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3 **Risk Assessment of PAHs and N-PAH Analogues in Sediment Cores from the Niger Delta**

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Abstract

Chemical-surveys of sediments are source of information about historical-pollution in aquatic-ecosystems, because ecological/human-health risks may arise from polycyclic-aromatic-hydrocarbons (PAHs) and nitrogen-PAHs presence in aquatic-environments, particularly sediments, where they partition. Despite this, sediment-PAHs/N-PAHs have not been reported in the Niger Delta. This study investigated vertical-profiles of PAHs/N-PAHs in 2cm-intervals-segments from Bonny Estuary, Niger Delta. Analysis showed that ΣPAHs/ΣN-PAHs in segments ranged from 8699-22528μg/kg and 503-2020μg/kg, respectively. Abundant-PAH/N-PAH are 2,6-dimethyl-naphthalene and benzo[a]acridine. PAHs/N-PAHs in the samples appeared to be from petrogenic and pyrogenic-sources. Petrogenic-PAHs/N-PAHs were predominated by 2-, 3-rings, alkylated-substituents, while, pyrogenic-PAHs/N-PAHs were dominated by 4-, 5-, 6-rings. Surface-sediments were dominated by petrogenic-PAHs/N-PAHs while, deeper-cores were heavily-contaminated with pyrogenic-PAHs/N-PAHs. ΣPAHs exceeded the ISQGs and PELs of CSQGs. Σ-quinoline/Σ-acridine exceeded the guidelines for protection of aquatic-life. Furthermore, there are concerns over toxic-ratios >70% in the estuary. Such surveys may be helpful in future sediment-management-decisions for contaminated-systems and long-term-monitoring of sediments to assess remediation/recovery.

Keywords: PAHs, N-PAHs, petrogenic, pyrogenic, Estuary, Niger Delta.

Capsule: Distinct sources of PAHs and N-PAHs exist in the Niger Delta ecosystem and, there are concerns over toxic ratios >70% in the oil rich region and the potential for adverse biological effects.

1. Introduction

For decades, polycyclic aromatic hydrocarbons (PAHs) contamination has been the focus of environmental investigation, mostly due to release from combustion, mining, industrial activities, and particularly oil and gas activities. PAHs are known mutagens, carcinogens, teratogens and genotoxins which tend to accumulate in sediments rather than water (Juhasz and Naidu, 2000; Santos et al., 2018; Davis et al., 2019) and their profiles in sediments are usually dominated by the hydrophobic 4–6-ring compounds (Wick et al., 2011). Studies have reported PAHs concentrations of 91,344 µg/kg (Paraiba do Sul Estuary, Brazil), 10–142,000 mg/kg (Wycoff/Eagle Habor, USA), 1,300–17,500 µg/kg (Persian Gulf, Kuwait), 20–344,600 µg/kg (Santander Bay, Spain) and 29–1059ng/g (Lake Macquarie, Australia) (Fowler et al., 1993; Stout et al., 2001; Viguri et al., 2002; Maioli et al., 2010; Idowu et al., 2020). Furthermore, concentrations of 65–331 µg/kg have been recorded in river sediments from the Niger Delta (Sojinu et al., 2010). However, in 2011, UNEP report revealed that total petroleum hydrocarbons (TPHs) in Niger Delta sediments ranged from 6,570–19,600 mg/kg which exceeded the Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN) value of 5,000 mg/kg, but, this did not give precise values of PAHs and the nitrogen-containing PAHs in the region.

In reality, PAHs do not exist alone; they are usually present as complex mixtures of many related compounds spanning a wide range of physico-chemical properties and toxicity to aquatic biota, and this varies widely depending on the sources and extent of degradation (Neff et al., 2005; Bandowe et al., 2019). While studies have reported the presence of PAHs in the aquatic environment, little is known about the historical trends and temporal fluxes of these contaminants or that of the heterocyclic (N-containing) analogues (N-PAHs) in the Niger Delta systems. N-PAHs have been known for some time (Blumer et al., 1977), and featured in the International Maritime Dangerous Goods Code dealing with packaged materials, where they were classified as toxic substances by the United Nations (Class 6.1) (UN 1973). N-PAH sources are similar to those of the PAHs (petroleum derived, combustion and biological sources). However, they can also be produced and used by industries (EC, 2011; IARC, 2012). It is now known that the heterocyclic aromatic compounds, such as N-PAHs, also contribute to the chemical inventory encountered in many contaminated sites and their polarity and lower k_{ow} values may lead to increased mobility and bioavailability compared to homocyclic analogues and, thus, exhibit potential toxic effects (EC, 2011; IARC, 2012; Anyanwu and Semple 2015a; 2016b; Anyanwu et al., 2017a). From both toxicological and epidemiological studies, many N-PAHs (quinoline, methyl-quinolines, benzo-quinolines, acridine, and dibenz-acridines) have been classified as toxins and human carcinogens (USDHHS, 2001; USEPA, 2011; EC, 2011; IARC, 1983; 2012; 2013). In addition, Jedy-Agba et al. (2012)

88 reported that Nigerian population is experiencing increased cancer incidents, some of which may be attributed to

89 environmental exposure and/or uptake of chemicals (PAHs/N-PAHs) through the food chain. Irrespective of

90 this, no study has been conducted in the Niger Delta to determine the occurrence, distributions, profiles, fluxes

91 and toxic ratios of PAHs and the N-PAH analogues in estuarine sediments.

92 An estuary is a semi-enclosed coastal waterbody that have a free connection with the open sea, extending from

93 rivers to the limits of the tidal zones, in which salt water is significantly diluted with fresh water derived from

94 land drainage (Pritchard, 1967; Santos et al., 2018). They are essential for majority of fauna, indicating global

95 importance due to their food sources and biodiversity. Yet, estuarine sediments, which act as food source and

96 final sink for many contaminants, have not been well investigated in developing countries. Nevertheless,

97 profiles of PAHs and N-PAHs in sediment cores can be used in historical records of estuarine contaminant

98 trends, fluxes and surface sediment recovery rates (USEPA, 2008).

99 Because the Niger Delta is of biological importance and possesses high socio-economic values, studies on

100 sources, trends, loads, distributions and toxicity of contaminants in sediments are necessary to evaluate the

101 impacts of oil exploration, transportation, waste disposal, industrial activities and consequently, pollution in the

102 area (Dienye and Sikoki, 2019). However, occurrence and distribution of PAHs and N-PAHs have not been

103 investigated in the region, especially the Bonny Estuary. Thus, in this study, vertical trend of PAHs and N-

104 PAHs in Bonny Estuary was investigated using 10 cm long sediment cores (sliced into 2 cm layers) collected

105 from three sampling stations, and control sediment (from underground drinking well). This is necessary for

106 ecological risk assessment and chemical action plan to protect human health and the environment.

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2. Materials and Methods

2.1 Study area

110 Niger Delta is an area of environmental interest not only because of economic development, but also because of

111 industrial activities with the related oil exploration and waste management. The Niger Delta region of Nigeria is

112 amongst the most sensitive and complex ecosystems in the world. Within it is the Bonny Estuary, a shallow

113 marine system (Data in Brief, Table 1; Fig. 1). Bonny Estuary is one of the largest arms of River Niger

114 emptying directly into the Atlantic Ocean. Furthermore, artisanal fishery is a major sustenance to communities

115 living on its banks. The water body has suffered from pollution and environmental degradation due to port

activities, human settlement, oil exploration / spills, operation of mechanized boats, deforestation and agricultural practices (Dienye and Sikoki, 2019). In addition, Bonny Estuary (BNN) receives effluents from cement factories, petroleum tank farms, medium size wharf, flour and sugar industries along its banks. These facilities may have contributed to the contamination of the aquatic ecosystem. Furthermore, the on-going degradation and stress would have resulted in changes in water quality, loss of biodiversity and extinction.

2.2 Sample collection.

This study was conducted in 2013. Sediment cores (10 cm long) were collected from 3 sampling stations (BNN 1, 2, 3) and sliced into 2 cm layers. Sediment samples were extruded vertically upward through the cores using an Uwitec manufactured Plexiglas's tubes mounted on a triple sediment corer type 90 mm. The collected core samples were pushed in 2 cm segments into 5 oz glass sample jars. Samples were identified by location and number beginning with 0–2 for the most-upper layer of sediment. Due to the level of oil pollution in the estuary and adjoining creek(s) / (tributaries), sediment sample was collected from an underground community well (drinking well) in the area to serve as control. Following collection and segmentation, samples were taken to the laboratory and oven dried at 50 °C, homogenised, sieved with 2 mm mesh size, stored in a container and transported to United Kingdom, where they were stored at 4 °C until analysis. In total, 15 sediment segments were analysed in this study (5 segments from each station); and the control (underground well sediment).

2.3 Chemicals

PAH and N-PAH standards were purchased from Thames Restek and Sigma-Aldrich, UK, respectively. Internal standard D_9-acridine was purchased from Cambridge Isotopes Laboratories, UK. HPLC grade acetonitrile, methanol and ethyl-acetate were used throughout the analysis. Calibration curves were performed at ten levels ranging from 2.5 to 2500 ng/ml for PAHs and six ranging from100 to 2000 ng/ml for N-PAHs in ethyl acetate. All calibrations had an accepted linearity (r^2 >0.99). Each calibration level contained internal standard (D_9-acridine) (2000 ng/ml). Individual target compound and their abbreviations are listed in (Data in Brief, Tables 2 and 3).

2.4 Extraction procedure

144   Pre-extractions were done with different solvents because of N-PAHs polarity, and a mixture of acetonitrile /

145   methanol was adopted for the experiment based on 73.5–106% recoveries. Because single extraction procedure

146   was used for the two physico-chemically varied compounds, recovery tests were performed by spiking known

147   concentrations (mixtures) into sediment samples. Samples, 1-2 g homogenised sediments, mixed with 2 g

148   anhydrous sodium sulphate ($NaSO_4$), was weighed into the pre-conditioned extraction thimble (after

149   conditioning for 4 h) and extracted in a Soxhlet device for 18 h using 300 ml solvent mixture of ACN/MeOH

150   (8:2). The extract was concentrated to 1 ml using rotary evaporator (Büchi Rotavap R-144). Clean-up of

151   concentrated extract was performed over a 5 mm glass column containing 6 g of 2% water deactivated

152   aluminium-oxide, topped with 1 g $NaSO_4$ (all baked overnight at 450 °C) (Anyanwu and Semple 2015b; 2016b).

153   The column was conditioned with 50 ml ACN/MeOH (8:2) and elution of extract was with 50 ml ACN/MeOH

154   (8:2). The elutes were rotary evaporated, solvent exchanged with ethyl-acetate and concentrate to 1 ml. Internal

155   standard (D_9-acridine) was added and samples were stored in the freezer until analysis with GC-MS (Anyanwu

156   and Semple 2015b; 2016b).

157   For quality assurance, samples were analysed in triplicates. All glass wares were soaked overnight in deacon,

158   washed, rinsed thoroughly with deionised water and dried. Prior use, all glass wares and cotton wool were baked

159   overnight in the furnace at 450 °C.

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161   *2.5 GC-MS analysis/Quantification*

162   GC-MS analysis was performed with Thermo Trace GC Ultra- DSQ. Column, ZB–Semi-Volatile 30 m × 0.25

163   mm × 0.25 μm (Phenomenex, USA) was used. The standards were injected (1 μl) into the GC SSL, splitless

164   mode. Source temperature was 250 °C; ion source was EI+ and MS interface was 300 °C. Different instrument

165   method was used for PAHs and N-PAHs analytes due to variation in physico-chemical properties. For PAHs,

166   the oven temperature was programmed at 65 °C for 5 min, 6 °C/min to 290 °C and 30 °C to 310 °C, held for 10

167   min. For N-PAHs, initial temperature was 70 °C for 2 min, 10°C/min to 150 °C, 4 °C to 250 °C for 10 min, and

168   50 °C to 300 °C, held for 10 min. Scan acquisition was performed by selected ion monitoring (SIM). Sample

169   concentrations were calculated from the peak area ratio between sample and internal standard, multiplied by the

170   reference factor between reference standard and internal standard. The instrumental detection limit (IDL) was

171   estimated to be 3 x the matrix-matched calibration curve (where the peak had signal-to-noise = 3) (Data in Brief,

172   Table 3) (Anyanwu and Semple 2015b; 2016b).

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2.6 Statistical analysis

Statistical analysis was carried out in SPSS 21 software package. Statistical analysis of PAHs and N-PAHs concentrations in the core segments with depth (cm) was determined by linear regression using depth profile (cm) as dependent variable. Comparison of PAHs and N-PAHs distribution across stations was also determined. Results were found to be statistically significant when $p<0.05$. Measured values were presented as mean ± standard error (SE) and graphs plotted with SigmaPlot 10.0 version.

3. Results

3.1 Concentration and distribution of PAHs in core segments from Bonny Estuary, Niger Delta

Mean concentrations of PAHs from the estuary is shown in Data in Brief, Table 4. From the analysis, sediment sample (control) collected from the community underground well in the area recorded high levels of PAHs. ΣPAHs in the well sediment was 4824 µg/kg. Surprisingly, B[a]P measured approx. 60 µg/kg. Perylene (a biogenic PAH) was also detected (Data in Brief, Table 4).

ΣPAHs measured in Bonny Estuary recorded high values ranging from 16635 µg/kg at 0–2 cm depth to 22528 µg/kg at 8–10cm depth (Data in Brief, Table 4). Data revealed that high ΣPAHs levels occurred at the bottom of the cores, mostly from depths 6-10 cm (Fig. 2). Although not consistent, a trend of increased concentration with increased depth was observed, and the core samples recorded high ΣPAHs values at 8–10 cm depth. Inspection of the core segments showed that individual PAH concentrations ranged from not detectable (nd) – 10069 ± 17 µg/kg. Low molecular PAHs contributed > 50% of the total-PAHs measured in the estuarine sediments (Fig. 4a). Alkylated–PAHs recorded high concentrations (Data in Brief, Fig. 1), with 2,6-dimethyl-naphthalene recording the highest concentration of 10069 ± 17 µg/kg in the segments (Data in Brief, Table 4). Furthermore, the biogenic PAH (perylene) was not detected in the samples, thus, did not contribute to the ΣPAHs measured. Distinct prints of hydrophobic PAHs (4-, 5-, 6-rings) was noted, with carcinogenic PAHs (B[a]A, chrysene, B[b]F, B[k]F, B[a]P, ID, and B[ghi]P) recording high values. Among the carcinogenic-PAHs, B[k]F measured the highest value of 2485 ± 4 µg/kg. In addition, HMW–PAHs dominated the estuary (> 40%) with BNN 1 and BNN 2 recording high concentrations at 6 cm, respectively (Fig. 4b).

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201   *3.2 Concentration and distribution of N-PAHs in core segments from Bonny Estuary, Niger Delta*

202   Data in Brief, Table 5 shows the mean concentrations of N-PAHs in Bonny Estuary core segments.

203   Concentrations of 8 N-PAHs in sediment sample from the underground well was 461 µg/kg. Similar to the

204   homologous PAHs, N-PAHs measured relatively high concentrations in control sediment from the community

205   well, with carcinogenic N-PAHs recording notable values (Data in Brief, Table 5).

206   In this study, N-PAHs exhibited lower values than the PAHs. Analysis of N-PAHs in core segments from the

207   estuary revealed that ΣN-PAHs ranged from 503 – 2020 µg/kg, and individual N-PAH concentrations ranged

208   from $39 \pm 0 – 376 \pm 18$ µg/kg. The 2- ring N-PAHs recorded low values of $39 \pm 0 – 167 \pm 70$ µg/kg. Among the

209   N-PAHs, B[a]A recorded the highest concentration of 376 ± 18 µg/kg. Also, dibenz-acridines and B[h]Q

210   recorded elevated values (Data in Brief, Table 5). Similar to parent PAHs, the highest ΣN-PAHs concentration

211   occurred at the bottom of the cores (depths 6–10 cm) (Fig. 3). Data revealed that high molecular weight /

212   carcinogenic N-PAHs dominated the estuarine segments. The 3 high molecular weight N-PAH analytes

213   accounted for > 60% N-PAHs measured in the estuary, with elevated concentrations recorded at BNN 3, depth

214   10 cm (Fig. 4d). Also, BNN 3 recorded greater levels of LMW and HMW N-PAHs (Figs. 4c, d)

215   To ascertain the distribution of PAHs and N-PAHs in the estuary, the data was analysed statistically using linear

216   regression. ANOVA showed statistically significant increase in ΣPAHs with increased depth (cm) ($p<0.05$).

217   Also, significant positive correlation was observed between PAHs and N-PAHs distribution in the estuary ($r =$

218   0.927, $p<0.01$).

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220   **4. Discussion**

221   Vertical profile of PAHs and N-PAHs were investigated in sediment core samples from Bonny Estuary, Niger

222   Delta, and an underground well sediment used as control. Analysis of 24 PAHs and 8 N-PAHs revealed mixed

223   petrogenic and pyrogenic sources from industrial processes, particularly the oil exploration industries (using the

224   LMW (2- to 3-ring) and HMW (4- to 6-ring) hydrocarbon predominance ratio classification) (Budzinski et al.,

225   1997). Furthermore, the study found elevated PAHs in control sediment collected from underground drinking

226   well in the area; revealing massive pollution and underground water contamination, probably due to vertical

227   migration of contaminants (UNEP, 2011).

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In this study, fingerprints revealed distinct peaks of 2-, 3-rings from alkylated-groups; suggesting that PAHs which dominated the core segments are from petrogenic sources (oil spills). Sojinu et al. (2010) in assessment of PAH ratios in the Niger Delta, reported that PAHs in most sediment samples were predominantly of petrogenic origin which may have resulted from oil pipeline leakages in the area. Elaborate fingerprinting methods have been used to differentiate petrogenic PAH sources in the environment (Budzinski et al., 1997; Neff et al., 2005) and alkylated substituents could also be useful in discerning PAHs from crude oil spills and other sources such as diesel fuel oil and weathered petroleum products (Neff, 2002; 2005). Also, alkyl-PAHs have been reported to be more abundant in petroleum contaminated sources than the parent PAH compounds (Stout et al., 2001; Neff et al., 2005). Thus, the high level of alkyl-PAHs (2,6-dimethyl-naphthalene, 2,3,6-trimethyl-naphthalene, 1-methyl-phenanthrene) (Data in Brief, Fig. 1) measured in this study, could be attributed to crude oil spills and/or by-products of parent PAHs biological or chemical degradation. Furthermore, elevated concentrations recorded at 0–2 cm (depth) indicates anthropogenic inputs (from oil spills), cement industry and/or shipping activities; and there is no indication that the aquatic systems are being covered by natural deposits of clean / uncontaminated sediments. This affirms the observation of Omokheyeke et al. (2015). In addition, high PAH concentrations measured at the bottom of the segments suggests massive pollution over time (UNEP, 2011; Omokheyeke et al., 2015).

Pyrogenic PAHs are formed during combustion processes; however, they are more complex and are dominated by 4- to 6-ring un-alkylated PAHs (Stout et al., 2001; Neff et al., 2005; Davis et al., 2019). It has also been reported that as oil products degrade, they become dominated by 4- to 6-ring PAHs resembling those found in pyrogenic sources (Stout et al., 2001; USEPA, 2008). In this study, the prominent presence of pyrogenic PAHs in the estuarine segments, suggests major anthropogenic sources (oil spills, shipping / cement bagging industry) and/or influx from surrounding polluted–Creeks during high tide. The is in harmony with other sediment studies in literature (Notar et al., 2001; Stout et al., 2001; Neff et al., 2005; Maioli et al., 2010; Domínguez et al., 2010; Sojinu et al., 2010; Nasher et al., 2013; Omokheyeke et al., 2015; Davis et al., 2019; Waszak et al., 2019; Idowu et al., 2020). Stout et al. (2001) recorded that creosote-impacted sediments in post-industrialized sediments contained high concentrations of pyrogenic PAHs associated with distilled / coal-derived liquids. However, it should be noted that high organic matter content, fast sedimentation rate (Omokheyeke et al., 2015), tremendous oil pollution, and human activities in the estuary can cause accumulation of PAHs; including pyrogenic ones. Also, the absence of biogenic PAH (in this study) may indicate a polluted system devoid of diagenic activities (Neff et al., 2005).

Concentration–profiles of PAHs and N-PAHs were different in the estuary. Variability could be expected due to differences in physico-chemical properties (chemical structure, chemical formula, molecular mass, solubility, K_{ow}, K_{oc}), anthropogenic sources (study area), environmental/human perturbation and/or sedimentation rate (Omokheyeke et al., 2015; Anyanwu et al., 2015a; 2015b). According to USEPA (2008), in contaminant profiling, maximum concentration of contaminants reveals the time at which the sediments were impacted by the contaminant source. In this study however, the observed increase in ΣPAHs and ΣN-PAHs with increased depth indicates immense and uncontrolled pollution over time, owing to industrial activities in the region (Martins et al., 2011; Vane et al., 2011; Idowu et al., 2020) and/or high sediment accumulation rate (dated 90s – 2000s) (Omokheyeke et al., 2015). USEPA (2008) documented that core sediments above the area of maximum concentration may show decreasing concentrations of contaminants as the source is limited and/or capped, and relatively clean sediments have to be deposited. However, this study revealed relatively high contamination of the upper segments indicating persistent anthropogenic input that has neither been limited nor capped (Data in Brief, Fig. 2).

The core samples showed a signature dominance of petrogenic PAHs in the upper sediments, while, deeper segments were heavily contaminated with un-alkylated/non-degraded compounds from weathering and/or industrial processes. This trend has been reported in literature (Stout et al., 2001; Neff et al., 2005; Domínguez et al., 2010; Davis et al., 2019). Stout et al. (2001) recorded dominance of HMW–PAH fingerprints mostly at the bottom halves of core segments and this was attributed to weathering. It has also been reported that surface sediment contamination of rivers located at industrial sites was dominated with urban run-off and weathered PAH fingerprints while, deeper sediments were heavily contaminated with relatively un-weathered and some pure-phase PAHs (USEPA, 2008). However, Shilla and Routh (2018) attributed the HMW-PAHs dominance to sequestration and deposition on bottom sediments.

This current study showed that B[a]A, dibenz-acridines, and B[h]Q were abundant in the estuary. The observed dominance of 3- and 4-rings N-PAHs is in agreement with Osborne et al. (1997) who reported that sediments contained higher proportions of 3-and 4-rings N-PAHs than air samples. This could be ascribed to the refractory nature of the compounds (Osborne et al. (1997), sequestration and/or persistence. Further assessment based on assumption that 1 µg/L = 1 µg/kg revealed that individual N-PAH concentrations measured in the drinking well sediment exceeded the 3.4 µg/L and 4.4 µg/L Canadian Council of Ministers of the Environment (CCME) interim guideline for quinoline and acridine in water, respectively; indicating potential for adverse effects. In addition, the positive correlation observed in this study suggests similar trend in fate and natural attenuation of

288   PAHs and N-PAHs in the aquatic environment. Furthermore, N-PAHs in the estuarine sediment recorded higher

289   values than other nitrogen heterocycles reported in literature (Table 2).

290   The estuary exhibited increased concentrations of PAHs with increase in depth (cm), and PAHs profile

291   portrayed distinct trends among the core segments. The first distinctive trend was observed at depth 2 cm. The

292   relative distribution at upper segment (0–2 cm) was proportionally very sharp indicating increased surface

293   sediment contamination. Distinct trends were also noted at 6 cm and 10 cm, respectively. Another trend was

294   observed in BNN 1, although to a varying level. The core consistently recorded elevated concentrations,

295   however, below 8 cm, a moderate but sharp elevation in contamination was found recording >22,000 µg/kg.

296   Generally, the estuary exhibited sharp PAHs increases at 0–2 cm, 4–6 cm and 8–10 cm, respectively (Fig. 2).

297   Examination of N-PAH profiles showed close resemblance to the homocyclic analogue. Similar trend of

298   consistent sharp curves at the upper (2 cm) and lower segments (4–6 cm, 6–8 cm) was noted. Also, BNN 1

299   showed a similar increase in concentration at 0–2 cm; however, at 6–8 cm, a different signature pattern was

300   observed; indicating elevated pollution. Furthermore, BNN 2 and BNN 3 showed a pattern of increased

301   concentrations at depths 4–6 cm, 6–8 cm and 8–10 cm, respectively (Fig. 3).

302   Temporal flux/load of the measured contaminants was further calculated by multiplying ΣPAHs/ΣN-PAHs

303   concentrations in the sediment layers by sediment accumulation rate, expressed in $ng/cm^2/year$ (Data in Brief,

304   Fig. 2) (Zaborska 2014; Omokheyeke et al., 2015). ΣPAHs/ΣN-PAHs showed variable deposition rates in the

305   estuary. The obtained results showed that relatively low PAHs/N-PAHs accumulation occurred in the 50s and

306   early 70s; implying that contaminant flux was low prior industrialization. However, high concentrations

307   emanated from early 90s to 2000s; agreeing with the massive oil spill and environmental perturbations reported

308   in the region (UNEP, 2011). The obvious PAHs/N-PAHs load at the surface sediments indicates persistent

309   contamination from anthropogenic inputs (oil spill and/or industrial activities). In addition, cement factories and

310   shipping harbour along the estuary banks (BNN 2; BNN 3) may have played significant role in generating

311   elevated levels of PAHs/N-PAHs in the estuary. However, immense deposition/flux observed during the late 30s

312   could be attributed to adverse weather conditions and/or flooding, since this happened during the pre-industrial

313   and/or crude oil pollution era. Studies on PAHs/N-PAHs flux have not been reported in the Niger Delta;

314   however, the findings agrees with the reports of Zaborska (2014) and Omokheyeke et al. (2015).

315   For risk assessment, individual PAH-levels were compared with the existing regulatory values of Canadian

316   sediment quality guidelines (CSQGs) (CCME, 1999). The results revealed that PAHs concentrations from the

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estuary exceeded the interim sediment quality guidelines (ISQG), and probable effect levels (PEL) (Table 1). Using the proportion of concentrations associated with effects in ranges below ISQG, between ISQG and PEL, and above PEL (CCME, 1999); percentage ratios of PAHs concentrations in the estuarine segments that are associated with adverse biological effects ranged from 51% – 83%; while, the drinking well sediment percentage ratios ranged from 20% – 70% (Table 1). This implies that PAHs concentrations in the drinking well may present a much higher risk, than the sediment concentrations in the estuary, because there could be a clearer pathway to human exposure (through consumptions). Bioavailability of sediment pollutants is another important factor, and LMW-PAHs are considered to be more bioavailable and acutely toxic to aquatic organisms (CCME, 1999). This suggests that PAHs in the sediments may have caused adverse biological effects such as decrease in benthic invertebrates, diversity, growth, development, physiological and behavioural changes (CCME 1999). However, elevated HMW-PAHs toxic ratios of 65% – 83% is a concern, because it could be the cause of increased cancer incidents experienced in the region.

For N-PAHs, quinoline and acridine have been listed in CCME (1999) water quality guidelines (with 3.4 and 4.4 µg/L interim guidelines for the protection of aquatic life). However, > 376 µg/kg measured in the estuarine segments is of great ecological concern. Furthermore, this study revealed that ΣPAHs concentrations in the estuarine segments was > 45% higher than DPR/EGASPIN intervention limit (Data in Brief, Table 4).

5. Conclusion

Remediation and monitoring the natural recovery as a risk reduction approach relies on understanding the trends, fate, fluxes and dynamics of contaminants in the environment. Analysis of sediment core samples from Bonny Estuary revealed trends and distinct sources that existed in the region. However, there are concerns over relatively high PAHs concentrations with toxic ratios over 70%, and N-PAH values greater than 3.4 and 4.4 µg/L in the oil-polluted region. Although natural attenuation may reduce sediment contamination, protecting the water column and biota from diffusion and advection of PAHs and N-PAHs from sediment; however, this may occur predominantly at the surface. Therefore, adequate control measures should be taken for the reduction of both the risk of re-suspension of contaminated sediments during high tide and the potential for contaminant transport into food chain.

Authors Contributions

346 FDS: Sample collection. INA: Methodology, Laboratory analysis, Writing original draft, Review and Editing.

347 KTS: Supervision, Review and Editing of first draft.

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479 **Table 1**

480 Toxicity comparison of concentrations measured in the Niger Delta with ISQGs and PELs for PAHs (µg/kg) in

481 estuarine sediments

LMW-PAHs	ISQG	PEL	This study				Toxic ratios (%)	
			Control	BNN 1	BNN 2	BNN 3	Control	BNN
Naphthalene	34.6	391	157.6	1322.2	1140.8	1475.7	19	71
2-Methylnaphthalene	20.2	201	64.9	445.1	1406.6	2178.9	23	82
Acenaphthylene	5.87	128	42.1	99.6	167.5	247.8	14	51
Acenaphthene	6.71	88.9	108.9	586.5	523.6	848.2	29	57
Fluorene	21.2	144	228.8	569.8	904.4	752.1	70	70
Phenanthrene	86.7	544	1232.4	665.2	1085.1	2347.9	23	28
Anthracene	46.9	245	159.7	333.7	279.9	210.7	20	75
HMW-PAHs								
Fluoranthene	113	1494	339.6	578.2	1030.9	415.5	20	80
Pyrene	153	1398	295.6	820.7	1324.3	516.1	19	83
Benz(a)anthracene	74.8	693	38.9	1200.1	1711.2	399.9	9	78
Chrysene	108	846	58.0	1069.5	598.7	355.7	9	72
Benzo(a)pyrene	88.8	763	61.7	127.7	386.6	343.5	8	22
Dibenz(a,h)anthracene	6.22	135	11.4	51.9	109.4	79.8	12	65

482 ISQGs = interim sediment quality guidelines, PELs = probable effect levels, BNN 1 = location 1, BNN 2 =

483 location 2, BNN 3 = location 3, Toxic ratios = the ratio of a chemical's LC_{50} estimated for baseline toxicity.

484

Table 2

Sediment comparison of N-PAHs concentrations in literature

Country	Aquatic system / site	2-ring	3-ring	4-ring	5-ring	ΣN-PAHs (µg/kg)	Reference
Nigeria	Bonny Estuary	39.3–168.6	43.7–241.8	75.7–376.8	66.9–354.4	461.9–2020.8	This study
Australia	Lake Macquarie	nd	-	-	-	36.4–291.7	Idowu et al., 2020
Germany	North Sea	1.0–66.4	3.9–63.5	7.0-36.0	-	1.0–125.0	de-Voogt and Lane, 2009
	Dutch Rivers	-	-	2.5-95.0	-	-	Kozin et al., 1997
China	Danshuei River	3.83–21.90	0.4–9.9	0.2–9.2	-	3.9–32.5	Chen et al., 2008
UK	Mersey	-	-	-	-	128.0–541.0	Osborne et al., 1997
USA	Lake Zuric	88.0	-	95.0	-	88.0–6000.0	Wakeman, 1979
	Puget Sound	-	43.0	-	-	-	Blumer et al., 1977
	Hamilton Harbour	-	-	-	-	8.0–63.0	Onusuka and Terry, 1989

| | St Mary River | - | - | - | - | 35.0–1200.0 | Fourlong and Carpenter, 1982 |

487   − = not determined

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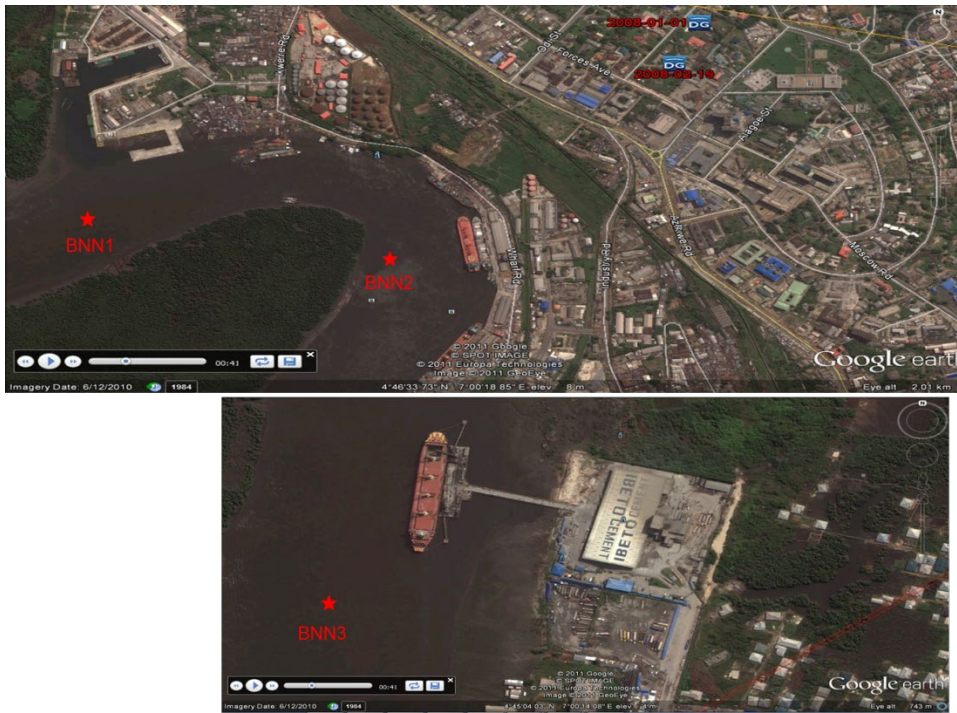
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490 **Fig. 1.** Map of Bonny Estuary in the Niger Delta showing sampling locations (Source: Google earth Retrieved,

491 December 2012). BNN 1 = location 1; BNN 2 = location 2; BNN 3 = location 3.

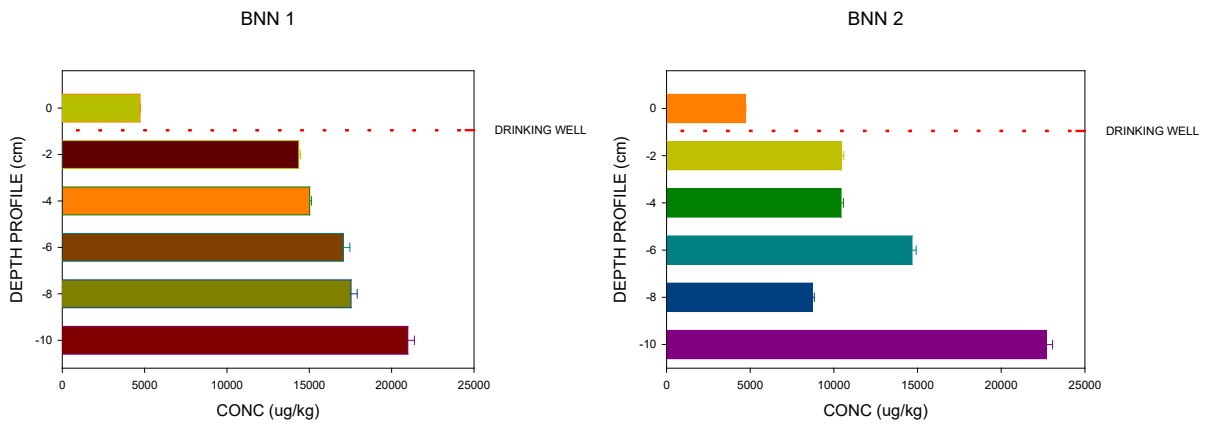492

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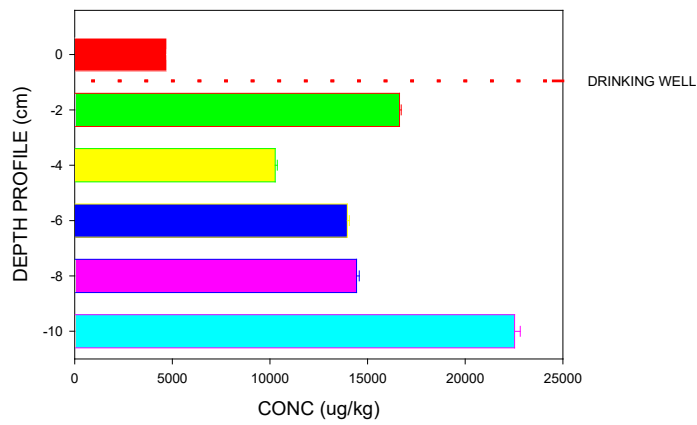496

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Fig. 2. Mean concentrations (μg/kg) of PAHs in core segments from Bonny Estuary, Niger Delta. Conc = concentration; BNN 1 = location 1; BNN 2 = location 2; BNN 3 = location 3. Y-axis depicts: 0 = control; –2 = 0–2 cm; –4 = 2–4 cm; –6 = 4–6 cm; –8 = 6–8 cm; –10 = 8–10 cm.

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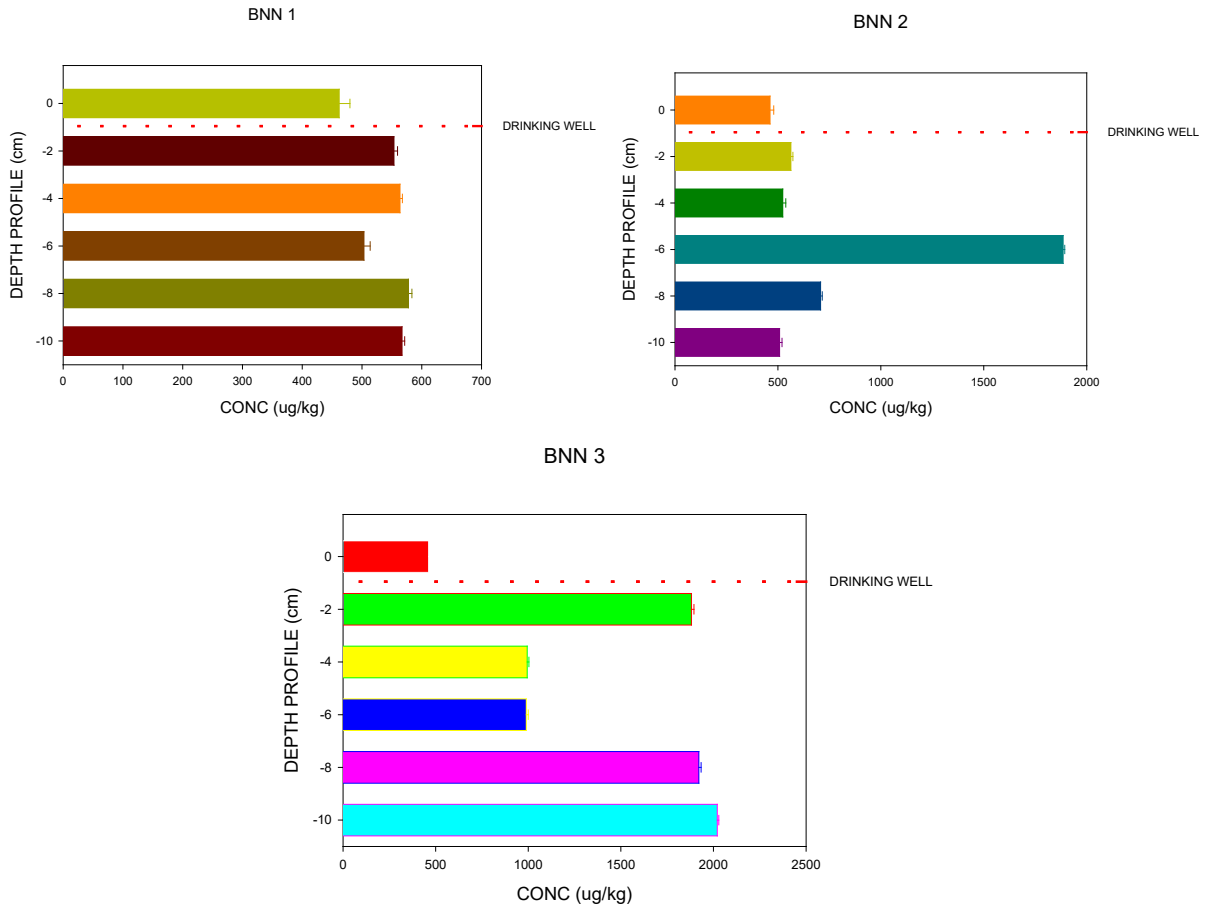
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Fig. 3. Mean concentrations (μg/kg) of N-PAHs in core segments from Bonny Estuary, Niger Delta. Conc = concentration; BNN 1 = location 1; BNN 2 = location 2; BNN 3 = location 3. Y-axis depicts: 0 = control; –2 = 0–2 cm; –4 = 2–4 cm; –6 = 4–6 cm; –8 = 6–8 cm; –10 = 8–10 cm.
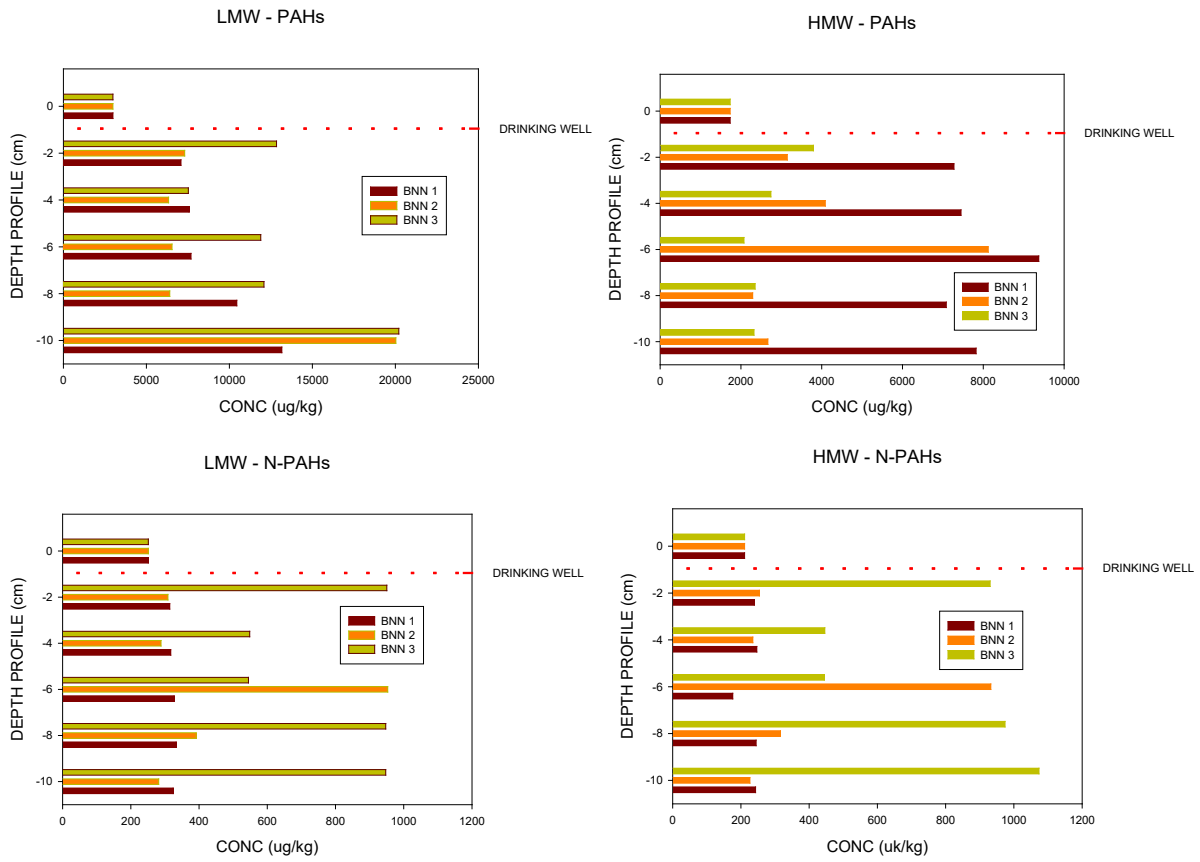
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Fig. 4. Mean concentrations (μg/kg) of LMW-HMW PAHs (**A, B**) and LMW-HMW N-PAHs (**C, D**) in core segments from Bonny Estuary, Niger Delta. Conc = concentration; LMW = Low Molecular Weight; HMW = High Molecular Weight; BNN 1 = location 1; BNN 2 = location 2; BNN 3 = location 3. Y-axis depicts: 0 = control; –2 = 0–2 cm; –4 = 2–4 cm; –6 = 4–6 cm; –8 = 6–8 cm; –10 = 8–10 cm.

539

1 **Data in Brief**

2

3 **Quantitative Assessment Data of PAHs and N-PAHs in Core Sediments from the Niger Delta, Nigeria**

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14

15 **Abstract**

16 Polycyclic aromatic compounds (PACs) pollution has been the focus of environmental research, mostly due to

17 their mutagenicity, carcinogenicity, teratogenicity and genotoxicity. Concentrations of polycyclic aromatic

18 hydrocarbons (PAHs) and the nitrogen-containing analogues (N-PAHs) (which tend to accumulate in sediments

19 rather than water) was measured in 2 cm intervals segments from Bonny Estuary, Niger Delta using GC-MS. Data

20 shows that PAHs/N-PAHs levels ranged from 8699–22528µg/kg and 503–2020µg/kg, respectively. Furthermore,

21 the data revealed that ΣPAHs levels in the estuarine segments was > 45% higher than DPR/EGASPIN intervention

22 limit. This gives insight on PAHs/N-PAHs contamination in the oil rich region.

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24 **Keywords:** PAHs, N-PAHs, Sediment cores, Niger Delta, Nigeria

25

26 **Specifications Table**

Subject area	Environmental Science

More specific subject area	Pollution
Type of data	Figures, Tables.
How data was acquired	GC-MS analysis (Thermo Trace GC Ultra- DSQ).
Data format	Analysed, Raw.
Parameters of Data Collection	Assessment of PAHs and N-PAHs levels in core sediments from Bonny Estuary, Niger Delta.
Description of Data Collection	Sediment samples were collected from 3 stations using Uwitec manufactured Plexiglas's tubes mounted on a triple sediment corer type 90 mm.
Data source location	Niger Delta, Nigeria
Data accessibility	Data available in the article
Related research article	I.N. Anyanwu, F.D. Sikoki, K.T. Semple. Risk assessment of PAHs and N-PAH analogues in sediment cores from the Niger Delta, Mar. Pollut. Bull. (2020). https://doi.org/10.1016/j.marpolbul.2020.111684.

Value of Data

❖ Data provides insight on PAHs/N-PAHs in the Niger Delta environment.

❖ The data could be useful to environmental scientists, toxicologists, limnologists and policy makers.

❖ Data can be compared with other scientific manuscripts and/or useful in monitoring of sediment recovery.

❖ Data revealed extent of PAHs/N-PAHs pollution and underground water contamination in the oil rich region.

1. **Data Description**

The data presents PAHs and N-PAHs concentrations encountered in contaminated sites [1–4].

Fig. 1 displays the LMW–ALKYL PAHs ranges (µg/kg) in core segments from Bonny Estuary, Niger Delta.

Fig. 2 reveals the temporal flux of PAHs and N-PAHs (ng/cm^2/yr) in core segments from Bonny Estuary, Niger Delta.

Table 1 describes the coordinates of sampling locations

Table 2 shows the analytes, abbreviations, chemical formula, chemical structure and molecular mass.

Table 3 illustrates the analyte list, abbreviations and detection limits.

43   Tables 4 and 5 highlights the profiles of PAHs and N-PAHs in segment core samples from the Niger Delta.

44   Fig. 1shows that Low molecular weight PAHs contributed > 50% ΣPAHs measured in the estuarine

45   sediments, with alkyl–PAHs recording high concentrations while high molecular weight N-PAHs recorded >

46   60% N-PAHs measured in the estuary and underground well recorded elevated values of PAHs/N-PAHs [5].

47   Fig. 2 portrays low PAHs/N-PAHs load in the 50s and early 70s; and high deposition in early 90s to 2000s

48   [5, 6–8]. Table 4 and 5 shows that ΣPAHs measured in the Estuary ranged from 16635 µg/kg (0–2 cm) to

49   22528 µg/kg (8–10cm) and ΣN-PAHs ranged from 503 – 2020 µg/kg with B[a]A, dibenz-acridines and B[h]Q

50   recording elevated values. Furthermore, data revealed that ΣPAHs concentrations in the estuary was > 45%

51   higher than DPR/EGASPIN intervention limit [5].

52

53   **2.   Experimental Design, Materials and Methods**
54   *2.1. Sample collection.*

55   Sample collection was as described in Anyanwu et al. [5]. In brief, sediment cores (10 cm long) were collected

56   from 3 stations in Bonny Estuary using Uwitec manufactured Plexiglas's tubes mounted on a triple sediment

57   corer (Table 1), and sliced into 2 cm layers. Due to high pollution in the estuary and the surrounding waters,

58   sediment sample was collected from an underground community well (drinking well) in the area to serve as

59   control. Following collection and segmentation, samples were taken to the laboratory, oven dried at 50 °C,

60   homogenised, sieved with 2 mm mesh size, stored in a container and transported to United Kingdom, where

61   they were stored at 4 °C until analysis [5].

62

63   *2.2. Chemicals*

64   Chemical standards (PAH and N-PAH) were purchased from Thames Restek and Sigma-Aldrich, UK,

65   respectively. Internal standard D_9-acridine was purchased from Cambridge Isotopes Laboratories, UK. HPLC

66   grade acetonitrile, methanol and ethyl-acetate were used for the analysis. Calibration curves were performed

67   at ten levels ranging from 2.5 to 2500 ng/ml for PAHs and six ranging from100 to 2000 ng/ml for N-PAHs

68   in ethyl acetate. Accepted linearity was obtained in all calibrations ($r^2 > 0.99$). The measured compounds are

69   listed in Tables 2 and 3 [5].

70

71   *2.3. Extraction procedure and GC-MS analysis/Quantification*

72   Sample extractions and GC-MS quantification was as reported in Anyanwu et al. [5]. In brief, 1-2 g sediments,

73   mixed with 2 g anhydrous sodium sulphate $NaSO_4$, was weighed into pre-conditioned extraction thimble

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(after conditioning for 4 h) and extracted in a Soxhlet device for 18 h using 300 ml solvent mixture of ACN/MeOH (8:2). Extract was concentrated to 1 ml (Büchi Rotavap R-144). Clean-up was performed over a 5 mm glass column containing 6 g of 2% water deactivated aluminium-oxide, topped with 1 g $NaSO_4$ (all baked overnight at 450 °C) [1, 4]. The column was conditioned with 50 ml ACN/MeOH (8:2) and elution was with 50 ml ACN/MeOH (8:2). Elutes were rotary evaporated, solvent exchanged with ethyl-acetate and concentrate to 1 ml. Internal standard (D_9-acridine) was added and samples were stored in the freezer until analysis with GC-MS. GC-MS analysis was performed with Thermo Trace GC Ultra- DSQ. ZB–Semi-Volatile column 30 m × 0.25 mm × 0.25 µm (Phenomenex, USA) was used. Scan acquisition was performed by selected ion monitoring (SIM) [5]. Data obtained from GC-MS analysis was used to derive the figures. The LMW PAHs/N-PAHs are 2- to 3-rings while, HMW group are 4- to 6-rings. Temporal flux was calculated according to Zaborska [7].

3. Authors Contributions

FDS: Sample collection. INA: Methodology, Laboratory analysis, Writing original draft, Review and Editing. KTS: Supervision, Review and Editing of first draft.

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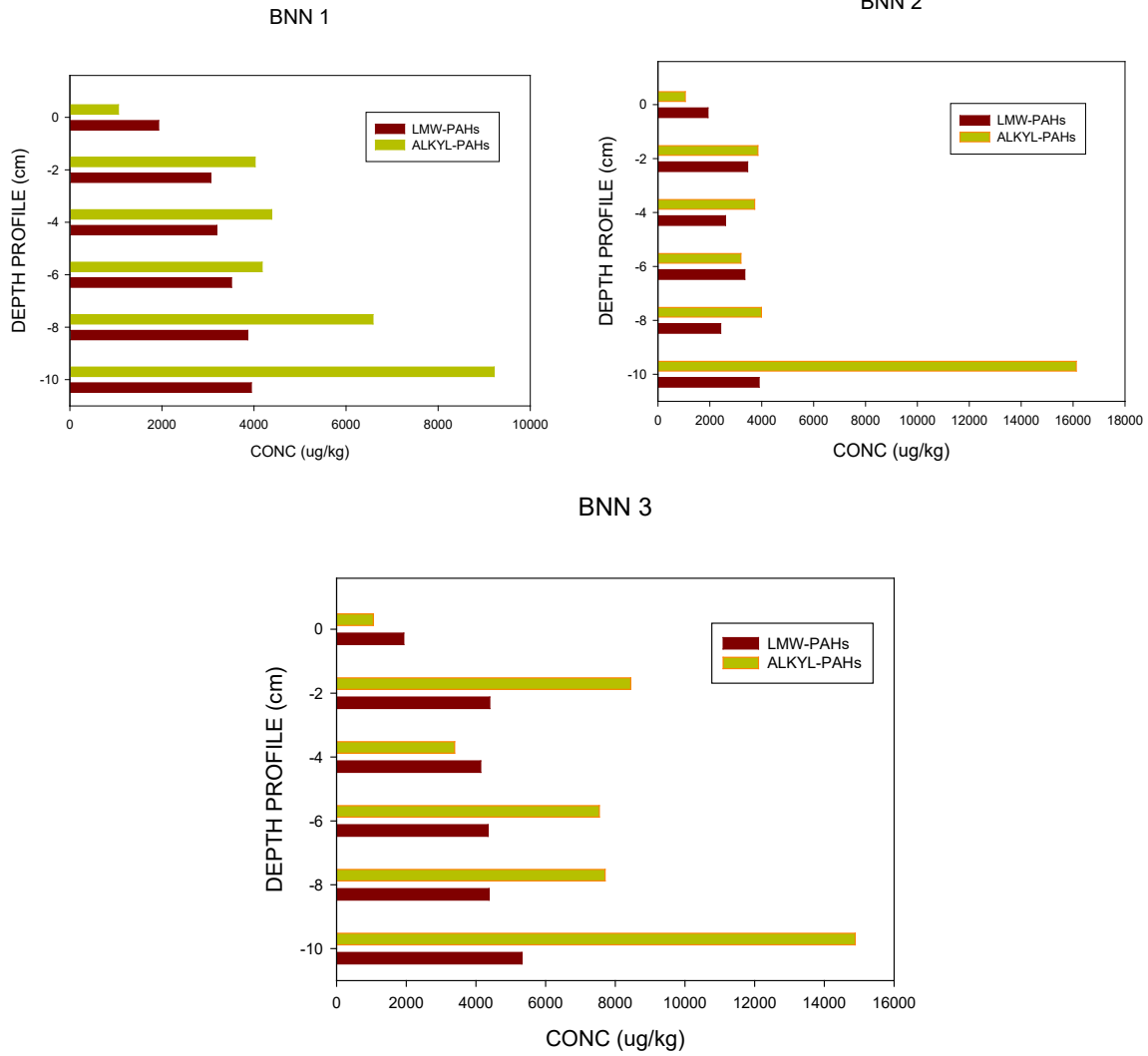
Fig. 1. LMW–ALKYL PAHs ranges (µg/kg) in core segments from Bonny Estuary, Niger Delta. Conc = concentration; LMW = Low Molecular Weight; ALKYL = Alkylated PAHs; BNN 1 = location 1; BNN 2 = location 2; BNN 3 = location 3. Y-axis depicts: 0 = control; –2 = 0–2 cm; –4 = 2–4 cm; –6 = 4–6 cm; –8 = 6–8 cm; –10 = 8–10 cm.

Fig. 2. Temporal flux of PAHs and N-PAHs (ng/cm^2/yr) in core segments from Bonny Estuary, Niger Delta. Y-axis depicts: 0 = control; –2 = 0–2 cm; –4 = 2–4 cm; –6 = 4–6 cm; –8 = 6–8 cm; –10 = 8–10 cm.

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Table 1

Description and coordinates of sampling locations

Location	Description	Coordinates	No of segment
BNN1	Station with no ongoing activity	N 4°46'33.73" E 7°00'.18.85"	5
BNN2	Port Harcourt Harbour (shipping)	N 4°46'02.43" E 7°00'.10.56"	5
BNN3	Area of Cement Bagging Factory	N 4°45'71.13" E 7°00'05.01"	5
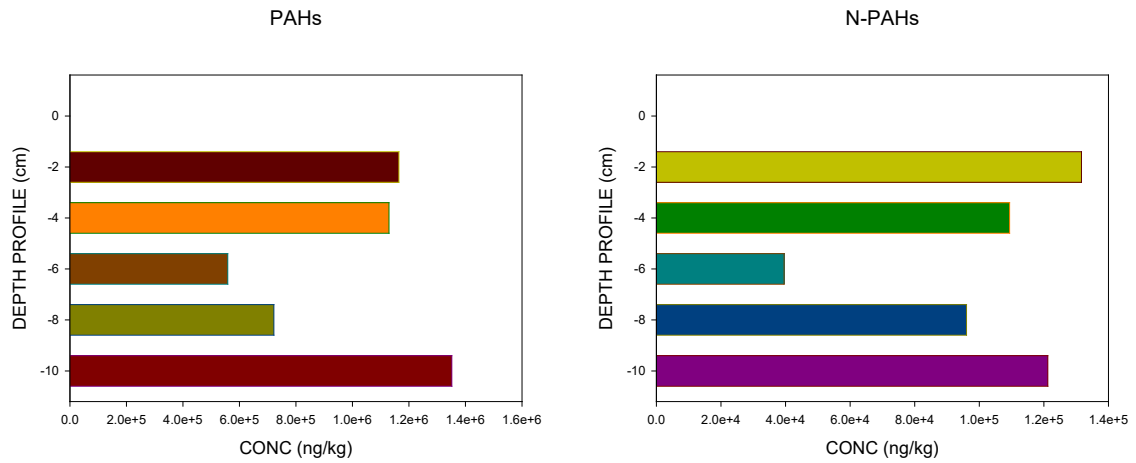
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Table 2

Analytes, abbreviations, chemical formula, chemical structure and molecular mass

Analyte(s) (**PAHs**)	Chem. formula	Chem. Structure	Mol. mass	Analyte(s)	Chem. formula	Chem. structure	Mol. mass
Naphthalene**＊**(N0)	$C_{10}H_8$		128.1	Benzo[k]fluoranthene**＊** (B[f]F)	$C_{20}H_{12}$		252.3
2-methyl-naphthalene (N1)	$C_{11}H_{10}$		142.2	Benzo[e]pyrene (B[e]P)	$C_{20}H_{12}$		252.3
1-methyl-naphthalene (N2)	$C_{11}H_{10}$		142.2	Benzo[a]pyrene**＊** (B[a]P)	$C_{20}H_{12}$		252.3
Biphenyl (Bph)	$C_{12}H_{10}$		154.2	Perylene (Per)	$C_{20}H_{12}$		252.3
2,6-dimethyl-naphthalene (N3)	$C_{12}H_{12}$		156.2	Dibenz[ah] anthracene**＊** (D[ah]A)	$C_{22}H_{14}$		278.3
Acenaphthylene**＊**(Acl)	$C_{12}H_8$		152.2	Indeno[123-cd] pyrene**＊** (ID)	$C_{22}H_{12}$		276.3
Acenphthene**＊**(Acc)	$C_{12}H_{10}$		154.2	Benzo[ghi]perylene**＊** (B[ghi]P)	$C_{22}H_{12}$		276.3
2,3,6-trimethyl naphthalene (N4)	$C_{13}H_{14}$		170.2	**N-PAHs**			
Fluorene**＊**(F0)	$C_{13}H_{10}$		166.2	Quinoline* (Quin.)	C_9H_7N		129.1
Phenanthrene**＊**(P0)	$C_{14}H_{10}$		178.2	Isoquinoline (Isoquin.)	C_9H_7N		129.1
Anthracene**＊**(AN)	$C_{14}H_{10}$		178.2	Benzo[h]quinoline* (B[h]Q)	$C_{13}H_9N$		179.2
1 methyl phenanthrene (P1)	$C_{15}H_{12}$		192.2	1,7-Phenanthroline (1,7-Phen)	$C_{12}H_8N_2$		180.2
Flouranthene**＊**(FL)	$C_{16}H_{10}$		202.2	4,7-Phenanthroline (4,7-Phen)	$C_{12}H_8N_2$		180.2
Pyrene**＊**(PY)	$C_{16}H_{10}$		202.2	Benzo[a]acridine* (B[a]A)	$C_{17}H_{11}N$		229.2
Benzo[a] anthracene**＊** (B[aA)	$C_{18}H_{12}$		228.2	Dibenz[a,h]acridine* (D[ah]A)	$C_{21}H_{13}N$		279.3
Chrysene**＊**(C0)	$C_{18}H_{12}$		228.2				
Benzo[b] fluoranthene**＊** (B[b]F)	$C_{20}H_{12}$		252.3	Dibenz[c,h]acridine* (D[ch]A)	$C_{21}H_{13}N$		279.3

16 EPA PAHs (**＊**); carcinogenic N-PAHs (*)

Table 3

Analyte list, abbreviations and detection limits.

PAHs	Abbreviation	IDL (ng/ml)	MDL (µg/kg)
Naphthalene	N0	0.1	25.7
2-methyl-naphthalene	N2	0.1	3.8
1-methyl-naphthalene	N1	0.3	ND
Biphenyl	Bph	0.5	23.7
2,6-dimethylnaphthalene	N3	0.9	46.2
Acenaphthylene	Acl	1.9	33.8
Acenaphthene	Ace	0.5	42.4
2,3,6-trimethyl-naphthalene	N4	1.5	48.4
Flourene	F0	1.3	32.3
Phenanthrene	P0	0.7	29.3
Anthracene	AN	0.2	41.1
1-methyl-phenanthrene	P1	2.5	23.3
Flouranthene	FL	0.1	24.5
Pyrene	PY	0.6	27.4
Benzo[a]anthracene	B[a]A	0.2	34.6
Chrysene	C0	0.1	27.9
Benzo[b]flouranthene	B[b]F	0.1	53.2
Benzo[k]flouranthene	B[k]F	0.2	67.8
Benzo[e]pyrene	B[e]P	0.1	20.7
Benzo[a]pyrene	B[a]P	0.2	24.3
Perylene	Per	0.2	36.1
Indeno[123-cd]pyrene	ID	0.5	19.6
Dibenz[ah]anthracene	D[h]A	1.5	11.8
Benzo[ghi]perylene	B[ghi]P	0.5	13.6
N-PAHs			
Quinoline	Quin	0.8	48.6
Isoquinoline	Isoquin	0.7	39.7
B[h]quinoline	B[h]Q	5.9	61.5
1,7-phenanthroline	1,7-Phen	1.9	54.3
4,7-phenanthroline	4,7-Phen	2.9	70.3
Benzo[a]acridine	B[a]A	0.2	82.2
Dibenz[ah]acridine	D[ah]A	0.1	75.3
Dibenz[ch]acridine	D[ch]A	0.2	76.1

IDL = instrument detection limit; MDL = method detection limit

187   **Table 4**

188   Profiles of PAHs in segment core samples from the Niger Delta

PAHs	Control (µg/kg)	BNN 1 (µg/kg)					BNN 2 (µg/kg)					BNN 3 (µg/kg)				
	0 cm	0-2 cm	2-4 cm	4-6 cm	6-8 cm	8-10 cm	0-2 cm	2-4 cm	4-6 cm	6-8 cm	8-10 cm	0-2 cm	2-4 cm	4-6 cm	6-8 cm	8-10 cm
N0	157.6 ± 3.2	1085.4 ± 63.2	1251.6 ± 77.2	1155.8 ±128.1	1155.8 ± 47.0	1322.2 ± 11.4	1140.8 ± 47.1	668.4± 7.9	758.0± 28.9	674.8 ± 44.1	671.1 ± 56.8	760.7 ± 78.9	1304.4 ± 90.0	1129.6 ± 15.6	1205.0 ± 10.3	1475.7 ± 71.1
N2	7.3 ± 0.0	408.6 ± 12.7	478.7 ± 9.8	486.1 ± 13.8	596.6 ± 19.7	695.1 ± 14.0	300.7 ± 1.9	282.6± 3.2	267.9 ± 29.4	320.31 ± 22.5	912.69 ± 86.7	210.6 ± 11.6	301.2 ± 5.6	835.3 ± 38.1	993.9 ± 7.9	1410.5 ± 46.1
N1	64.9 ± 0.9	234.5 ± 14.4	339.1 ± 15.1	327.9 ± 25.9	345.8 ± 17.9	445.1 ± 14.1	485.2 ± 22.8	461.4 ± 8.9	490.5 ± 15.4	550.2 ± 9.8	1406.6 ± 12.3	487.2 ± 30.9	586.3 ± 44.4	1386.0 ± 12.4	1480.4 ± 69.5	2178.9 ± 22.6
Bph	46.5 ± 0.1	312.1 ± 2.9	373.8 ± 25.1	384.4 ± 24.9	466.0 ± 30.0	518.1 ± 17.8	285.9 ± 18.2	253.9± 4.8	372.5 ± 9.6	209.5 ± 15.5	442.8 ±48.6	140.8 ± 1.2	223.5 ± 12.4	272.2 ± 26.9	265.8 ± 18.1	442.1 ± 2.9
N3	220.9 ± 0.3	1532.7 ± 33.3	1665.4 ± 57.9	1579.3 ± 71.5	3460.4 ± 50.1	5463.9 ± 99.0	2031.8 ± 16.6	2118.2 ± 41.9	1320.3 ±48.7	2281.1 ± 78.9	10069.1 ± 17.6	1370.0 ± 2.2	1289.8 ± 19.5	4064.1 ± 150.7	3748.4 ± 66.4	8148.5 ± 156.7
Acl	42.1 ± 0.1	76.8 ± 0.6	91.3 ± 3.9	86.7 ± 2.7	99.6 ± 4.5	99.6 ± 1.0	55.8 ± 3.1	67.8 ± 6.1	167.5 ± 63.9	62.7 ± 3.6	104.7 ± 0.4	174.5 ± 3.9	93.4 ± 1.9	113.9 ± 4.9	159.4 ± 5.4	247.8 ± 7.7
Acc	108.9± 0.8	340.0 ± 2.4	431.1 ± 41.4	462.8 ± 19.6	573.4 ± 22.2	586.5 ± 2.6	374.6 ± 24.2	345.1 ± 2.7	381.1 ± 20.1	283.3 ± 10.1	523.6 ± 36.8	281.1 ± 36.8	378.5 ± 26.5	418.3 ± 35.2	275.1 ± 150.8	848.2 ± 34.8
N4	736.3 ± 1.0	1218.5 ± 65.1	1314.0 ± 1.0	1181.8 ± 29.4	1611.6 ± 55.2	2080.2 ± 69.5	587.6 ± 17.9	587.8 ± 22.9	619.0 ± 49.4	522.7 ± 74.8	3199.7 ± 281.3	5721.7 ± 171.5	663.9± 16.9	811.3 ± 62.5	1166.2 ± 64.3	2731.5 ± 54.2
F0	228.8 ± 3.6	356.3 ± 8.6	339.2 ± 23.4	433.2 ± 11.7	569.8 ± 19.1	541.3 ± 30.4	396.5 ± 25.8	346.2 ± 17.1	414.7 ± 1.3	326.3 ± 10.1	904.4 ± 9.6	483.2 ± 2.4	574.9 ± 11.9	630.8 ± 37.9	752.1 ± 2.2	126.3 ± 19.1
P0	1232.4 ± 4.1	603.6 ± 6.0	409.3 ± 0.7	655.1 ± 16.0	665.2 ± 2.0	566.5 ± 43.3	996.6 ± 19.8	733.0 ± 13.2	974.7 ± 9.2	667.6 ± 24.1	1085.1± 21.9	2347.9 ± 141.6	1409.9 ± 23.2	1696.0 ± 12.2	1546.2 ± 42.1	1997.3 ± 105.0
AN	151.4 ± 0.7	288.7 ± 15.2	297.4 ± 0.1	334.3 ± 16.1	333.7 ± 2.6	308.7± 17.1	206.6 ± 5.8	192.1 ± 15.7	279.9 ± 7.6	193.7 ± 1.4	170.4 ± 0.8	210.7 ± 1.1	152.3 ± 21.1	88.2 ± 2.8	174.6 ± 1.0	180.5 ± 13.8
P1	151.5 ± 0.3	629.4 ± 51.9	586.2 ± 5.2	601.8 ± 2.8	570.1 ± 11.7	533.0 ± 2.0	446.9 ± 46.9	279.3 ± 4.9	500.1 ± 22.6	316.0 ± 5.9	537.4 ± 15.9	651.6 ± 95.8	546.8 ± 23.7	443.4 ± 9.6	318.6 ± 15.9	417.8 ± 1.9
FL	331.4 ± 0.5	525.3 ± 6.4	521.9 ± 30.2	578.2 ± 62.4	537.8 ± 9.8	568.8 ± 1.0	386.3 ± 37.4	481.1 ± 17.1	1030.9 ± 56.3	312.8 ± 13.0	339.2 ± 31.9	415.5 ± 47.1	277.0 ± 0.8	245.7 ± 9.9	216.9 ± 35.2	229.9 ± 20.9
PY	295.6 ± 0.7	731.1 ± 18.5	731.7 ± 14.1	820.7 ± 38.5	764.7 ± 10.6	813.1 ± 11.4	553.1 ± 49.6	671.4 ± 15.4	1324.3 ± 43.0	475.8 ± 20.9	521.4 ± 35.6	516.1 ± 55.2	473.8 ± 2.5	314.9 ± 0.7	241.4 ± 22.6	304.3 ± 60.9
B[a]A	38.9 ± 0.5	817.6 ± 52.7	866.6 ± 27.2	1200.1 ± 22.7	836.5 ± 24.4	964.5 ± 5.5	508.6 ± 84.7	1091.1 ± 34.7	1711.2 ± 26.8	424.6 ± 15.7	582.2 ± 36.7	399.9 ± 44.1	372.8 ± 2.7	213.6 ± 1.1	198.2 ± 7.7	233.8 ± 7.7
C0	56.9 ± 0.1	795.3 ± 65.7	784.9 ± 11.7	1069.5 ± 60.3	785.3 ± 31.8	905.0 ± 5.4	598.7 ± 41.4	144.1 ± 17.7	275.9 ± 20.9	63.9 ± 9.4	88.4 ± 2.4	355.7 ± 34.6	331.27 ± 10.7	192.1 ± 3.6	171.6 ± 1.9	194.9 ± 4.5
B[b]F	336.6 ± 1.4	1568.7 ± 113.4	1623.1 ± 76.7	2115.6 ± 48.1	1532.4 ± 22.7	1663.8 ± 52.1	336.5 ± 33.4	204.3 ± 12.6	1470.7 ± 52.1	298.5 ± 10.8	127.9 ± 4.1	1189.9 ± 65.6	741.0 ± 30.3	697.1 ± 1.8	884.7 ± 44.6	527.2 ± 1.1
B[k]F	410.1 ± 0.1	1990.8 ± 14.8	2000.7 ± 15.3	2485.2 ± 4.3	1767.4 ± 13.2	2021.5 ± 46.0	221.2 ± 81.2	673.5 ± 68.9	1068.7 ± 42.3	303.9 ± 57.9	483.3 ± 87.5	304.3 ± 23.2	241.1 ± 2.9	156.0 ± 0.2	195.8 ± 0.6	279.4 ± 15.0

B[e]P	35.8 ± 0.1	158.3 ± 10.0	173.5 ± 0.1	188.6 ± 5.1	160.7 ± 3.1	164.9 ± 4.1	120.4 ± 2.2	129.9 ± 1.5	175.5 ± 13.7	83.6 ± 1.5	127.9 ± 5.2	35.1 ± 3.5	45.0 ± 0.1	0.0 ± 0.0	67.2 ± 0.6	68.7 ± 3.9
B[a]P	59.5 ± 0.1	113.6 ± 3.9	123.4 ± 4.8	190.1 ± 1.1	120.1 ± 3.5	127.7 ± 0.8	130.7 ± 6.6	206.7 ± 13.5	386.6 ± 10.7	134.2 ± 4.7	128.2 ± 1.7	343.5 ± 43.6	101.8 ± 1.2	160.1 ± 1.6	216.5 ± 23.7	243.1 ± 5.9
Per	25.7 ± 0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
D[ah]A	10.2 ± 0.2	51.9± 1.1	32.2 ± 0.2	51.2 ± 2.2	49.8 ± 1.0	39.5 ± 4.5	31.1 ± 0.8	34.1 ± 0.4	109.4 ± 0.4	26.7 ± 1.1	31.6 ± 0.7	64.5 ± 1.3	32.8 ± 0.1	26.1 ± 0.6	54.0 ± 0.4	79.8 ± 0.8
ID	43.6 ± 0.1	219.7 ± 11.4	258.4 ± 19.3	311.4 ± 25.1	244.1 ± 2.4	246.3 ± 1.2	132.6 ± 3.9	203.8 ± 1.7	294.0 ± 6.9	80.2 ± 6.1	111.5 ± 3.4	99.2 ± 1.6	72.9 ± 1.8	42.7 ± 1.5	65.8 ± 0.6	94.0 ± 2.4
B[ghi]P	39.1 ± 0.1	301.1 ± 5.5	332.3 ± 1.5	363.1 ± 3.9	285.4 ± 4.7	306.8 ± 8.1	130.0 ± 4.1	249.0 ± 46.0	275.5 ± 3.5	87.1 ± 0.4	125.6 ± 3.1	72.2 ± 0.7	53.7 ± 3.9	27.7 ± 0.5	39.2 ± 1.6	68.6 ± 1.9
∑PAHs (μg/kg)	4824.7	14360.0	15025.8	17062.9	17532.2	20982.1	10458.2	10424.8	14668.9	8699.5	22694.8	16635.9	10268.1	13965.1	14437.0	22528.8
∑PAHs (mg/kg)	4.8	85.0					67.0					77.8				
DPR / EGASPIN Interv. Limit (mg/kg)	40.0	40.0					40.0					40.0				

189 Values = mean ± SE

190 ND = PAHs not detected during analysis

191 DPR = Department of Petroleum Resources

192 EGASPIN = Environmental Guidelines and Standards for the Petroleum Industry in Nigeria

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201   **Table 5**

202   Profiles of N-PAHs in segment core samples from the Niger Delta

N-PAHs	Control (µg/kg)	BNN 1 (µg/kg)					BNN 2 (µg/kg)					BNN 3 (µg/kg)				
	0 cm	0-2 cm	2-4 cm	4-6 cm	6-8 cm	8-10 cm	0-2 cm	2-4 cm	4-6 cm	6-8 cm	8-10 cm	0-2 cm	2-4 cm	4-6 cm	6-8 cm	8-10 cm
Quin*	43.8 ± 0.0	49.0 ± 0.1	49.7 ± 0.10	49.8 ± 0.4	50.3 ± 0.1	51.4 ± 0.5	54.5 ± 4.7	50.7 ± 1.1	168.6 ± 70.5	68.3 ± 19.4	49.8 ± 0.1	167.5 ± 70.8	96.4 ± 0.3	96.9 ± 0.1	167.7 ± 70.5	167.6 ± 71.2
Isoquin	34.6 ± 0.1	39.3 ± 0.0	39.5 ± 0.0	39.3 ± 0.2	39.7 ± 0.3	39.8 ± 0.1	42.9 ± 3.4	40.4 ± 1.0	136.7 ± 58.5	55.2 ± 15.8	39.4 ± 0.1	136.5 ± 58.6	78.2 ± 0.1	78.4 ± 0.0	136.8 ± 58.5	137.1 ± 58.8
B[h]Q*	63.3 ± 0.3	93.1 ± 1.0	95.6 ± 1.7	101.3 ± 0.5	104.1 ± 2.0	96.8 ± 1.0	76.5 ± 6.5	70.6 ± 2.0	221.5 ± 90.8	95.0 ± 24.0	67.1 ± 0.0	219.0 ± 90.8	128.9 ± 0.8	124.2 ± 0.2	214.4 ± 90.5	213.4 ± 90.8
1,7-Phen	43.9 ± 0.4	51.0 ± 0.0	50.6 ± 0.1	50.2 ± 0.9	56.3 ± 0.1	52.5 ± 0.6	57.6 ± 4.7	54.0 ± 1.0	185.2 ± 79.1	73.9 ± 21.8	53.0 ± 0.2	184.9 ± 78.8	105.8 ± 0.1	106.7 ± 0.3	186.5 ± 79.7	187.7 ± 80.3
4,7-Phen	65.6 ± 0.1	81.8 ± 0.0	81.7 ± 0.6	86.5 ± 5.9	82.7 ± 2.0	83.6 ±0.3	77.4 ± 5.8	72.9 ± 1.6	241.1 ± 101.5	99.0 ± 27.9	72.4 ± 0.1	242.6 ± 103.2	139.2 ± 0.0	138.6 ± 0.1	241.8 ± 102.6	241.4 ± 103.9
B[a]A*	75.7 ± 0.6	93.8 ± 3.0	101.3 ± 1.0	98.3 ± 2.5	99.4 ± 0.6	98.0 ± 1.3	88.3 ± 7.5	85.1 ± 1.9	330.0 ± 67.8	114.1 ± 31.8	81.5 ± 0.2	329.2 ± 69'8	160.9 ± 0.2	159.2 ± 0.1	376.8 ± 18.6	376.3 ± 18.7
D[ah]A*	68.1 ± 1.2	72.9 ± 0.0	72.8 ± 0.1	77.9 ± 0.0	72.9 ± 0.0	73.0 ± 0.3	85.3 ± 7.5	75.3 ± 1.6	304.4 ± 58.8	101.9 ± 29.6	72.4 ± 0.0	303.1 ± 57.6	144.7 ± 0.0	145.1 ± 0.2	302.2 ± 57.8	352.4 ± 8.2
D[ch]A*	66.9 ± 0.4	72.7 ± 0.6	72.5 ± 0.3	77. ± 0.7	72.3 ± 0.7	71.9 ± 0.3	80.5 ± 5.2	74.5 ± 1.8	297.9 ± 53.9	100.0 ± 28.0	72.6 ± 1.8	298.0 ± 56.2	140.4 ± 0.1	140.2 ± 0.0	295.0 ± 55.0	344.9 ± 5.0
∑N-PAHs (µg/kg)	461.9	553.6	563.7	503.3	577.7	567.0	563.0	523.5	1885.4	707.4	508.2	1880.8	994.5	989.3	1921.2	2020.8
∑NPAHs (mg/kg)	0.5	2.8					4.2					7.8				

203   * = carcinogenic N-PAHs (IARC, 2012; 2013)
204   Values = mean ± SE of triplicates

1   **Water, Air and Soil Pollution**

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3   **Baseline PAHs, N-PAHs and ^{210}Pb in Segment Samples from Bodo Creek: Comparison with Bonny Estuary,**

4   **Niger Delta**

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Abstract

Polycyclic aromatic hydrocarbons (PAHs), the nitrogen-containing analogues (N-PAHs), and lead 210 (^{210}Pb) were measured in 2-cm interval core segments from Bodo Creek to evaluate impact of oil pollution in the waterbody. PAHs and N-PAHs were measured by gas chromatography analysis with mass spectrometry detection, and ^{210}Pb activity concentration was determined by alpha spectrometry measurement. Data shows that ΣPAHs and ΣN-PAHs ranged from 12774.3 – 18470.2µg/kg and 524.0 – 672.2µg/kg, respectively. Concentrations were found to increase with increase in depth (cm). Petrogenic-PAHs predominated the surface sediment (with elevated levels of 2,3,6-trimethyl-naphthalene, phenanthrene and 1-methyl-phenanthrene), while, pyrogenic-PAHs dominated the deeper segments (with high levels of pyrene, benzo[a]anthracene, chrysene and benzo[k]fluoranthene). For N-PAHs, benzo[h]quinoline, 4,7-phenanthroline and benzo[a]acridine recorded high values. Chemicals comparison with values measured from Bonny Estuary revealed greater PAHs contamination in the estuary, while, N-PAHs recorded elevated values in the creek. ^{210}Pb activity concentration in the creek showed relatively low activity compared to the Estuary, and similar distribution with the aromatic hydrocarbons. The measured hydrocarbons were high and exceeded the Canadian sediment quality guidelines. However, there are concerns over toxic ratios >70% and radioactivity (EPR-D-values) >3 – 4.E ± 01 Bq measured in the polluted creek. This gives insight on the level of radioactivity, PAHs, N-PAHs, and PAHs toxic ratios in Bodo creek which would be useful in future remediation studies and/or monitoring the ability of sediments to recover under natural conditions.

Key words: PAHs, N-PAHs, ^{210}Pb, Toxic ratios, Bodo Creek, Bonny Estuary, Niger Delta

Introduction

Industrial development generated significant economic growth in Nigeria, however, the resulting anthropogenic activities have caused severe pollution that has damaged the country's fragile ecosystems. One of the affected ecosystems is Bodo Creek, located in Bodo town, Niger Delta. This fragile ecosystem was exposed to two oil spillages in 2008 resulting from major leaks (large spills) in the Trans Niger Pipeline operated by the Shell Petroleum Development Company of Nigeria Ltd (SPDC) (Bonte et al., 2019). Previous reports showed that the number of oil spills in the area has been relatively low prior to the 2008 SPDC spill. Example, about 17 spills were reported between 1986 and 2008 of which 10 were from illegal activities; however, the spills increased to > 30 in 2010–2011 (Gundlach, 2018; Little et al., 2018; Bonte et al., 2019). Prior the oil pollution saga, the creek and mangroves are known to provide nutrient filtration, fish nursery, bird staging areas and local transport corridors for human access to vital natural resources such as food and wood for building, fuel and making of cultural artifacts (Fentiman & Zabbey, 2015).

Oil pollution in Bodo town has been of serious concern and researchers are recently investigating the impacts of oil spills on Bodo Creek and its surrounding (Zabbey & Uyi, 2014, Vincent-Akpu et al., 2015; Zabbey et al., 2017; Little et al., 2018; Gundlach, 2018; Chikere et al., 2019; Bonte et al., 2019; Anyanwu et al., 2020a, b). For example, Zabbey & Uyi (2014) studied the intertidal soft-bottom macro-zoobenthic community and observed that surface and infauna communities suffered severe reduction, with species reduced by 81% after spills, and two of the sampled stations recorded no taxa at all. Vincent-Akpu et al. (2015) assessed the heavy metals content and physico-chemical properties of water and sediments from Bodo Creek and reported that some metals and physico-chemical parameters were higher than the World Health Organization permissible limit for both surface and drinking water; making the water unfit for domestic use. Little et al. (2018) measured total aliphatic and aromatic hydrocarbon concentrations in sediments and reported high contamination of TPHs, aliphatic and aromatic hydrocarbons in the equivalent C_{12}–C_{44} range (EC_{12}– EC_{44}) in surface and subsurface sediments. Bonte et al. (2019) found high levels of TPHs in sediments from Bodo Creek at depth 2–4 m, and reported that majority of petroleum hydrocarbons are restrict to depths <50 cm. Also, Anyanwu et al. (2020a, b) recorded elevated PAHs and N-PAHs concentrations, with toxic values >70% in core sediments from Bodo surrounding estuary (Bonny Estuary). In addition, UNEP report on Ogoniland revealed TPHs range of 6,570–19,600 mg/kg in Bodo sediments which exceeds the Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN) limit of 5,000 mg/kg

80   (UNEP, 2011). However, these reports on Bodo ecosystem did not give precise level of PAHs in the Creek. Also,

81   the nitrogen-containing analogues and ^{210}Pb levels were not considered.

82   N-PAHs occur in conjunction with PAHs in contaminated sediments and despite the known toxicity of some N-

83   PAHs, their occurrence in segment cores remain to be elucidated in developing countries (Anyanwu & Semple,

84   2015; 2016; Anyanwu et al., 2017). Recent studies have reported quantitative ecological and human health risk

85   associated with the presence of PAHs and their nitrogen-containing analogues in aquatic environment, particularly

86   sediments, where they partition (Tian et al., 2017; Idowu et al., 2020; Vila et al., 2020; Anyanwu et al., 2020a, b).

87   However, such data is lacking for ecosystems in Bodo, Niger Delta. Furthermore, polar PAHs (such as N-PAHs)

88   have been reported to be more leachable than parent PAHs of the same number of rings; thus, causing misleading

89   information on the precise risks of contaminated sites when only PAHs were analyzed (Larsson et al., 2018).

90   Moreover, ^{210}Pb which is a naturally occurring radionuclides of uranium (^{238}U) radioactive series, can also be

91   released from industrial processes (Jia, 2013). ^{210}Pb and its grand-daughter radionuclide (^{210}Po) provide major

92   internal natural radiation dose to man (Ebaid & Khater, 2006), and are included in the group of most highly toxic

93   radioisotopes. Owing to its chemical properties, ^{210}Pb cannot be removed from the human body, and exposure (via

94   ingestion or inhalation) of the radionuclide can be fatal or result to effects that are life threatening (IAEA, 2006).

95   According to Bonczyk (2013), ^{210}Pb is an extreme mobile nuclide, and there are dangers of it escaping into the

96   environment from areas of sediment deposition or industrial activities. Thus, the risk of this radioisotope migrating

97   becomes quite significant as it could find its way into the aquatic environment, resulting in contamination of

98   surface drinking water, underground water and/or bioaccumulation in aquatic organisms/seafoods.

99   Irrespective of the potential risks, ^{210}Pb, PAHs and the nitrogen heterocyclic aromatics (N-PAHs) have received

100   little attention in the Niger Delta. In addition, toxic ratios which is the ratio of a chemical's LC_{50} estimated for

101   baseline toxicity have not been ascertained for these chemicals in the region. This current study provides the first

102   overview of PAHs, N-PAHs and ^{210}Pb activity composition and distribution in core sediments from Bodo Creek

103   and ^{210}Pb activity composition and distribution in core sediments from Bonny Estuary. The study measured their

104   concentrations, quantitative risk assessment in the core samples, and the PAHs/ N-PAHs data were compared with

105   values obtained from the surrounding Bonny Estuary. This is necessary for identification of potential health risk

106   posed to humans, and provide helpful information to support management of the ecological systems of the region.

107   PAHs are known to incorporate into the sediment through association with particulate matter. Due to variety of

108   aquatic organisms living in contact with sediments, sediments are important exposure routes for these organisms

109   to PAHs (CCME, 1999). Thus, Canadian interim sediment quality guidelines (ISQGs) and probable effects levels

110   (PELs) for PAHs was used to evaluate the degree to which adverse biological effects are likely to occur as a result

111   of exposure to PAHs in the Bodo core sediments. Toxic ratios indicate the distribution of chemical concentrations

112   in marine and estuarine sediments that are associated with adverse biological effects and no adverse biological

113   effects. The percentages indicate proportions of concentrations associated with effects in ranges below the ISQG,

114   between the ISQG and the PEL, and above the PEL (CCME, 1999).

115

116   **Materials and Methods**

117   **Study Area**

118   Bodo area is part of the interconnected Bonny and Andoni river systems that are tidal embayment un-connected

119   to the Niger Delta distributary system (NDES, 1997; Little et al., 2018). Bodo creek (brackish in nature), located

120   in Bodo town, Gokana Local Government Area (Ogoniland) on the Bonny River, Niger Delta has over 228,828

121   residents (Little at al., 2018). The sediment core samples were collected in 2013 (Fig 1). The creek and close

122   shorelines / tributaries which are used by fishers on a regular basis have experienced repeated oil pollution over

123   time (Baker, 1983; Little et al., 2018).

124

125   **Sample Collection**

126   Sample collections were based on the methods used by Anyanwu et al. (2020a, b). Briefly, sediment core samples

127   were collected from Bodo Creek and the surrounding Bonny Estuary, and extruded vertically upward from Uwitec

128   manufactured Plexiglas's tubes mounted on a triple sediment corer type 90 mm. The samples were pushed in 2 cm

129   segments with number 0–2 for the most surface sediment sample. Due to pollution in the creek and its surrounding,

130   sediment was collected from underground community well (drinking well) to serve as control. Following

131   segmentation, samples were oven dried, sieved with 2 mm mesh size and transported to United Kingdom, where

132   they were stored at 4 °C until analysis. A total, 10 segments were analyzed in this study (5 from each location),

133   and the control (underground drinking well sediment).

134

Chemicals

136   As reported in Anyanwu et al. (2020a), PAH and N-PAH standards were purchased from Thames Restek and

137   Sigma-Aldrich, UK, respectively. Internal standard D_9-acridine was purchased from Cambridge Isotopes

138   Laboratories, UK. HPLC grade acetonitrile, methanol and ethyl-acetate were used. Calibration curves were

139   performed at ten levels ranging from 2.5 to 2500 ng/ml (for PAHs) and six ranging from100 to 2000 ng/ml (for N-

140   PAHs) in ethyl acetate. All the calibrations had an accepted linearity ($r^2 > 0.99$).

141

Sample Analysis

Core Sediments Physico-chemical Parameters Determination

144   Bodo core sediments were analyzed using the Mastersizer 2000 (Malverin Instrument), pH was with pH radiometer

145   model PHM 93 (Copenhagen) and organic matter content by loss of ignition method. The cation-exchange capacity

146   (CEC) was determined using Flame Photometer 410 (Sherwood), based on Ross & Ketterings (1995) (Table 1).

147

Core Sediments Sample Extraction

149   Sample extractions, GC oven and MS parameters were as recorded in Anyanwu et al. (2020a, b). In brief, 1-2 g

150   sediment samples were mixed with 2 g anhydrous sodium sulphate ($NaSO_4$) and weighed into the pre-conditioned

151   extraction thimbles. The thimbles containing the samples were extracted for 18 h using 300 ml solvent mixture of

152   ACN/MeOH (8:2) in Soxhlet device. The extracts were rotary evaporated to 1 ml using Büchi Rotavap R-144.

153   Clean-up of extracts were carried out using 5 mm glass column containing 6 g of 2% water deactivated aluminum-

154   oxide, topped with 1 g $NaSO_4$ (Anyanwu et al., 2020a, b). Columns were first conditioned with 50 ml ACN/MeOH

155   (8:2) and elution of extracts was with 50 ml ACN/MeOH (8:2). Eluted samples were concentrated and solvent

156   exchanged with ethyl-acetate. Internal standard (D_9-acridine) was added, and samples were stored in the freezer

157 until analysis with GC-MS. GC-MS analysis was performed with Thermo Trace GC Ultra- DSQ. ZB–Semi-

158 Volatile column 30 m $\times$ 0.25 mm $\times$ 0.25 μm (Phenomenex, USA). Scan acquisition was by selected ion monitoring

159 (SIM). Source temperature was 250 ºC; ion source EI+ and MS interface 300 ºC. Different methods were used for

160 the PAHs and N-PAHs analytes. In PAH samples, oven temperature was set at 65 ºC for 5 min, 6 ºC/min to 290

161 ºC and 30 ºC to 310 ºC, held for 10 min. In N-PAH samples, initial temperature was 70 ºC for 2 min, 10ºC/min to

162 150 ºC, 4 ºC to 250 ºC for 10 min, and 50 ºC to 300 ºC, held for 10 min. Sample concentrations were calculated

163 from the peak area ratio between sample and internal standard, multiplied by the reference factor between reference

164 standard and internal standard (Anyanwu et al. 2020a, b).

165

Core Sediments ^{210}Pb Analysis

167 ^{210}Pb isotope is relatively common in sediments, but environmental pollution from oil industry has been an

168 exposure problem for humans. In this study, polonium (Po) analysis of sediment using total dissolution and copper

169 was used to analyze ^{210}Pb in the sediments by assuming equilibrium with its granddaughter ^{210}Po. The method

170 aims at complete dissolution of the sediment samples (although some organic material may remain undigested),

171 therefore the total ^{210}Pb was analyzed supported and unsupported (Bonczyk, 2013; Szarlowicz, 2019).

172 Here, approximately 0.5 g dry and homogenized samples were weighed into a PTFE beaker and 50 μg tracer

173 (^{209}Po) was added as a yield monitor/tracer prior to total digestion of the samples. Then, 6 M HCl (10 ml) was

174 added and carefully taken to dryness. The samples were allowed to cool, and 20 ml H_2O_2 was added and taken to

175 dryness. After, 10 ml each of concentrated HCl, HNO_3 and HF were added to the samples, respectively. Samples

176 were then refluxed for approximately 4 h before taken to dryness, and 25 ml 6 M HCl was added, and gently heated

177 for 30 min to get the isotopes into solution. The digested samples were later filtered through a hardened filter (to

178 remove undigested materials) and plated with 2.5 x 2.5 Cu disc by heating at 95 ºC with stirring for 3 h. The discs

179 were allowed to dry overnight and activity of ^{210}Pb was determined by alpha spectrometry.

180

Statistical Analysis

182 Statistical analysis was carried out in SPSS 21 software package. Statistical analysis of PAHs and N-PAHs

183 concentrations in the core segments with depth (cm) was determined by linear regression using depth profiles (cm)

184   as dependent variables. Values were presented as mean ± standard error (SE) and graphs plotted with Sigma-Plot

185   10.0 version.

186

187   **Results and Discussion**

188   **Physico-chemical Parameters of Core Sediments from Bodo Creek**

189   Physico-chemical characteristics of the core sediments is presented in Table 1. From the sediment texture, Bodo

190   Creek can be categorized as silt loam and silt clay loam, respectively; with high organic matter content (> 5.0%).

191   A trend of decreased pH and CEC with increase in depth was also observed. High organic-rich systems are known

192   to provide good sedimentary environment for the accumulation of organic contaminants; hence, the high-level

193   PAHs and N-PAHs concentrations observed in the creek. Furthermore, the fine-particle sizes (silt and clay) and

194   high organic matter may have facilitated the accumulation of aromatic hydrocarbons in the core segments. Elevated

195   organic matter content was measured at depths 0–2 and 6–8 cm, corresponding with the high level of PAHs, N-

196   PAHs and ^{210}Pb concentrations measured in the segments. Biological productivity and/or high sedimentation rate

197   could be ascribed (Anyanwu et al., 2020a, b).

198

199   **Concentrations of PAHs in Core Sediments from Bodo Creek**

200   The underground community well sediment (used as control) recorded ∑PAHs of 4719.50, with elevated values

201   of carcinogenic PAHs (including benzo[a]pyrene), and phenanthrene measured highest value of 1231.90 ± 4.06.

202   Although the control sample recorded high levels of PAHs, ΣPAHs from Bodo core segments ranged from 12774.7

203   μg/kg at depth 4–6 cm to 18470.20 μg/kg at 6–8 cm, while individual PAH concentrations ranged from not

204   detectable (nd) – 24980 ± 27.30 μg/kg (Table S2). Among the PAHs, 1-methyl phenanthrene measured the highest

205   concentration of 24980 ± 27.30 μg/kg at depth 6–8 cm. B[a]P was not detected at depths 4–10 cm, however, 61.70

206   ± 0.50 μg/kg was measured in the control sample. Similarly, perylene was not detected at depths 6–10 cm.

207   Assessment of PAHs distribution showed that elevated concentrations (>21%) occurred at the upper segment (0–

208   2 cm) (Fig 2a). Variation of low molecular weight (LMW) and high molecular weight (HMW) was noted. The

209   measured LMW-PAHs ranged from 5.90 ± 0.00 – 1231.90 ± 4.06 (control) and 47.90 ± 1.70 – 24980 ± 27.30

8

210   (Bodo creek), while HMW-PAHs ranged from $11.40 \pm 0.70 - 427.60 \pm 1.70$ (control) and, nd $- 1806.90 \pm 26.10$

211   (Bodo creek). Data showed that LMW-PAHs were prominent in the Creek (>68.1%) compared to HMW-PAHs

212   (Fig 3a). Also, GC-MS fingerprint depicts dominance of 2-, 3-rings and the methyl-group (2,6-dimethyl-

213   naphthalene, 2,3,6-trimethyl-naphthalene and 1-methyl-phenanathrene) than the parent compounds (Table S2).

214   Diversity and abundance of PAHs and their methyl-derivatives have been recorded in PAH-contaminated

215   environmental samples (Tian et al., 2017; Larsson et al., 2018; Idowu et al., 2019; Vila et al., 2020; Anyanwu et

216   al., 2020a). However, PAHs fingerprints from Bodo Creek shows to primarily composed of weathered crude oil.

217   Bonte et al. (2019) in their study (vibra-coring and analyses used to monitor and verify when Phase 1 clean-up of

218   Bodo creek was adequately performed) found high levels of TPH in sediments from Bodo Creek at depths 2–4 m.

219   The authors reported heavy TPH fractions (>C16) dominating the pre- and post-clean-up conditions with reports

220   that majority of petroleum hydrocarbons are restricted to depths <50 cm. Hence, high concentrations of PAHs

221   measured at the bottom segments (this study) suggests massive pollution over time. Furthermore, elevated

222   concentrations observed at depth 0–2 cm indicates persistent anthropogenic input. These could be the cause of

223   underground water contamination (due to vertical migration of contaminants) as reported by UNEP (2011) on

224   Ogoniland. This also agrees with the elevated values measured in control samples (this study). Dominance of

225   LMW-PAHs in the Creek agrees with the reports that lighter aromatics concentrations increase significantly with

226   depth due to their higher volatility and potential to penetrate fine-grained sediments compared to the heavier

227   hydrocarbons (Little at al., 2018; Bonte et al., 2019). In addition, ANOVA showed statistically significant increase

228   in ΣPAHs with increased depth (cm) ($p<0.05$). The toxic ratio (the ratio of a chemical's LC_{50} estimated for baseline

229   toxicity) of PAHs (µg/kg) in Bodo Creek was derived based on the interim sediment quality guidelines (ISQGs)

230   and probable effect levels (PELs) for marine/estuarine sediment (CCME, 1999). The results showed that PAHs

231   toxic ratios in the area ranged from 8% – 78% (control) and 8% – 83% (Bodo creek) (Table 2). This suggests that

232   PAHs in the drinking well and creek may present higher risk, because there could be a clearer pathway to human

233   exposure (via consumptions) and/or risk of bioaccumulation in fishes and other seafoods (Anyanwu et al., 2020a).

234   This could be the cause of increased cancer incidents experienced by Nigerian population according to Jedy-Agba

235   et al. (2012) and Anyanwu et al. (2020a).

236

237   **Concentrations of N-PAHs in Core Sediments from Bodo Creek**

9

238 ΣN-PAHs in the core samples ranged from 524.00 μg/kg at depth 2–4 cm to 672.20 μg/kg at depth 6–8 cm, while

239 individual N-PAHs ranged from 35.50 ± 0.00 – 79.90 ± 0.50 (control) μg/kg and 39.50 ± 0.40 – 161.20 ± 3.90

240 μg/kg (Bodo creek); with carcinogenic N-PAHs recording high concentrations (Table S3). B[a]A measured the

241 highest concentration of 161.20 ± 3.90 μg/kg at depth 6–8 cm. The highest ΣN-PAH concentrations occurred at

242 the bottom of the segments (depth 6–10 cm) (Fig 2b). Like PAHs, data showed that LMW-N-PAHs (B[h]Q, 4-7-

243 Phen) and B[a]A were abundant in the creek (Fig 3b; Table S3). High concentrations of N-PAHs and dominance

244 of 3-, 4-ring N-PAHs have been reported (Osborne et al., 1997; Tian et al., 2017). Anyanwu et al. (2020a, b) also

245 observed that core segments from Bonny estuary Niger Delta contained elevated levels of N-PAHs, and dominance

246 of 3-, 4-ring N-PAHs. Potential risk to human health and associated consequences may be higher for the polar

247 PAHs because they elicit direct toxic effects at comparatively low concentrations (Goodale et al., 2015; Lemieux

248 et al., 2015; Anyanwu et al., 2017; Tian et al., 2017; Vila et al., 2020; Anyanwu et al., 2020a). Values of aromatic

249 hydrocarbons measured in Bodo Creek were compared with those in Bonny Estuary (Table 3), and greater PAHs

250 contamination was recorded in the estuary. However, N-PAHs measured elevated values in the creek (Table 3).

251

Concentrations of ^{210}Pb isotope in Core Sediments from Bodo Creek

253 ^{210}Pb isotope ratio determined for Bodo aquatic ecosystem ranged from 75.1 ± 2.45 – 89.78 ± 2.82 activity/Bq.

254 Similar to the PAHs and N-PAHs distribution, increased activity concentration was recorded at upper 0–2 cm and

255 lower 6–8 cm depth (Figs 2a, b; 4a). Variation was observed when compared with values measured in Bonny

256 Estuary (Fig 4b). The Estuary showed higher range of 127.34 ± 4.00 – 138.47 ± 4.35 activity/Bq. The recorded

257 ^{210}Pb activity in the two aquatic ecosystems were higher than the EPR-D-value recommendation (IAEA, 2006).

258 Although ^{210}Pb toxicity have not been reported in the Niger Delta environment, there are concerns over the

259 implications of this isotope migrating to underground water sources and/or its bioaccumulation in fishes and other

260 seafoods consumed in the region.

261 This study found that PAHs, N-PAHs and ^{210}Pb activity concentrations in the core segments recorded increased

262 levels with increase in depth (cm) (Figs 2, 4). Also, contaminant distribution showed distinct trend at depths 0 –2

263 cm and 6–8 cm, respectively. Similarity in sources could be attributable. This reveals the dangers of industrial

264 activities and oil spills in the Niger Delta environment. There are also concerns over risk of re-suspension of

265 contaminated sediments during high tide and the potential for contaminant transport into food chain. In addition,

266 PAHs concentration measured in Bodo segments exceeds the DPR/EGASPIN intervention limit of 40 mg/kg

267 (Table S2), and Environment Canada Sediment Quality Guidelines for PAHs (Table S1) (CCME, 1999).

268 Similarly, Little et al. (2018) reported that samples collected from Bodo Creek exceeded Environment Canada

269 Sediment Quality Guidelines for the sum of sixteen PAHs. However, there are serious concerns over toxic ratios

270 >70% (Table 2), and radioisotope D-values >3 – 4.E ± 01 Bq, with half-life of 22.3 years in the creek / estuary

271 and its implications on human and ecosystems health.

Conclusions

274 The baseline analysis of core sediment samples shows a picture of dangers associated with crude oil contamination

275 in the Niger Delta. There are concerns over elevated concentrations of N-PAHs and PAHs toxic ratios >70% and

276 radioisotope D-values >3 – 4.E ± 01 Bq, with half-life of 22.3 years in the creek. The findings of this study will

277 help in understanding the levels, sources, and ecological risks of PAHs, N-PAHs and ^{210}Pb activity in Bodo creek

278 and surrounding ecosystems, and provides valuable information for remediation and/or implementing pollution

279 reduction policies thereby protecting water resources and human health in the region. It is further recommended

280 that adequate risk assessment of environmental samples (water, sediments, fishes, seafoods) should focus on both

281 PAHs, N-PAHs, ^{210}Pb radioactivity and other radionuclides, which will provide support to future research in

282 environmental monitoring and/or bioremediation of contaminated systems in the Niger Delta.

289 **Authors Contributions**

290 FDS: Sample collection. INA: Methodology, Laboratory analysis, Writing original draft, Review and Editing.

291 KTS: Supervision, Review and Editing of first draft.

292

293 **Declaration of Interest**

294 The authors declare that they have no known competing interests.

295

296 **Data Availability Statement**

297 All data generated or analyzed during this study are included in this published article [and its supplementary
298 information files].

299

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391 **Table 1:** Physico-chemical Characteristics of Core Segments from Bodo Creek

Sample	Depth (cm)	O M (%)	pH	CEC (cmol+/kg)	Texture	Clay (%)	Silt (%)	Sand (%)
Control	-	0.08	7.23	1.63	Silt Loam	20.65	51.91	27.44
Bodo Creek	0-2	5.14	6.73	11.00	Silt Loam	20.42	76.79	2.79
	2-4	5.10	6.50	11.70	Silt Loam	27.41	76.79	17.46
	4-6	5.02	6.34	10.20	Silty Clay Loam	31.51	55.36	13.13
	6-8	6.36	6.17	10.90	Silty Clay Loam	28.94	65.95	5.11
	8-10	5.38	5.33	8.50	Silty Clay Loam	30.48	55.14	14.38

392 OM = organic matter content; CEC = cation-exchange capacity; pH = hydrogen ion level

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409 **Table 2:** Toxic Ratios and Comparison of PAHs (µg/kg) in Bodo Creek with the ISQGs and PELs for

410 Marine/Estuarine Sediments (CCME 1999)

PAHs	Sediment Quality Guidelines (mg/kg)		This Study (mg/kg)		Toxic Ratios (%)	
LMW-PAHs	ISQG	PEL	Control	Bodo	Control	Bodo
Naphthalene	34.6	391	132.7	362.5	19	19
2-Methylnaphthalene	20.2	201	55.5	230.6	23	82
Acenaphthylene	5.87	128	40.5	64.5	14	14
Acenaphthene	6.71	88.9	106.1	331.8	57	57
Fluorene	21.2	144	213.6	767.6	70	70
Phenanthrene	86.7	544	1231.9	3128.5	78	78
Anthracene	46.9	245	159.7	397.8	20	75
HMW-PAHs						
Fluoranthene	113	1494	339.6	1016.8	20	80
Pyrene	153	1398	295.5	1068.0	19	83
Benz[a]anthracene	74.8	693	37.5	1806.9	9	78
Chrysene	108	846	58.0	1615.5	9	72
Benzo[a]pyrene	88.8	763	61.7	38.5	8	8
Dibenz[ah]anthrcene	6.22	135	11.4	30.0	12	12

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412 ISQGs = interim sediment quality guidelines, PELs = probable effect levels, Toxic ratios = the ratio of a

413 chemical's LC_{50} estimated for baseline toxicity.

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Table 3: Sediment Comparison of PAHs and N-PAHs Levels in Bodo Creek and Bonny Estuary

Depth (cm)	∑PAHs (µg/kg)		∑N-PAHs (µg/kg)	
	Bodo Creek	Bonny Estuary	Bodo Creek	Bonny Estuary
0 – 2	15829.40	14360.0	535.80	553.6
2 – 4	13727.70	15025.70	524.00	563.7
4 – 6	12774.30	17062.90	549.00	503.3
6 – 8	18470.20	17532.10	672.20	577.7
8 – 10	16215.50	20982.00	630.80	567.0
Reference	**This study**	**Anyanwu et al. 2020a, b**	**This study**	**Anyanwu et al. 2020a, b**

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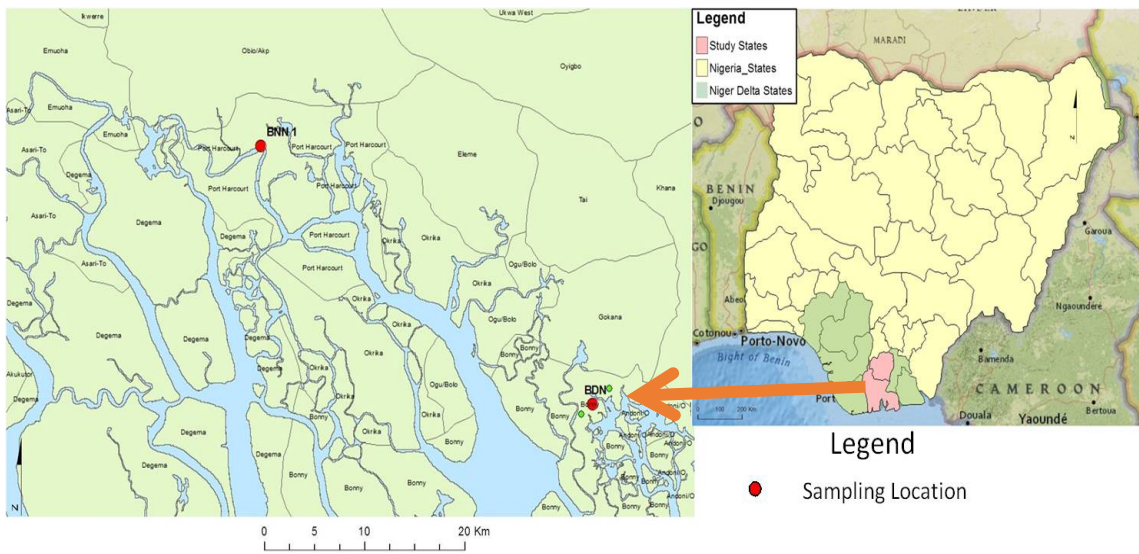
Fig 1. Map of Nigeria showing the study area and sampling locations. BDN = Bodo Creek, BNN = Bonny

Estuary.

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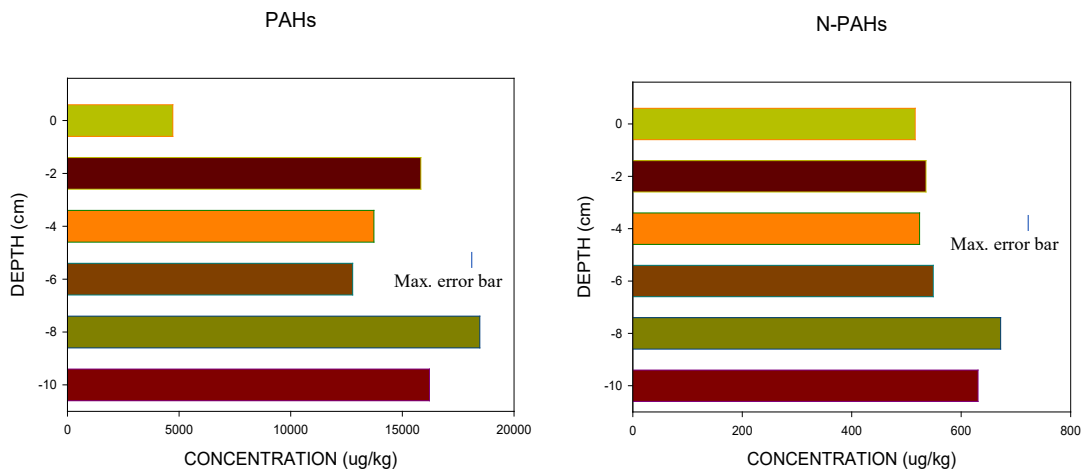
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Fig 2. Mean concentrations (μg/kg) of PAHs and N-PAHs in core segments from Bodo Creek, Niger

Delta. Y-axis shows: 0 = control; –2 = 0–2 cm; –4 = 2–4 cm; –6 = 4–6 cm; –8 = 6–8 cm; –10 = 8–10 cm.
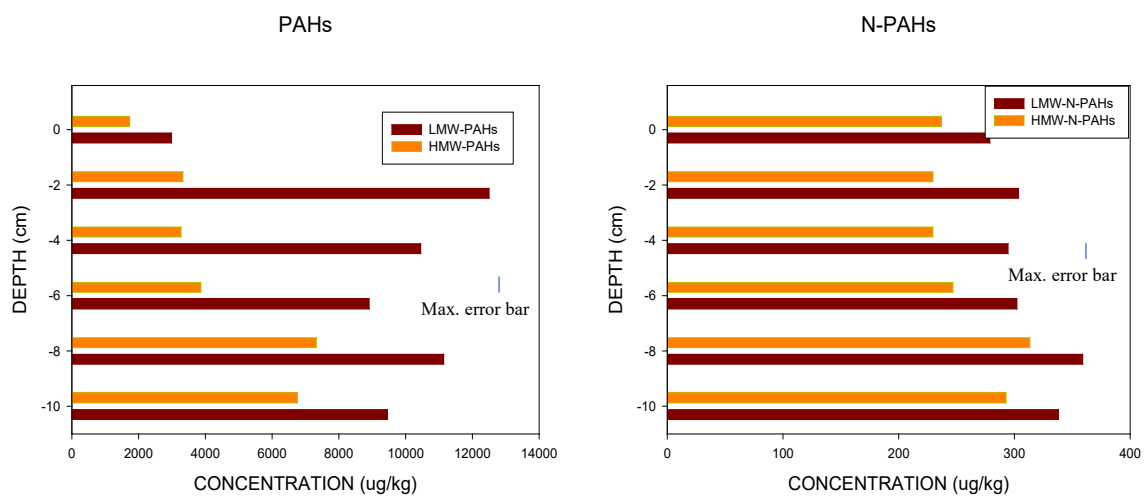
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Fig 3. Mean concentrations (μg/kg) of LMW–HMW PAHs and N-PAHs in core segments from Bodo Creek, Niger Delta. LMW = Low Molecular Weight; HMW = High Molecular Y-axis depicts: 0 = control; –2 = 0–2 cm; –4 = 2–4 cm; –6 = 4–6 cm; –8 = 6–8 cm; –10 = 8–10 cm.
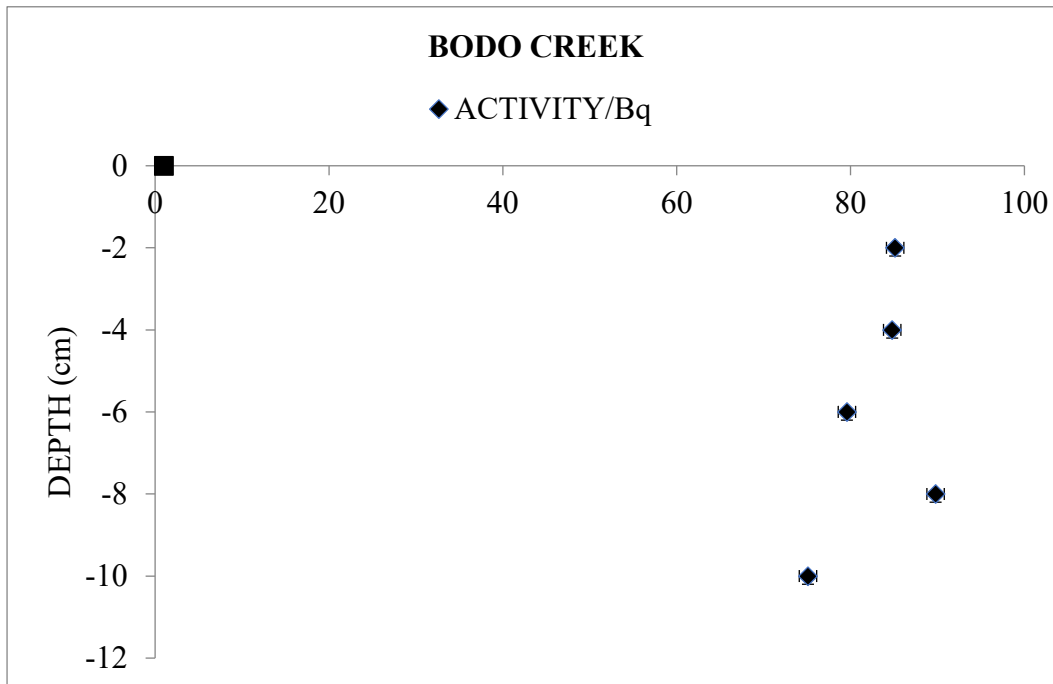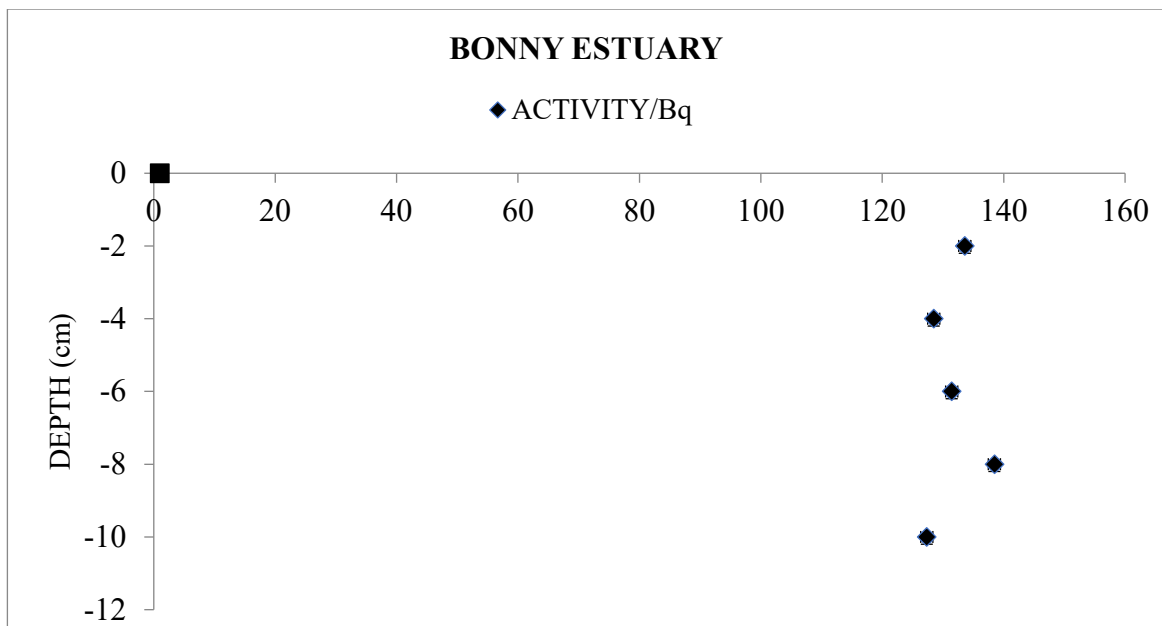
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Fig 4. Radioactivity concentrations of ^{210}Pb in core segments from Bodo Creek and Bonny Estuary, Niger Delta.

Y-axis depicts: 0 = control; –2 = 0–2 cm; –4 = 2–4 cm; –6 = 4–6 cm; –8 = 6–8 cm; –10 = 8–10 cm.