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CHEMICAL COMPONENTS AND NUTRIENTS IN MANGAL SEDIMENTS OF CROSS AND QUA IBOE RIVERS, SOUTH-EAST NIGERIA

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ABSTRACT

The coastal area of south-east Nigeria is extensively fringed by mangroves species which include *Avicennia africana* (white mangrove), *Rhizophora mangle, Rhizophora racemosa, Rhizophora harrisonii* (red mangroves), and *Languncularia racemosa* (black mangrove). This study examined the chemical components of the mangrove sediments and the extent of impact by human activities. The mangal sediments were characteristically acidic and non-sodic especially at the eastern Cross river flank. Texture of the sediments ranged from silty-clay (SC) to sandy-clay (S-CL) with the abundance of silt/clay in the lower reaches (estuary) and sandy mud in the upper reaches. These sediment characteristics predict a high retention potential for pollutants. The average chemical components and nutrient levels were low indicating constant flux of minerals between the mangrove vegetation and the associated surficial sediments. The pollutant levels, Fe and total hydrocarbons, clearly indicate high anthropogenic impact of the Cross and Qua Iboe rivers estuarine system.

INTRODUCTION

The Nigerian coastline stretches more than 800 km and is marked by sandy beaches, estuaries, lagoons, and a delta (Asuquo, 1997). The coastline can be

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divided into four distinct regions, the strand coast in the eastern area characterized by terrestrial riverine ecosystem with exposed fine sand beaches of flat topography and the Niger delta region consisting of extensive mangrove deltaic environment with numerous networks of rivers and creeks bordered by tracks of mangrove trees. On the western region is the western Mahin mud coast consisting of low lying coastal creeks, organic-rich mud flats and beaches, and the barrier-lagoon region which includes the Lagos lagoon system and the barrier islands characterized by extensive areas of low-energy sheltered lagoon (Dublin-Green, Awobamise, & Ajoa, 1997). The Badagry area has a steep profile with medium to coarse sandy texture (Asuquo, 1997).

In the south-south area of Nigeria, two major rivers traverse the coastal area and discharge into the sea. These are the Qua Iboe river (a drowned river valley system) and the coastal plain Cross river system, which is the largest estuary in the West Africa (Asuquo, Ewa-Oboho, Asuquo, & Udo, 2004), receiving inland drainages from Calabar river, Mbo river, Great Kwa river, and Akpayefe rivers. The areas of Qua Iboe river and the Cross river estuaries investigated are located between longitude 7° 55’ and 8° 30’ E and latitude 4° 30 and 5° 25 N (see Figure 1). In this area, the estuarine sediments are characteristically unique in nature and play the significant role of hosting different species of biota, epifauna, and mangrove trees especially *Avicennia africana* (white mangrove), *Rhizophora mangle, Rhizophora racemosa, Rhizophora harrisonii* (red mangrove), and *Languncularia racemosa* (black mangrove) species, and the former being the least abundant specie. The major threats to the coastal areas are pollution (mainly from oil spillages), mangrove deforestation (for firewood/ house building), agriculture, Nypa palm (*Nypa fruticans*) encroachment and coastal erosion.

However, the Cross River State Conservation Edicts of 2001 has designated some areas of the mangrove to be preserved as national parks while the Akwa Ibom State Government have instituted the Stubbs creek Conservation Project (all in the area) to protect and conserve the mangrove resources from further encroachment by humans.

Besides the above threats, other human activities such as sand winning, channelization (dredging) and dumping of municipal wastes into these estuaries are indisputable agents of sediment mobilization, distribution, and dissolved mineral recycling in the estuarine system. With the muddy substratum of the mangrove sediments, dissolved mineral nutrients are absorbed, utilized, and redistributed in the ecosystem.

This study was designed to examine the chemical components and mineral elements in the estuarine mangrove sediments. The investigation also aimed at determining their distributions between the intertidal and subtidal areas of the mangrove ecosystem and the hydrocarbon content in the estuarine sediments.

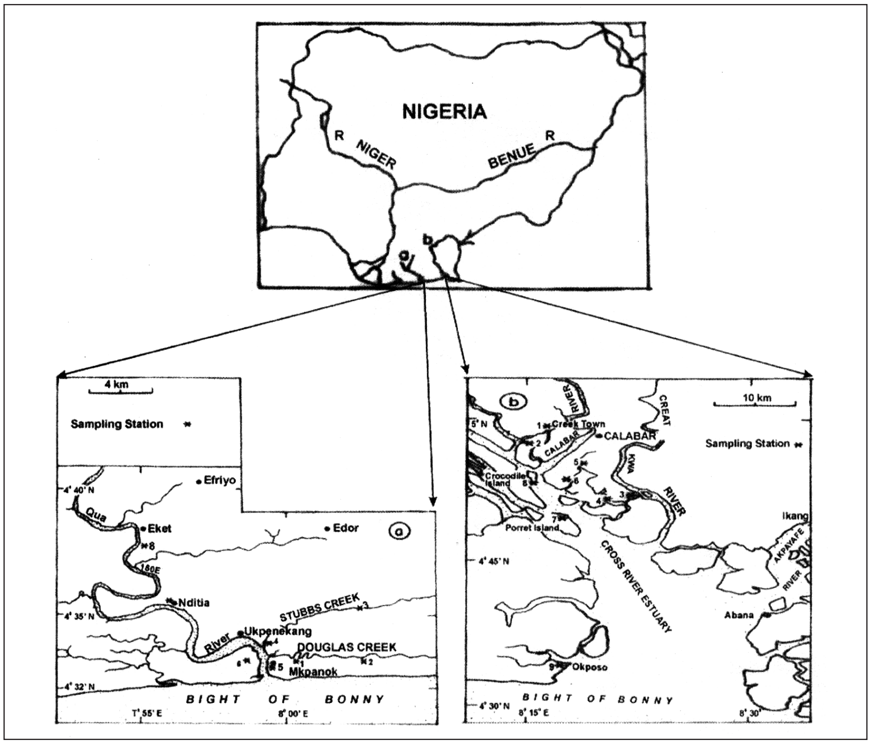


Figure 1. The location maps of Qua Iboe river (a) and Cross river (b) showing the distribution of the sampling stations with the map of Nigeria as inset. (Qua Iboe: 1 – Douglas creek behind flare basin, 2 – Douglas creek 5 km upstream, 3 – Stubbs Creek 5 km upstream, 4 – Stubbs Creek at the mouth, 5 – Qua Iboe R, close to Mkpanak, 6 – QIR opposite Upenekang, 7 – QIR at Nditia, 8 – QIR at UAC, Eket; Cross river: 1 – Creek Town Creek 4 km, 2 – Inlet of Creek Town Creek, 3 – Aqua Vista creek, 10 km from the estuary, 4 – Aqua Vista creek, 5 km from the estuary, 5 – Abitu Creek, 6 – Edita's Creek, 7 – Cross river at Parrot Island, 8 – Cross river at Crocodile island, 9 – Cross river at Okposo.

MATERIALS AND METHODS

Sample Collection

Sampling started in January 1997 and ended in August 1998. Seventeen sampling sites were chosen, eight at the Qua Iboe area (designated a), and nine from Cross river area (designated b, Figure 1). Sampling quadrats measuring 5 m^2 were mapped out at each location and composite samples obtained at the intertidal and subtidal levels. Surface sediments (0-10 cm) were collected using the hand auger for the intertidal and the Van veen grab sampler for the subtidal sediments. Samples were stored in polythene bags and preserved in ice chess for laboratory analysis.

Sample Processing and Laboratory Measurements

The samples were air dried, ground with wooden-roller, and reserved through 2 mm mesh. The sediment pH was determined in 1:2 sediment/water ratio. The electrical conductivity (EC) was measured in 1:2 sediment-water extract using an electrical conductivity meter. Particle size determination was carried out by Bouyoucos (1951) hydrometer method. The method of Walkey and Black (1934) was used in the determination of organic carbon. Available phosphorus was determined by Bray and Kurtz (1945) No. 1 method. Exchangeable acidity was extracted with IN KCL solution and measured by titration with 0.01 M NaOH. Exchangeable bases were extracted with neutral IM NH_4OAC, pH 7.0, the potassium and sodium in the extract were determined by flame photometry while Ca and Mg by Versenate EDTA titration (Jackson, 1962). Total Nitrogen was determined by the micro-kjeldahl digestion method (Jackson, 1962). Total hydrocarbon (THC) was determined by extracting the sediment samples with redistilled n-hexane and measuring the total hydrocarbon content at 430 nm using DR/3000 Hach spectrophotometer. Fe was extracted from the sediment samples by digestion of the samples with a mixture of nitric and perchloric acids (Baruhnisel & Bertsch, 1982). The metal concentrations (Fe) in the extracts were read on computerized Atomic Absorption Spectrophotometer (Model 2350). The analytical precision gave a coefficient of variation between 2 to 5%.

RESULTS

The physicochemical composition of the mangrove sediments for the Qua Iboe river system (QIRS) and Cross river system (CRS) are presented in Tables 1 and 2.

A comparative assessment of the mean levels of sediment quality parameters between the two locations, QIRS and CRS, are shown in Figures 2 and 3 for the intertidal and sub-tidal sediments respectively. The sediment reaction were dominantly acidic with a mean of 2.68 ± 0.4 and 3.82 ± 0.2 for the QIRS and CRS mangrove sediments. The electrical conductivity was high and variable (1.0 - 17.3 ECds/m) for QIRS but low for CRS (0.1-1.50 ECds/m). The % N (0.16-0.69% and 3.6-6.0%), avail. P (2-9.0 mg/kg, 1.6 -6.4 mg/kg), % TOC (1.94-8.38%, 6.2-9.1%) were low for QIRS and CRS. Marked levels of exch., Ca (3.84-24.96 cmol/kg), Na (0.25-11.9 cmol/kg), Fe (18.0-331.2 mg/kg) were measured in QIRS as compared to low values of exch., Ca (< 6.4 cmol/kg) and exch., Na (< 0.4 cmol/kg) except Fe (< 2228 mg/kg) in CRS. The latter was attributed to anthropogenic sources (Ntekim, Ekwere, & Ukpong, 1993). The intertidal and sub-tidal sediments of both QIRS and CRS were impacted by hydrocarbons (5.0-127.0 mg/kg

Table 1. Ranges of Physicochemical and Mineralogical Composition of the Qua Iboe River Mangrove Sediments, Nigeria, with Maximum Tolerable Limits

Parameters	QIR intertidal sediments	QIR subtidal sediments	Maximum tolerable limits
pH	2.5-5.2	3.8-5.5	5.1-6.5
EC ds/m	2.35-16.83	1-17.28	4.0
Tot N %	0.06-0.87	0.16-0.69	100[a]
Org. carbon %	1.07-10.32	1.94-8.38	0.2[b]
Base Sat %	21-97	46-97	2.0[b]
ESP	1.3-36	0.6-42	15.0
Sand %	26.4-92.4	46.4-92.4	—
Silt %	2.6-42.6	6.4-8.4	—
Clay %	3.0-27.0	3.0-23.0	—
Textures	S-Cl	S-SCL	—
Avail. P mg/kg	3-37	2-9	20[b]
Exch. Ca cmol/kg	1.6-19.52	3.84-24.92	10-100[b]
Exch. Mg cmol/kg	1.0-14.4	1.0-16.01	3-8[b]
Exch. K cmol/kg	0.15-7.24	0.2	8.31[b]
Exch. Na cmol/kg	0.57-9.52	0.25	11.9[b]
Exch. EA cmol/kg	1-20.5	0.8-18.3	4.0
ECEC cmol/kg	12.4-49	10.27-48	10-100
Fe	40-212	18-331.2	20,000-60,000[c]
THC mg/kg	5-105	18-127	20[d]

[a]Chemical Society of Britain (1975). [b]Black, Evans, White, Esminger, and Clark (1973). Robertson and Carpenter (1976), DPR (1991). [c]Robertson and Carpenter (1976). [d]DPR (1991).

Table 2. Ranges of Physicochemical and Mineralogical Composition of the Cross River Mangrove Sediments, Nigeria, with Maximum Tolerable Limits

Parameters	CR intertidal sediments	CR subtidal sediments	Maximum tolerable limits
pH	3.2-6.1	3.7-6.1	5.1-6.5
EC ds/m	0.1-1.50	0.096-1.47	4.0
Tot N %	4.71-6.4	3.1-4.72	100[a]
Org. carbon %	6.3-9.2	6.2-9.1	0.2[b]
Base Sat %	62-84	61-84	2.0[b]
ESP	—	—	15.0
Sand %	60-80	461-87	—
Silt %	8.2-28.3	7.2-24.6	—
Clay %	8-15.7	5-19	—
Textures	S-Cl	S-SCL	—
Avail. P mg/kg	4.1-6.4	1.6-6.0	20[b]
Exch. Ca cmol/kg	2.0-6.4	1.92-6.4	10-100[b]
Exch. Mg cmol/kg	4.2-10.2	2.1-3.4	3-8[b]
Exch. K cmol/kg	2.1-3.1	1.04-1.1	8.31[b]
Exch. Na cmol/kg	0.3-0.8	0.26-0.35	11.9[b]
Exch. EA cmol/kg	1.8-3.6	1.6-3.2	4.0
ECEC cmol/kg	7.1-10.2	6.47-12.1	10-100
Fe	871.1-2228	780-2168	20,000-60,000[c]
THC mg/kg	160-760	140-758	20[d]

[a]Chemical Society of Britain (1975). [b]Black et al. (1973). [c]Robertson and Carpenter (1976). [d]DPR (1991).

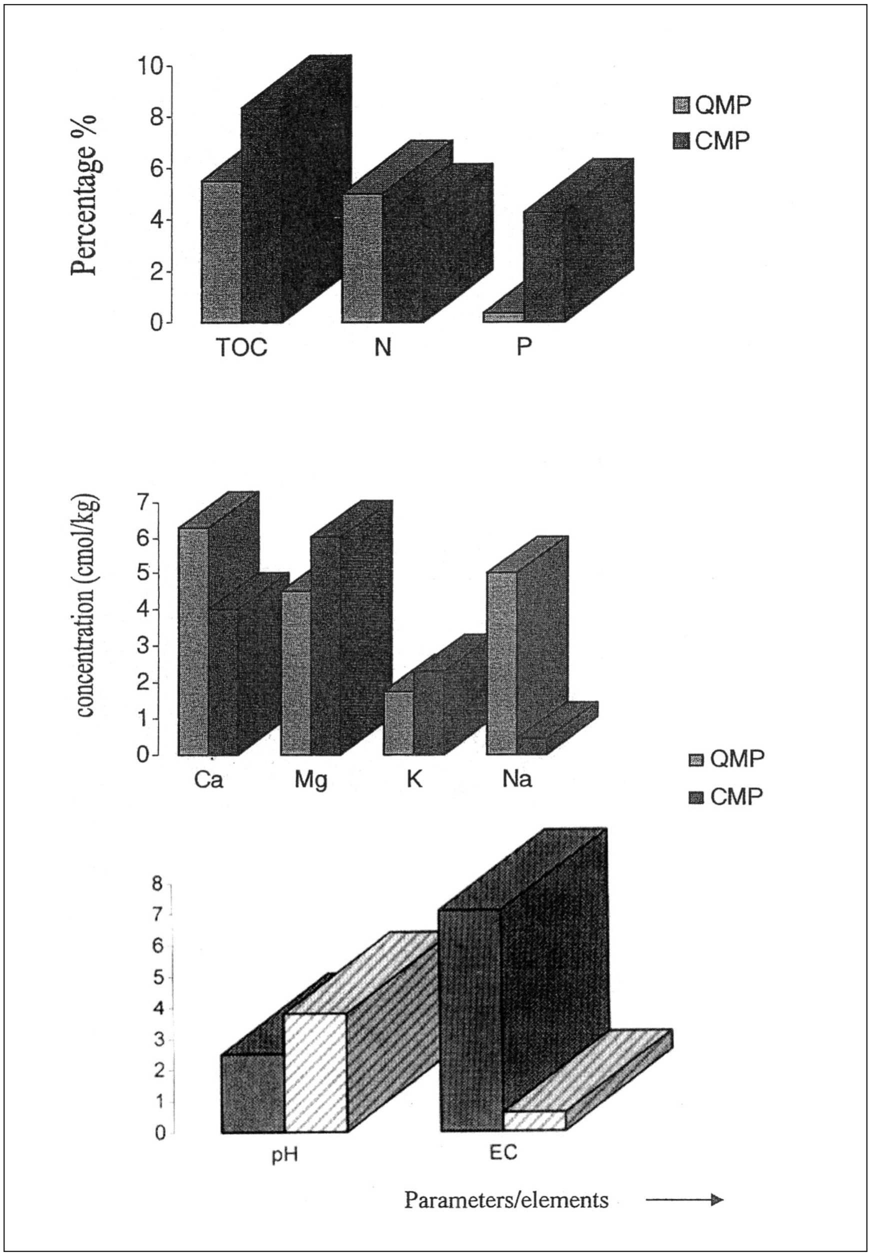


Figure 2. Mean levels of pH, EC, TOC, N, P, Ca, Mg, K, and Na in intertidal sediments of Qua Iboe and Cross river mangrove ecosystem, Nigeria. (QMP – Qua Iboe Mangrove Project; CMP – Cross river mangrove Project)

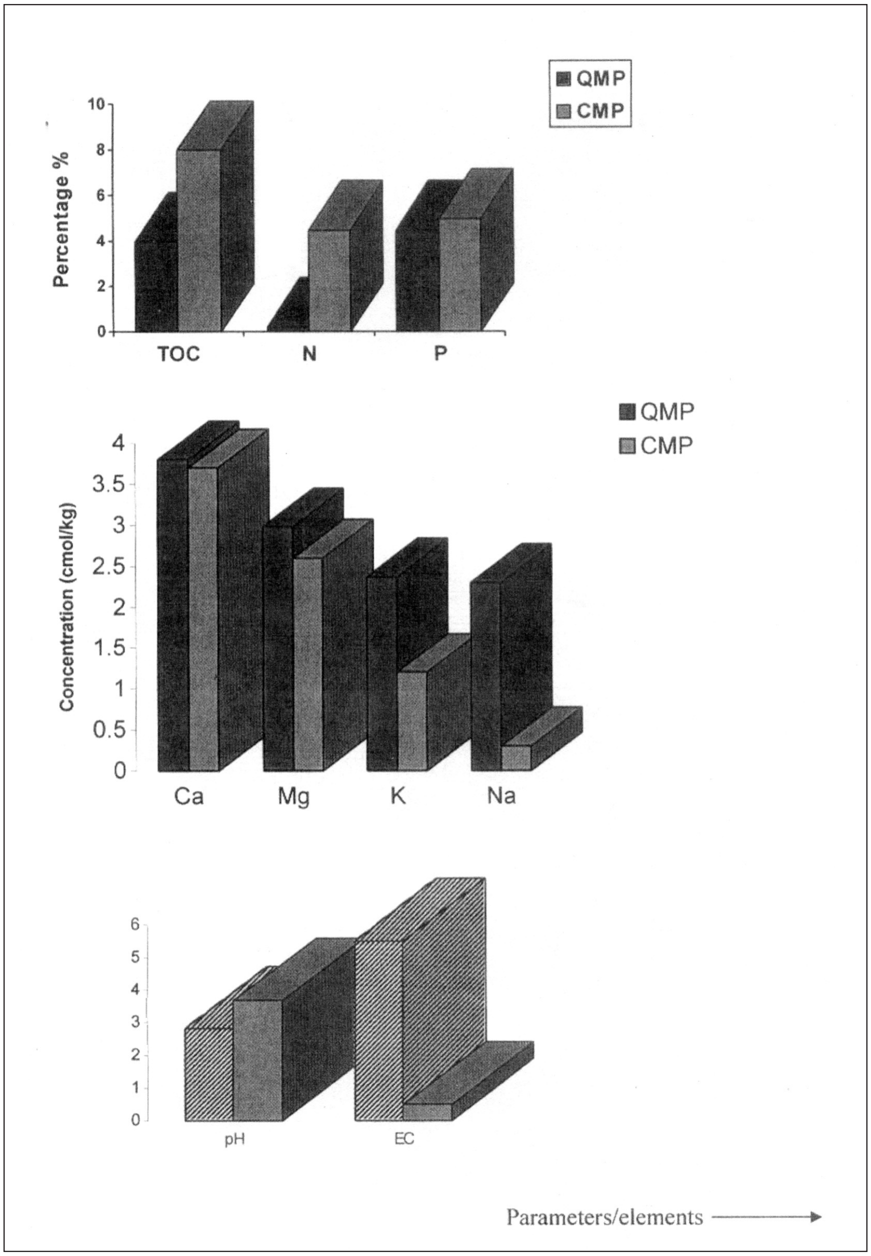


Figure 3. Mean levels of pH, EC, TOC, N, P, Ca, Mg, K, and Na in subtidal sediments of Qua Iboe and Cross river mangrove ecosystem, Nigeria. (QMP – Qua Iboe Mangrove Project; CMP – Cross river mangrove Project)

and 140-758.0 mg/kg respectively). The hydrocarbon levels were above the permissible limit of 20.0 mg/kg specified by Department of Petroleum Resources (DPR, 1991), Nigeria.

Figures 2 and 3 show the mean amounts of chemical components and micronutrients in the intertidal and subtidal sediments from the two estuarine systems. The concentrations of micronutrients (nitrogen and phosphorus) were markedly low (< 8%) for the intertidal and subtidal sediments. Inputs of constituents into the systems were high for P, Mg, and K in the intertidal sediments and N and P for subtidal of the Cross river system. This is attributed to the minimal addition of nutrients from coastal development activities such as agricultural farms, flour factories, and oil palm mills located in these areas. Whereas for the QIRS, N, Ca, and Na were high in the intertidal as well as Ca, Mg, K, and Na occurrences in the subtidal. %TOC were comparable for the two estuarine systems with levels in CRS (9.1%) being relatively higher than % TOC in QIRS (8.38%). Figure 4 presents for mean concentrations of THC and Fe in the mangal sediments. The spatial variations and distribution of the chemical components in the sediments are shown in Figures 5 and 6, with the Cross river system exhibiting a regular variation than Qua Iboe river system attributed to a higher degree of turbulence of the latter.

DISCUSSION

The pH of the intertidal sediment samples from QIRS was significantly ($p < 0.01$) lower than the intertidal sediments from Cross river system (CRS). The lower pH in the intertidal sediments than the subtidal is probably attributed to the 6-hourly flood and ebb tides phenomena, which permits aeration of the sediment interstices through absorption of air within the pore spaces. In the subtidal zone, due to the absence of oxygen, anaerobic activities prevails which support the breakdown of carbohydrates and the production of H_2S, a less acidic gas than CO_2. Most subtidal mangrove sediments contain H_2S at relative concentrations known to inhibit activities of enzymes (Mckee, 1996a; Mckee, Mendelssohn, & Hester, 1988). According to Landon (1992), in soils that are very strongly acidic (pH 4-5.5) to moderately acidic (pH 5.5-6.0), micro nutrient elements except P become more available as phosphate combine with iron to form iron phosphates which makes it unavailable. In such acidic medium, Fe, Al, and Mn are the most abundant mineral elements, whereas Ca, Mg, and K are likely to be in low abundance. This is in agreement with the results obtained during this assessment. Fe concentrations (< 2000 mg/kg) were markedly higher than other mineral elements especially in the intertidal sediments.

In acidic soils, N and P nutrients are bound as Fe and Al phosphates, as well as Fe and Al nitrates (Landon, 1992). Their unavailability permits the utilization of other organic matter principally, the mineral elements as plant nutrients for metabolic activities. Ca and Mg occurred at amounts higher than 10 cmol/kg in the

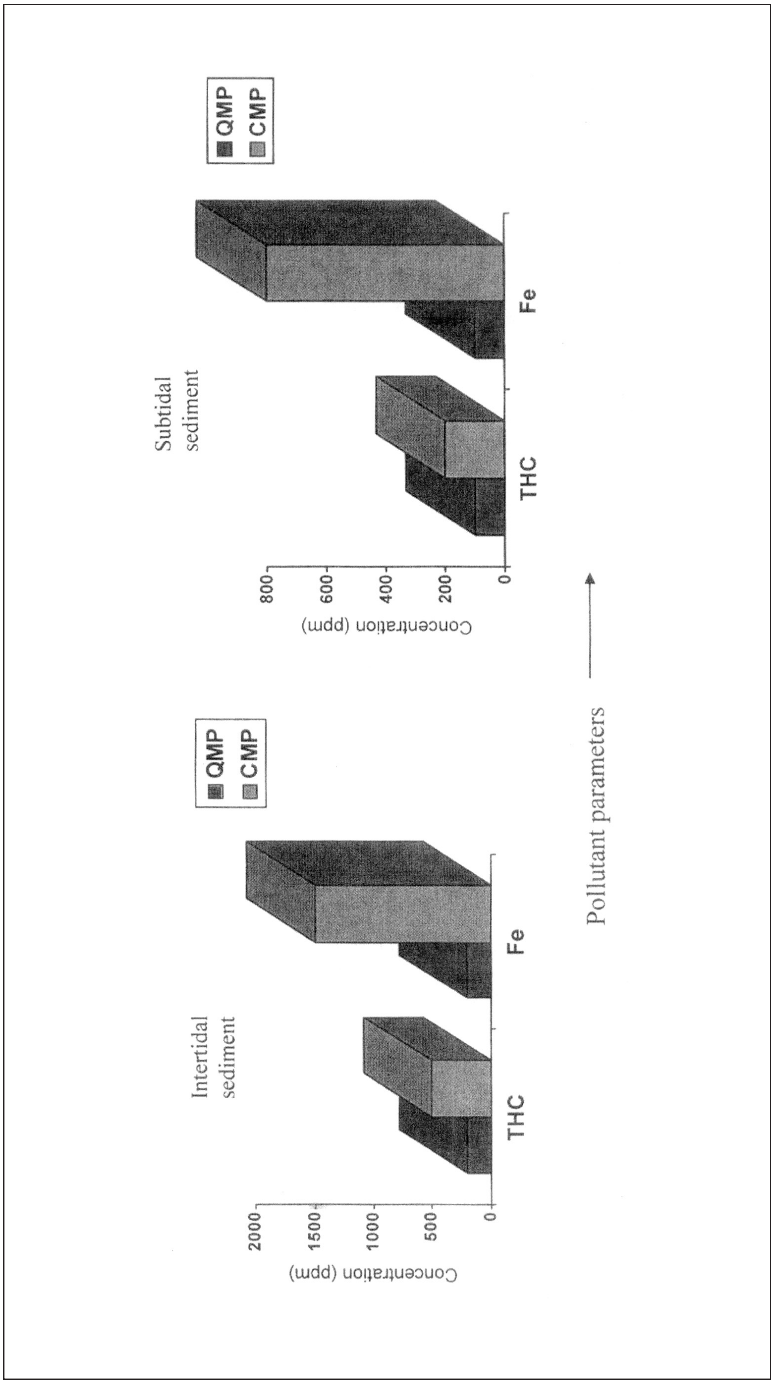
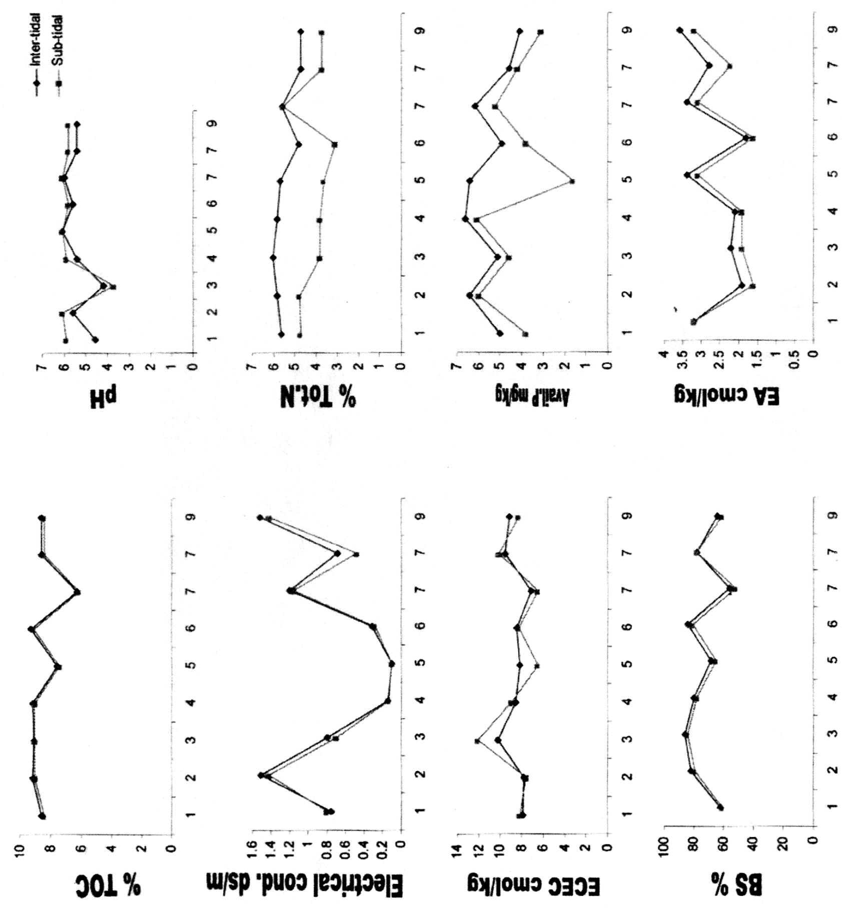


Figure 4. Intertidal and subtidal distribution of pollution indicators in the mangrove sediments of Qua Iboe and Cross river ecosystems, Nigeria.

mangrove soils of QIRS except K. Values of the exchangeable bases were lower in the subtidal sediments of CRS than the intertidal area except Na. Generally, Ca and Mg concentrations were higher in the sediments than Na especially for the Cross river system indicating that the sediments are non-sodic (Na < 1.0 cmol /kg). These enhance the release of these components thus making them available for plant utilization and subsequent metabolism. Of course, calcium deficiency is expected whenever Na is high in sediment (sodic sediments). Magnesium concentrations were comparable to Ca concentrations during the period. Ca:Mg ratios were almost 1:1 for the locations investigated for both the intertidal and subtidal sediments. The characteristic non-sodic sediment also permitted the availability of Mg and its utilization for plant nutrition. It therefore appears that in non-sodic sediments, Fe, Ca, and Mg may serve as limiting mineral nutrients for plant growth (Landon, 1992).

Electrical conductivity values measured indicated slightly saline (4-5 mS/cm) for Qua Iboe mangrove ecosystem to relatively salt free sediment (< 1.0 mS/cm) for Cross river sediments. Presently, it is well established that salinity or high electrical content of the ecosystem is not a requirement for mangrove growth as most mangrove species can thrive well in fresh water habitats (Ball, 1988; Mckee, 1996b; Tomlinson, 1996). The low salinity encountered could be attributed to the semidiurnal tidal flushing of the intertidal and shallow subtidal creeks and channels. Such continuous erosivity by high freshwater discharge of the Cross river (Lowenberg & Kunzel, 1991), is capable of reducing sediments salinity vis-à-vis the electrical conductivity. The total hydrocarbon (THC) levels determined in the mangrove sediments ranged from 160-760 mg/kg in the intertidal sediments and 140-758 mg/kg for the subtidal sediments. Hydrocarbon levels in the Qua Iboe river were higher than values in the Cross river ecosystem probably due to the enclosed nature of the Qua Iboe estuarine system which restricts movements of tidal incursions and spilled crude oil persists and are recirculated within the system before absorption onto the muddy sediments of the mangrove swamps. Reports of environmental contamination of the Qua Iboe coastline by petroleum residues abounds (Asuquo, 1997; Mobil Report, 1998; Olagbende, Ede, & Inyang, 1999; PIA, 1998). Most Nigerian oil wells are located onshore in the mangrove ecosystem resulting in direct impact from oil during accidental spills. Reports of marine organism such as *Crassostrea tulipa* (mangrove oysters), barnacles, *Callinectes* sp (swimming crab), and *Thais callifera* have been made (Asuquo et al., 2004; Mobil Report, 1998; PIA, 1998).

Fe concentrations were low in the estuarine sediments (800-2000 ppm) compared to maximum tolerable levels in soil or sediments (> 20,000 ppm). Correspondingly, Fe concentrations were lower in the subtidal than the intertidal sediments (see Figure 4) partly due to the acidic nature of the sediments. Generally, the low level is attributed to the utilization of Fe by the dominant mangrove species (*Avicennia* and *Rhizophora* spp) thereby suggesting Fe as one of the limiting nutrients for plant growth in non-sodic sediments.


Inter-tidal
Sub-tidal
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Avail.P mg/kg
EA cmol/kg
% TOC
Electrical cond. ds/m
ECEC cmol/kg
BS %

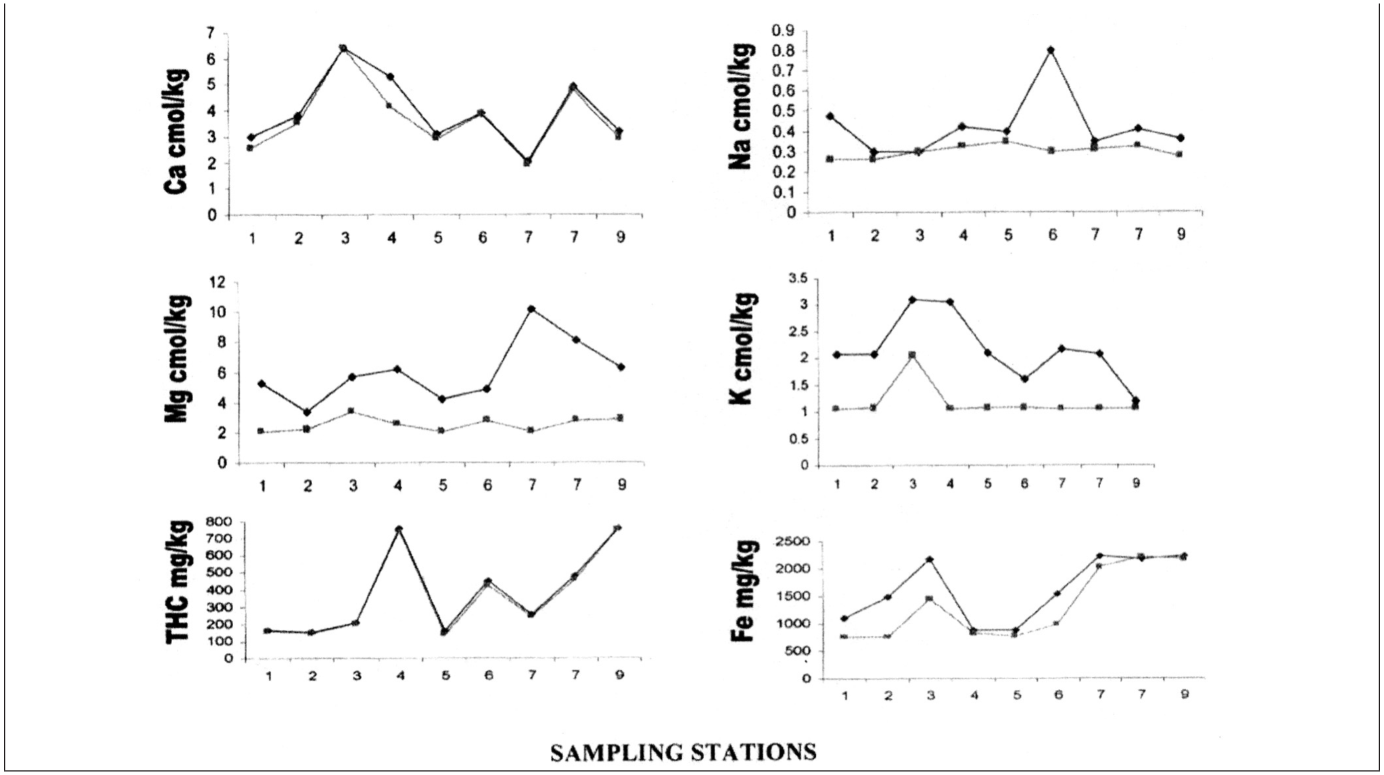
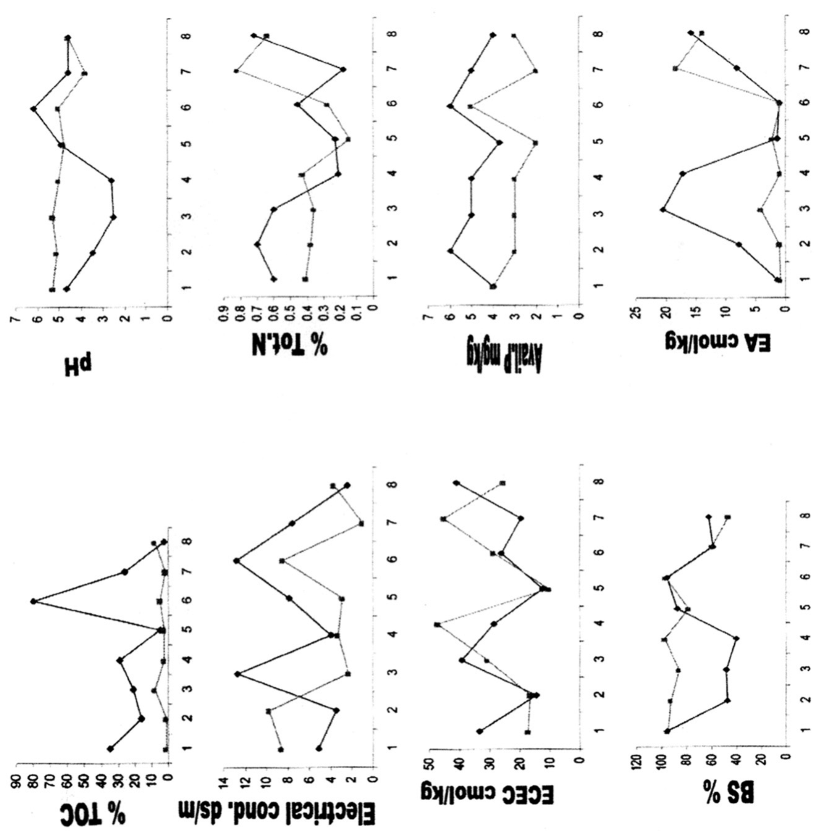


Figure 5. Spatial variation of sediment quality parameters in the intertidal (IT) and subtidal (ST) regions of Cross river mangrove ecosystem.



pH
% Tot.N
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EA cmol/kg
% TOC
Electrical cond. ds/m
ECEC cmol/kg
BS %

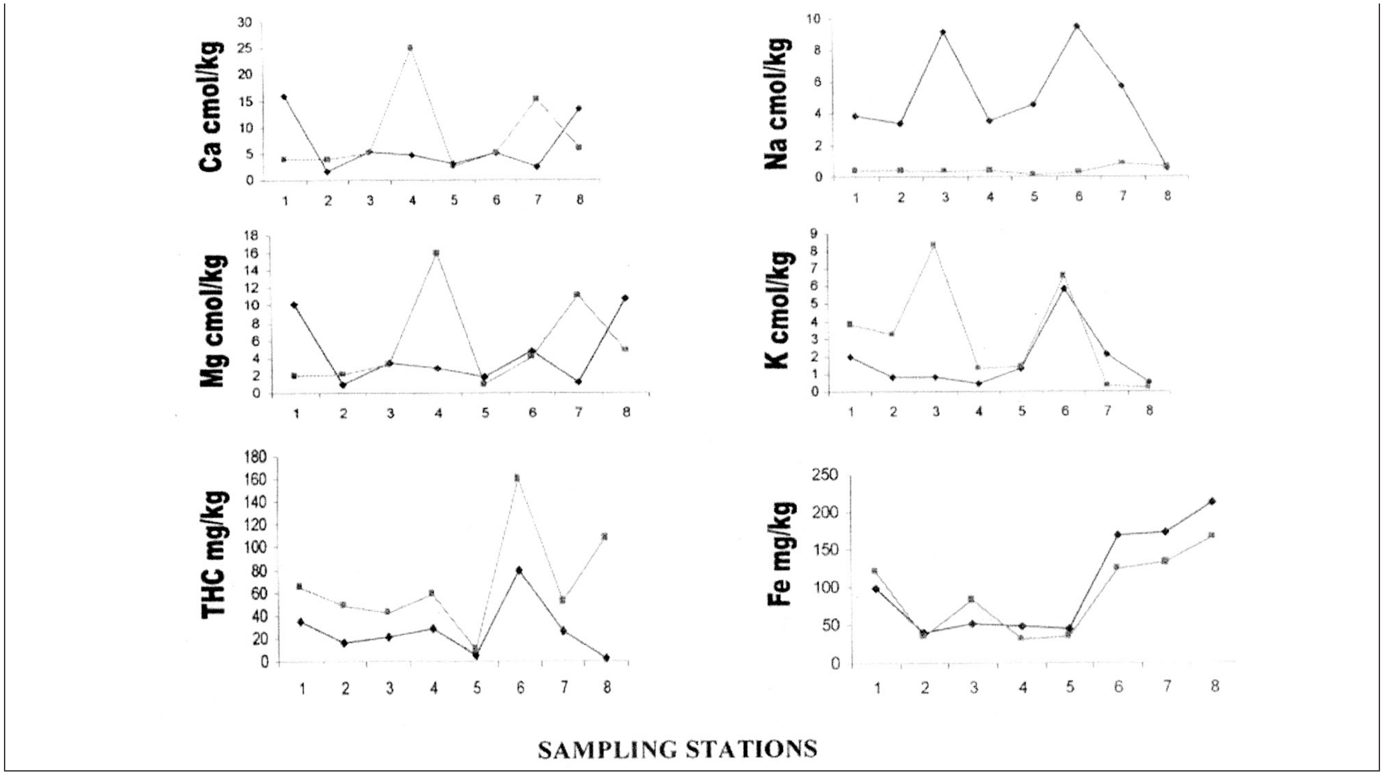

Figure 6. Spatial variation of sediment quality parameters in the intertidal (IT) and subtidal (ST) regions of Qua Iboe river mangrove ecosystem.

SPATIAL DISTRIBUTION OF PHYSICOCHEMICAL AND GROWTH FACTORS IN SEDIMENTS

In the Cross river, the spatial distribution of the physicochemical and growth limiting factors showed similar pattern of behavior in the sediments (see Figure 5). pH, % TOC, and ECEC also indicated the same fluctuation pattern in almost all the locations whereas other factors showed remarkable variable with stations. The variations appeared to be influenced by the texture of the substratum (silt loam absorbing more than sandy loam), erosional force of semi-diurnal tidal waves on the intertidal sediments and exchange processes of dissolved minerals at the water-sediment interfaces. The latter factors seem to balance the mineral element concentration so that there is no remarkable loss of the nutrients. The observed variation were of course within maximum tolerable limits for these parameters but total P and Fe showed marked depletion partly attributed to the formation of iron phosphate in the acid soils and to the utilization by the mangrove species for growth. In the Qua Iboe river sediments, marked spatial variation occurred for almost all the parameters. This condition depicts the highly dynamic nature of the ecosystem and the resultant effect on sediment mobilization processes. It appears that there is a continuous exchange of dissolved substances between the sediment fluff layer and the overlying water which invariably depends on the degree of sediment perturbation arising from human activities such as sand winning, mangrove deforestation for partisan agriculture and crude oil pipe-laying along the network of creeks and rivulets in these areas.

Generally, in the estuarine ecosystem, diffusion and spread of dissolved minerals and pollutants are facilitated by tidal movements and storm surges especially during the wet season (April to September) when these contaminants are transported into shallow coastal regions such as the marshlands which supports large population of the mangrove vegetation. Subsequent sediment deposition processes occur and may create mineral/pollutant bedding in the wetlands and nearshore environments. The obvious effect of the contaminants especially Fe and hydrocarbon is that most benthic organisms may become enriched in the aquatic food chain thereby posing a serious health threat for the dependent human population. This study have described the mineralogical composition of the mangal environment of Qua Iboe river and Cross river systems, the dynamics and flux of the minerals at the water-sediment interface and the possible factors causing the observed flux between the sediment and overlying waters.

CONCLUSION

Mangal ecosystems are areas of constant hydrodynamic activities involving onshore prospecting/drilling for oil, maritime transportation along creeks/network of channels, seasonal agriculture (deforestation), dredging among others. These processes facilitate either the enrichment/depletion of the mangrove ecosystem of mineral elements and nutrients which supports the biochemical activities of the mangal flora and fauna or project the system as a sink for contaminants. Abundance of silt/clay and sandy mud textured sediments predict a high retention potential for minerals and pollutants. Due to their shallow nature, mangal systems are highly exposed to ebb-flood tidal influence (flooding) and the flux of minerals between the mangrove vegetation and the associated surficial sediments, accompanied by erosive action of tides, determine the retention time, distribution, and speciation of chemical components. In areas of high turbulence such as the Qua river system, the availability of chemical constituents or contaminants are highly randomized depicting a short retention time for absorbed or deposited constituents in the mangal sediments.

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