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Sediment Quality Status of Two Creeks in the Upper Bonny Estuary, Niger Delta, in Relation to Urban/Industrial Activities

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Abstract Two creeks (Azuabie and Obufe) in the upper Bonny Estuary, Nigeria were studied to determine how industrial and other anthropogenic activities have influenced their relative sediment qualities. Total organic carbon, total hydrocarbons, zinc, lead, cadmium and iron were significantly higher in the Azuabie creek, while phosphate, nitrate, copper and chromium did not show significant differences between the two creeks. Principal component analysis (PCA) ordinations discriminated all locations in the Obufe creek into a cluster along with the less-contaminated sites in the Azuabie creek. The other two sites in the Azuabie creek clustered separately, showing that they were contamination hot-spots.

Keywords Hydrocarbons · heavy metals · organic carbon · estuary · Niger Delta

The Niger Delta is one of the richest and largest deltaic formations in the world with a high abundance and diversity of natural flora and fauna (Powell, 1995). Over the last three decades, increasing urbanization and industrialization have drawn attention to the environment in the Niger Delta. The Bonny estuary is a mangrove swamp with similar species to those found in the rest of the estuarine portion of the Niger Delta. It is a busy transport route for vessels and the presence of a number of industries such as petroleum refinery, petrochemical industries, tire industries, bottling companies and other oil and gas companies sited along or close to the banks of the estuary exposes it to a range of pressures, some of which are capable of inducing environmental stress. Most studies in the estuary have focused on the main channel of the estuary (Snowden and Ekweozor, 1990) or larger creeks, especially near major industries (Ebere, 2002, Otokunefor and Obiukwu, 2005) with less attention being paid to some small but strategic creeks.

The Azuabie and Obufe creeks lie adjacent (running roughly parallel to one another) in the upper Bonny estuary; at the eastern flank of Port Harcourt – a rapidly urbanizing city with heavy oil and other industrial presence (e.g. tire manufacturing, breweries, canning, plastic industries, metal fabrications). The Azuabie creek runs towards an industrial area and is exposed to inputs from industrial operations, near-shore direct-discharge lavatories, waste from a sprawling waterfront settlement, and a large abattoir. The main activity in the Obufe creek is dredging of sand (for sale and occasionally to make the creeks navigable), which also takes place in the Azuabie creek. This paper reports the sediment characteristics of these creeks with the aim of evaluating how industrial and other human activities have influenced the sediment quality of the Azuabie creek with reference to the adjacent Obufe creek, and by small-scale spatial variations along the creeks. Sediment was chosen for the study as it represents the ultimate sink for almost every class of environmental pollutants (Bryan and Langston, 1992).

Materials and Methods

A total of eight sites were chosen (four from each creek located at approximate spatial equivalents along two 4 km gradients) taking into consideration possible sources of

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contamination (Fig. 1). These were coded (upstream to downstream) as AA to AD in the Azuabie creek and OA to OD in the Obufe creek.

Sediment samples were collected randomly in triplicate per station with an Ekman grab from September 2003 to February 2004, covering both the rainy and dry seasons. Conductivity was determined on fresh (wet) samples using a conductivity meter. A subsample of each sediment sample was placed in a labeled polythene bag, transferred to the laboratory and dried at room temperature for the analysis of sediment characteristics. For sediment particle-size analysis samples were disaggregated using a mortar and pestle and sieved through a graded series of standard sieves suited to the intervals of the Wentworth scale (Buchanan, 1984). The median particle size (mdϕ) was determined by graphical interpolation after plotting the cumulative percentage of each sediment fraction against the particle size (mdϕ). Samples (sieved through 500 μm mesh sieves) were used to perform the analysis of nitrate, phosphate, total hydrocarbons, total organic carbon and heavy metals. Total organic carbon (TOC) was determined by the wet combustion method of Walkley and Black (1934). The total hydrocarbon content (THC) was determined by extracting 5 g of sediment with 10 ml carbon tetrachloride (toluene) and then measuring the absorbance spectrophotometrically. Nitrate levels were determined after Kjedahl digestion, while available phosphorus in sediment was determined by the Bray no. 1 method (Jackson, 1962). For heavy-metal analysis (October 2003 and February 2004 samples representing wet and dry seasons, respectively), the sediment fraction (< 500 μm) was digested using HCl/HNO_3 following the method of the American Society for Testing and Materials (ASTM, 1986). The concentrations of iron, copper, zinc, cadmium, lead, chromium, were determined using an atomic absorption spectrophotometer (AAS), a Unicam 969 with a UNICAM SOLAR datastation V6.15; the detection limits were Fe, 0.01 mg/l; Cu, 0.001 mg/l; Zn 0.001 mg/l; Cd, 0.001; Pb, 0.01 mg/l; Cr, 0.01 mg/l. The concentrations were blank-corrected and expressed as $\mu g g^{-1}$ dry sediment. Concentrations of metals in reference estuarine sediment samples (European Community Bureau of Reference – BCR 227) were within 10 % of the certified values.

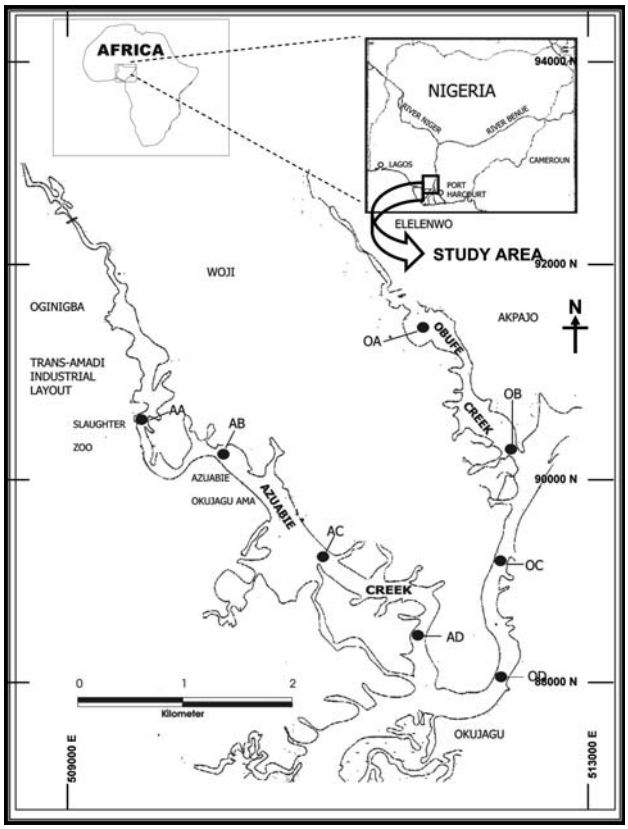

Fig. 1 Location of the study site and sampling stations

Three-way ANOVA was applied to the sediment data (for heavy metals, the concentrations obtained were normalized against the concentration of iron; enrichment factors [EFs] were calculated and the values used for ANOVA) to test for significant differences at each level of the creek, location (within the creek) and time. Where significant interactions were found between creek and location, two-way ANOVA was performed, which also enabled pairwise comparison between the stations (and time) using Tukey tests. Data were log (x+1) transformed (except the EF values) before statistical analysis. Principal component analysis (PCA, correlation-based because of the differences in the units of variables) was performed to visualize the multivariate ordinations in the sediment data. MINITAB R14 was used for the ANOVA while PRIMER v. 5.13 was used for PCA.

Results and Discussion

The sediments were generally sandy to muddy sand. Median particle size analysis also showed sand fractions as the median particle size (Fig. 2A). The mean sediment conductivity ranged from 900 (± 58) μScm^{-1} at station OA in October to 4133 (± 348) μScm^{-1} at station OD in February (Fig. 2B). There was no significant difference in conductivity between the creeks but significant differences were found between locations as well as period (Table 1); the interaction between creek and location was not significant. The significant differences between locations as well as periods are indicative of the natural gradients and influence of freshwater inputs during the rainy season.

TOC ranged from an average of 0.97 (± 0.03) % to 8.37 (± 0.33) %. The mean TOC values were consistently higher in the Azuabie than Obufe creek (Fig. 2C) in all sampling

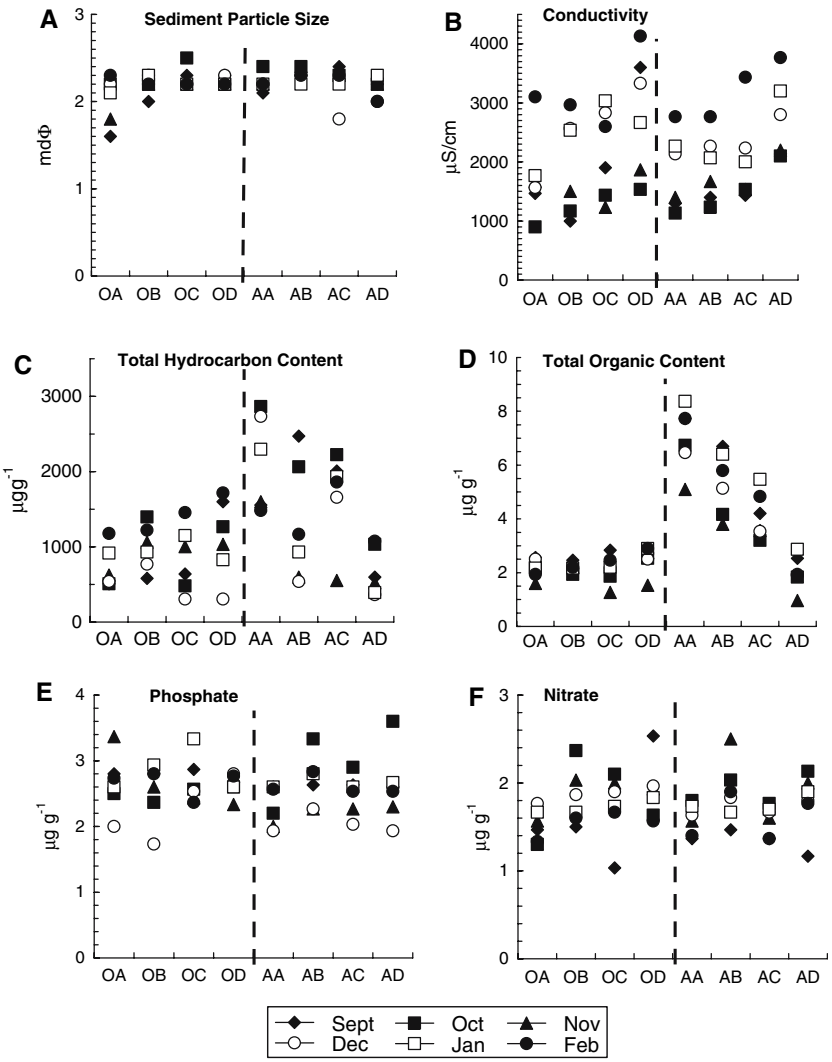

Fig. 2 Some physicochemical variables of the sediments (mean values, $n = 18$) in the study area

Table 1 *F* values from ANOVA to test for significant differences for some sediment variables

		Cond.	TOC	THC	NO_3	PO_4
Source of variation	*df*	*F*	*F*	*F*	*F*	*F*
Creek	1	0.03	83.12***	7.92**	0.97	1.36
Location	3	24.61***	24.34***	3.75***	9.25***	0.67
Period	5	35.89***	5.71***	3.50**	9.37***	7.43***
Location × creek	3	0.2	32.5***	9.46***	1.23	1.55
Location × period	15	1.68	0.5	1.23	2.09*	1.06
Creek × period	5	0.65	1.04	1.47	3.12*	2.23

*$p < 0.05$, **$p < 0.01$, ***$p < 0.001$

months, showing significant differences between creeks, locations as well as time (Table 1). Creek and location had significant interactions while locations and time did not. In each month, the highest TOC value in the Azuabie creek was recorded at location AA with an upstream gradient such that the values at station AD were similar to those in the Obufe creek. Tukey tests indicated significance ($p < 0.05$) as AA = AB = AC > OA = OB = OC = OD = AD. The appreciably high organic carbon in the upstream stations of Azuabie creek is attributed to the presence of the abattoir and the large quantities of organic waste discharged into the near-shore sediments at these stations.

Waste spills from abattoir operations could introduce excess nutrients into the surface waters (Meadows, 1995), which may have been reflected in the high TOC levels in the Azuabie creek.

The lowest mean THC value (305.4 ± 25.2 μgg^{-1}) was recorded at stations OC and OD in December while the highest mean value (2865.0 ± 240.3 μgg^{-1}) was obtained at station AA in October (Fig. 2D). THC was clearly higher in the Azuabie creek (except at station AD) in September and October but less so in January and February with some inconsistency in November. Significant differences in THC occurred between creeks, locations and time (Table 1). Creeks and location also showed significant interactions, but no significant interactions between locations and time, creeks and time. Tukey tests indicated that THC levels at station AA were significantly higher than at the stations OA, OB, OC, OD and AD while station AC was higher than OC, and AB higher than AD. The THC values observed in this study fall within the range reported by Ekweozor et al., (2004) at various locations along the Bonny estuary and are generally lower than the values of 3,584–19,981 μgg^{-1} recorded by Ebere (2002). The high values recorded by Ebere could be due to the influence of refinery effluent and loading of petroleum products at the Okrika jetty, which was part of his sampling sites. The elevated THC levels at stations AA, AB, and AC are attributable to industrial waste discharge by some industries present in the area and the materials washed off from the large volume of burnt tires used for roasting at the abattoir.

There were minimal spatial variations in the mean concentrations of nitrate (Fig. 2E) and phosphate (Fig. 2F) and no significant variations between creeks were found for either variable (Table 1). The mean concentration of nitrate in sediment ranged from (1.03 ± 0.07) μgg^{-1} to 2.53 (± 0.35) μgg^{-1}, both recorded in September, while phosphate values ranged from 1.73 (± 0.09) μgg^{-1} at station OB in December to 3.6 (± 0.25) μgg^{-1} at station AD in October.

The concentrations of Zn, Pb, Cu and Cd were higher during the wet season (October) than the dry season (February) but Fe and Cr did not show such seasonal trends (Fig. 3). Also, the concentrations measured in October gave the highest mean values of Zn (214.4 μgg^{-1}, Fig. 3A), Pb (30 μgg^{-1}, Fig. 3B), Cu (17.26 μgg^{-1}, Fig. 3C) and Cd (0.62 μgg^{-1}, Fig. 3D) at station AA in the Azuabie creek; followed by station AB, which had higher levels than the other stations in the Azuabie creek as well as locations in Obufe creek. The enrichment factor (EF) was used as an index to evaluate anthropogenic influences of heavy metals in the sediments; it is the observed metal-to-iron ratio in the sample of interest divided by the background metal-to-iron ratio. Normalization of trace-metal concentrations in sediments using Fe or Al is effective in reducing textural control of trace-metal concentrations; this is evident for Fe, an element that is not substantially enriched by anthropogenic contamination due to its high natural concentrations (Niencheski et al., 1994). The EF is expressed mathematically (adapted from Feng et al., 2004, who used Al in place of Fe) by:

$$EF = [(Me_{Sample})/(Fe_{Sample})]/ [(Me_{Background})/(Fe_{Background})]$$

where $(Me/Fe)_{Sample}$ is the metal-to-iron ratio in the sample of interest and $(Me/Fe)_{Background}$ is the natural background value of the metal-to-iron ratio.

Background values were obtained from Nweke (2000) for locations in the upper Bonny Estuary that are not exposed to industrial pollution. Average background concentrations (n = 12) of metals used were 13.0 μgg^{-1} Zn, 2.08 μgg^{-1} Pb, 1.47 μgg^{-1} Cu, 0.07 μgg^{-1} Cd, 2080 μgg^{-1} Fe; no value was available for Cr. The enrichment factor (EF) is a useful indicator reflecting the status of environmental contamination (Aloupi and Angelidis Feng et al., 2004). An EF value less than 1.5 suggests that the trace metals may be entirely from crustal materials or natural weathering processes (Zhang and Liu, 2002; Feng et al., 2004). However, an EF value greater than 1.5 suggests that a significant portion of the trace metal is delivered from non-crustal materials, or non-natural weathering processes and that the trace metals are provided by other sources (Feng et al., 2004). The EF values for Zn, Pb, Cu and Cd are presented in Table 2. Zn, Pb and Cd were found to have EF values above 1.5 at stations AA and AB during the wet season sampling period (October) but in February only Pb fell above the threshold value. EF values for Cu were higher than 1.5 at all stations in the Azuabie creek in addition to two stations in Obufe creek. Analysis of variance showed significant differences in the EF value at the levels of creek, locations and seasons as well as for interactions between creek and location (Table 3). Tukey tests show that stations AA and AB had significantly higher ($p < 0.01$) EF values for zinc, lead and cadmium than all other sites. Copper, for which the EF values showed enrichment at most sites or verged on it, significant differences were only found between station AB and the other sites.

The relationships between the various sediment quality variables were determined by correlation .TOC was significantly positively correlated with THC, silt-clay sediment fraction, Cu, Pb, Zn and Cd. Most metal–metal correlations (Cu, Pb, Zn and Cd) were positive and significant. Correlations between median particle size and silt-clay fraction with most metals were also significantly positive but correlations with silt-clay were stronger in most cases.

The overall order in the concentrations of metals in sediments was: Fe > Zn > Pb > Cu > Cr > Cd. Although the spatial profiles depicted elevated concentrations of some

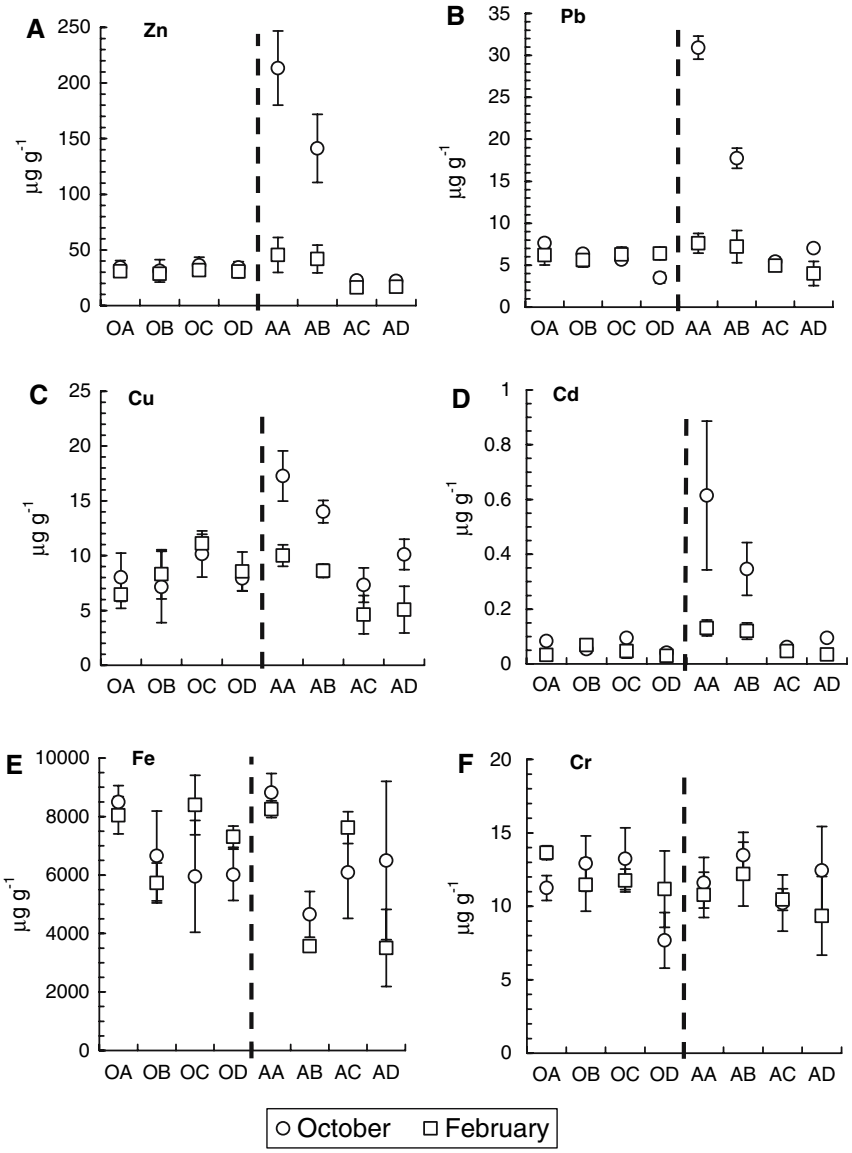

Fig. 3 Concentrations of heavy metals (mean ± SD, $n = 3$) in sediments from the study area

Table 2 Enrichment factors (x and SD, mean and standard deviation, $n = 3$) of zinc, lead, copper and cadmium in sediments from the study area. Values in bold are enriched

Site	Zinc				Lead				Copper				Cadmium			
	Oct		Feb		Oct		Feb		Oct		Feb		Oct		Feb	
	x	SD	x	SD	x	SD	x	SD	x	SD	x	SD	x	SD	x	SD
OA	0.7	0.2	0.6	0.01	0.9	0.0	0.8	0.2	1.4	0.5	1.1	0.1	0.3	0.1	0.1	0.0
OB	0.7	0.1	0.8	0.03	1.0	0.3	1.0	0.0	1.5	0.4	**2.0**	0.3	0.2	0.0	0.4	0.0
OC	1.0	0.1	0.6	0.04	1.0	0.4	0.7	0.1	**2.7**	1.4	**1.9**	0.1	0.5	0.2	0.2	0.1
OD	0.9	0.3	0.7	0.1	0.6	0.2	0.9	0.1	**1.9**	0.6	**1.7**	0.3	0.2	0.1	0.1	0.0
AA	**3.9**	0.9	0.9	0.3	**3.5**	0.4	0.9	0.2	**2.8**	0.6	**1.7**	0.1	**2.1**	1.1	0.5	0.1
AB	**5.1**	1.8	**1.9**	0.6	**3.9**	0.9	**2.0**	0.6	**4.4**	1.0	**3.4**	0.4	**2.3**	1.0	1.0	0.3
AC	0.6	0.1	0.3	0.1	0.9	0.3	0.6	0.0	**1.7**	0.1	0.9	0.4	0.3	0.0	0.2	0.0
AD	0.6	0.4	0.8	0.2	1.2	0.5	1.2	0.1	**2.5**	1.3	**2.0**	0.3	0.5	0.2	0.3	0.0

Table 3 *F* values from ANOVA to test for significance in the enrichment factor (EF) values for heavy metals in sediment

		Zn	Pb	Cu	Cd
Source of variation	*df*	*F*	*F*	*F*	*F*
Creek	1	23.3***	50.9***	13.9**	27.3***
Season	1	16.7***	22.9***	8.3**	14.9***
Location	3	10.8***	16.3***	7.8*	8.1***
Creek × season	1	11.1**	20.1***	3.3^{ns}	7.9**
Creek × location	3	12.0***	12.7***	13.5***	7.9***
Season × location	3	3.5*	6.3**	0.6^{ns}	2.0^{ns}

*$p < 0.05$, **$p < 0.01$, ***$p < 0.001$, ns = not significant

metals in the Azuabie creek, particularly at stations AA and AB (which also had the highest EF values), the highest mean values obtained were lower than the values recorded in heavily polluted mining areas (Daka et al., 2003) or industrialized areas (Bryan and Langston, 1992). Industrial activities capable of contributing to elevated concentrations of heavy metals include the plastic industry, automobile and boat fuel, construction, galvanizing iron and steel products, and electroplating (Förstner and Wittmann, 1979; Moore and Romamoorthy, 1984). A number of industries in the trans-Amadi industrial zone fall into these categories, thus leading to elevated concentrations of Zn, Pb, Cu and Cd in the Azuabie creek. The high concentrations of these metals at stations AA and AB are attributable to their proximity to these sources of contamination. Also, there were higher levels of TOC at these stations with significant positive correlations between the metals and TOC ($p < 0.05$), showing that incorporation of metals by flocculation with organics influenced the concentration in sediment. It is, however, possible that the frequent dredging in the creeks results in the removal and export of contaminated sediment particles such that a build up of metal levels is ameliorated. This may also explain the variable status of enrichment between periods.

The result of PCA ordinations (Fig. 4) using sediment quality characteristics indicates three groupings. This was much clearer in the February samples than in October. Stations AA and AB (the most heavily impacted areas in the Azuabie creek) each stood out separately, while the four stations in the Obufe creek (OA, OB, OC and OD) were grouped together with AC and AD (the less-contaminated sites in Azuabie creek). The graphs (especially Fig. 4A) show that the main factor (first axis) is decreasing pollution from upstream to downstream, opposing AA to OA. The second organizing factor (second axis) is the trivial upstream-to- downstream gradient, opposing AA and OA to AD and OD. This is more marked for the Azuabie creek. The two factors (pollution and downstream gradient) are correlated; this explains the Guttman effect observed on the two graphs. This indicates that stations AA and AB are hot-spots of contamination because of their proximity to sources of anthropogenic impacts.

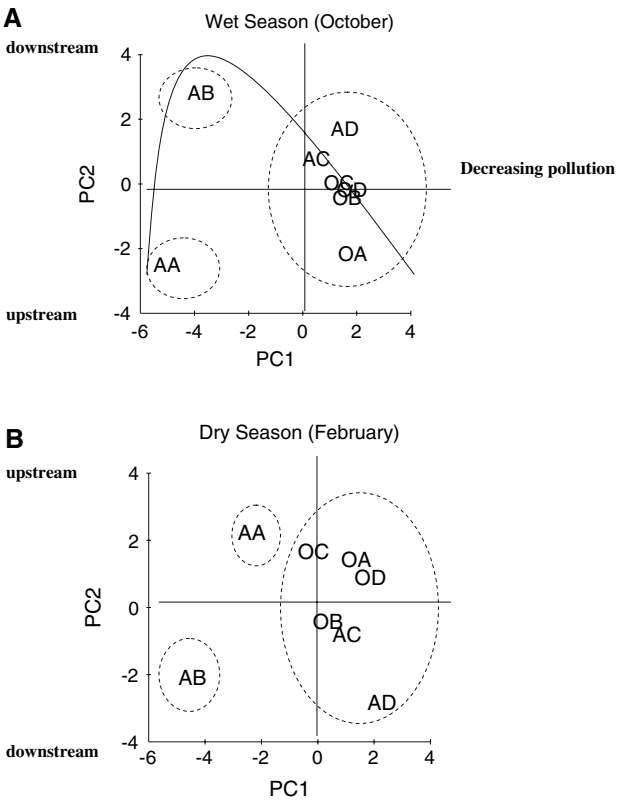

Fig. 4 Discrimination of sites by principal component analysis (PCA) using sediment data

In conclusion, this study shows that the Azuabie creek has higher levels of contamination with organic matter and heavy metals than the adjacent Obufe creek, with gradients of contamination showing higher values in the upstream reaches. Pollution is the strongest organizing factor, which partially hides the trivial upstream–downstream gradient. However, the level of contamination with hydrocarbons is lower than that obtained from areas chronically contaminated with petroleum hydrocarbons in the Bonny Estuary. Continual pollution could have ecological consequences by

affecting the species composition and diversity of benthic organisms in the area.

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