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Sawmill Activities Near the Lagos Lagoon, Nigeria: Polycyclic Aromatic Hydrocarbons and Embryotoxic Evaluations of Sediment Extracts Using *Clarias gariepinus*

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Abstract

The physicochemical parameters and 16 priority PAHs in surface water, porewater and sediment at a sawmill wastes-impacted and High-Rise study sites on the Lagos lagoon in Nigeria were assessed. Further, the embryotoxic effects of sediment organic and porewater extracts from the study sites were evaluated in *Clarias gariepinus* (African sharptooth catfish) embryos for 26 h. High molecular weight PAHs dominated the PAHs profile especially in the sediment. Source apportionment of the PAHs in the three environmental matrices revealed mainly pyrogenic sources. Developmental abnormalities and decreased hatching success were observed in *C. gariepinus* embryos exposed to extracts from the Okobaba site compared to High-Rise study site. The results demonstrate the potential though non-significant ecological risk of sawmill activities near the lagoon on water quality and fisheries. Further studies are recommended to provide holistic evidence-based information to promote sustainable fisheries in the lagoon in support of the UN SDGs 13 (climate action) and 14 (life below water).

Keywords African sharptooth catfish · PAHs · Sediment organic extracts · SDGs · Lagos lagoon

The Lagos lagoon is the largest brackish coastal lagoon in the West African coast. It is a major coastal water in Nigeria that is of immense ecological and economic value including being a major source of seafood for the people of Lagos (Alo et al. 2014). Human activities such as oil transportation, industrial wastewater discharges and urban runoff have adversely impacted the water quality and biodiversity of the lagoon (Bawa-Allah et al. 2018). These impacts such as reduced fisheries diversity and fish catch over the years have been reported (Ajagbe et al. 2012). The lagoon's biodiversity is further threatened by polluting activities such as saw milling and burning of wood shavings at the Okobaba bank of the lagoon which is the hub of a thriving logging and saw milling industry (Buraimoh et al. 2015). The continuous burning of saw dusts and wood shavings near the lagoon are potential point sources of priority pollutants like polycyclic aromatic hydrocarbons (PAHs) into the lagoon which are known to be carcinogenic and mutagenic (Kim et al. 2011).

Embryotoxic (adverse effects on embryos/early life stages of animals) and teratogenic (effects on ontogeny/development of an animal) effects of sediment organic extracts have been observed in vivo, such as in zebrafish (*Danio rerio*) embryos (Sogbanmu et al. 2016) and in vitro as in cell lines (Perez-Albaladejo et al. 2016). Also, sediment porewater has been shown to induce toxic responses including acute developmental toxicity and cardiac teratogenesis in *D. rerio* (Fang et al. 2014). The effects of pollutants on the early life stages of fish provides a forecast on the availability and sustainability of fisheries in aquatic ecosystems. The advocacy for animal alternatives in research and rapid high-throughput assays to provide bases for environmental management and policies has informed the use of the early life stages of fish species as a globally ratified method relating to the principle of the 3Rs (replacement, refinement and reduction) (OECD 2013). Model fish species indigenous to various countries have been utilised such as the zebrafish (*Danio*

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rerio), fathead minnow (*Pimephales promelas*), rainbow trout (*Onchoryhncus mykiss*), and Japanese medaka (*Oryzias latipes*) (Nguyen and Janssen 2001). The African Sharptooth Catfish (*Clarias gariepinus)*, a commercially and ecologically important fish species in Nigeria is a suitable model with a well-documented general biology, transparent eggs, easy to culture and year-round reproduction (Nguyen and Janssen 2001). The embryos can be spawned artificially and development from fertilization to hatching occurs within 24 to 29 h post-fertilization at 28–29℃ (Mumuni and Sogbanmu 2018).

The dearth of information on the impact of sediments potentially laden with pollutants on native fish species in general, particularly their early life stages provided an impetus for this study. Consequently, the aim of the study was to investigate the impacts of sawmill activities at the Okobaba hub of the Lagos lagoon on sediment and surface water physicochemistry, PAHs input and developmental effects of sediment organic extracts on the embryos of *Clarias gariepinus*. Findings from this study can aid understanding of the nature and extent of biological impacts of the associated pollutants on fish species for the purpose of targeted environmental management.

Materials and Methods

The study areas were Okobaba (sawmills waste-impacted study site) and University of Lagos high rise building area (High-Rise study site) on the Lagos lagoon (Fig. 1; Plate 1). The Lagos Lagoon is a tidal water with an average tidal water height ranging from 0.3 to 1.3 m and suffers from longshore drift. The lagoon has an average depth of 2 m and a maximum depth of about 5 m in the main body which is dependent on the tidal regime and season (Ajao and Fagade 1990; Nkwoji et al 2020). It receives water from the Atlantic Ocean during high tides and returns water during low tides. During this process there is mixing of water (Badejo et al. 2014). Okobaba is a hub of sawmills, timber transport and municipal waste discharge (Akpata 1987) while the High-Rise study site is located adjacent to the University of Lagos staff quarters and relatively close to the Okobaba study site (Plate 1). Three (3) stations were sampled at each of the two study sites. The stations were geo-referenced with the aid of Global Positioning System (GPS) and recorded as coordinates of the locations (Fig. 1).

Three (3) surface water and sediment samples each were collected monthly in the wet (June to August, 2016) and dry (December 2016 to January 2017) seasons at each study site. The surface water samples were collected at a depth of 0.5 cm and stored in amber-coloured glass bottles.

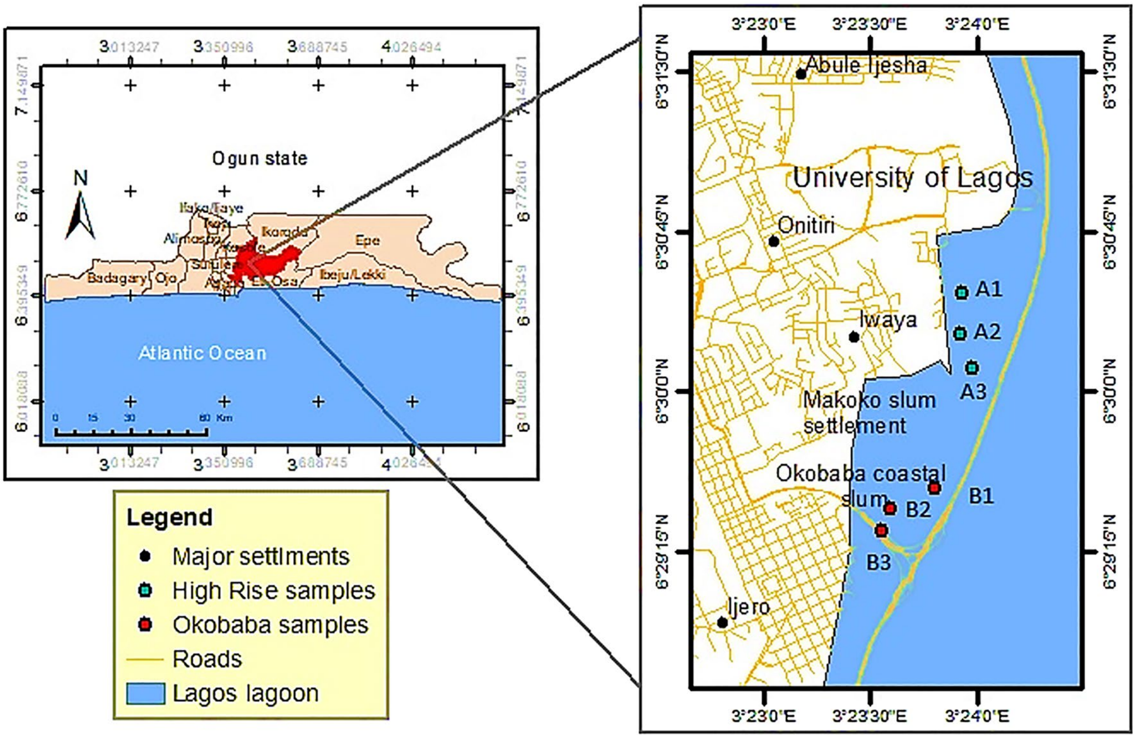

Fig. 1 Map of the study area showing sampling locations on the Lagos lagoon, Nigeria

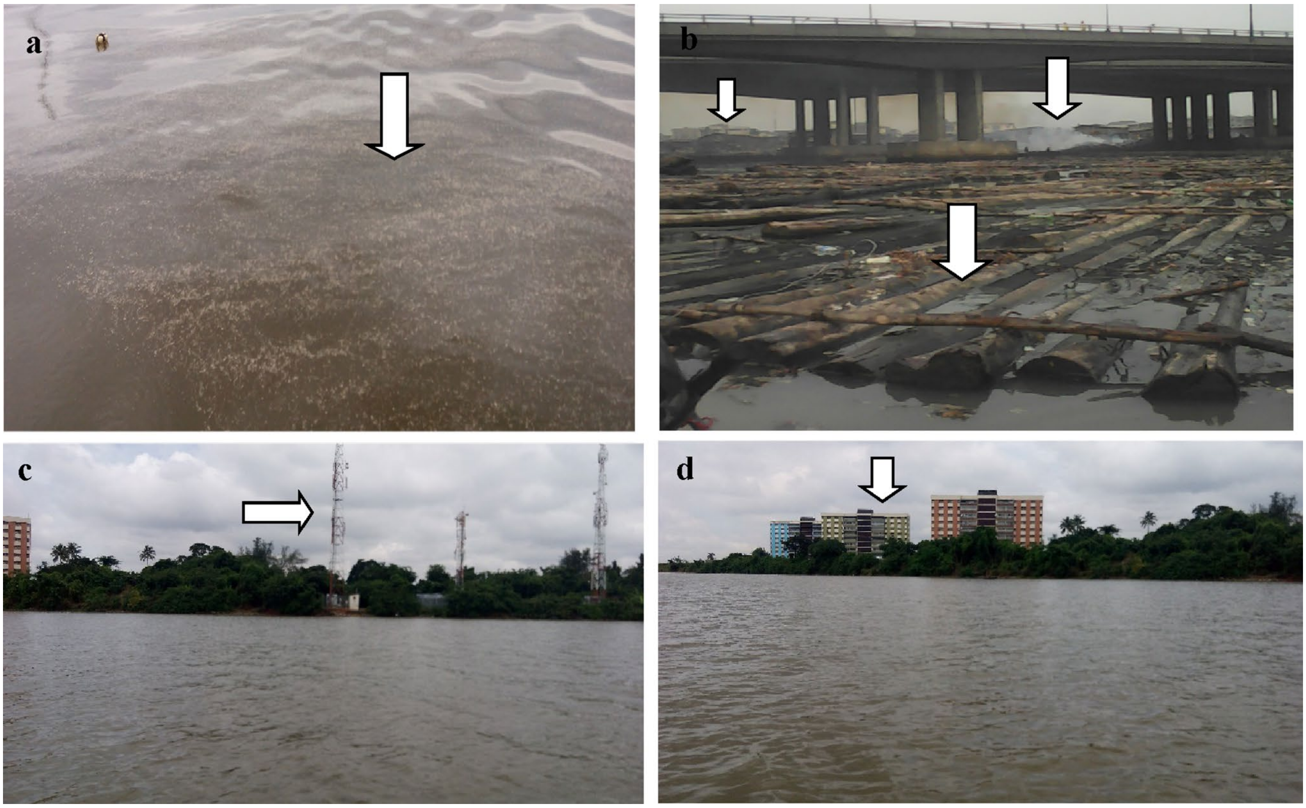

Plate 1 Pictures showing the nature of activities and state of the environment at the Okobaba and High-Rise Study sites on the Lagos lagoon, Nigeria. Arrows showing (**a**) saw dust on the water, (**b**) sawmills, burning of saw dust and thick mass of wood logs on the Lagos lagoon at the Okobaba study site (**c**) University of Lagos High Rise building and (**d**) Masts at the High Rise study sites on the Lagos lagoon. Photo credit—**a**, **c**, **d**: Sogbanmu, T. O.—June to August 2016 (wet season) sampling pictures; **b** Sogbanmu, T. O.—February 2017 (dry season) sampling pictures

The sediment samples were collected at depths of 0–10 cm with Van Veen grab sampler and stored in aluminum foil papers from three (3) sampling points each at the Okobaba and High-Rise study sites on the Lagos lagoon (Sogbanmu et al. 2019). All samples were labelled and stored in ice-packed (temperature: 4°C) coolers before transportation to the analytical laboratory at the Department of Chemistry, University of Lagos, Nigeria for analysis. The samples from the three sampling points at each site were composite prior to analyses (Sogbanmu et al. 2016).

Surface water physicochemical parameters (temperature, pH, conductivity, dissolved oxygen, TDS and salinity) were measured in situ using Horiba U50G Multi-water sampler (HORIBA Advanced Techno, USA).

For the sediments, physicochemical parameters such as total organic carbon, particle size, pH, conductivity and physical appearance were determined. Particle size distribution of the sediments was determined by a wet sieving and sedimentation technique according to the British Standard Method for soils using Adetunde et al. (2014). Sediment pH was determined after adding 0.01 mol/L $CaCl_2$ (10 mL) to 5 g of each sediment and shaken for 1 h. Walkley–Black titrimetric method was used to determine total organic carbon and total organic matter. Oil and grease content was extracted ultrasonically (acetone: *n*-hexane, 50:50 v/v) and quantified gravimetrically (Hong et al. 2003). The concentration of analyte in blanks were subtracted from field samples.

For water samples extraction, 250 mL of water samples were extracted by liquid–liquid extraction using hexane and dichloromethane (DCM) mixture (1:1 v/v) according to Sogbanmu et al. (2019). Water samples were extracted thrice using 50, 30 and 20 mL of the solvent mixture. The solvents were combined, dried with anhydrous sodium sulphate and concentrated using nitrogen gas. The extract was re-constituted with 2 mL of n-hexane and DCM (1:1) and analysed for PAHs using Gas Chromatograph (Agilent Technologies 6890 N, GC system) coupled with Flame Ionisation Detector (GC-FID) (Sogbanmu et al. 2019).

Sediment porewater samples extraction were conducted according to Fang et al. (2014). Briefly, 5 g of sediment was centrifuged in glass centrifuge tubes at 3000 rpm for 30 min to separate the porewater from the sediment. The porewater was collected, filtered into glass vials (this served as the crude porewater), extracted and analysed in a similar manner to the water sample. Briefly, 5 mL of porewater was liquid–liquid extracted as the water samples using 5, 2 and 1 mL of extracting solvent. The extract was reconstituted using 1 mL of hexane/DCM (1:1) and kept in amber vials for analysis of PAHs with GC-FID.

For sediment organics extraction, 5 g of sediment samples were freeze-dried and 2 g of treated copper turnings (copper turnings were treated by adding 0.1 M concentrated nitric acid until the outer layers were corroded after which the copper turnings were washed thoroughly with distilled water and kept in methanol for use to prevent sulphur interference) were added to the sample and left overnight for 24 h (Sojinu et al. 2013). Thereafter, the sediment samples were ultrasonicated thrice using 10 mL, 6 mL and 3 mL hexane/acetone (1:1 v/v) mixture for 30 min respectively. The extracts were combined and concentrated using nitrogen. The extracts were reconstituted with 5 mL of hexane. Sample cleanup was done using Supelco solid phase extraction C18 cartridges that have been conditioned with methanol. Elution of the PAHs was done using 2 mL of hexane/DCM (1:1 v/v). The eluate was analysed using GC-FID.

Blanks were carried out with distilled water extracted with hexane/DCM solvent used for the liquid–liquid extraction. Recovery studies were also carried out on both the water and pore water sample in triplicates per level by spiking the water samples with mixed PAHs standards. For the sediment sample, a certified reference material (clay loam 2 soil CRM 131 by Sigma Aldrich) was used. The certified reference material (CRM) was ultrasonicated and extracted for PAHs like the sediment samples. Spiked recovery method was used for validation studies of the sediment samples. The sediment samples were spiked with 1 µL of 100 ppm standard mixture containing the 16 priority PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a) anthracene, chrysene, benzo(b)fluoranthene, benzo(k) fluoranathene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h) anthracene and benzo(g,h,i)perylene (Supelco)) before extraction. The final extracts were made up to 1 mL. The spiked samples were extracted and analysed. The recoveries were between 75 and 105% for both the spiked and certified reference standard (CRM) and certified levels were obtained for PAHs in the CRM and spiked samples. Napthalene recorded the least recoveries and benzo(g,h,i)perylene recorded the highest recoveries.

A mixed standard of the 16 priority PAHs was used for external calibration of the instrument. Calibration standards were prepared by serial dilution of stock solution with DCM. A calibration curve was plotted for each of the PAHs. All the calibration plots for the 16 PAHs had R^2 value of 0.98 to 0.99 and were used to quantify the PAHs. Limits of detection were determined for each of the PAHs in water, pore water and sediments using a signal to noise ratio of 1 to 3 and the values were 0.009 mg/L or mg/kg respectively or less.

The concentrations of the PAHs were determined using a GC-FID (Singh et al. 2019). Nitrogen gas was used as the carrier gas with a flow rate of 40 mL/min, hydrogen with air produced the flame. Temperature for sample injection was 250°C and the volume of sample injected manually was 3 µL in a split mode with a split ratio of 100:1. The GC oven temperature was programmed from 70°C to 175°C at 15°C/min then to 215°C at 10°C/min then to 265°C at a rate of 2.5°C/min, finally at a temperature of 265°C it was ramped at a rate of 20°C/min to 290 °C and held for 8 min. The run time was 42.25 min. The column was HP5 and the length of column was 30 m with internal diameter of 0.32 mm and thickness of 0.25 µm.

Source apportionment of PAHs was carried out using ratios of the levels (or concentrations) of phenanthrene to anthracene (Stogiannidis and Laane 2015), anthracene/anthracene + phenanthrene (A/A + P) (Edokpayi et al. 2016) and fluoranthene/fluoranthrene + pyrene (F/F + P) (Tobiszewski 2014)

Sediment organics extraction was conducted as described in the samples extraction procedure detailed above and was solvent exchanged with acetone. The crude sediment organic extract (CSE) stock solution was equivalent to 1 g dry weight sediment equivalent extract (eQsed) per millilitre while the cleaned-up sediment organic extract (CUSE) stock solution was equivalent to 2.5 g dry weight sediment equivalent extract (eQsed) per mL. Sediment porewater was extracted (as described in samples extraction) (Sogbanmu et al. 2016). The crude sediment porewater (CPW) stock solution was equivalent to 1 g wet weight sediment (eQsed) per mL while the cleaned-up sediment pore water extract (CUPW) stock solution was equivalent to 5 g wet weight sediment porewater equivalent extract (eQsed)/mL. Acetone was used as a control. Cleaned up extract refers to further processing (removal of interferences/contaminants extracted from the matrix leaving only the analytes of interest (PAHs) of the extract to make it suitable for instrumental analysis (Silva et al. 2009).

Clarias gariepinus (chordata, osteichthyes, siluriformes, clariidae) embryos were spawned from unexposed broodstock (1 female and 2 males) purchased from the University of Lagos fish farm according to OECD (2013) and Sogbanmu et al. (2018). Briefly, one (1) female broodstock *C. gariepinus* (weight: 1.1 kg; length: 45 cm) was injected with Ovaprim (Syndel laboratories Ltd, Canada) hormone (a potent ovulating agent to facilitate spawn in fish species) at 0.5 mL per kg of fish. The hormone was drawn with a 2 mL syringe and injected intra-muscularly at an angle of 45° into dorsal muscle of the female broodstock (Ayoola 2009). After 10 h latency period, a slight pressure was applied on the abdomen of the female allowing the

Table 1 Physicochemical parameters of Lagos lagoon surface water in the wet and dry season, 2016–2017

Parameter	Wet season		Dry season		NESREA limits
	Okobaba	High rise	Okobaba	High rise	
Temperature (°C)	26.12 ± 1.17	26.69 ± 1.06	28.29 ± 0.40	29.25 ± 0.16	< 40
pH	8.16 ± 0.57	9.35 ± 1.57	6.75 ± 0.06	6.67 ± 0.15	6.5–8.5
Conductivity (mS/cm)	0.97 ± 0.18	1.22 ± 0.29	28.83 ± 1.68	30.83 ± 0.06	NS
Dissolved oxygen (mg/L)	9.68 ± 5.18	8.85 ± 3.39	4.34 ± 0.74	9.72 ± 3.96	> 6.0
Total Dissolved solids (g/L)	0.65 ± 0.06	0.76 ± 0.20	17.90 ± 1.04	18.83 ± 0.06	2
Salinity (‰)	0.44 ± 0.10	0.61 ± 0.14	17.40 ± 1.01	19.13 ± 0.06	NS

Values are Mean ± SD (n = 3); NESREA 2010; *NS* Not specified

release of the eggs which were collected into a dry plastic bowl. Two (2) males (weight range: 1.0 ± 0.5 kg; length range: 48 ± 1.1 cm) were euthanized and the testes were carefully removed with the aid of a new razor blade. An incision was carefully made on each testis to let out the milt used for fertilizing the eggs. Fertilization was aided with the addition of 1 mL of saline water (composition: 9 g of table salt (NaCl) in 1 L of dechlorinated water) to the mixture and the bowl was gently swirled to ensure adequate mixing of the milt with the eggs (Idahor et al. 2014). Fertilized eggs were identified and confirmed with the aid of a stereomicroscope (Ceti Star-13 ED Stereomicroscope, Medline Scientific, United Kingdom). Fertilization was considered to have occurred when the egg-yolk was transparent greenish-orange and cell division was clearly visible in the blastodisc (Mumuni and Sogbanmu 2018). All applicable international, national, and/or institutional guidelines for the care and use of animals were followed (AVMA 2013).

A total of 30 embryos (10 embryos in triplicates) per concentration were exposed to sediment organic extracts (crude and cleaned up) and porewater (crude and cleaned up) in separate petri dishes containing 40 mL of dechlorinated water from 0 to 26 h post-fertilization (hpf) (Sogbanmu et al. 2016). The exposure concentrations were; 1 mg eQsed/mL (crude porewater (CPW)), 250 µg eQsed/mL (crude sediment organic extracts (CSE)), 1.25 mg eQsed/mL (cleaned up pore water (CUPW) and 250 µg eQsed/mL (cleaned up sediment organic extracts (CUSE)). Two controls were included; embryos in dechlorinated water alone (40 mL) and embryos exposed to acetone (0.25 µL/mL (0.025% of highest concentration of sediment extract) (Sogbanmu et al., 2016). The endpoints that were assessed in the embryos were mortality, hatching success and developmental abnormalities using a stereomicroscope (Ceti Star-13 ED Stereomicroscope, Medline Scientific, United Kingdom). Mortality was measured as the percentage of coagulated embryos with no structures and/or embryos with no visible heartbeat (Kumar et al. 2013). Hatching success was measured as the percentage of embryos that hatched (fully emerge from the chorion) at 26 hpf. Developmental abnormalities were calculated as the percentage of embryos observed under the dissecting microscope with one or more developmental abnormalities such as pericardial oedema, yolk-sac oedema, scoliosis, curved/stunted tail (Mumuni and Sogbanmu 2018).

Physicochemical parameters and PAH levels in surface water and sediments as expressed as mean ± standard deviation. The embryotoxicity (mortality, hatching success and developmental abnormalities) data are expressed as mean ± standard error. Test for adherence to normality and equal variance among groups were applied and one-way non-parametric Analysis of Variance (ANOVA) (Kruskal–Wallis test) was used to test for significant differences between treatment means (embryotoxicity data) and controls (Sogbanmu et al. 2016). T-test was used to test the significant differences in PAHs data between sites and seasons. Post-hoc tests were conducted using Duncan's Multiple Range Test (Duncan 1955) with the level of significance set at $p < 0.05$. Statistical analyses were conducted using SPSS version 22.0.

Results and Discussion

The surface water physicochemical parameters at both sites and seasons were within set limits by the National Environmental Standards and Regulations Enforcement Agency (NESREA), Nigeria except for DO values in the dry season at Okobaba which was lower than the set limit (Table 1). However, conductivity, TDS and salinity values were higher in the dry season compared to the wet season at both sites. The low surface water DO could be attributed to the presence of organic pollutants (sawdusts) which could result in anoxic conditions due to the action of microorganisms (Buraimoh et al. 2015). Also, the low DO may be related to the high TDS value in the dry season at the Okobaba study site though a higher value was recorded at the High-Rise study site.

In the dry season, the water is more concentrated, slightly acidic, had more dissolved solids and ions which gave rise to higher conductivity and salinity. The

Table 2 Physicochemical parameters of Lagos lagoon sediments in wet and dry seasons, 2016–2017

Parameters	Wet season		Dry season	
	Okobaba	High rise	Okobaba	High rise
TOC (%)	2.32 ± 1.30	0.88 ± 0.44	1.64 ± 1.30	0.58 ± 0.63
Grain particule size (%)	Gravel; 0 Sand: 15–22 Silt: 28–31 Clay: 50–54	Gravel: 0 Sand: 23–25 Silt: 35–37 Clay: 42–45	Gravel:0 Sand: 7.1–10 Silt: 27–30 Clay: 63–67	Gravel:0 Sand:21–23 Silt:33–35 Clay: 40–42
pH	4.13 ± 0.50	4.86 ± 0.92	5.92 ± 0.50	5.25 ± 1.00
Conductivity (dS/cm^3)	4927 ± 2546	2522 ± 1379	772 ± 254	9473 ± 139
Physical apperance	Dark grey, organic silty clay	Dark grey, organic silty clay	Dark grey, organic silty clay	Dark grey, organic silty clay

TOC total organic carbon; n = 3, Values are Mean ± SD

temperature of the Lagoon was higher in the dry season which is usually hotter. There were no significant differences ($p > 0.05$) in the physicochemical parameters' values between the High Rise and Okobaba study sites in either of the seasons (Table 1) which is rather puzzling. The High-Rise study site was selected based on a lack of visible anthropogenic activity except for its proximity to the University of Lagos staff quarters. Thus, this result may point to the high pollution status of the lagoon over the years. Since the water is not stagnant, tidal movement across the lagoon could transport pollutants from highly polluted sections to hitherto unpolluted polluted areas (High Rise study site which is close to the Okobaba study site).

The percentage total organic carbon (TOC) in the sediment was higher at the Okobaba study site compared to the High-Rise study site in both seasons. Further, the % TOC was higher in the wet season compared to the dry season at both sites (Table 2). The sediment pH was generally acidic across the two sites and seasons though, the acidity was higher in the wet season compared to the dry season. Conductivity was higher at the Okobaba study site in the wet season compared to the dry season while the reverse was the case for the High-Rise study site (Table 2).

The higher TOC values recorded in sediments at the Okobaba study site may be because of the continuous deposition of wood wastes at the site that are majorly composed of carbon. According to Olafimihan (2009), the sawmill industry at Okobaba has been run for over 50 years with timber being exported to the sawmill from Ondo state, Nigeria via tug boats. Hence, the associated wood wastes are estimated to have been accumulating for over six (6) decades as at the time of this study. Over the years, this contributes to siltation of sediment at this site as evidenced by the high percentage of silt and clay particle size in this study. Furthermore, the characteristic colour of the sediments is associated with sediments that have organic matter present in them (Akpata 1987). The high percentage TOC observed in the wet season may be due to a higher deposition of wood wastes into the surface water via run-offs during the heavy rains which eventually sink to the bottom of the lagoon. Microorganisms act on this in the sediment further compacting it (Buraimoh et al. 2015). This might be responsible for the lower sediment pH observed in the wet season compared to the dry season. Sediment pH was noted to be more acidic than surface water pH which could be as a result of accumulation of organics at the bottom of the lagoon. Also, the sediment conductivity values were higher than the water samples showing that there were more ions in the sediments probably due to accumulated debris. The higher percentage of sand and silt observed in the wet season may be due to run-off during rainfall from the bank of the lagoon laden with sawmill wastes.

The highest total PAHs concentration in this study was recorded in the sediments from the High Rise study site in the wet season which was significantly higher ($p < 0.05$) than values recorded for sediments from Okobaba (Table 3). Total PAHs concentration in Okobaba porewater and surface water were higher than the values for the High-Rise study site. In the dry season, the total PAHs concentration in the sediment at the High-Rise study site was higher than the values recorded for Okobaba (Table 3). However, this value was significantly lower ($p < 0.05$) than the value recorded at the High-Rise study site in the wet season. Furthermore, the total PAHs in the Okobaba porewater was significantly lower ($p < 0.05$) in the dry season compared to the wet season. There were no significant differences ($p < 0.05$) in the total

Table 3 Polycyclic aromatic hydrocarbons concentration in surface water, sediments and porewater of the Lagos lagoon in wet and dry seasons, 2016–2017

PAHs (mg/L or mg/kg)	Wet season						Dry season					
	Okobaba			High rise			Okobaba			High rise		
	Surface water	Pore water	Sediment	Surface water	Pore water	Sediment	Surface water	Pore water	Sediment	Surface water	Pore water	Sediment
Naphthalene	0.03 ± 0.03	0.75 ± 0.93	1.37 ± 1.65	0.03 ± 0.03	0.75 ± 0.93	1.66 ± 2.15	0.01 ± 0.00	0.21 ± 0.00	0.81 ± 0.55	0.01 ± 0.01	0.21 ± 0.00	0.22 ± 0.29
Acenaphthylene	0.03 ± 0.01	0.67 ± 0.28	1.27 ± 0.46	0.03 ± 0.03	0.63 ± 0.22	1.48 ± 0.80	0.02 ± 0.00	0.50 ± 0.00	1.05 ± 0.07	0.01 ± 0.01	0.50 ± 0.00	0.55 ± 0.65
Acenaphthene	0.29 ± 0.47	0.78 ± 0.48	1.47 ± 0.80	0.15 ± 0.23	0.73 ± 0.40	4.38 ± 7.75	0.02 ± 0.00	0.50 ± 0.00	1.01 ± 0.01	0.01 ± 0.01	0.50 ± 0.00	1.01 ± 0.00
Fluorene	0.03 ± 0.01	0.53 ± 0.06	0.95 ± 0.63	0.02 ± 0.01	0.49 ± 0.00	1.69 ± 1.20	0.02 ± 0.00	0.49 ± 0.00	0.99 ± 0.00	0.01 ± 0.01	0.50 ± 0.00	0.59 ± 0.58
Phenanthrene	0.16 ± 0.21	0.45 ± 0.12	0.88 ± 0.28	0.02 ± 0.00	0.45 ± 0.12	2.06 ± 0.89	0.05 ± 0.04	0.52 ± 0.01	1.04 ± 0.01	0.01 ± 0.01	0.52 ± 0.00	1.33 ± 0.41
Anthracene	0.13 ± 0.11	2.23 ± 2.96	4.43 ± 5.95	0.09 ± 0.11	2.23 ± 2.96	5.53 ± 5.32	0.02 ± 0.00	0.56 ± 0.00	1.13 ± 0.00	0.01 ± 0.01	0.57 ± 0.00	0.77 ± 0.51
Fluoranthene	2.11 ± 1.61	0.65 ± 0.09	1.26 ± 0.10	0.03 ± 0.01	0.65 ± 0.09	1.35 ± 0.24	0.10 ± 0.11	0.60 ± 0.00	1.20 ± 0.00	0.13 ± 0.01	0.60 ± 0.00	1.51 ± 0.44
Pyrene	0.09 ± 0.12	2.16 ± 2.98	4.30 ± 5.98	0.09 ± 0.13	2.16 ± 2.98	4.41 ± 5.88	0.02 ± 0.00	0.56 ± 0.00	1.13 ± 0.01	0.02 ± 0.01	0.56 ± 0.00	1.59 ± 0.66
Benz(a) anthracene	0.06 ± 0.04	0.78 ± 0.37	1.54 ± 0.59	0.03 ± 0.02	0.71 ± 0.27	4.57 ± 6.00	0.02 ± 0.00	0.56 ± 0.01	1.11 ± 0.00	0.01 ± 0.01	0.35 ± 0.30	1.11 ± 0.00
Chrysene	0.17 ± 0.26	0.36 ± 0.28	0.75 ± 0.50	0.02 ± 0.01	0.36 ± 0.28	0.81 ± 0.39	0.02 ± 0.00	0.52 ± 0.01	1.035 ± 0.01	0.01 ± 0.01	0.42 ± 0.15	1.04 ± 0.00
Benzo(b) fluoranthene	0.37 ± 0.53	1.05 ± 0.78	1.99 ± 1.32	0.04 ± 0.04	1.03 ± 0.76	7.06 ± 9.99	0.02 ± 0.00	0.60 ± 0.01	1.19 ± 0.00	0.02 ± 0.02	0.40 ± 0.28	1.20 ± 0.00
Benzo(k) fluoranthene	0.06 ± 0.03	0.68 ± 0.58	1.36 ± 1.17	0.03 ± 0.02	0.68 ± 0.58	2.72 ± 1.17	0.04 ± 0.00	1.02 ± 0.00	2.04 ± 0.00	0.03 ± 0.03	1.02 ± 0.00	2.05 ± 0.00
Benzo(a)pyrene	0.03 ± 0	0.78 ± 0.01	1.51 ± 0.08	0.03 ± 0	0.78 ± 0.01	1.63 ± 0.11	0.03 ± 0.00	0.78 ± 0.00	1.55 ± 0.00	0.02 ± 0.02	0.46 ± 0.44	1.55 ± 0.00
Indeno(1,2,3,c-d) pyrene	0.03 ± 0.01	0.54 ± 0.06	1.03 ± 0.06	0.02 ± 0.01	0.53 ± 0.07	4.82 ± 6.29	0.02 ± 0.00	0.52 ± 0.02	1.03 ± 0.05	0.01 ± 0.01	0.68 ± 0.00	1.53 ± 0.00
Dibenz(a,h) anthracene	0.03 ± 0.02	0.71 ± 0.18	1.23 ± 0.30	0.03 ± 0.01	0.65 ± 0.20	2.30 ± 1.26	0.03 ± 0.01	0.53 ± 0.00	1.06 ± 0.00	0.01 ± 0.01	0.68 ± 0.00	1.53 ± 0.00
Benzo(g,h,i) perylene	0.56 ± 0.87	0.54 ± 0.42	0.97 ± 0.75	0.39 ± 0.65	0.52 ± 0.43	8.00 ± 8.56	0.02 ± 0.00	0.27 ± 0.00	0.59 ± 0.06	0.02 ± 0.01	0.74 ± 0.00	0.63 ± 0.00
∑PAHs	4.18 ± 4.33	13.66 ± 10.58*	26.31 ± 20.1^{a}	1.05 ± 1.00	13.35 ± 9.45	54.57 ± 50.00^{b}*	0.46 ± 0.11	8.74 ± 0.06*	17.38 ± 0.77	0.46 ± 0.20	8.74 ± 1.17	17.97 ± 3.54*

n = 3, units for surface water and porewater are in mg/L while sediments are in mg kg^{-1}; results are presented as mean ± SD; * represents significant difference between seasons for the same media while different alphabet superscripts represent significant differences between Okobaba and High-Rise study sites for the same medium and season at $p < 0.05$

PAHs between the Okobaba and High-Rise study sites in the dry season. Generally, in the wet and dry seasons, the order of decreasing total PAHs was sediment > porewater > surface water.

The higher level of PAHs (especially high molecular weight (4–6 rings) PAHs) in the sediments compared to the surface water and porewater is consistent with the findings of Sogbanmu et al. (2016) who reported higher levels of PAHs in the sediments compared to the surface water. Also, organic pollutants such as organochlorine pesticides have been found to be highest in sediments followed by porewater and least in surface water (Gakuba et al. 2018). Sediments have been shown to act as sinks for PAHs due to the hydrophobic nature of the latter. PAHs adhere to organic matter in soil and sediments (Wang et al. 2014). Moreover, the organic nature of the sediment, in this case, may have contributed to the binding of organic compounds such as PAHs to it (Ukalska-Jaruga et al. 2019). The significant decrease of PAHs in the porewater from the Okobaba study site in the dry season might be because of the reduced remobilisation of sediment PAHs into the water column. Also, the observation may be related to wet deposition from the atmosphere, preferential partitioning between air–water and sediment–water interfaces, all of which may be temperature /season dependent (Zhang et al. 2003). The findings in this study were similar to that of Adekunle et al. (2017) where higher concentrations of PAHs were recorded during the wet season than in the dry season.

The ratio of phenanthrene/anthracene (P/A) levels in the surface water, porewater and sediments at the Okobaba and High-Rise study sites ranged from 0.2 to 2.5 (Table 4). The highest P/A levels (1.23 and 2.5) were observed in the surface water from the Okobaba study site at both wet and dry seasons respectively (Table 4). All the P/A ratios were less than 5. Thus, the PAHs were from pyrogenic (combustion) sources (Stogiannidis and Laane 2015). A value of < 0.1 and > 0.1 for A/A + P ratio shows the PAHs present are petrogenic and pyrogenic respectively (Edokpayi et al. 2016). In this study, A/A + P ratios were between 0.29 and 0.83 (Table 4). These values are all greater than 0.1 which indicates that the source was pyrogenic. However, another ratio, F/F + P gave values that suggested that the source of PAHs in the lagoon were of mixed sources (Table 4). Some values of F/F + P were higher than 0.5 which suggest pyrogenic origin due to wood, grass or coal while some values were lower than 0.4 which suggest some PAHs in the lagoon were of petrogenic origin (Tobiszewski 2014).

Mortality was highest in the cleaned up porewater from the high-rise study site (CUPW-HR) followed by the crude porewater-high rise (CPW-HR), crude porewater-Okobaba (CPW-OB), crude sediment organic extract-Okobaba (CSE-OB) compared to the controls (Fig. 2). Hatching success was highest in the controls (dechlorinated water and acetone

Table 4 Source apportionment ratios for PAHs at the Okobaba and high-rise study sites on the Lagos Lagoon

Ratios	Okobaba (wet season)			High rise (wet Season)			Okobaba (dry season)			High rise (dry season)		
	Lagoon water	Pore water	Sediment	Lagoon water	Pore water	Sediment	Lagoon water	Pore water	Sediment	Lagoon water	Pore water	Sediment
P/A	1.23	0.20	0.20	0.22	0.20	0.37	2.50	0.93	0.92	1.00	0.91	1.73
A/A + P	0.45	0.83	0.83	0.82	0.83	0.73	0.29	0.52	0.52	0.50	0.52	0.37
F/F + P	0.96	0.23	0.23	0.25	0.23	0.23	0.83	0.52	0.52	0.87	0.52	0.49

P/A phenanthrene/anthracene (Stogiannidis and Laane 2015), *A/A + P* anthracene/anthracene + phenanthrene (Edokpayi et al. 2016), *F/F + P* fluoranthene/fluoranthene + phenanthrene (Tobiszewski 2014)

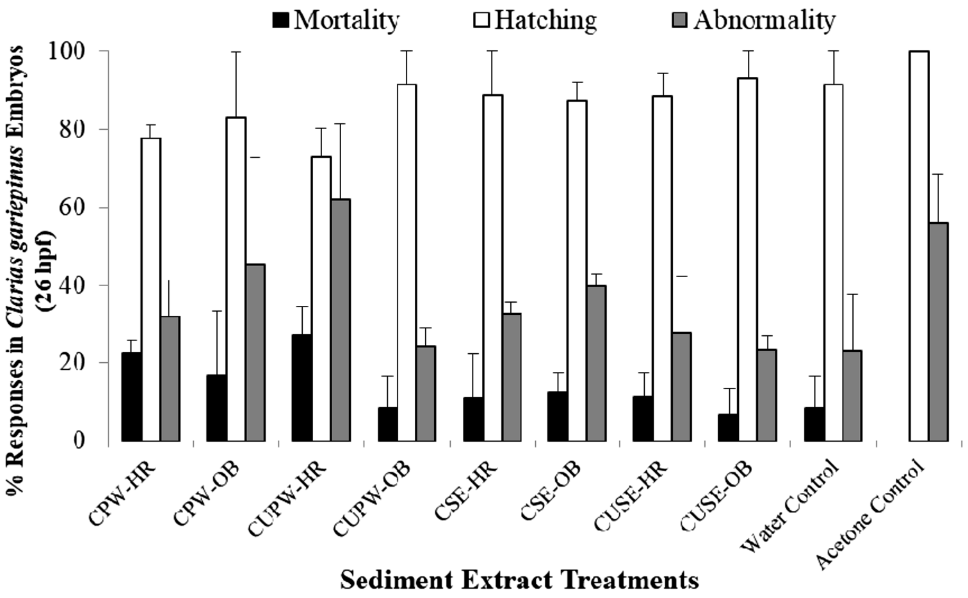

Fig. 2 Embryotoxicity indices in *Clarias gariepinus* embryos exposed to extracts of sediments from Okobaba and High-Rise study sites on the Lagos Lagoon from 0 to 26 h post-fertilization. n = 3 replicates, values are represented as % mean ± standard error (SE). *CPW-HR* crude pore water high rise, *CPW-OB* crude pore water Okobaba, *CUPW-HR* cleaned up pore water high rise, *CUPW-OB* cleaned up pore water Okobaba, *CSE-HR* crude sediment extract high rise, *CSE-OB* crude sediment extract Okobaba, *CUSE-HR* cleaned up sediment extract high rise, *CUSE-OB* cleaned up sediment extract Okobaba. *Dechlorinated Water* Alone—Water Control, Solvent Control—Acetone. *Exposure Concentrations* 1 mg eQsed/mL (CPW), 250 µg eQsed/mL (CSE), 1.25 mg eQsed/mL (CUPW), 250 µg eQsed/mL (CUSE), 0.25 µL/mL (acetone)

controls), cleaned up sediment organic extracts (CUSE-OB) and porewater (CUPW-OB) from Okobaba. Hatching success was lowest though higher than 50% in cleaned up porewater from the High-Rise study site (CUPW-HR) (Fig. 2). The percentage abnormalities was highest in the cleaned up porewater from the High-Rise study site (CUPW-HR) and lowest in water control. No significant differences ($p > 0.05$) were observed in the mortality, hatching success and abnormalities of the crude and cleaned up sediment organic extracts, porewater and controls (Fig. 2).

As observed in the previous results on physicochemical parameters and PAHs values for the Okobaba and High-Rise study sites, embryotoxic responses were highest in the extracts from the High-Rise study site compared to the Okobaba study site. Furthermore, the cleaned up porewater (CUPW-HR) and sediment organic extracts (CUSE-HR) (containing PAHs only) elicited higher embryotoxic responses compared to the crude porewater (CPW-HR) and sediment organic extracts (CSE-HR) at the High-Rise study site. This points to an unexpected source of pollution by PAHs at the High-Rise study site which is not related to significant anthropogenic activity as opposed to activities seen at Okobaba. Possible sources could be oil spills from boats that cross the area, atmospheric PAHs deposition from diffuse sources including burning of sawmill wastes (Zhang and Tao 2009) at Okobaba which is relatively close to the High-Rise study site, proximity to the University of Lagos lagoon front which is the berthing point for boats used by some departments in the University. Conversely, the crude porewater (containing inorganic pollutants) and sediment organic extracts (containing organic pollutants including PAHs) from Okobaba study site elicited higher embryotoxic responses compared to the cleaned up extracts from the same site. This may point to other pollutants (both inorganic and organic) at the site which are capable of eliciting higher embryotoxic and perhaps more biotoxic effects than PAHs alone. For example, elevated levels of heavy metals (Cd, Pb, Cu and Zn) have been reported in surface water, sediment and tissues of the edible blue crab (*Callinectes amnicola*) from the Okobaba study area (Jerome and Chukwuka 2016; Jerome et al. 2017). The non-significant ($p > 0.05$) embryotoxic responses between extracts and controls could be due to the low concentrations tested (250 µg eQsed/mL) compared to the concentrations (2.5 to 25 mg eQsed/mL) that elicited significant embryotoxic effects in *Danio rerio* embryos exposed to Lagos lagoon sediment organic extracts in a previous study (Sogbanmu et al. 2016). Further, sediment organic extract concentrations at 7 mg eQsed/mL from 11 sampling sites on the Lagos lagoon elicited significant DNA damage in rainbow trout gill-W1 cells (Amaeze et al. 2015). Also, previous studies on sediment extracts from Makoko and Ikorodu areas of the Lagos lagoon had reported that polar and water extracts in Rat hepatoma H4IIE and fish PLHC-1 cell-lines did not exert high cytotoxic effects (except the non-polar extracts) though significantly modulated phase I biotransformation responses (Mennillo et al. 2020). Conversely, significantly high ($p < 0.05$) % developmental abnormalities were observed in *C. gariepinus* embryos exposed to sublethal concentrations of Cracker 282 (endosulfan:deltamethrin mixture) (Mumuni and Sogbanmu, 2018).

Our results demonstrate non-significant differences in embryotoxic and teratogenic responses of crude and cleaned up sediment organic extracts from both study locations. However, the observed high mortality, low hatching success and high developmental abnormalities though non-significant compared to the controls points to the need for future studies with high extract concentration, evaluation of non-polar/inorganic contaminants as well as biomarkers at sub-organismal (molecular and cellular) levels of biological organization in order to provide holistic and evidence-based information for management of the study sites on the lagoon. Also, further studies are recommended such as in situ monitoring studies using indigenous fish and macro-invertebrates, evaluation of other biomarkers in model aquatic organisms, comparative embryotoxicity studies with mixture of PAHs standards at levels detected in the extracts in this study, evaluation of other pollutants such as pesticides and heavy metals in the sediment and water, animal species diversity studies and stakeholders' engagement for holistic evaluation and management of pollution in the study area. This will forestall further coastal degradation and promote sustainable fisheries in the lagoon in support of the United Nations sustainable development goals 14 (life below water).

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Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

Research Involving Human and Animal Rights This study followed the principles in the Declaration of Helsinki on the humane treatment of animals used in research (https://www.wma.net/en/30publications/10policies/a18/) and the principles in the AVMA Guidelines for the euthanasia of animals (AVMA 2013).

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