments can lower sediment total nitrate and TOC concentrations because inorganic constituents (minerals and clays) can dilute organic matter concentrations (Radke, 2002). Also, catchment erosion can increase sediment TP concentrations because phosphorus attaches to a wide variety of mineral surfaces (Froelich, 1988). Sediment carbon and nutrient concentrations increase with decreasing grain size because organic matter adsorbs onto mineral surfaces and has a high affinity for fine-grained sediment (Hedges and Keil, 1995).

STUDY AREA

Umutu oil field lies between latitude $5^0 50'$ and

$6^0 00'$ North; and longitude $6^0 10'$ and $6^0 20'$E East within the Niger Delta (Figure 1). The region is one of the wetlands of the world referred to as inland areas of the coast. It has a slightly undulating topography ranging from 10-100 meters from the lower landscape to the highest points. The area is well drained and porous with moderate surface runoff of about 100mm/year. It is effectively drained by the River Ethiope and its tributaries that form a very coarse textured dendritic drainage pattern devoid of structural control and characteristic of homogenous and uniform earth materials. The drainage pattern follows a course that is a direct consequence of the original slope of the region, taking advantage of the north-southwest trending depression, thus creating a relationship between the drainage topography and sediment dip.

The area is characterized by two seasons, the wet and dry season. The wet season begins in April and last till October while the dry season prevails from November to March. Thunderstorms usually accompany late rains at the beginning of the rainy season and the beginning of dry season. The mean annual rainfall is between 2000-3000mm (Offodile, 1992). The mean annual temperature lies between the range of 28-32^{0}C (Etu-efeotor and Odigi, 1983). Regionally the vegetation consists of forests in some places, mangrove swamps, smaller trees and shrubs as typified by tropical zones with high temperature and rainfall, but most natural forest have been destroyed by human activities leaving behind only secondary re-growth vegetation.

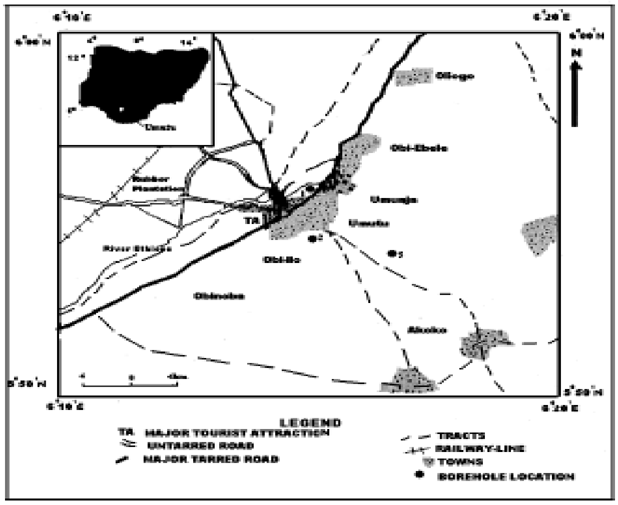

Figure 1: Map of Study Area.

METHOD OF STUDY

30 ditch cuttings samples from the Umutu oil well-2, were collected at 30ft (sometimes 15ft) intervals, washed and analyzed the lithostratigraphic log of the well was built from grain size analysis. Standard methods were used to determine the organic contents. Determination of Total Nitrogen was by Macro-Kjeldahl Method. Determination of Phosphorus in sediment extract was done using L-Ascorbic Acid Molybdate Blue Method (Morphy and Riley Method). Organic Carbon Determination was by Walkley-Black Wet Oxidation Method. For the determination Of Total Hydrocarbon (THC), 5gm of the air-dried sediment sample was weighed out into a clean plastic bottle. 20ml of n-hexane was added into the plastic bottle, and placed on the mechanical shaker and agitated for 15minutes. The solution was allowed to settle down and the hexane layer was decanted. The absorbance was measured at 460nm through a set of working standard of the order 0, 5, 10, 15, 20 and 25ppm and values recorded. The absorbance of the sample extract was read and calculated.

RESULTS AND DISCUSSION

The results of analysis on TOC, N, P, THC, C/N and C/P ratios obtained from the study are presented in Table 1.

Table 1: Contents of Total Organic Carbon, Nitrogen, Organic Matter, Phosphorus and Total Hydrocarbon of Umutu Well 2.

Units	Depth (ft)	TOC(%)	N(%)	C/N	OM(%)	P(ppm)	THC(ppm)	C/P	C/P mole ratio
S_2	4570	3.8	0.23	16.52	6.57	34.04	0.96	1116.33	2881.44
S_1	4870	3.68	0.21	17.52	6.36	32.47	0.83	1133.35	2925.38
	4930	3.52	0.19	18.53	6.09	25.78	0.7	1365.40	3524.32
T	5820	3.88	0.24	16.17	6.71	26.73	0.74	1451.55	3746.70
U	6015	3.04	0.18	16.89	5.26	21.09	0.82	1441.44	3720.60
	6105	4.2	0.27	15.56	7.26	25.83	0.87	1626.02	4197.02
	6195	3.64	0.2	18.2	6.29	30.91	0.44	1177.61	3039.61
	6585	3.7	0.22	16.82	6.4	24.05	0.79	1538.46	3971.03
	6765	1.91	0.12	15.92	3.3	20.64	0.74	925.38	2388.58
	6975	2.4	0.14	17.14	4.15	37.22	0.72	644.815	1664.37
	7005	2.72	0.17	16.12	4.7	36.44	0.81	746.43	1926.67
V	7125	1.32	0.08	16.92	2.28	28.68	0.65	460.25	1187.98
	7215	2.96	0.16	18.5	5.12	25.89	0.57	1143.30	2951.04
	7425	1.6	0.09	17.98	2.77	23.27	0.52	687.58	1774.76
	7455	1.28	0.07	17.53	2.21	26.34	0.61	485.96	1254.33
	7605	3.2	0.19	16.84	5.53	31.64	0.66	1011.38	2610.54
	8085	2.24	0.13	17.23	3.87	24.83	0.57	902.14	2328.56
W	8385	3.52	0.2	17.6	6.09	23.6	0.48	1491.53	3849.88
	8445	1.44	0.08	17.14	2.49	25.05	0.66	574.85	1483.78
	8655	3.52	0.1	16.76	6.09	36.6	0.83	961.75	2482.43
X	8925	3.48	0.19	18.32	6.02	35.49	0.57	980.56	2530.98
Y	8985	3.36	0.18	17.68	5.81	26.89	0.79	1249.54	3225.26
	9285	3.52	0.2	16	6.09	20.87	0.92	1686.63	4353.48
	9345	3.64	0.1	17.33	6.29	32.08	0.83	1134.67	2928.76
	9465	1.92	0.13	14.77	3.32	37.61	0.61	510.50	1317.69
	9735	2.24	0.14	16	3.87	26.56	0.89	843.37	2176.89
	9825	1.76	0.1	17.96	3.04	31.52	0.94	558.38	1441.26
Z_1	9945	2.08	0.12	17.33	3.6	35.43	0.98	587.07	1515.33
	9975	1.76	0.1	17.6	3.04	26.67	0.95	659.92	1703.34
	10005	2.72	0.16	17	4.7	28.12	0.92	967.28	2496.72

From the result of this study, the C/N ratio varied from14.77 – 18.53 with a mean of 17.00. This indicates that the source of sediment organic content is from plant remains (Dietrich *et al.,* 1972; Miller, 1977). The C/P ratio varied throughout the length of well- 2 (510-1134, mean 751.6) for units Y and Z_1. Units X, W and V, ranged from 460.3-1686.3, mean 912.3. These ratios lie within the 3900 values for laminated shale (Ingal *et al.,* 1993). However, high ratios have been obtained in sediments linked to sedimentary accumulation under oxic bottom waters (Ingal and Janike, 1994). The C/P ratios for the lithologic sandstone units U,T,S, and S_2 vary from 925.4 – 1626.0 (mean 1308.4) with two lower values 644.8 and 746.4 at the boundary contact with the V-subunit.

Sediment organic matter can be a source of 'recycled nutrients' for water column productivity (including algal blooms) when it degrades. Dissolved oxygen concentrations are usually lowered when organic matter is degraded by aerobic bacteria, and anoxic & hypoxic conditions may develop under stratified conditions. Organic matter is also a source of food and energy, and its nutritional balance (TOC:TN:TP ratio) plays an important role in material flow through ecosystems. Decomposition rates of organic matter increase as nitrogen and phosphorus contents increase (Goldman *et al.,* 1987), and as TOC/TN and TOC/TP ratios decrease (Enriquez *et al.,* 1993).

The nitrogen present in sediments is derived predominantly from the proteins of plants and microorganisms. Very little amount is, however, present as inorganic nitrogen in form of ammonium, nitrate and NH_4^+ in illite lattice. Most of them are transformation products of organic matter by reactions by which these different nitrogenous compounds are formed. The total nitrogen content of a given sediment therefore gives a general ideal of the original organic sedimentation since the fixed ammonium nitrogen comes from organic matter. The weight ratio of the organic carbon content and the total nitrogen (C/N) expresses the measure of the protein contents of an organic matter and is a measure of paleoproductivity from planktons. Living organisms rich in protein show low C/N ratio e.g. for zooplankton, mean ratio is 5.9. Animal compounds contain more protein than plants, however, lower plants the main source of organic matter in sea are relatively rich in protein also. Hence show low C/N ratios, e.g. blue-green algae (6.5) and diatoms (5.5 – 7.5) (Dietrich *et al.,* 1977). Higher plants contain less than 20% protein and therefore have higher C/N ratio. In terrestrial and near shore environments the C/N ratio is higher than in marine sediments; but the terrestrial organic input is of minor importance in the open sea.

Phosphorus is one of the essential micronutrients for life and although only present in minor amounts in soft parts of living organisms, it usually constitutes the major hard parts of vertebrates and invertebrates. Phosphorus materials in the marine environment consist of inorganic phosphorus (dissolved orthophosphates), organic phosphorus in solution and particulates phosphorus (Riley and Skirrow, 1975). Large inorganic phosphate contents are associated with clay minerals. Most organic productivity utilizes the dissolved orthophosphates in the upper surface waters in the ocean, so the phosphate concentration controls the organic productivity. The C/P ratio for oxic bioturbated shale is about 150 while for laminated shale, it is about 3900 (Ingall *et al.,* 1993). In modern terrestrial environment, the ratio ranges 300-1300. Decomposition of organic matter decreases C/P ratio. Demineralisation of P relative to C in ocean bottom can result in burial of organic matter with high C/P ratio around 250:1 and can lead to higher ratios in sediments linked to sedimentary accumulation under anoxic bottom waters (Ingall and Jahnike, 1994).

The availability of nitrogen and phosphorus exerts primary controls on biological productivity in marine environments (Holland, 1978). Because certain organisms can fix atmospheric nitrogen, phosphorus is considered to be the ultimate limiting nutrient in the marine environment (Redfield, 1958: Broecker and Peng, 1982). Variation in Phosphorus contents may be related to variations in continental weathering (Pedersen and Calvert, 1990; Algeo *et al.,* 1995; and Algeo and Scheckler, 1998), changes in the C/P ratio of sedimentary organic matter (Broecker and Peng, 1982), or variations in the P-flux under anoxic or very low O_2 bottom water conditions (Ingall and Jahnke, 1994). Whereas marine phytoplankton has an original C/P ratio of 106:1 (Redfield, 1958), ratio for modern terrestrial Organic Matter are 300-1300 which is lower Phosphorus content, and 7-80 for bacterial Organic Matter. Even with a predominantly marine Organic Matter source, preferential remineralization of Phosphorus relative to Carbon at the ocean bottom can result in the burial of Organic Matter with high C/P ratios, around 250:1 (Van Capellen and Ingall, 1994). Still higher C/P ratios in sediments have been linked to sediment accumulation under anoxic or very low O2 bottom water conditions (Ingall and Jahnke, 1994). The result here show very high ratios, suggestive of bottom water accumulation.

Ingall *et. al*. (1993) equated the presence of lamination to deposition under anoxic conditions and reported average $C_{organic}$ /P mole ratios of 150 for oxic, bioturbated shales and 3900 for anoxic laminated shales. This is consistent with the definition of Savrda *et al.* (1984), although the model of Rhoads and Morse (1971) suggests that laminae can occur also in lower dysaerobic (dysoxic) environment. Ingall *et al* (1993) ascribed C/P ratios of 150 for oxic bioturbated shales and C/P ratios of 3900 and above for anoxic shales. It therefore suggest that using C/P ratios may not fully confirm anoxicity or ortherwise, the source of the environment. The ratios obtained in this study (925 – 1626) in far below values for anoxic shales. However, according to Redfield (1958), terrestrial organic matter (plants) has C/P ratios between 300 – 1300. Hence the study shows that the source of organic matter is plant remains.

TOC and OM

The concentration of total organic carbon in the sediments ranged between 1.32-4.20% (Table 1). Burial of this organic matter and development of suboxic condition may enhance the mobility of trace metals through the sediment pore water to upper oxygenated condition at the sediment/water interface where subsequent reprecipitation of the trace metals takes place in suitable Eh-pH conditions (Banerjee, 1985). Vine et al. (1958) has shown that sapropelic matter in marine sediments increase seaward owing to contributions to total organic matter present by remains of marine plankton (largely sapropelic). The most likely environment for deposition and preservation of such organic rich sediments (with large concentration of humic matter) are nearshore marine, deltaic and also some non-marine areas. Thus, the deltaic environment is suggested for these sediments under study.

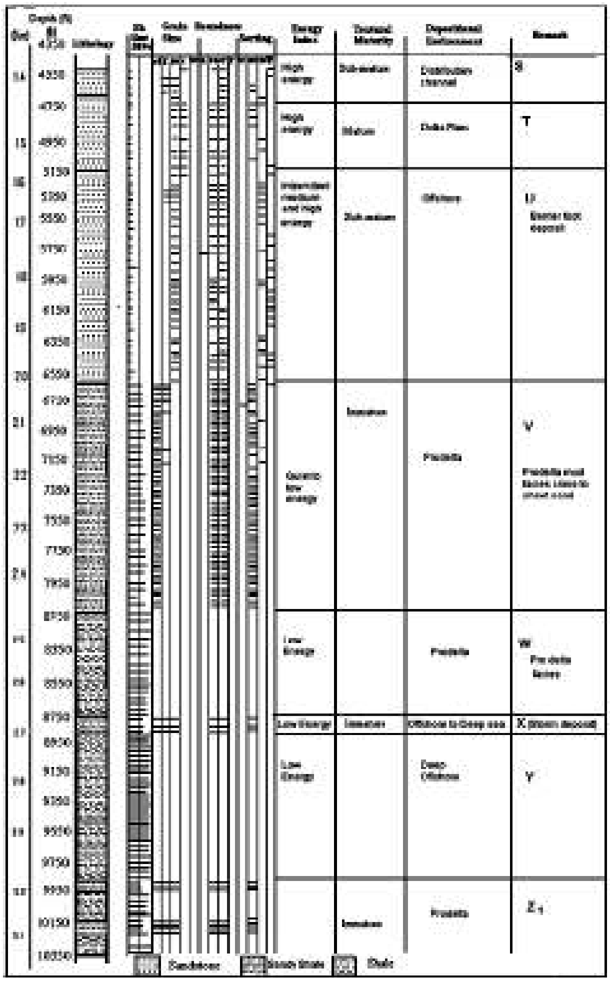

Figure 2*. Composite log for Umutu Well 2*

Bustin (1988), studied side-wall core and cuttings from the Agbada-Akata transition or uppermost Akata Formation and concluded that there are no rich source rocks in the delta but that this is compensated for when considering the oil potentials, by the great volume of sediments, excellent migration pathways, and excellent drainage. The oil potential is further enhanced by permeable interbedded sandstone and rapid hydrocarbon generation resulting from high sedimentation rates. The TOC values for sediments in the Umutu Well-2 ranges from 2.18% in Sandy shale to 3.68% in Sandstone unit (Figure 3). This values group the zones of Umutu Well studied into fair to good (0.5<TOC<2.0) with potentials for gas and oil and good to excellent (TOC>2.0%) with potential for oil. Figure 3 shows that the lithologic units U to S_2 are characterized by good to excellent, indicative of oil habitat while Z_1 to V are fair to good, indicative of moderate oil impregnation. Those rocks containing less than 0.5% TOC are considered to have negligible hydrocarbon source potential. The amount of hydrocarbon generated in such rocks is so small that expulsion simply cannot occur. Rocks containing between 0.5% and 1%TOC are marginal and will not function as highly effective source rocks; they may expel small quantities of hydrocarbon and thus should not be discounted completely. Kerogen in rocks containing less than 1%TOC, are generally oxidized and of limited source potential. Rocks containing more than 1%TOC values often have substantial source potential. Between 1% and 2% are associated with depositional environments intermediate between oxidizing and reducing where preservation of Lipid organic matter with source potential for oil can occur.

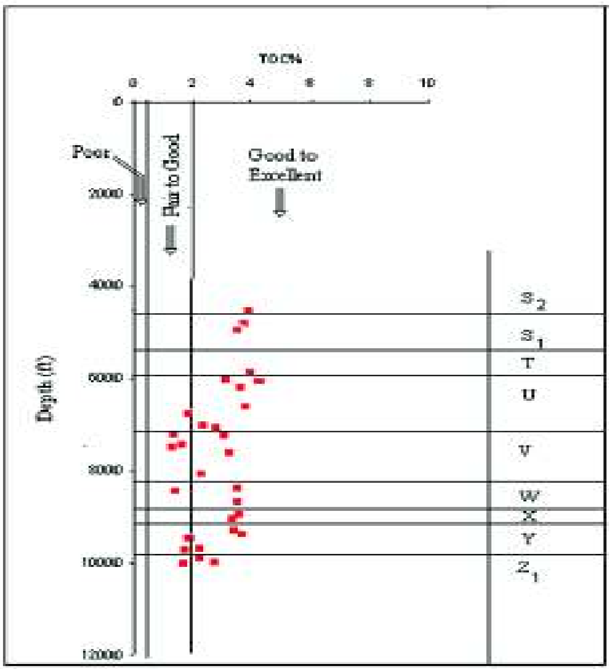

Figure 3. *Plot of TOC Versus Depth in Umutu Well- 2*

The total organic carbon (TOC) content of sandstone and shale in Bustin (1988) work is essentially the same (average of 1.4 to 1.6%TOC). Bustin's Eocene TOC average compares well with the averages of 2.5% and 2.3% obtained for Agbada-Akata shales in two wells (Udo and Ekweozor, 1988). Ekweozor and Okoye (1980) reported TOC values as high as 5.2% in paralic shales from western part of the delta. The higher TOC contents are limited to thin beds and are only easily recognised in conventional cores (Doust and Omatsola, 1990). The varying concentrations of TOC at different lithostratigraphic units are indicators of periodic anoxicity during their deposition. Those with high TOC indicate rapid sedimentation rates where there was no time for oxic condition to prevail. Anoxia is of tremendous importance in the preservation of organic matter which in turn preserves organic carbon in sediments, because when the availability of oxygen is limited, diagenesis is restricted to anaerobic processes. These processes are inefficient compared with aerobic diagenesis and are usually limited in scope by the availability of sulphates and nitrates. Thus, the development of anoxia conditions will enhance the preservation of organic carbon. Anoxia sediments are not always easy to recognize but total organic carbon content had served as an important indicator since anoxic sediment contain elevated TOC generally above 2% and always above 1%.

CONCLUSION

TOC analysis from the study samples were similar to those described for the broad Niger Delta area. Ten lithostratigraphic units (Z_o-S_2) were identified and composed of sandstone, sandy shale and shale. TOC versus depth plot classified the lithologic units into fair – good and good – excellent source rocks with potentials for gas and oil, and oil respectively. C/N ratio varied from 14.77-18.53 (mean=17.00) indicating that the source of hydrocarbon sediments is plants remains. C/P ratios also varied throughout the depth and were lower than 3900values for laminated shales.

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