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Research Article

Spatial and Temporal Variation of Physico-Chemical Parameters of Sediment from Azuabie Creek of the Upper Bonny Estuary, Niger Delta

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Abstract: The impacts of human and industrial activities on the physico-chemical quality of sediment of Azuabie Creek in the upper Bonny Estuary of the Niger Delta, Nigeria were studied. Major waste inputs into the creek include run-off from surrounding lands, animal wastes from a major abattoir, human/domestic waste from a high density settlements along the creek and industrial effluents from Trans-Amadi industrial area, hosting a number of manufacturing and oil servicing companies. Sediment samples were collected from ten sampling stations, seven (st. 1, 2, 6, 7, 8, 9 and 10) along the main creek and three (st. 3, 4 and 5) along a creeklet that empties into the main creek. These stations were selected to reflect various points of domestic and industrial waste inputs along the creek. Particle size distribution indicated sediments were generally sandy-mud in nature with higher proportions of clay. Seasonal and spatial variations were observed in mean pH values of sediments while the oxidation-reduction potential of the sediment varied remarkably. TOC in the study area were generally above 1% across all stations during the study while mean values of THC, ranged from 210±0.01 to 10750±0.71.3 mg/kg. NO_3 and PO_4 also varied significantly ($p \leq 0.001$). It is concluded that physicochemical variables of sediment from Azuabie Creek are influenced by pollution sources and these would affect the benthic community in the estuarine creek.

Keywords: Bonny estuary, effluents, Nigeria, nutrients, redox potential, sediment

INTRODUCTION

Shallow coastal sediments are temporally dynamic and spatially heterogenous environments characterized by fluctuations in physicochemical and biological factors (Fenchel and Glud, 2000). These factors can influence many important processes occurring within the sediment and affect the exchange of solute across the sediment-water interface. Since contaminated sediments are a major source of pollution in estuaries and are repositories for many different organic and inorganic contaminants they are capable of accumulating such contaminants to concentrations of concern in aquatic ecosystems (Bryan and Langston, 1992).

In the Niger Delta, the problem of water and sediment pollution has been of concern to all stakeholders, following the rate and extent of degeneration of the environment and water bodies by human activities, particularly from industrial and domestic sources. The oil exploration and exploitation activities in the Niger Delta have increased the surge of human population to major activity areas in the region and one of the major cities is Port Harcourt.The presence of several companies and the high population density in coastal cities have caused adverse effects in the area (Odu *et al*., 1985; Nwankwo, 1991). This population growth has inadvertently increased effluents and solid wastes generated and discharged into the environment, which finally find their way into the natural water bodies (Chindah *et al*., 2006). The Azuabie Creek located on the eastern part of Port Harcourt is part of the upper Bonny estuary of the Niger Delta**.** The Okolo-Azuabie creeklet receives industrial effluent from the Trans-Amadi Industrial Layout drains and empties into the main Azuabie creek. A coastal settlement (Azuabie Town) is also found along the Azuabie creek from where numerous domestic wastes are generated and dumped along the creek. A major abattoir and some other companies are located upstream of the Azuabie creek. The Azuabie Creek is open to different kinds of human activities; which ultimately translate into the discharge of various kinds of wastes into this environment. Some of these activities relate to artisanal fishing, transportation, dredging operations, near shore lavatories, oil industry activities and other industrial operations, water front settlement, major abattoir activities and in recent times, illegal bunkering activities. Wastewater, oil and grease, cow dung, domestic wastes and bones are major wastes discharged into the Azuabie Creek.

Daka *et al.* (2007) conducted a comparative study of the sediment characteristics of Azuabie and Obufe

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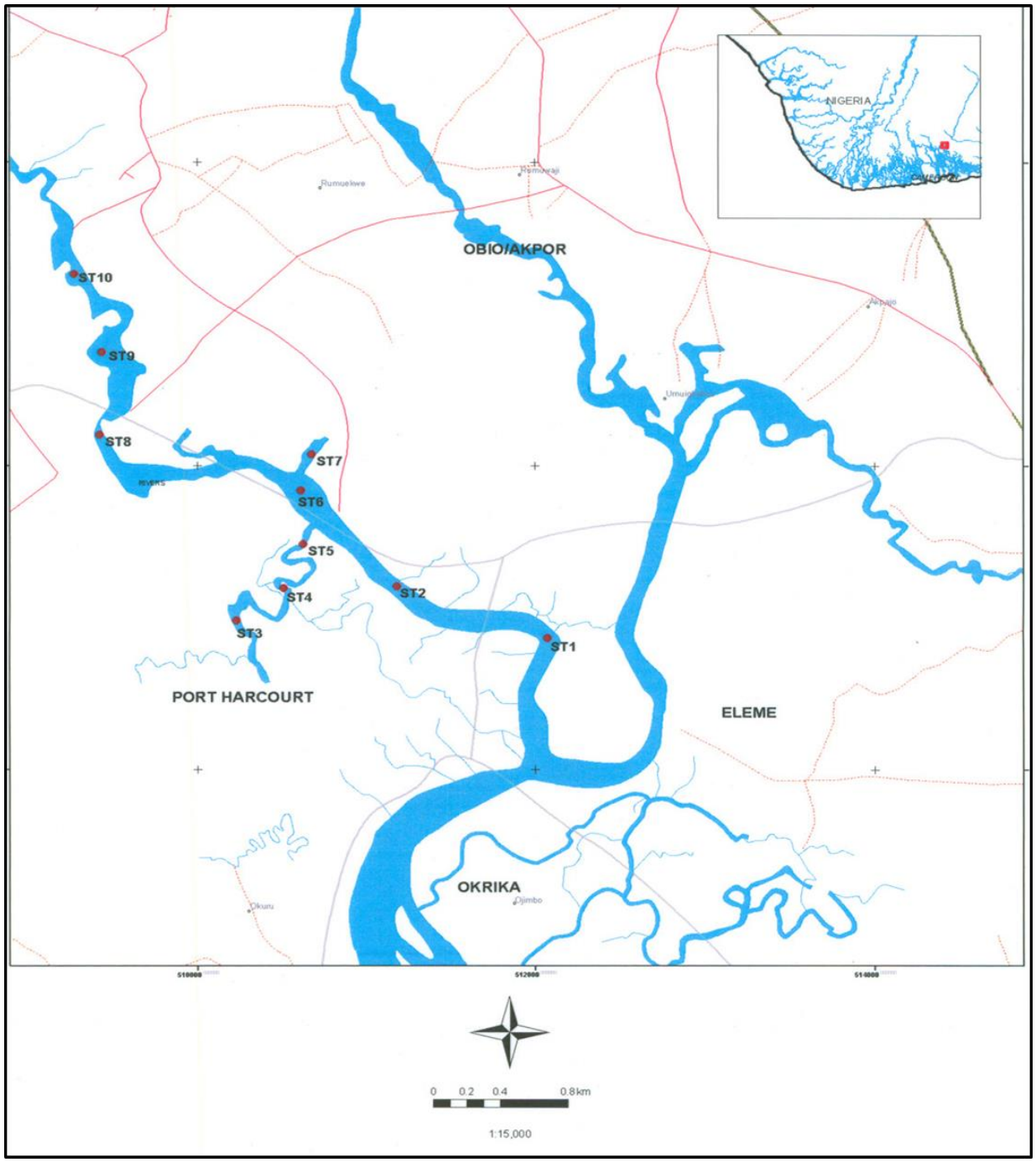
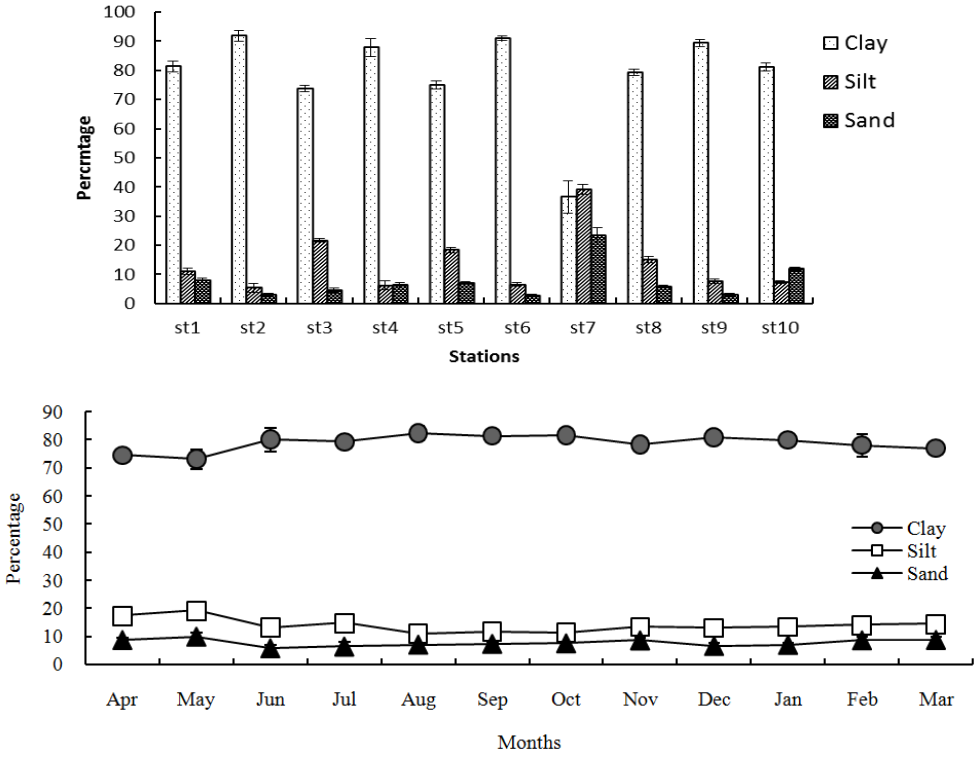


Fig. 1: Map showing sampling sites in the study area

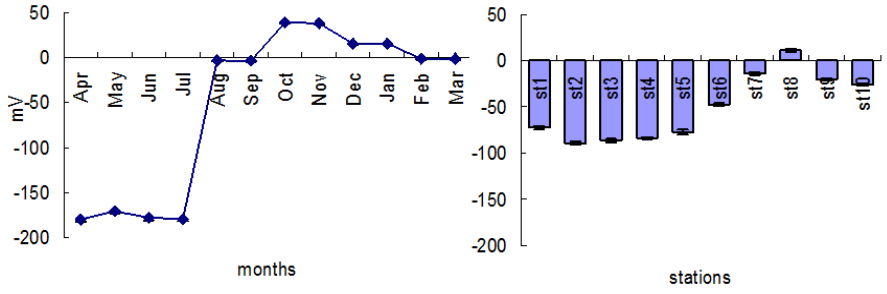
creeks; to evaluate how industrial and other human activities have influenced the sediment quality of Azuabie creek with reference to the adjacent Obufe creek and by small-scale spatial variation along the creeks. They established that anthropogenic and industrial activities led to lower relative quality of the Azuabie creek. This study is therefore a more detailed study of the Azuabie creek to determine spatial and temporal patterns in sediment physico-chemistry.

MATERIALS AND METHODS

Study sites: Ten sampling stations were located along the Azuabie Creek, to cover land-based sources of contaminant inputs into the creek as well as presumably uncontaminated loactions (Fig. 1). The sampling stations and their geographical coordinates of these stations are as follows: Stations 1 (4°48'08.871"N, 7°04'15.763") and 2 (4°48'19.958"N, 7°03'46.932"E)



(a) Particle size distribution



(b) Redox potential

Fig. 2: Sediment particle fractions and redox potentials (mean±S.E., n = 20 for months and 24 for stations) of sediments

were relatively away from any visible anthropogenic influence but stations 3 (4°48'28.591"N, 7°03'29.218"E) 4 (4°48'12.462"N, 7°03'16.906"E) and 5 (4°48'18.675"N, 7°03'25.946"E) were located along the creeklet that receives industrial effluents from Trans-Amadi Industrial drains in addition to a waste dump site that is close to station 3. Stations 6 (4°48'40.150"N, 7°03'28.370"E) and 7 (4°48'48.411"N, 7°03'30.411"E) were close to a domestic waste dumpsite and a pier latrine. Station 8 (4°48'52.041"N, 7°02'49.661"E) was close to a major abattoir and some industries while stations 9 (4°49'09.796"N, 7°02'50.446"E) and 10 (4°49'26.711"N, 7°02'44.237") were also close to domestic waste inputs upstream of the creek.

Sample collection and analyses: Sediment samples were collected monthly with an Ekman grab (15 cm by 15 cm) at each of the stations for a period of 1 year from April 2006 to March 2007. Replicate grabs samples were collected for physicochemical analysis of the sediment. These were transported to the laboratory in ice-cooled boxes.

The sediment samples were air-dried, sieved and used to perform the following physicochemical analysis except pH and conductivity for which wet samples were also analyzed. The Bouyoucos hydrometer method was used for the particle size analysis. The pH and conductivity of the sediment were determined using a meter (model H1 8314, membrane HANNA instrument). The sediment samples were mixed in a

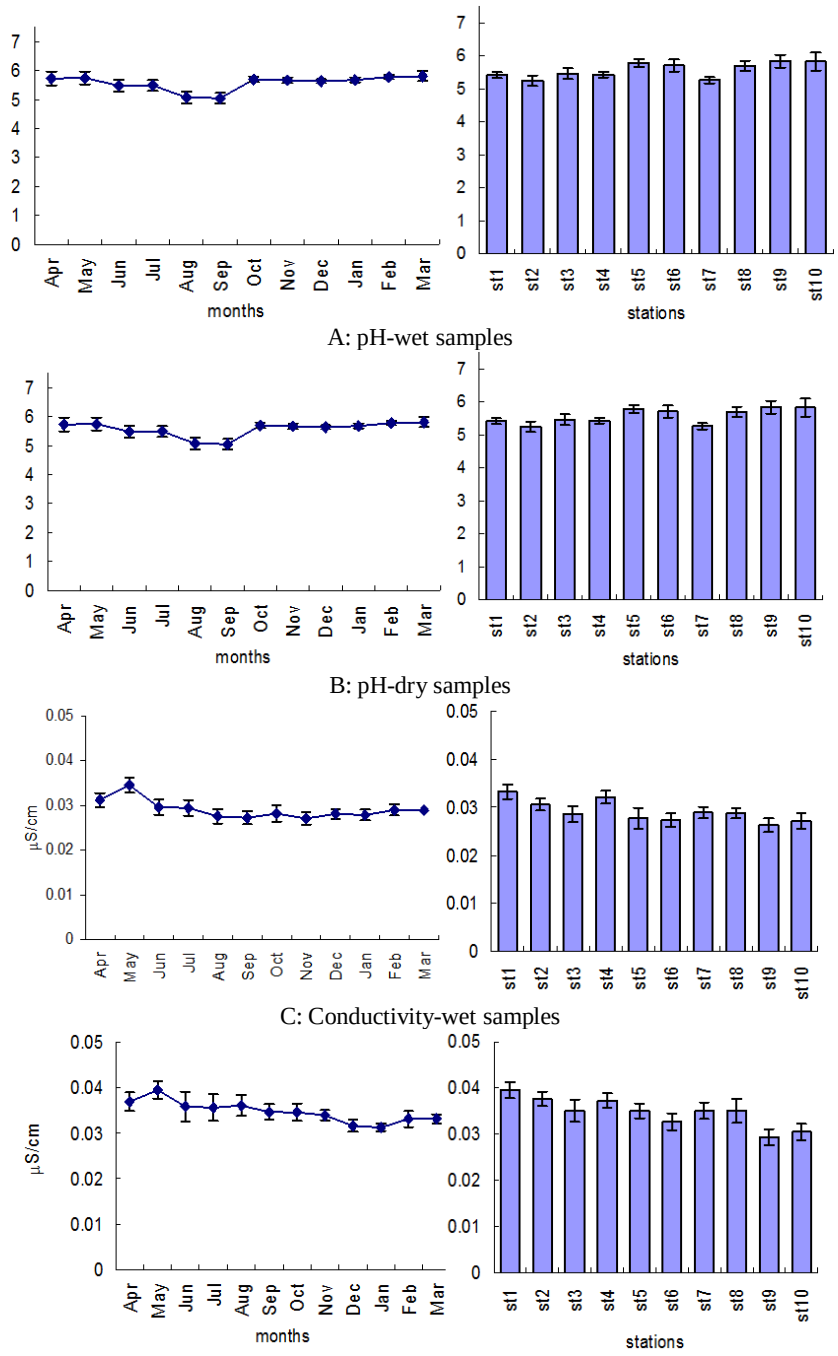


Fig. 3: pH and conductivity values (mean±S.E., n = 20 for months and 24 for stations) of sediments

ratio of 1:1 with distilled water in a beaker before inserting the probes. Readings were taken after allowing the instrument to stabilize.

Total Organic Carbon (TOC) in percentage was determined by the wet combustion method of Walkley and Black (1934). Nitrate (NO_3) levels in sediment were determined following the Brucine Method (APHA, 1976, 1998), while available phosphorus in sediment was determined by Bray and Kurt (1945). The total hydrocarbon content of the sediment was determined spectrophoto metrically after extraction with toluene (Odu *et al*., 1985).

Data analysis: Two-way ANOVA with replicate was used for statistical analysis of each sediment variable. Where ANOVA result showed a significant difference,

Bonferoni test were performed for mean separation. MINITAB (R14) was used to carry out the statistical analysis.

RESULTS

The results of the particle size distribution indicated that sediments were generally sandy mud in nature and could be said to be clay>silt>sand (Fig. 2A). Mean percentage composition of sand ranged from 0.4±0.42-45.85±2.16%. The highest percentage of sand was recorded at station 7 in the month of May while the least was recorded at station 2 in the month of April. The lowest mean value (1.57±0.49%) of silt particle was observed at station 4 in the month of July while the highest mean value (54.50±6.37%) in the same month was at station 7 but clay value (5.51±2.68%) was minimum at station 7 in May and maximum (96.70±1.98%) at station 4 in April. There were significant differences ($p<0.001$) between location, time and also a significant interaction between location and periods for sand, silt and clay particles in the study area (Table 1).

There were remarkable seasonal and spatial variations in the mean values of the oxidation-reduction potential of the sediment in the study area (Fig. 2B). The values ranged from -285.5±0.71 mV at station 4 in April to 87.00±1.41 mV at station 10 in November. The negative values indicate reducing conditions whereas the positive values indicate oxidizing conditions. There were significant differences ($p<0.001$) in the oxidation-reduction potential of the sediment between locations, time and also a significant interaction between location and time (Table 1). All pairwise comparisons show that station 1 was significantly different from all stations except station 7; station 2 was significantly different from other stations except stations 3 and 4. Station 3 was not significantly different from 7 and 9 while station 4 was also not significantly different from stations 5 and 10. Temporally, the month of April differed significantly from other months except May, June July but the period of May was not significantly different June and July. Values in the month of June were also not significantly different from those in the month of July but those in July differed significantly from values in the month of August to March.

Minimal variations in space and time were observed in the pH of sediment of the study area (Fig. 3A and B). The mean pH values for wet sediment ranged from 6.18±0.09 at station 10 in the month of May to 7.30±0.06 at station 1 in November. There were significance differences between locations ($p<0.001$), between time ($p<0.001$) and also a significant interaction ($p<0.001$) between location and time (Table 1). Significance difference between locations occurred between station 8 and those of 1, 3, 5, 7 and 9 while that of time occurred between April, May, June, July and October, November, December, January, February and March indicating that the difference is mainly between the wet and dry season months.

Table 1: Summary of ANOVA tables for physicochemical parameters of sediment

	F-values		
Parameters	Location	Time	Location*time
Sand	221.08***	24.92***	8.69***
Silt	215.50***	7.92***	6.43***
Clay	335.81***	20.63***	15.07***
Redox potential	227.51***	1673.71***	65.61***
pH (wet sediment)	3.29***	32.32***	2.21***
pH (dry sediment)	30.91***	33.46***	4.00***
Cond. (wet sediment)	40.50***	28.34***	8.37***
Cond. (dry sediment)	47.38***	21.21***	5.15***
Total organic carbon	28.62***	6.50***	2.47***
Total hydrocarbon content	61.77***	102.44***	8.88***
Nitrate	41.77***	10.23***	2.71***
Phosphate	475.87***	13.88***	14.63***

***: $p\leq0.001$; **: $p\leq0.01$; *: $p\leq0.05$

Spatial and temporal differences were observed in the mean conductivity values of the sediment (Fig. 3C and D). Values obtained showed that the conductivity of the wet sediment were generally lower than those of the dried sediment. The mean values ranged from 22.0±0.001-48.0±0.001 µS/cm (wet sediment) and 23.0±0.002-47.0±0.003 µS/cm (dry sediment), respectively. Stations 8, 9 and 10 (upstream) generally had lower conductivity values than stations 1 and 2 (downstream), which could be due to dilution effects from fresh water inputs upstream. Analysis of Variance (ANOVA) for both wet and dry sediment values showed significant differences between locations, time and significant interaction between location and time ($p<0.001$) (Table 1).

The nitrate level in Azuabie creek was generally high and varied across the study sites and periods (Fig. 4A). The mean concentration of nitrate in sediment varied from 2.32±0.04 mg/kg at station 7 in April to 7.84±0.71 mg/kg in March at Station 5 (Fig. 4A). Significant differences were observed between location, time and also the interaction between location and time was significant ($p<0.001$) (Table 1). Bonferroni test also indicated significant differences between stations 1, 2 and stations 3, 4, 5, 7 and 10 as well as between station 3 and stations 6, 7, 8 and 9. Station Values for April and May were significantly different from those of August, September, November, December, January, February and March while values for June and July were also significantly different from those of March but the month of October did not differ from other months except January, February and March.

Phosphate levels in the study area were observed to be generally lower than nitrate levels but higher at stations 8, 9 and 10 upstream of the study area (Fig. 4B). The mean values ranged from 0.50±0.04 mg/kg at station 7 in April to 8.10±0.16 mg/kg at station 8 in May. ANOVA showed significant difference in mean phosphate concentrations between periods, locations and significant interaction between periods and locations (Table 1). Bonferroni test for

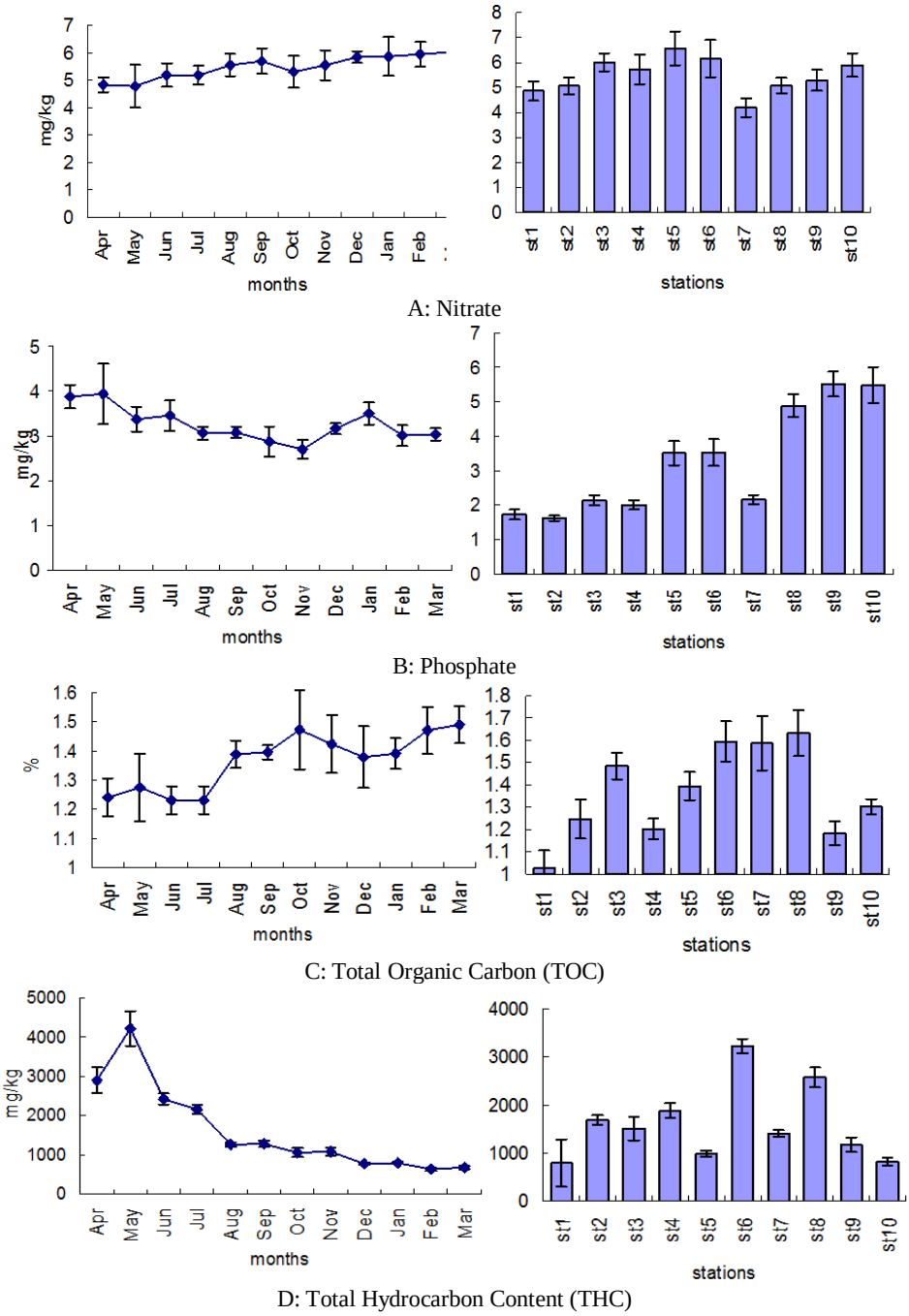


Fig. 4: Nitrate, phosphate, TOC and THC values (mean±S.E., n = 20 for months and 24 for stations) of sediments

mean separation indicate as follows, stations 1 and 2<3 = 4 = 5 = 6 = 7 = 8 = 9 = 10, stations 3 and 4<5 = 6 = 8 = 9 = 10, stations 5 and 6<7 = 8 = 9 = 10, station 7<8 = 9 = 10 and station 8<9 = 10 ($p<0.05$). The significant difference in time occurred as follows, April and May <August = September = October = November = January = February = March.

The values of total organic carbon in the study area varied greatly in space and time with higher values observed during the dry season (Fig. 4C). TOC in the study area were generally above 1% across all stations during the study period. The lowest mean value recorded was 0.84±0.08% at station 1 in the month of November while the highest mean value observed was 2.16±0.07% at station 7 in the month of August. TOC values were observed to be higher at stations 3, 6, 7 and 8. Significant differences were observed in the ANOVA results between locations, time and also the interplay of location and time ($p<0.001$) (Table 1). Bonferroni test among levels of location showed that station 1 varied

significantly with all stations but 9 while station 2 had a significant variation with stations 3, 6, 7 and 8. The significant variation in time was found between April and February, March as well as May and March. Significant variation was also seen between the months of June, July and October, February, March as well as between the months of August, September, December and January and December.

There were remarkable variations in THC values between stations and time in the study area (Fig. 4D). The lowest mean value (210±0.01 mg/kg) was recorded at stations 10 in December while the highest mean value (10750±0.71.3 mg/kg) was obtained at station 8 in May. The ANOVA output show statistical difference in THC between locations and also time (Table 1). Locations and time also showed significant interactions. Bonferroni test indicated station 1 to be significantly different from stations 2, 3, 4, 6, 7 and 8 while stations 2 and 3 were also significantly different from stations 5, 6, 8, 9 and 10. THC values in April were significantly different from those of other months except June while values in May were significantly different from those of other months. The month of June was not significantly different from July but July differed significantly from August, September, October, December, January and February.

DISCUSSION

In general, coarse fractions tend to be deposited in areas with high hydrodynamic energy and fine fractions in areas with low hydrodynamic energy (Suguio, 1973). Grain size analysis show that sediments from the Azuabie creek were generally sandy-mud in nature with textural characteristics being fairly constant over the study period. However, station 7 had higher silt-sand compositions than other stations which had more clay-silt compositions. Sediments with fine particles provide better surface areas for pollutants to adsorb than those with coarse particles. The nature of the sediment and the organic matter composition also determine the benthic community structure found in particular sediments.

Obvious variations were observed in the oxidation-reduction potential of the sediment with negative values recorded during the first four months across all stations. The lowest negative potential recorded was -285.5 mV in the month of April. There was a gradual increase towards the dry season months with values reaching a maximum of 87.0 mV in November but in December 2006 and January 2007, all stations except 2 had positive oxidation-reduction potentials. This indicates the effects of seasons on sediment oxidation-reduction potential in the study area. Also, benthic organisms can alter the chemistry of sediments through their circulatory, respiratory and excretory behaviour and notably altar the oxidationa-reduction potential discontinuity of the sediment. Stations (1, 2, 3 and 4) downstream of the creek were generally low in redox potential compared to ones (7, 8, 9 and 10) upstream of the creek which were higher but values in station 8 was exceptionally higher than others in the first four months. This could be attributed to sediment composition and organic matter content as station 8 is influenced by anthropogenic inputs from major abattoir. Benthic organisms can alter the chemistry of sediments through their circulatory, respiratory and excretory behavior and altar the redox potential discontinuity of the sediment. Warnken *et al*. (2008), stated that that the majority of carbon oxidation occurred at the sediment water interface via O_2 reduction. This likely result from the high frequency of sediment re-suspension events combined with the shallow sediment mixing zone, leaving anaerobic oxidants responsible for only -10-15% of the carbon oxidized in these sediments.

There were minimal seasonal and spatial variations in the mean pH values of sediment in the study area except for wet sediment where spatial variations were quite unnoticeable. The pH values were higher during the dry season months and lower during the wet season months with pH of the wet sediments generally higher than those of the dried sediment indicating that the dried sediments tended to be more acidic than the wet sediments. Moslen (2005) noted that the acidic nature of the dried sediment would pose serious challenges to benthic organisms in nature. Dry and wet sediment pH and conductivity values were measured during the study. It was observed that values from the wet sediments were generally higher than values from the dried sediment for both parameters. Higher values were observed at stations 1 and 2 (more saline end of the creek) than stations 8, 9 and 10. With mean pH values such as 6.18 to 7.30 (wet sediment) and 4.30 to 6.40 (dried sediment), it could be stated that drying of the sediment has effects on the pH. The values obtained for dried sediment pH during this study were consistent with those of Umesi (1999), Ebere (2002) and Daka *et al*. (2007) who recorded ranges of 2.7-5.5, 4.27-4.8 and 2.5-3.5, respectively. These values are rather highly acidic and would pose serious challenges to organisms in nature. However, the values are the result of the chemical reactions that take place in pyrite-rich sediments during drying, resulting in low pH values.

Seasonal variations in conductivity of the sediments were also observed as a result of dilution due to rainfall. The conductivity values of the wet sediment are also a better reflector of the sediments conditions in situ. The upstream stations (stations 8, 9 and 10 generally had lower conductivity values than downstream (stations 1 and 2), which could be due to dilution effects from fresh water inputs upstream.

Nitrate and phosphates normally give an indication of the nutrient level in the study area. Variations across sites were observed in the concentration of these

nutrients. Nutrient levels were found to be generally lower at stations 1and 2 than other stations. Domestic waste input from human settlements near these stations and surface run-offs into the creek could be responsible for the appreciably high nutrient level recorded at these stations. However, the concentration (2.32-7.84 mg/g) of nitrates observed in sediments of the Azuabie creek is in agreement with the range (3.07-6.46 mg/g) recorded by Umesi (1999) in a study in the upper Bonny estuary. Similarly, the phosphate values (0.5-8.10 mg/g) observed in this study also fall within the range (0.2-4.18 mg/g) recorded by Umesi (1999) and that (4.95-14.73 mg/g) observed by Ebere (2002) at other polluted sites in the upper Bonny estuary. Benthic organisms and bacteria living at or near the sediment-water interface can profoundly affect the exchange of nutrients by directly taking up dissolved constituents, such as phosphates before releasing them to the overlying water column (Sundback *et al*., 1991). In addition, benthic processes, such as bioturbation (physical mixing) and bio-irrigation (pore water pumping), can enhance the exchange of dissolved constituents with the overlying water (Hammond *et al*., 1985). Although, Nitrogen (N) is most common limiting nutrient in the marine environment, Phosphorus (P) and Silicon (Si) can be locally and temporally important. The importance of these nutrients is accentuated in estuarine systems where anthropogenic influences have caused changes in the nutrient loading ratios of biologically available N:p and N:Si. Desorption of Phosphate from sediment surfaces can regulate the availability of dissolved P in sediment under oxic conditions.

Organic matter content is commonly associated with the amount of silt and clay present in the sediment. Fine sediment particles have larger relative surface areas than coarse particles and can absorb colloidal and dissolved organic matter forming sedimentary complexes. Once deposited, these complexes are capable of incorporating organic matter into the bottom. Stations 1 and 2 were generally lower in organic carbon than all other sites with mean values of organic carbon rarely exceeding 1.3% but stations 6, 7 and 8 were hotspots of organic pollution The appreciably high organic carbon is traced to the presence of wastes dump sites due to a major abattoir and the large quantities of organic wastes discharged into the near-shore sediments at these stations. The average percentage of organic carbon (0.82-2.16%) observed in the Azuabie Creek show good correspondence with that (1.82-4%) reported by Bernard *et al.* (1996) in an estuary with fringing mangrove environment in the Caribbean Island of Guadelope but below that (10.52-10%) reported by Venturini and Tomassi (2004) in Santos Bay, Brazil. It also agrees with the range of values (1.3-6.8%) reported by Ebere (2002) in a study of the impact of Refinery effluent in the upper Bonny estuary, however, Griggs (1975) reported that sediments with values exceeding 1% are said to have high organic carbon. Other studies with similar range of values include: Umesi (1999): 2.7-16%, Ugbomeh (1987): 3.68-26.07% and Ekeh (2005). Organic carbon residing in pores too small to allow the penetration of enzymes could be preserved, which might work in tandem with other preservation process, such as humification, leaving sedimentation rates as important control on carbon burial rates (Mayer, 1994). Benthic communities in most organically enriched with the most disturbed environment are occupied solely by small, thread-like polychaets, which include several species belonging to sibling species complex of *Capitellacapitata*. Such polychaets often reach very high densities (Pearson and Rosenberg, 1978). These simple benthic communities, lacking in diversity, are gradually replaced by more diverse communities after a decrease in the additional organic discharge into the bottom environment.

Hydrocarbon enters the marine environment through natural pathways and anthropogenic process. Natural sources include forest fires, natural petroleum seeps and post-depositional transformation of bioorganic precursors (Young and Cerniglia, 1995). Urban runoff, Swage disposal, industrial effluents, oil production and transportation activities are some of the most important sources of anthropogenic hydrocarbons (Kim *et al*., 1999). Chronic pollution resulting from these kinds of inputs has effects on marine organisms, which are necessary to study and quantify. The total hydrocarbon concentration of the Azuabie Creek was appreciably high with mean values of THC ranging from 210-10,750 μg/g during the study. In this study, high levels of THC were observed at stations 6, 7 and 8 while moderately high concentrations were recorded at stations 2, 3, 4 and 9 mostly during the early months of the study period. The high concentrations observed at stations 6, 7 and 8 could be attributed to spills due to bunkering activities close to those stations in addition to industrial waste discharge by some oil companies present in the area and the materials washed off from burnt tyres at the abattoir while the moderate values observed at stations 2, 3, 4 and 9 farther away could be due to tidal effects. The values observed during this study are consistent with that (50-10,000 ppm) recorded by Ekweozor (1991) and that (3,584.62-19,981.42 μg/g) recorded by Ebere (2002). Data obtained in this study also corresponds with that of Bernard *et al*. (1996) who also recorded values (25.4-4104.4 μg/g) that are similar to those found in the Azuabie Creek in the Caribbean Island of Guadelope. There was a significant positive correlation between TOC and THC. Dubin-Green (1990), noted that, continuous release of petroleum effluent and extensive pollution, such as oil spill would cause measurable changes in the physicochemical parameters of an aquatic ecosystem. He found that the

main effects of petroleum and hydrocarbon on macrobenthic organisms is sharp reduction in species diversity, reduction in population density, elimination of sensitive species, changes in the location of significant biotype boundaries and increase in the relative abundance of pollution tolerant species such as *Millammina fusca*, *Trechommina inflata Elghidum excavatum* and *Ammonia beccari*.

CONCLUSION

It is concluded that the Azuabie creek has the following attributes as a result of a mix of anthropogenic stresses and natural variation. Physicochemical variables are influenced by pollution sources and these would affect the benthic community in the estuarine creek:

- Minimal seasonal and spatial variations were observed in the mean pH values of sediment of the study area.
- Remarkable seasonal and spatial variations were noticed in oxidation-reduction potential of the sediment with higher values during the dry season at upstream stations (stations 7, 8, 9 and 10).
- Stations 3, 6, 7 and 8 generally had higher levels of contaminants such as TOC, THC than other stations reflecting their proximity to sources of contamination.

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