TIDAL CHARACTERISTICS AND THE CHEMICAL WATER QUALITY OF BONNY ESTUARY IN THE NIGER DELTA BASIN OF NIGERIA

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Abstract

This study focused on the horizontal changes in some chemical variables of water quality along Bonny Estuary, the estuary with the second largest tidal area and the highest discharge of all the estuaries in the Niger Delta of Nigeria. Surface water samples were collected from seventeen sampling stations over the dry and the rainy seasons of one annual cycle and analysed for pH, electrolytic conductivity, major anions and cations, organic matter, plant micronutrients (NO^-_3, PO^{3-}_4 and SiO_2), dissolved oxygen, BOD_5 and some heavy metals, using standard analytical methods mostly within 1-10% precision levels. With regard to the horizontal variation along the major axes of the estuary, the investigated chemical variables fell into two sharply defined groups, the abiotic and the biogenic variables. The former showed steady decrease in concentration from the brackish waters through tidal fresh to fresh waters while the latter varied inversely. The waters of the basin were all strongly influenced by the sea and, in view of the basin's low lying configuration and the extensive penetration of polyhaline water into it, the estuary can be classified among the coastal plain or drowned valley estuaries of the world. The estuary is influenced (at the Bonny bar area) by a tide regime with a maximum possible range of 2.5 m, mean range of spring tides of 1.66 m, mean range of neap tides of 1.31 m and an overall mean tide level of 1.39 $\pm$ 0.79 m above reference datum of the bar. The fresh waters were slightly acidic in pH (range = 5.7 – 6.3; mean $\pm$ s.d = 6.0 $\pm$ 0.3), of low oxygen concentration (1.0 – 2.5; 1.3 $\pm$ 1.1 mgl^{-1}) low oxygen saturation (generally less 50%) and very poor in electrolytes. On the other hand, they were rich in organic matter, silicate, and nitrate, compared to the brackish waters. In this respect and in their characteristic dark brown colouration, they are similar to temperate bogs and humid tropical swamps, especially the blackwaters of Amazonia, and suggestive of relatively high content of organic matter decay products. The brackish waters varied from near neutral to alkaline in pH (6.7 – 8.3; 8.0 $\pm$ 0.4), of relatively high oxygen concentration (6.0 – 8.1 mgO_21^{-1}; 6.3 $\pm$ 1.2 mgO_2^{-1}) and very similar to sea water both in ionic order of dominance and in their probable salt composition. However, their levels of heavy metals (chromium, cobalt, copper, and nickel) were high compared to the average concentrations in the open sea. The relatively high levels of biogenic variables in waters in the residential areas of the basin is suggestive of organic pollution (most probably of domestic origin) while the relatively high levels of heavy metals at the estuary's mouth was related to the heavy water traffic and the many activities of the petroleum industry in that area of the basin. Variation in tidal hydrology had a more pronounced effect on the water quality of the estuary than seasonal variation.

Keywords: Horizontal variation, tidal characteristics, water quality, fresh waters, brackish waters, Bonny Estuary, Niger Delta.

Introduction

The Niger Delta of Nigeria is remarkable in many respects. It is a difficult forest terrain riddled with an intricate network of natural water channels through which R. Niger, its tributaries and distributaries drain about one-third of West Africa (2.09 x 10^6 km^2) into the Atlantic Ocean through the Bights of Benin and Bonny. Before the mouths of most of the river channels were blocked by bars, the Niger Delta provided the largest number of sheltered port sites along the coastline of West Africa, and such historic ports as Bonny, Warri, Brass and Forcados were located in the region (Udo 1970). Covering an area of about 6000 km^2 (NEST 1991) i.e., about 20% of the entire delta basin, the mangrove forest zone of the Niger Delta is one of the largest in the world. It forms a vegetative band about 15 – 45 km wide, parallel to the coast with the widest areas being in the tidal basins of Bonny, New Calabar and Sombreiro Rivers and the Escravos-Forcardos Rivers.

Today, the Niger Delta is the nerve centre of the Nigerian crude oil and petro-chemical industries. In spite of this, little is known about the chemical water quality of the region. Even the reports of the Netherland Engineering Consultants, NEDECO (NEDECO, 1959; 1961) which are the best known in the literature (being the most comprehensive and the most widely circulated) on the waters of the basin, contain virtually no information on the chemical conditions of the waters. Perhaps, the first major work relating to the chemical water quality of the basin is that of the Research Planning Institute Inc. (Research Planning Institute Inc., 1985), a technical report on the environmental baseline studies of the Niger Delta. In that work however, the Bonny River system was combined with that of the adjacent New Calabar River. This paucity of information on the water quality of the delta is one of the major issues highlighted in the reports to the Niger Delta Environmental Survey (NDES), a registered NGO on the Niger Delta of Nigeria (NDES 1997).

In this work, information collected over one annual cycle on the chemical conditions of the Bonny River along the two main zones of the delta (the freshwater zone and the brackish mangrove zone) is presented. The work focused on the horizontal changes in some chemical variables along the estuary from its mouth near Bonny town upwards to Port Harcourt conurbation over a distance of about 70 km. In order to have some knowledge of the temporal patterns of variation in the chemical conditions of the estuary, information was also obtained on the extent of seasonal and tidal changes in the investigated variables. As a background to the tidal changes, data on predicted tidal movements at Bonny bar for the year of study was analysed for the characterization of the tidal hydrology of the estuary. Having regard to the likely effect of the basin's general environmental features (including climate) and high level of industrialization on its water quality, rather detailed review information on these aspects of the study area is provided.

Area of study

The general features of Bonny River Basin

River Bonny is one of the major natural network of rivers in the Niger Delta Basin of Nigeria (Fig. 1). The river basin is located in the eastern part of the arcuate Niger delta and bordered by the Andoni-Imo River Basins to the east and the New Calabar River Basin to the west. Its coastline along the Bight of Bonny (syn=Bright of Biafra) extends roughly from longitude 007^{o} 00'E to 007^{o} 20' E (*ca*. 35 km stretch). With a tidal area of about 600 km^2, the Bonny estuary is the fourth largest estuary in the Niger Delta (NEDECO, 1961). However it has the second largest water mass area to total tidal basin area (about 30%) as well as the highest discharge (*ca*. 33,000 m^3 s^{-1}) of all the estuaries in the delta (NEDECO 1961). Freshwater discharge into the Bonny estuary is limited and is mainly through Woji and Amadi Creeks both rising locally from the higher plains immediately north of Port Harcourt. The tidal regime in the estuary is essentially semi-diurnal with diel inequality. The mean water depth at mean water level is 13.8 m at Bonny (007^{0} 11^{1} E, 04^{0} 35^{1} N) and 9.4 m at Port Harcourt (007^{o} 00' E, 04^{o} 45' N) with a corresponding cross-sectional width of 2550 m^2 and 250 m^2, respectively. Fig. 2 provides information on some meteorological variables in the basin during the year of study. The basin falls within the A_2 of the rainfall zones of Nigeria (Ojo 1977) while the climate is the Semi-Hot Equatorial type (Papadakis 1965). Warri (5^{o} 31'N, 005^{o} 44'E) and Port Harcourt are often cited as typical locations of the A_2 rainfall zone in Nigeria (Ojo, 1977). The zone is

Fig. 1: A map of the Niger Delta Basin of Nigeria showing the Bonny Estuary and the investigated sampling station.

Fig. 2. Meteorological information on the Bonny River Basin. 1990.

characterized by the highest rainfall intensity in the country, with rain all months and an annual variability of approximately 10-16%. The semi-hot equatorial climate type is characterized by moderate maximum temperature (highest monthly daily maximum of the warmest month below 33.5^{0}C or 92.3^{0}F) and annual rainfall greater than annual potential evapotranspiration (Papadakis, *op. cit.*). There is rain virtually throughout the year with a regime characterized by dual maxima (July and September) and dual minima (February and August). Average annual rainfall is about 250 cm in Port Harcourt and 420 cm in Bonny with rainfall surplus of about 100 cm and 200 cm, respectively.

Industrial development in Bonny River basin

Bonny River basin is well known for its many oil fields, heavy industrialization and water traffic. The Port Harcourt conurbation (located at the head of the estuary) is the most industrialized town in southeast Nigeria and the second largest port in the country. The major oilfields in the basin include: Bomu, Cawthorne, Alakiri and Bonny. Others are the Bodo West, Ebubu, Apara, Akpori, and Onne oilfields. Most of these oilfields date back to the late 1950s and early 1960s and altogether contain about 180 oil wells about 70% of which are still producing. With a production rate of about 100,000 barrels/day (Ikein 1990) the Bonny oilfields account for about 5% of the current Nigerian daily crude production of about 2.05 million b/d. The Bonny light crude is one of the bench mark crudes in the world oil market.

The Trans-Amadi industrial estate in Port Harcourt is one of the largest industrial estates in the country. It has close to one hundred medium – large scale industries (i.e., industries that consume more than 50 m^3 /days of water), including both light and heavy industries. The major industries there are manufacturing, food and beverages, plastic and rubber and metallurgical. Also located within the basin are two of the four oil refineries in Nigeria, *viz*: the Port Harcourt Refinining Company Limited (established in 1965 and expanded in 1971) and the second Port-Harcourt Refinery (Commissioned in 1989) both with installed capacity of 210,000 b/d i.e. 47% of the current total capacity for all the Nigerian refineries (John West, 1989). Other facilities located in the basin include the National

Fertilizer Company of Nigeria (NAFCON) at Onne, five of the nineteen ports in the country (Port Harcourt, Okrika, Onne lighterate Terminal, Bonny onshore and Bonny offshore). These probably explain why the basin is rated to be the most stressed in the entire Niger delta (RPI 1985).

Materials and methods

Sampling Stations

The seventeen stations from which water samples were collected for investigations (Fig. 1) can be grouped broadly into two sets: thirteen occasional stations and four regular stations. Each regular station was sampled at least three times during the year of study (once during each of the following three periods of the year: late dry season/early rainy season, mid-rainy season, and at one of the two rainfall peaks of the year). On the other hand, the occasional stations were sampled only during the July to August flood peak of the study year. Almost all the occasional stations were located within or close to the Port Harcourt conurbation (this was to be able to relate their water quality to urbanisation/industrialization and other anthropogenic influences in the area). Some of the stations (stations 2, 3 and 10) were selected because they had been noted by some earlier workers (Powell 1987) to lack shrimps and/or characterized by unusual/abnormal shrimp fauna, most probably as a result of water pollution.

Most of the stations located close to the mouth of the estuary (especially the two outermost stations, stations 16 and 17) seemed prone to water pollution that might result from crude oil operation sources and/or related activities, including the heavy traffic of oil tankers from and to the Bonny Terminal. With regard to spatial distribution, the seventeen stations could also be grouped broadly into three categories consisting of six stations located on tributary streams and small creeks (stations 1, 2, 3, 6, 7 and 8), six on the major creeks (4, 5, 10, 11, 12, 13) and the remaining stations located on the main body of the estuary (9, 14, 15, 16, 17). The stations in the first category were likely to be affected by effluents from the domestic and industrial areas they drain.

Sampling Programme and Sample Collection

Sampling to show horizontal variation in chemical conditions along the estuary was undertaken from the end of July through the first week of August, 1990. This time of the year coincided with a considerable increase in fresh water flood discharge resulting from the first of the two rainfall peaks in the year. Sampling to show broad seasonal variation in the investigated chemical variables was limited to the four regular stations. This set of samples was collected at alternate months from one end of the dry season (February, 1990) through the entire rainy season to the onset of another dry season (November, 1990).

The effect of tidal variation on water quality was investigated on the samples collected from the four stations (stations 4, 5, 10 and 11) located on Woji and Amadi Creeks (tidal variation in terms of shore exposure is pronounced in these creeks and in the entire Port Harcourt area). High tide and low tide samples were collected from the four stations on the same day in November, 1990, during full moon. This time of the year is commonly regarded as onset of dry season although late flood water is usually still high. In all cases, sample collection was from about 5 cm below the water surface. Glass reagent bottles of 125 or 250 cm^3 capacity were used for collecting dissolved oxygen and BOD_5 samples while 5-litre capacity polyvinylchloride (P.V.C.) plastic bottles were used for collecting the samples for the other chemical determinations. Sample bottles were always rinsed with the sample waters before collection.

Chemical Analyses of Samples

Chemical determinations were carried out directly on unfiltered samples (the samples were usually very clear in spite of the brownish colouration, i.e., they were coloured but not turbid). pH was determined on the field immediately after collection using a Lovibond pH comparator while the dissolved oxygen concentrations of the samples were fixed using Winkler's reagents. All the other chemical determinations, especially those of plant micronutrients (NO^-_3, PO_4^{3-} and SiO_2), were carried out soon on returning to the laboratory. Usually, all analyses were completed within a fortnight of sample collection. Samples were stored in a deep freezer (away from other materials) until full analyses were to be carried out on them.

Conductivity (specific conductance) was determined at 25 ^oC using a conductivity meter. The following variables were determined titrimetrically: dissolved oxygen by Winkler's method (Mackereth *et al.* 1978), Biochemical Oxygen Demand (BOD_5) as for dissolved oxygen after five days of incubation, and total alkalinity using standard sulphuric acid solution and mixed indicator of Methyl Red and Bromocresol Green (A.P.H.A. 1985).

The organic matter content (estimated as organic carbon x 1.724) was determined by oxidation with chromic acid (Jackson 1958). In this determination, correction was made for the high level of chloride in the brackish water samples by the addition of mercuric sulphate. Calcium and magnesium concentrations were determined by compleximetric titration using disodium dihydrogen ethylenediaminetetra-acetate, Na_2 EDTA (Golterman *et al.* 1978), while sodium and potassium were determined using a flame emission analyser. A number of samples (collected towards the end of the dry season from stations 10, 13, 15, 16 and 17) were analysed for copper (Cu), nickel (Ni) chromium (Cr), cobalt (Co) and elemental iron (Fe), using an atomic absorption spectrophotometer (AAS).

Nitrate, ortho-phosphate, reactive silicate (expressed as silica), and total soluble iron were all determined colorimetrically according to the standard methods of A.P.H.A. (1985). Nitrate determination was by the phenoldisulphonic acid method; orthophosphate by the modified Denige's method using ammonium molybdate and stannous chloride reagents; reactive silicate using sulphuric-molybdate solution; and total iron by the thioglycollic acid method. Sulphate was determined by the turbidimetric technique (A.P.H.A., 1985). Chloride was determined using an automatic chloride titrator, while salinity was estimated roughly as the total mass concentration of all the major ions and silica. Most of the analytical methods employed were within the precision range of 1-10% (Golterman *et al.*, 1978).

Calculation of dissolved acids, bases and probable salt contents

In order to examine changes in the chemical composition of the basin's waters apart from those relating to salinity and/or those due to mere dilution or concentration, the percentage equivalent concentrations of the various acids and bases likely to occur or dissolved in the waters were estimated by the methods of Kemp, (1971). The variation in the concentrations of the acids and bases were related to that of carbonic acid (as it was obvious from the pH values that the chemistry of the water was under the control of the CO_2 – carbonate/bicarbonate – carbonic acid equilibrium system). The concentrations of the probable salt contents of the waters were calculated by the method of Holden, (1970) based on the mass concentration values of the major anions (CO_3^{2-}, SO_4^{2-}, and Cl^-) and major cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+).

Analysis of Tide Data

The tidal regime of the area was characterized based on the daily tide data for one annual cycle (1990) comprising about 1400 specific tide measurements, i.e., about 4 readings per day for the year. The separation of tide phases into neap and spring tides was with regard to moon phases. The abbreviations of tide levels used as well as the development of tide emersion curve for Bonny bar were in accordance with the work of Lewis, (1964) and Olaniyan, (1975).

Results

Tidal Hydrology

Highlights of the tidal hydrology of Bonny estuary based on tide measurements at the Bonny bar are presented in Table 1. The highest (or extreme) high water individual spring tide (EHWS) recorded over the one-year period was over the levels of 0.1 – 2.6 m, giving a range of 2.5 m (about 8 ft). This reading was recorded 2 days after full moon in September of the study year, i.e., during the equinoctial spring when the sun was passing the equator. The highest tide range values during the other spring periods (mostly 0.2 – 2.3 m) also occurred about one or two days after full moon and/or the new moon phases.

On the whole, mean high water of springs (MHWS) and mean low water of springs (MLWS) were 2.18 $\pm$ 0.24 m and 0.52 $\pm$ 0.27 m respectively, thus giving a mean range of spring tides values of 1.66 m (which is about 70% of the observed extreme range of spring tides). On the other hand, the mean range water level of neap tides (MHWN) and mean low water level of neap tides (MLWN) were 2.00 $\pm$ 0.34 m and 0.69 $\pm$ 0.24 m, respectively, giving a mean range of neap tides values of 1.31 m, which is about 55% of the observed extreme range of spring tides and about 80% of the mean range of spring tides. Average high tide level (AHTL) and average low tide level (ALTL) were 2.10 $\pm$ 0.35 m and 0.60 $\pm$ 0.25 m, respectively, while mid-tide level (MTL) for all recorded tides (n = 1400) was 1.39 $\pm$ 0.79 m.

Table 1. Frequency of some specific tidal levels at Bonny bar of Bonny estuary.

Tide description	**Abbreviation**	**n**	**Value ± s.d.**
Extreme high water of spring tides	(EHWS)	1	2.6 m
Mean high water of spring tides	(MHWS)	382	2.18 ± 0.24 m
Average high tide level	(AHTL)	716	2.10 ± 0.35 m
Mean high water level of Neap tides	(MHIWN)	334	2.00 ± 0.34 m
Midtide level	(MTL)	1400	1.39 ± 0.79 m
Mean low water level of Neap tide	(MLWN)	327	0.69 ± 0.24 m
Average low tide level	(ALTL)	684	0.60 ± 0.25 m
Mean low water level of spring tides	(MLWS)	357	0.52 ± 0.27 m
Extreme low water of spring tides	(ELWS)	1	0.10 m

The mean range of spring tides could be divided broadly into the three commonly observed shore zones: the upper shore zone (the portion above the mean range of neap tides), the middle shore zone (corresponding to the mean range of neap tides), and the lower shore zone (corresponding to the portion below the mean range of neap tides). The proportion of these three zones for Bonny bar for the year of study was 0.11, 0.79 and 0.10 for the upper shore, middle shore and lower shore, respectively. Figure 3 is the "tide emersion curve" for Bonny bar. It shows that emersion did not increase uniformly from low to high water mark, it was less rapid between MLWN and MHWN than above (MHWN–MHWS) and below (MLWN–MLWS) the two intermediate levels. Estimates from this curve also show that the splash–upper shore zone was exposed to air for 67–100% of the time, while the middle shore zone was exposed to air for 29–67% of the time and the lower shore zone exposed to air for 1 – 29% of Neap–spring tide regime.

Figure 3: Emersion curve for tides at Bonny bar.

Spatial Variations in Chemical Composition

Based on the samples collected at the time of the year when fresh water discharge into the estuary was rising to a peak (July to August), water salinity varied in the estuary from very dilute fresh water (< 0.5‰) at Station 1 to 25.4‰ in Station 17, i.e., over a distance of about 70 km. Following the salinity classification adopted in earlier work in the area, (e.g. Powell, 1987 and RPI, 1985) the investigated sampling stations covering the entire area occurred within the following four brackish water types, namely: freshwater/tidal freshwater ($\leq$ 0.50 ‰ salinity), oligohaline brackish water (0.51–5.00 ‰), mesohaline brackish water (5.01–18.0 ‰) and polyhaline brackish water (18.01–30.0 ‰).

By this classification, all the stations along the main body of Bonny estuary from Station 9 to the estuary mouth were of polyhaline brackish waters, while the stations located within the channels of the Okirika islands (commonly called the Okirika arm) upstream into the two major creeks (Woji Creek and Amadi Creek) as well as Ogu Creek were of mesohaline waters (Fig. 1). The stations located close to the junctions of these creeks and their tributary fresh water/tidal streams were oligohaline brackish while those located between the sources of the tributary streams and their middle reaches were either fresh/or tidal fresh waters, depending on their location away from the stream source. This distribution shows that polyhaline water penetrated up to about 55 km into the estuary while mesohaline water extended about 10 km further beyond, towards Port Harcourt. The extent of variation in each of the investigated variables with respect to salinity classification of the waters is presented in Table 2.

The pattern of horizontal variation in salinity and the other chemical variables along the main body of the estuary through the different grades of brackish waters (Stations 17, 16, 14, 10, 7, 6) are depicted in Fig. 4 while the pattern along another horizontal transect from oligohaline brackish water stations through tidal fresh to fresh water (stations 5, 4, 3, 2 and 1) is shown in Fig. 5. These presentations and the information in Table 3 reveal that most of the investigated variables could be grouped broadly into two categories: the abiotic and the biogenic chemical variables.

Figure 4: Horizontal variations in the investigated chemical variables along the main axis of Bonny Estuary (from polyhaline through mesohaline to oligohaline brackish waters).

The variables in the abiotic category were: conductivity, pH, dissolved oxygen, and the major anions and cations. The concentration of this group of variables showed a decrease from the brackish waters to tidal fresh and fresh waters. The rates of decrease from polyhaline to mesohaline brackish waters were generally small but, more or less, exponential from mesohaline through oligohaline water (Fig. 4) as well as from oligohaline to fresh waters (Fig. 5). On the other hand, the biogenic variables: reactive silicate, nitrate, orthophosphate, total soluble iron, and organic matter, generally showed negative correlation with salinity as they increased in concentration away from the brackish waters to the fresh waters (Table 3). Spatial variation in most of the variables showed definite trends (a decrease in the biotic variables towards the estuary mouth but an increase in the abiotic variables along the same direction).

Table 2. The mean (± std. error) concentrations of chemical variables in different waters of Bonny Estuary, Niger Delta, Nigeria.

Chemical variable	*Unit*	Fresh/Tidal fresh waters (n=4)	Oligohaline waters (n=2)	Mesohaline waters (n=6)	Polyhaline waters (n=5)
Hydrogen ion con. (H^+)	pH	6.0 $\pm$ 0.3	6.3 $\pm$ 0.3	7.3 $\pm$ 0.2	8.0 $\pm$ 0.1
Conductivity at 25 °C	mS cm^{-1}	0.5 $\pm$ 1.9	4.1$\pm$ 1.2	22.0 $\pm$ 2.7	36.0 $\pm$ 2.1
Salinity (estimated)	‰	0.1$\pm$ 0.4	0.9 $\pm$ 1.1	13.1 $\pm$ 0.9	21.4 $\pm$ 1.5
Dissolved oxygen (O_2)	mgl^{-1}	1.3 $\pm$ 1.5	4.6 $\pm$ 0.8	6.4 $\pm$ 0.4	7.5 $\pm$ 0.4
Calcium (Ca^{+2})	mgl^{-1}	23.4 $\pm$ 7.2	32.8 $\pm$ 6.1	96 $\pm$ 8.2	223 $\pm$ 15.6
Magnesium (Mg^{+2})	mgl^{-1}	7.5 $\pm$ 6.3	113.6$\pm$ 15.5	389 $\pm$ 20.2	647 $\pm$ 27.3
Sodium (Na^+)	mgl^{-1}	0.6 $\pm$ 7.0	231.0$\pm$ 36.5	4685 $\pm$ 120	6784 $\pm$ 143
Potassium (K^+)	mgl^{-1}	0.0$\pm$ 1.9	35.2 $\pm$ 7.3	152 $\pm$ 15.2	245 $\pm$ 11.2
Total alkalinity, ($CaCO_3$)	mgl^{-1}	23.0 $\pm$ 7.8	27.0 $\pm$ 4.3	57 $\pm$ 5.3	82 $\pm$ 4.0
Sulphate (SO_4^{-2})	mgl^{-1}	3.8 $\pm$ 1.1	115.0$\pm$ 10.5	650 $\pm$ 15.5	1343 $\pm$ 30.5
Chloride (CI^-)	mgl^{-1}	22.8 $\pm$ 5.2	321.5 $\pm$ 8.1	7629 $\pm$ 8.5	10111$\pm$10.5
Silicate (SiO_2)	mgl^{-1}	2.4 $\pm$ 0.6	6.8 $\pm$ 0.8	2.3 $\pm$ 0.4	1.9 $\pm$ 0.5
Nitrate (NO_3^-)	ugl^{-1}	543 $\pm$ 30	262 $\pm$ 50	266 $\pm$ 42	209 $\pm$ 50
Phosphate (PO_4^{-3})	ugl^{-1}	46$\pm$ 10	32 $\pm$ 15	60 $\pm$ 16	53 $\pm$ 15
Iron (Fe)	ugl^{-1}	216 $\pm$ 50	8 $\pm$ 10	521$\pm$ 50	131 $\pm$ 40
Organic matter	mgl^{-1}	2.3 $\pm$ 0.4	2.1 $\pm$ 0.3	1.4 $\pm$ 0.4	1.3 $\pm$ 0.5

Table 3. Linear regression of water chemical variables (y) on water conductivity (x) of Bonny Estuary, Niger Delta, Nigeria.

	Linear regression equation (y = a+bx $\pm$ s.e)			
Chemical variable (y)	A	b	s.e	r
Hydrogen ion con. (pH)	6.1	0.05	0.10	0.929***
Estimated salinity (‰)	0.9	0.50	1.7	0.972***
Dissolved oxygen, O_2 (mgl^{-1})	3.2	0.13	0.9	0.896***
Calcium, Ca^{+2} (mgl^{-1})	5.9	5.45	42.2	0.884***
Magnesium, Mg^{+2} (mgl^{-1})	40.2	16.72	45.6	0.983***
Sodium, Na^+ (mgl^{-1})	72.1	185.8	843.1	0.955***
Potassium, K^+ (mgl^{-1})	8.0	6.5	27.5	0.960***
Total alkalinity (mg$CaCO_3$l^{-1})	20.8	1.7	8.0	0.951***
Sulphate, SO_4^{-2} (mgl^{-1})	- 20.8	36.3	190.8	0.942***
Chloride, CI^- (mgl^{-1})	75.3	265.0	821.4	0.978***
Silicate, SiO_2 (mgl^{-1})	4.6	-0.08	1.77	- 0.553*
Nitrate, NO^-_3 (ugl^{-1})	435.0	- 7.06	222.9	- 0.421

Ortho-phosphate, PO_4^{-3} (ugl^{-1})	60.0	- 0.39	101.7	- 0.063
Soluble iron, Fe (ugl^{-1})	279.0	- 2.44	446.7	- 0.080
Total organic matter (mgl^{-1})	2.0	- 0.02	0.7	- 0.370

s.e = standard error of estimate   r = correlation coefficient
* = $P \leq 0.05$
*** = $P \leq 0.001$

Table 4. Regression equations of the molar percentage carbonic acid (x) against the molar percentage of other acids and bases in Bonny Estuary.

Water type	**Molar percentage (y)**	**Regression on molar % of H_2CO_3 (x)**	**Standard error of estimate**
Brackish waters (n = 13)	$Ca(OH)_2$	0.7 – 0.33 x	0.29
	$Mg(OH)_2$	4.8 – 2.56 x	0.90
	NaOH	53.3 – 21.86 x	4.80
	KOH	1.1 – 0.52 x	0.14
	H_2SO_4	1.4 + 0.43 x	0.77
	HCl	37.9 + 25.74 x	5.90
Fresh / Tidal freshwaters (n = 4)	$Ca(OH)_2$	-0.2 + 1.21 x	1.04
	$Mg(OH)_2$	13.5 – 0.01 x	9.26
	NaOH	35.5 – 1.64 x	7.86
	KOH	3.3 – 0.15 x	2.62
	H_2SO_4	6.0 – 0.17 x	2.54
	HCl	41.9 – 0.24 x	16.55

Fig. 5: Horizontal variations in the investigated chemical variables of Bonny Estuary from oligohaline brackish water to fresh water.

pH, Conductivity, Oxygen and BOD_5

Although pH values varied over a wide range (5.7 – 8.3) they were mostly between 6.0 and 7.6. In general, water was acidic in the freshwater/tidal freshwater streams, slightly acidic to neutral in the oligohaline brackish, and slightly alkaline to alkaline in the mesohaline and polyhaline brackish waters. Within the main body of the estuary, pH values were generally above 7.8, increasing steadily to the mouth of the estuary where they were mostly above 8. Among the abiotic group of variables, pH was characterised with the lowest rate of decrease through the estuary, inward from its mouth, while conductivity showed the highest rate of decrease, although it also varied over a wide range of values, 16 μScm^{-1} – 39500 μScm^{-1} at 25 ^{o}C.

Isopleths showing broad spatial variation in mass concentration and percentage saturation of dissolved oxygen in the upper reaches of the estuary, i.e., the region of most rapid rates of change, are shown in Fig. 6. On the whole, dissolved oxygen concentration occurred over a wide range of 1.0 – 8.1 mgl^{-1}, increasing steadily towards the mouth of the estuary, more or less, following the pattern exhibited by the other abiotic variables (pH, conductivity, salinity, and the major ions). The mesohaline and polyhaline waters were significantly higher in oxygen content and percent saturation than the oligohaline and tidal fresh/freshwaters. All the stations to the north-west of Okirika arm of the estuary were poorly saturated with oxygen (being only about 50% at best, and as low as 10% saturation in the headwaters of the tributary creeks). The values of BOD_5 ranged from 0.3 mgO_21^{-1} to 7.7 mgO_21^{-1}, consisting of 0.3 – 3.1 mgO_21^{-1} for mesohaline brackish and the less dilute waters, and 5.8 – 7.7mgO_21^{-1} for the polyhaline brackish waters.

The Major Ions, Acid-Bases and Probable Salts.

Sodium and potassium were, respectively, the most dominant and the least abundant cations (their ranges were 0–7680 Na^+ mgl^{-1} and 0–270$K^+$$mg1^{-1}$, respectively). Chloride, with a range of 5.9 $mg1^{-1}$ to 10,393.0 mgl^{-1}, was not only the dominant anion but also the most dominant of all the investigated variables. Sulphate varied between 3.6 mgl^{-1} and 1633 mgl^{-1} while total alkalinity (the least of the major ions) ranged from 2 mg $CaCO_31^{-1}$ to 88 mg $CaCO_31^{-1}$; it consisted solely of bicarbonate ions. All the major ions were characterised, more or less, by the same rate of decrease in concentration into the estuary from its mouth.

Fig. 6. Above: Isopleths of mass concentration (mgl^{-1}) of dissolved oxygen in the upper reach of Bonny Estuary during early floodwater. Below: Isopleths of percentage (%) of dissolved oxygen in the Upper Bonny Estuary during early flood water.

Although the relative contribution of each of the three major anions to their total sum (expressed in % milliequivalent concentration) was slightly different for the different waters, the general order of ionic dominance among them was the same for all the waters, this order being: $C1^{-} > SO_4^{-2} > CO_3^{-2}$. The order of dominance among the four major cations was: $Ca^{+2} > Mg^{+2} > Na^{+} > K^{+}$ in the fresh and tidal fresh waters, and $Na^{+} > Mg^{+2} > Ca^{+2} > K^{+}$ in the brackish waters. The regression equations of percent molar concentrations of carbonic acid (H_2CO_3) to other acids and bases in Bonny waters are presented in Table 4. All the waters, both brackish and fresh, belong to the chlorided water series of the world, following the scheme of Kemp, (1971). However, the relative contribution of each of the major ions to water salinity indicates that the polyhaline and the mesohaline brackish waters were essentially mixohaline brackish waters, i.e., having their ions in the same proportion as in seawater or simply diluted sea water.

The contribution of probable salt content of the estuarine water at different levels of salinity are indicated and compared with that of sea water in Table 5. The relative contribution of $CaCO_3$ to water salinity showed a steady decrease from the freshwater/tidal freshwater (32.1 $\pm$ 22.5%) through the various grades of brackish waters to only 0.34% in the sea. On the other hand, the relative contribution of NaCl to salinity showed an inverse pattern to that of $CaCO_3$. The relative contribution of NaCl as well as total chloride salts to water salinity increased steadily from fresh/tidal freshwater through the brackish water to the sea where NaCl accounts for about 78% of salinity. Thus, unlike the typical freshwater in which $CaCO_3$ and $MgCO_3$ are dominant, in the freshwater/tidal freshwater of Bonny estuary $CaCl_2$ is the dominant salt.

Organic Matter, Micronutrients and Heavy Metals

The concentration of total organic matter in the estuary was generally less than 4.0 mgl^{-1}. In general, organic matter was higher but varied much more widely in the fresh waters than in the brackish waters. However, among the biotic group of the investigated chemical variables, organic matter had the lowest rate of increase inward from the estuary mouth. It was highest in Station 1 (3.6 mgl^{-1}) a residential area, followed by Station 3 (a station near an abattoir). The average concentration for the six stations located on the tributary streams and minor creeks was 1.8 $\pm$ 1.2 mgl^{-1} as opposed to 1.5 $\pm$ 0.5 mgl^{-1} for the six stations on the major creeks, and 1.2 $\pm$ 0.3 mgl^{-1} for the five stations along the main axis of the estuary.

Table 5. The percentage contribution of different probable salts to the salinity of Bonny Estuary.

Salt	Freshwater/Tidal freshwater (mean $\pm$ s.d.)	Oligohaline brackish water (mean $\pm$ s.d.)	Mesohaline/ Polyhaline brackish water (mean $\pm$ s.d.)	Sea water *
$CaCO_3$	32.1 $\pm$ 22.5	5.3 $\pm$ 1.5	0.7 $\pm$ 0.2	0.34
$MgCO_3$	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.1 $\pm$ 0.2	0.0
$CaSO_4$	8.4 $\pm$ 5.8	6.0 $\pm$ 4.5	2.0 $\pm$ 0.9	3.6
$MgSO_4$	1.2 $\pm$ 0.6	14.7 $\pm$ 11.5	5.0 $\pm$ 2.0	4.7
Na_2SO_4	8.0 $\pm$ 11.7	6.8 $\pm$ 9.5	0.0 $\pm$ 0.0	0
$CaCl_2$	44.0 $\pm$ 18.3	0.0 $\pm$ 0.0	1.6 $\pm$ 3.3	0
$MgCl_2$	6.1 $\pm$ 7.2	14.4 $\pm$ 20.3	6.8 $\pm$ 3.9	10.9
NaCl	0.0 $\pm$ 0.0	41.6 $\pm$ 2.2	75.6 $\pm$ 5.3	77.8
KCl	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	1.3 $\pm$ 1.2	0
Others	0.2 $\pm$ .17	11.2 $\pm$ 4.6	6.9 $\pm$ 4.5	0

*Source: Gaskell (1964)
s.d. = standard deviation

Reactive silicate varied from 0.7 $mgSiO_2l^{-1}$ to 8.8 $mgSiO_2l^{-1}$ with a decrease from the tributary stream stations to the main estuary. The values of total soluble iron all occurred within the range of 0–1688 $\mu gFel^{-1}$ while those of the other plant micronutrients were: 0 – 862 $\mu gNO^{-}_{3}1^{-1}$ and 0–266 $\mu gPO_4^{-3}l^{-1}$. The mean values of these three variables were higher but less varied in the tributary stream stations (398$\pm$290 $\mu gNO^{-}_{3}1^{-1}$, 277 $\pm$ 269 $\mu g1^{-1}$ soluble Fe, and 70 $\pm$ 102 $\mu gPO_4^{-3}1^{-1}$) than for the main estuary stations (194 $\pm$ 212 $\mu gNO_3 1^{-1}$, 193 $\pm$ 364 $\mu gFel^{-1}$ and 67 $\pm$ 133

$\mu gPO_4^{-3}l^{-1}$). These three variables were not even detected in some stations (nitrate was not detected in three stations, soluble iron in five stations and ortho-phosphate in ten stations). Most of the stations from which these micronutrients were not detected were either on the main creeks or on the main estuary.

Cobalt was detected in four of the five stations investigated for the heavy metals (stations 10, 13, 15 and 16) copper in three of the stations (stations 10, 13 and 16) and chromium and nickel were each detected in only two of the stations, stations 15 and 17. The range of values were: 0–20 $\mu gCul^{-1}$, 0–320 $\mu gCrl^{-1}$, 0–340 $\mu gCol^{-1}$, 530–1100 $\mu gFel^{-1}$, and 0–1460 $\mu gNil^{-1}$. In general, the concentration of these heavy metals tended to increase from the oligohaline through mesohaline to polyhaline brackish waters. Indeed, nickel and chromium were only recorded near the estuary's mouth with the peak value at Station 17, which is close to the Bonny Terminal.

Temporal Variations in Chemical Composition

Information on the chemical composition of water in the four regular stations at three selected periods of the year is presented in Table 6. Conductivity, salinity and most of the major ions decreased steadily from the late dry season (February/March) through the mid-rainy season (May) to the peak of the rainy season (July). The amplitude of variation in each variable over the entire study period decreased from the less saline water to the more saline waters. For instance, in Station 13 (a mesohaline water), conductivity dropped from 31.5 $mScm^{-1}$ in March to 21.5 $mScm^{-1}$ in July at the rise of early flood water, thus giving an amplitude of 10 $mScm^{-1}$ over the four-month period. On the other hand, the corresponding amplitude of conductivity values at Stations 15 and 16 (polyhaline waters) over the four months were 2.6 $mScm^{-1}$ and 2.5 $mScm^{-1}$, respectively. The biogenic variables did not show a clearly discernible pattern of temporal variation. However, nitrate and soluble iron were generally higher during the rainy season than during the dry season. The mean ratio of dry season to rainy season values for these variables also decreased inversely with water salinity. The value for the mesohaline waters was 1.7 $\pm$ 0.8 (range = 0.4 – 3.8) as opposed to 1.5 $\pm$ 0.7 (range = 0.9 – 3.4) for polyhaline waters, for all the variables considered.

The mean chemical composition of water in relation to reversal in tide regime (i.e., the change from low tide to high tide and vice versa) is summarised in Table 7. Waters were significantly more alkaline and saline at high tide than at low tide. To varying degrees, this also applied to the specific chemical variables except silicate which was significantly higher at low tide than at high tide. Again, the extent of variation (expressed as the ratio

Table 6. The seasonal variations in the chemical composition of Bonny River, Niger Delta, Nigeria (based on four regular stations)

Table 7: The mean concentrations of chemical variables in Bonny Estuary at high and low tides (based on mesohaline waters)

Chemical variable	Unit	Tide Regime (mean ± s.d)		HT/LT
		High Tide (HT)	**Low Tide (LT)**	
Hydrogen ion con.	pH	6.7 ± 0.5	6.3 ± 0.5	1.04 ± 0.03
Conductivity @ 25^0C	mS cm^{-1}	4.8 ± 2.6	3.76 ± 2.34	1.4 ± 0.3
Estimated salinity	‰	6.0 ± 4.0	2.5 ± 2.0	2.6 ± 1.1
Calcium, Ca^{+2}	mgl^{-1}	116 ± 106	40 ± 35	2.5 ± 1.2
Magnesium, Mg^{+2}	mgl^{-1}	253 ± 200	124 ± 101	2.1 ± 0.2
Sodium, Na^{+}	mgl^{-1}	2886 ± 1851	1117 ± 834	3.2 ± 2.7
Potassium K^{+}	mgl^{-1}	122 ± 133	108 ± 133	1.5 ± 0.6
Total alkalinity, $CaCO_3$	mgl^{-1}	36 ± 19	25 ± 15	1.5 ± 0.2
Sulphate, SO_4^{-2}	mgl^{-1}	451 ± 33	181 ± 142	2.5 ± 0.7
Chloride, CI^{-}	mgl^{-1}	2.134 ± 1781	948 ± 1008	2.8 ± 2.7
Silicate, SiO_2	mgl^{-1}	2.2 ± 1.2	3.1 ± 1.0	0.7 ± 0.2
Nitrate, NO_3^{-}	μgl^{-1}	27 ± 29	20 ± 23	1.7 ± 0
Soluble iron, Fe	μgl^{-1}	528 ± 710	105 ± 95	4.9 ± 5.5

of high tide to low tide values) differed slightly from station to station. On the whole, the mean ratio of high tide to low tide values was 2.3 ± 1.1 for all the variables considered.

Discussion

The extent of polyhaline brackish water penetration into Bonny estuary as well as the order of ionic dominance of its water (which suggest that they are all chlorided waters), show that the estuary is strongly influenced by the sea. This influence can be attributed to the low lying nature of the basin, the extensive fetch available both to wind and tidal movements (about 10 km at the mouth and 0.3 km at Port Harcourt) and to the location of the estuary's mouth along the long-shore current of the Bight of Bonny which is such that water from the bight can enter directly and penetrate far inward into the estuary. Again, unlike the distributaries of the Niger within the delta (notably Rivers Nun and Forcados - Fig. 1) which are characterised by high discharge of fresh water throughout the year, fresh water input into Bonny estuary is relatively small (even at the peak of flood discharge) and input is derived solely from the locally rising coastal streams. Thus, Bonny estuary can be classified among the drowned river valley estuaries or coastal plain estuaries which are essentially extensions of the sea surrounded by land. These are the most common types of estuary in the region and most of them are believed to have been formed by a rise in sea-level relative to land, as a result of the release of ice-held water at the end of the last glaciation (Barnes, 1974).

In the Bonny estuary, the patterns of horizontal variations (increasing inshore from the estuary mouth) in the concentrations of the biogenic group of variables show that these variables are derived mainly from within the fresh water basin and residential areas. The observed sources of organic matter from the residential areas included open sewage discharge, waste run off, waste from abattoir, refuse and garbage tips as well as organic waste from other cultural activities of man. With a solid waste generation of about 3.6 kg per household per day in 1982 (Filani and Abumere, 1986) and 265,000 tonnes per year in 1990 (Agabi *et al.*, 1995), Port Harcourt is among the towns in Nigeria with the highest rates of solid waste generation and accumulation. The leaching of such wastes into waterways probably accounted for the relatively high organic matter content of streams draining the residential areas investigated.

The fact that some components of organic matter such as humic acid (which was suspected in Bonny River from its characteristic dark brown colouration) may gradually precipitate in contact with sea water can partly explain the reduction in the concentration of organic matter and the attendant increase in dissolved oxygen as we move downstream (sea ward) along in Bonny estuary. The reduction can also be attributed to the mineralization of the organic matter. As a major product of organic matter mineralization, it was not surprising that the concentration of nitrate was generally much higher in the fresh waters and in the Port Harcourt areas than in the brackish waters and the non-residential areas of the basin. Compared with a number of major African lake waters, viz: Lakes Asejire, Kainji, Volta, Kariba, Victoria, and Nyansa (Egborge 1971) and the rivers and streams in central Nigeria (Adeniyi and Oakhumen 1989) the levels of nitrate in the investigated fresh waters and residential areas were fairly high while the levels of ortho-phosphate were relatively low. The bonding of nitrate to organic particles is fairly uncomplicated and it is expected to be readily liberated by ion-exchange reaction as well as leaching from organic matter especially under heavy rainfall and low lying water-shed like the Bonny basin. The low levels of ortho-phosphate and its absence in many stations in Bonny basin suggest that inorganic phosphorus may be a critical limiting factor for biological primary production in the basin.

With regard to their low mineral content, characteristic humic acid water colouration and low pH, the fresh waters of Bonny estuary are similar to the black waters of the humid tropics in South America and some Congo streams (Egler and Schassmann 1961), the coastal swamps waters of River Jong in Sierra Leone (Wright 1985) and the Black waters of the Niger Delta (RPI, 1985). Compared with other African fresh waters, they can be classified among the most dilute waters of the continent (Talling and Talling 1965). The low conductivity of the waters can be attributed to at least one other reason apart from the effect of high organic matter content on the waters. The fresh water tributaries of Bonny River all drain small catchment areas (each less than 10 km^2) and in entirely flat low lying watershed. With such relief, sediment loads from the basin (which are mostly of sandy materials) are generally small and contribute little or nothing to the dissolved chemical load of recipient waters.

The data on heavy metals in the estuary suggest that most of them (cobalt, copper, nickel, and chromium) were rather high compared with their corresponding average concentrations in the open sea (Gaskell, 1964) or in relation to recommended standards for drinking water quality (WHO 1971; Hattingh 1977). Of the five major sources of heavy metal pollution in the environment as listed by Forstner and Prosi (1979), two of them namely: heavy metals in animal and human excretion, and the leaching of metals from garbage and solid waste dumps are the most probable sources in the Port Harcourt area. On the other hand, the crude oil activities within and around the Bonny Terminal are the most likely sources of heavy metals at the estuary mouth stations (as suggested by the relatively high levels of both chromium and nickel in those stations). In the Niger Delta, oil pollution results mainly from blow-out, equipment failure, maintenance error, and sabotage (Awobajo 1981). Others are accidental discharges and spills from crude oil, oil cargo, oil storage and handling, and refinery effluent disposal. Imevbore and Ekundayo, (1987) reported monthly average concentrations of 4.6 – 58.8 ppm (mean $\pm$ s.d = 13.6 $\pm$ 7.7 ppm, n = 60) of crude oil in the Bonny Terminal effluent water from January 1979 to December 1983, while Adeyemi and Akinluyi (1983), recorded oil concentrations of 4464–26278 ppm in sediments and 9.05–64.65 ppm in waters of the Niger delta between June and August, 1980. This portends likely heavy metal pollution of the estuarine water especially in the Terminal area.

Compared with some recommended/suggested water quality standards (Table 8), it is obvious that the high salinity of the brackish waters (including the high hardness and S.A.R. values) will impose serious limitations on them with regard to their usefulness to the riparian communities (especially for domestic use, life-stock production and irrigated agriculture), although the waters were apparently free from organic pollution. On the other hand, the waters in the Port Harcourt area were characterised by chemical properties (notably low oxygen levels) which suggest organic enrichment in the area (probably from the effect of urbanisation and industrialisation).

The tidal characteristics of the Bonny estuary as revealed in the present work have many features in common with those of the typical Atlantic coast. Typically, tides of the Atlantic coasts are dominated with the semi-diurnal pattern often with two unequal high water and two low waters occurring within each 24 hours (King 1975). As applicable to most of the locations around Britain (King 1975; Lewis, 1964), the diurnal inequalities in

Table 8. Comparative water quality of Bonny Estuary, Niger Delta Nigeria (based on some primary quality criteria)

the Bonny tides are small. This is evident from the small coefficient of variation associated with the mean tide levels, especially those of the high tides (MHWS, AHTL, MHWN) which are generally less than 20% coefficient of variation (values for low tides have about 40% coefficient of variation). These low inequalities are probably due to the wide tidal area of the Bonny estuary as well as its relatively deep basin and flat topography (Port Harcourt is less than 20 m above the mean sea level) of extensive alluvium deposits. Unlike the British coasts where the mean neap range amounts to between 0.45 and 0.55 of the mean spring range (Lewis, 1964), in Bonny estuary, like some localities around north-east Ireland, the mean value is 0.79. Such a disproportionally large neap range is typical of locations where tidal ranges are small. However, the overall mean range of about 1.7m (MHWS – MLWS) at Bonny bar corresponds to the mean value of 1.70 $\pm$ 0.82 m for various locations (n = 30) on the West and Central Atlantic coasts of Africa (UNEP 1985). In Nigeria, the mean value of 1.7 m for Bonny bar is surpassed only by the tidal range in Calabar (2 m).

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