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Spatial characteristics and risk assessment of polychlorinated biphenyls in surficial sediments around crude oil production facilities in the Escravos River Basin, Niger Delta, Nigeria

Chukwujindu M.A. Iwegbue[a,*], Ernest Bebenimibo[a], Godswill O. Tesi[b], Francis E. Egobueze[c], Bice S. Martincigh[d]

[a] Department of Chemistry, Delta State University, P.M.B. 1, Abraka, Nigeria
[b] Department of Chemical Sciences, University of Africa, Toru-Orua, Bayelsa State, Nigeria
[c] Environment Department, Nigerian Agip Oil Company, Rumueme, Port Harcourt, Nigeria
[d] School of Chemistry and Physics, University of KwaZulu-Natal, Westville Campus, Private Bag X54001, Durban 4000, South Africa

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ABSTRACT

In this study, the concentrations of 28 polychlorinated biphenyl (PCB) congeners, including 12 dioxin-like PCBs and 7 indicator PCBs, were determined in sediments around oil production facilities in the Escravos River Basin of the Niger Delta in Nigeria. The aim was to describe the spatial patterns, sources, and ecosystem risks associated with exposure to PCBs in sediments of this river basin. Gas chromatography-mass spectrometry (GC–MS) was used to determine the concentrations of PCBs in the sediments. The Σ28 PCB concentrations in sediments from the Escravos River Basin ranged between 226 and 31,900 ng g^{-1} with a median concentration of 2300 ng g^{-1}. The results indicated that sediments around crude oil production facilities, such as, wellheads, flow stations, and truck lines, had significantly higher levels of Σ28 PCBs ($p < 0.05$) than those collected near residential communities within the river basin. The median concentrations of PCB homologues in sediments from this river basin followed the sequence: hexaPCBs > penta-PCBs > tetra-PCBs > hepta-PCBs > tri-PCBs > di-PCBs > deca-PCBs > octa-PCBs > nona-PCBs. The risk assessment of PCBs in sediments from this river basin suggest very high potential risks for both organisms and humans.

1. Introduction

Polychlorinated biphenyls (PCBs) are widespread synthetic organic pollutants that are capable of exhibiting ecotoxicity effects far away from their point of emission due to their ability to undergo long distance migration. At the Stockholm Convection of 2001, PCBs were among the compounds classified as persistent organic pollutants (POPs). These compounds are environmentally stable (i.e. they are resistant to microbial- and photo-degradation), lipophilic and have the capacity to bioaccumulate in organs and tissues of organisms, and magnify through the food chain (Nouira et al., 2013). PCBs show a wide variety of toxic effects, including cancer, hepatic effects, dermal and ocular effects, immunotoxicity, neurological disorders, and endocrine-disrupting characteristics, as well as, reproductive and developmental disorders (Iwegbue et al., 2019). PCBs have been used as electrical transformer oils, insulating liquids in power capacitors, plasticisers in paints, plastics and rubber products, pesticide extenders, fire retardants, hydraulic fluids, cutting oils, printing inks, carbonless copy papers, casting agents, sealants, and wood floor finishes (Batterman et al., 2009; Halfadji et al., 2013; Iwegbue et al., 2019). The PCB load in the environment comes through atmospheric circulation and deposition, as well as discharges from anthropogenic processes such as waste incineration, effluents from industrial processes, leaks from electrical transformers containing PCBs, oil leaks and surface runoffs, and disposal of PCB-containing consumer products (Duan et al., 2013).

In the aquatic setting, PCBs are adsorbed onto particulate matter, and undergo sedimentation processes and, consequently, build up in sediments. Sediment has a high retention capacity for PCBs, owing to its surface area, and can be a secondary source of PCBs to the overlying water body through mechanical or physical turbation or changes in the geochemical properties of the sediments (Sakan et al., 2017). Therefore, sediment plays a significant role in determining the fate and global cycling of PCBs. In addition, PCBs enter the human food chain through interactions between sediment, benthic organisms and edible fish.

* Corresponding author.
E-mail address: cmaiwegbue@delsu.edu.ng (C.M.A. Iwegbue).

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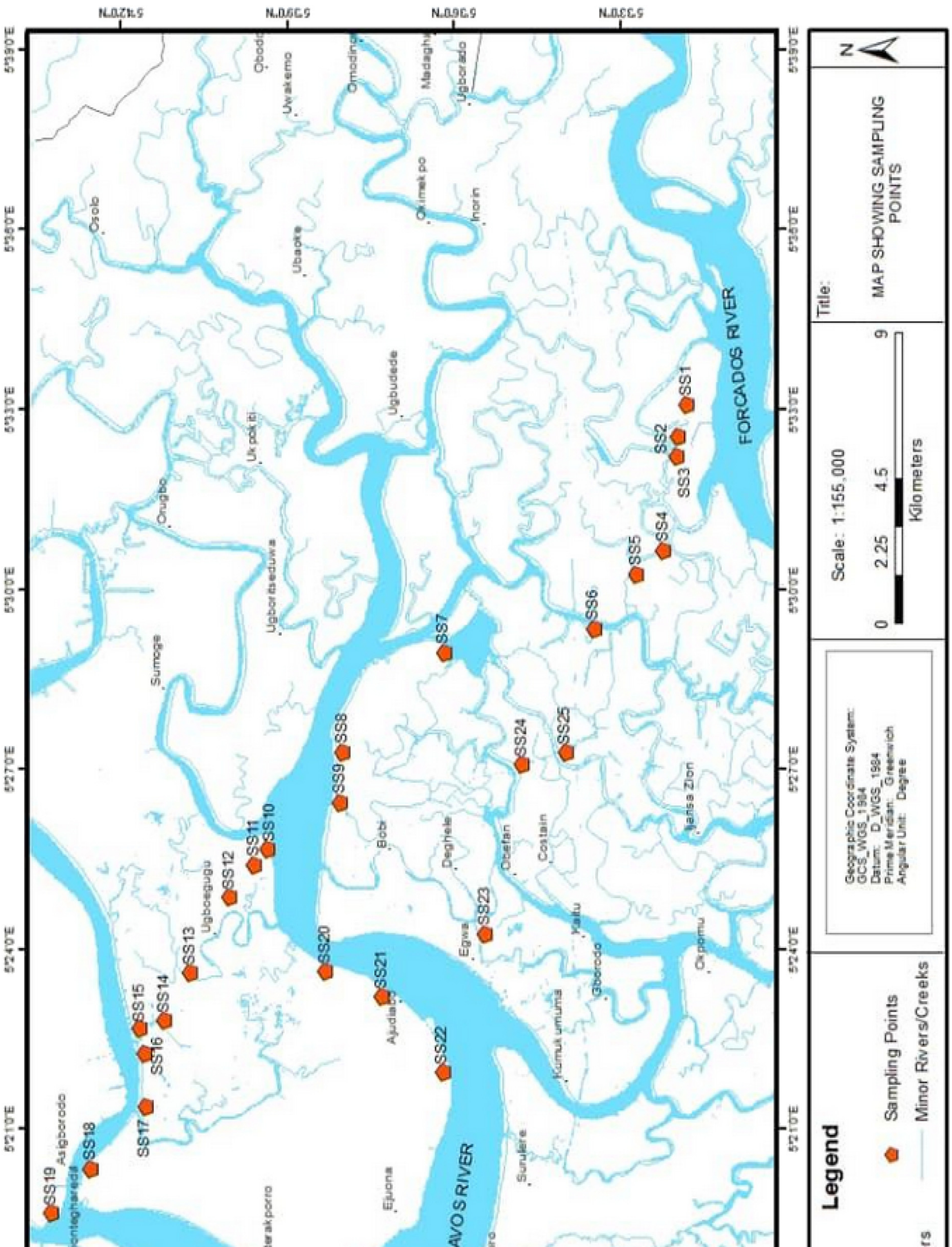


Fig. 1. Map of study area showing sampling locations SS1 to SS25.

Therefore, sediment can be used as a marker for measuring the extent of pollution and potential environmental risks (Barakat et al., 2013).

In Nigeria, the primary sources of PCBs are the power generating companies as PCBs are contained in transformers. PCBs are not manufactured in Nigeria but are imported as components of transformers from South Africa, Europe (England, Belgium, Italy, and Sweden), and Asia (especially Japan, India and South Korea) (Ministry of Environment, 2009). In 2009, Nigeria as a contracting party to the Stockholm Convention of 2001 and other treaties on the control of persistent organic pollutants, compiled an inventory of PCBs contained in oils and equipment although the list is not exhaustive. The report indicated that the total amount of PCB-contaminated waste in Nigeria stands at 3410 tons; PCBs contained in oil amounted to 421 tons and the combined weight of PCB-contaminated equipment was 1061 tons, with the possibility of these values increasing with a comprehensive inventory (Federal Ministry of the Environment, 2009; Okoh, 2015). However, Nigeria has not developed policy guidelines and legislative frame works for monitoring and control of PCBs in the environment.

The production, distribution, sale and use of PCBs are either prohibited or restricted by legislation in most countries. However, PCBs are still found in environmental media today due to legacy use or discharges from old electrical equipment and transformers that are yet to be decommissioned. Against this background, there is a clear need to determine the extent and effectiveness of compliance to the jurisdictions and control measures by monitoring the spatiotemporal trends of PCBs in the environment. Analysis of surface sediment can provide useful information on PCB concentrations, distribution patterns and the influence of contemporary anthropogenic inputs arising from factors such as population growth, urbanization, agriculture and industrial developments.

The Escravos River Basin hosts one of the major crude oil and gas production and processing facilities in the western part of the Niger Delta in Nigeria. Most of these operations are powered by energy generated from gas-fired turbines. However, most studies on the impacts of production and processing of crude oil on the environment of the Niger Delta are restricted to evaluation of concentrations of petroleum hydrocarbons and metals with little or no attention paid to other organic contaminants such as halogenated organic compounds. Therefore, this study aimed to determine the concentrations, spatial distribution patterns, sources and risks of PCBs in sediments from water bodies around oil production facilities in the Escravos River Basin. This study is the first of its kind in this basin and provides a comprehensive framework for understanding the extent and patterns of PCBs in this river basin, and identifying the impacts of anthropogenic pressures, and likely threat to humans and the ecosystem of the Escravos River basin. Such data are useful for developing surveillance programs, environmental quality management plans, and evaluating the extent of compliance and effectiveness of national and global prohibition policies on the production, trade and application of technical PCB mixtures.

2. Materials and methods

2.1. Description of study area

The Escravos River is approximately 56 km (35 mile) in length, and is one of the distributaries of the River Niger in the western part of the Niger Delta in Nigeria. The river flows through zones of mangrove swamps and coastal sand ridges into the Bight of Benin in the Gulf of Guinea where it joins the Atlantic Ocean. The crude oil production facility has an oil terminal pump with a capacity of 73000 m^3/d (https://en.wikipedia.org/wiki/Escravos_River). The Escravos River has no port, but it is linked with other rivers, such as the Forcados, Warri, Benin, and Ethiope, through a maze of interconnected waterways. The river subsumed the Forcados River as the main route to the Delta ports of Burutu, Forcados, Koko, Sapele and Warri (https://www.britannica.com/place/Escravos-River). Today, the river serves as the only channel for oceangoing vessels to these ports. However, prior to 1960 and the completion of the Escravos Bar Project in 1964, the depth of the natural passageway was only 12 ft (4 m) at the ocean exit of the Escravos Bar.

2.2. Sample collection

Surface sediments (0–5 cm depth) were obtained from 25 locations (Fig. 1) within the Escravos River basin including sites close to wellheads, flow stations, truck lines, gas flare points, dockyards and residential communities. Information on the individual site characteristics are provided in Supplementary Material Table S1. The sediments were collected using a modified Ekman grab sampler, and then wrapped in aluminum foil and packed in zip-locked polyethylene bags. The samples were transported to the laboratory in an ice chest. The samples were allowed to dry, and were then sieved through a 0.2 mm mesh sieve, and kept at < -4 °C before the extraction process.

2.3. Reagents and chemicals

The solvents for extraction (acetone, dichloromethane (DCM) and *n*-hexane) were of pesticide grade (Merck, Darmstadt, Germany). A PCB standard mixture containing 28 PCBs (PCB-8, 18, 28, 44, 52, 60, 77, 81, 101, 105, 114, 118, 123, 126, 128, 138, 153, 156, 157, 167, 169, 170, 180, 185, 189, 195, 206, 209) was used for calibration (AccuStandard Inc., CT, USA). A standard mixture containing isotopically labeled PCBs, namely, $^{13}C_{12}$PCB-28, 52, 118, 153, 180 and 209 (Cambridge Isotope Laboratories, Inc., MA, USA), was used as a source of surrogate standards. Anhydrous sodium sulfate, silica gel, and alumina (analytical grade) were products of Sigma-Aldrich, Inc., USA.

2.4. Sediment physicochemical characteristics

The sediment pH values were measured in a sediment/water suspension (1:2.5 sediment/water ratio). The total organic carbon content of the samples was evaluated according to the Walkley and Black (Walkley and Black, 1934) wet oxidation method (Radojevic and Bashkin, 1996). The electrical conductivities of the sediments were determined by inserting the conductivity electrode in the filtrate of the sediment/water suspension used for pH measurement.

2.5. Extraction of PCBs

A mass of 10 g of the sediment sample was homogenized with 5.0 g of anhydrous Na_2SO_4 until the homogenate was free-flowing. The homogenate was spiked with the standard mixture containing 200 ng g^{-1} of $^{13}C_{12}$-labeled PCBs and transferred to an extraction thimble, and Soxhlet extracted for 16 h with 100 mL of a 1:1:1 acetone/DCM/*n*-hexane mixture. The extract was concentrated to 2 mL with the aid of a rotary evaporator, and the concentrated extract was subjected to purification in a multi-layer silica gel and alumina column consisting of 4.0 g of anhydrous Na_2SO_4, 4.0 g of alumina and 4.0 g of silica gel packed from top to bottom. The elution of PCBs from the column was carried out with a 30 mL aliquot of a 1:1 *n*-hexane/DCM mixture and the eluate was concentrated to 2 mL under a slow flowing stream of pure nitrogen gas.

2.6. Chemical analysis

The concentrations of the 28 PCBs in the sample extracts were determined by using an Agilent 7890A gas chromatograph interfaced with a 5876C mass selective detector (MSD) (Agilent Technologies Inc., Palo Alto, CA, USA). The separation column was a DB-7 capillary column (30 m length, 0.25 mm internal diameter and 0. 25 µm film thickness,). The mobile phase was high purity helium gas at a constant flow velocity of 1 mL/min. The initial temperature of the column was fixed at 85 °C, held for 1 min, and stepped up to 200 °C at 35 °C/min, and then increased from 200 to 300 °C at 10 °C/min. The injector temperature and that of the transfer line was maintained at 280 °C. The mass spectrometer was operated at an electron impact energy of 70 eV and data acquisition was by selected ion monitoring (SIM) scanning from 35 to 500 *m/z*. The PCB congeners were identified from the target ions, and confirmation ions, in addition to matching the retention times of the PCBs in these samples with those obtained from authentic PCB standards.

2.7. Quality assurance/control

All glassware was washed with detergent, rinsed thoroughly with double-distilled water and acetone, and subsequently baked for 4 h at 450 °C in a muffle furnace. The performance of the analytical procedure was evaluated from the recoveries of the $^{13}C_{12}$-PCBs and matrix spike methods. The surrogate PCB recoveries were 82 to 96.7%, while those of the spiked matrix samples were 89 to 99.6%. The quantification of the PCBs was achieved by using an external calibration method consisting of 5-point calibration lines obtained as a plot of the congener peak areas versus the standard concentrations. The regression coefficients (r^2) for the calibration lines ranged from 0.9991 to 0.9999. The limits of detection and quantification (3 and 10 times the noise levels of the baseline, respectively) for the PCBs were 0.1 to 0.5 and 0.3 to 1.5 ng g^{-1} respectively. Procedural blanks ($n = 4$) were analyzed following all the analysis steps but omitting the samples. The PCB levels of the blanks were below the limits of detection. The precision of the method for replicate analyses was less than 8% relative standard deviation (RSD).

2.8. Statistical analysis

Microsoft Excel® and SPSS software version 15.1 were used to performed all the statistical analyses. Analysis of variance was used to assess the difference in contamination levels between the studied sites, while multivariate statistics (principal component analysis [PCA] and cluster analysis [CA]) and the Pearson correlation were used to establish relationships among the PCB congeners and with other sediment properties. All statistical analyses were carried out at a significance level of $p = .05$.

2.9. Data treatment

2.9.1. Toxicity equivalence of dioxin-like PCBs

The toxicity equivalence (TEQ) of dioxin-like PCBs (*dl*-PCBs) was determined from Eq. (1). The TEQ is obtained as the sum of the product of the concentration of a particular *dl*-PCB and its respective toxic equivalency factor (TEF) value.

$$TEQ = \Sigma C_i \times TEF_i \quad (1)$$

where C_i is the concentration of a particular *dl*-PCB, and TEF_i is the toxicity equivalency factor for the particular *dl*-PCB. The International Programme on Chemical Safety (IPCS) of the World Health Organization (WHO) in 2005 specified the TEF values for *dl*-PCBs. For PCB-77, PCB-81, PCB-105, PCB-114, PCB-118, PCB-123, PCB-126, PCB-156, PCB-157, PCB-167, PCB-169 and PCB-189 the TEF values are1×10^{-4}, 3×10^{-4}, 3×10^{-5}, 3×10^{-5}, 3×10^{-5}, 3×10^{-5}, 1×10^{-1}, 3×10^{-5}, 3×10^{-5}, 3×10^{-5}, 3×10^{-2} and 3×10^{-5}respectively (Van den Berg et al., 2006).

2.9.2. Ecosystem risk assessment

The ecotoxicological risk of PCBs in sediments from the Escravos River Basin was evaluated by making use of two approaches, the potential ecological risk index (PERI) procedure introduced by Hakanson (1980) and the sediment quality guidelines (SQGs) (MacDonald et al., 1996, Long and Morgan, 1990; Long et al., 1995; Gómez-Gutiérrez et al., 2007). The PERI of PCBs in sediments from the Escravos River basin is given by Eq. 2. The PERI approach has been adopted in a number of studies to determine the ecotoxicity risk of PCBs in sediments (Lai et al., 2015; Cui et al., 2016; Baqar et al., 2017).

$$PERI = \sum_{i=1}^{n} E_r^i \quad (2)$$

where $E_r^i = T_f^i \times C_f^i$and $C_f^i = \frac{C_s^i}{C_r^i}$

C_s^i and C_r^i represent the sample and background concentrations of PCBs respectively. The background concentrations of total PCBs used was 10 ng g^{-1}(Hakanson, 1980). C_f^i, E_r^i and *PERI* represent the contamination factor, ecological risk factor and potential ecological risk index respectively, while T_f^i represents the toxic response factor for PCBs and is equal to 40 (Hakanson, 1980). The interpretation and significance of PERI is given as follows: low potential ecological risk $E_r^i < 40$; moderate potential ecological risk $E_r^i = 40–79$; considerable potential ecological risk $E_r^i = 80–159$; high potential ecological risk $E_r^i = 160–319$; and very high potential ecological risk $E_r^i > 320$ (Hakanson, 1980).

3. Results and discussion

3.1. Total concentrations and congener distribution

The concentrations of Σ28 PCBs in sediments from the Escravos River Basin ranged between 226 and 31,900 ng g^{-1} with a median concentration of 2300 ng g^{-1} dry weight (Table 1, Supplementary Material Table S2). One-way analysis of variance showed that there were significant spatial discrepancies ($p < 0.05$) in the concentrations of PCBs in sediments from the Escravos River Basin. Generally, differences in PCB concentrations in sediments may be related to differences in source inputs, sediment geochemical properties, tidal action, flow velocity, topographic features and the relationship with adsorption, horizontal distribution and transport behaviours of PCBs (Yang et al., 2009; Yang et al., 2011; Barhoumi et al., 2014; Cui et al., 2016). In this study, sediments from sites 1 to 5 and 18 contained higher concentrations of PCBs than the other sites. The highest level of Σ28 PCBs (31,900 ng g^{-1}) was detected in site 5, followed by sites 2 (26,800 ng g^{-1}) and 1 (21,400 ng g^{-1}) (Supplementary Material Table S2). Sites with higher PCB concentrations are those around wellheads and flow stations. Generally, the concentrations of PCBs in sediments around oil production facilities, e.g. wellheads, flow stations, and truck lines, were greater than those found in sediments collected around residential communities (e.g. sites 19, 20 and 21) and dockyards. This could be related to discharge of PCBs from these facilities into the river system. Nigeria has no specified regulatory control limits for PCBs in sediments. However, we applied the guideline values for PCBs in soil specified by some international regulatory bodies as indicative values for evaluating the significance of PCBs in these sediments. For example, the Dutch action value, and the Australian and New Zealand Ecological Investigation Level is specified as 1000 ng g^{-1} PCBs (VROM, 1994; ANZECC/NHMRC, 1992), while 1300 ng g^{-1} is specified by the Canadian authority as the soil quality guideline (CCME, 2007), and 220 ng $g^{-1}$is the United States Environmental Protection Agency (US EPA) health-based screening level for total PCBs which intends to prevent adverse health effects related to chronic exposure (Rudel et al., 2008). The PCB concentrations in sediments from the Escravos River basin were above these guideline values except for sites 14, 19, 20, and 21.

Table 2 presents a comparison of the Σ28 PCB concentrations in sediments from the Escravos River basin with those reported for some other river systems in the world. Such a comparison is often difficult given the discrepancies in the number of samples and congeners analyzed, and the extraction and instrumental analytical methods employed. However, this does not invalidate the need to establish the global occurrence, trends and concentration patterns of PCBs in

Table 1
Concentrations (ng g^{-1} dry weight) of PCBs in sediments of the Escravos River.

	Mean	SD	Median	Min	Max
PCB-8	805	1807	156	3.6	8360
PCB-18	1298	3615	70.0	6.0	14,100
PCB-28	156	160	114	36.0	666
PCB-44	123	189	68	2.0	814
PCB-52	131	128	118	12.0	628
PCB-60	128	107	117	2.0	488
PCB-77	138	122	92.0	10.0	570
PCB-81	135	182	78.0	14.0	792
PCB-101	145	155	104	2.0	664
PCB-105	542	1530	124	4.0	6030
PCB-114	151	179	120	28.0	858
PCB-118	91.7	68.3	66.0	14.0	230
PCB-123	136	151	100	22.0	738
PCB-126	102	67.1	76.0	6.0	254
PCB-128	151	160	104	4.0	756
PCB-138	180	195	133	4.0	838
PCB-153	156	207	140	10.0	1030
PCB-156	143	206	99.0	2.0	882
PCB-157	156	192	132	4.0	738
PCB-167	124	218	70.0	4.0	844
PCB-169	104	56.8	100	34.0	194
PCB-170	160	169	126	48.0	706
PCB-180	160	212	103	14.0	876
PCB-185	122	133	94.0	2.0	516
PCB-189	212	276	136	2.0	932
PCB-195	172	292	97.0	2.0	1080
PCB-206	102	75.8	78.0	6.0	310
PCB-209	1780	2330	148	8.0	7630
TOTAL	5610	8500	2300	226	31,900
Di-PCB	805	1810	156	4	8360
Tri-PCBs	1400	3610	178	8	14,100
Tetra-PCBs	540	594	436	124	3290
Penta-PCBs	803	1420	442	0	6880
Hexa-PCBs	661	997	510	0	5240
Hepta-PCBs	318	598	192	0	3030
Octa-PCBs	172	292	97	2	1080
Nona-PCBs	102	76	78	6	310
Deca-PCBs	1790	2330	148	8	7630
Non-ortho *dl*-PCBs	374	311	376	42	1660
Mono-ortho *dl*-PCBs	931	1660	538	0	6750
Σ*dl*-PCBs	1310	1900	868	42	7620
i-PCBs	709	936	554	0	4930
LC-PCBs	3550	6170	1290	226	23,300
HC-PCBs	2060	2930	948	0	11,900

dl-PCBs - dioxin-like PCBs, *i*-PCBs - indicator PCBs, LC-PCBs - low chlorinated PCBs (2Cl-5Cl), HC-PCBs (6Cl-10Cl).

sediments of river systems. Higher levels of PCBs were observed in sediments from the Escravos River basin than those reported for some other Nigerian river systems, e.g. the Forcados River (Iwegbue, 2016), Ethiope and Benin Rivers (Ezemonye, 2005), Ogun and Ona Rivers (Adeogun et al., 2016), River Niger and Nicholas River (Unyimadu, 2017), and New Calabar River (Ilechukwu et al., 2018). Sediments of the Escravos River basin also contained higher levels of PCBs than those reported for other African countries and other regions of the world. For example, these include the Pangani River, Tanzania (Hellar-Kihampa et al., 2013); Umgeni River (Gakuba et al., 2015), Swartkops River and Sundays River estuaries (Olisah et al., 2020), South Africa; Awash River Basin, Ethiopia (Dirbaba et al., 2018); Congo River Basin (Verhaert et al., 2013); Yamuna River, India (Kumar et al., 2013); Chenab (Eqani et al., 2012) and River Ravi and its tributaries, Pakistan (Baqar et al., 2017); Seine River basin, France (Lorgeoux et al., 2016); Thames River, England (Lu et al., 2017); Missouri River (Echols et al., 2008) and Chicago Ship Canal (Pervely et al., 2014), USA; Ankara Creek, Turkey (Özyürek et al., 2013); Shongua (Cui et al., 2016), Haihe and its estuary (Zhao et al., 2010) and Lijiang (Leung et al., 2006) Rivers in China. However, PCB concentrations in sediments from the Northwest Persian Gulf, Iran (Zahed et al., 2009) and Belford Harbour, Massachussetts, USA (Subedi et al., 2014) were higher than those found in sediments from the Escravos River basin.

Among the 28 congeners that were analyzed, lower chlorinated (2-Cl to 5-Cl) PCBs dominated higher chlorinated (6-Cl to 10-Cl) PCBs in these sites. The lower chlorinated PCBs accounted for 22.2 to 100%, while the higher chlorinated PCBs explained 0 to 77.8%, of the Σ28 PCBs in these sites. The prominence of low chlorinated PCBs in these sediments could be related to the susceptibility of these compounds to build up in the atmosphere and be washed down by precipitation, and thereby entering the aquatic system through runoff and ultimately being deposited in sediments (Gao et al., 2013; Shi et al., 2016). The lower chlorinated PCBs are products of dechlorination, but are generally not prone to further dechlorination. Given the high concentrations of lower chlorinated PCBs detected, it is highly unlikely that long-range transportation processes are a significant source of PCBs in these sediments. Therefore, both low and high chlorinated PCBs are related to local sources and contaminated areas (Tolosa et al., 1995; Borja et al., 2005; Combi et al., 2016). In China and Nepal, lower chlorinated PCBs were prominently used in capacitors, lubricants and transformers, while the higher chlorinated PCBs were applied as plasticizers in plastics and paints (Wu et al., 2011; Yadav et al., 2017). However, this may not be the case in Nigeria. Nevertheless, there are a number of sites where the concentrations of the higher chlorinated PCBs dominate those of lower chlorinated PCBs (e.g. sites 1, 4, 8, 12, 13 and 18) which could be linked to the high K_{ow} values that promote their association with suspended particulate matter and consequent deposition (Hong et al., 2003; Liu et al., 2017). Furthermore, the low detection frequencies of higher chlorinated PCBs in these sediments can be linked to their low water solubility and poor migration capacity (Liu et al., 2017). Conversely, the lighter PCB homologues such as di-PCBs, tri-PCBs and tetra-PCBs are susceptible to microbial degradation and volatilization after discharge into the environment (Zhang et al., 2003; Eqani et al., 2013; Baqar et al., 2017). The contributions of the individual PCB homologues to the total PCB concentrations in sediments from the Escravos River basin were 0.0 to 26.2%, 0.5 to 49.1%, 1.0 to 97% and 0 to 40.2% for di-, tri-, tetra- and penta-PCBs respectively. In the case of higher chlorinated homologues, the percentage contributions of the hexa-, hepta-, octa-, nona- and deca-PCBs to the total PCB concentrations in these sediments were 0 to 41.5%, 0 to 19.3%, 0 to 0.75%, 0 to 7.8% and 0 to 58.7% respectively (Fig. 2). The median concentrations of the PCB homologues in the Escravos River basin sediments followed the sequence: hexaPCBs > penta-PCBs > tetra-PCBs > hepta-PCBs > tri-PCBs > di-PCBs > deca-PCBs > octa-PCBs > nona-PCBs. Of the 28 PCB congeners measured in this study, the hexaPCBs, penta-PCBs and tetra-PCBs were the three top homologues in sediments from this river basin. PCB-138, PCB-153 and PCB-157 were the top congeners of the hexaPCBs in these sediments, while PCB-105 and PCB-114 were the prominent congeners of the penta-homologues. In the case of tetra-PCBs, the prominent congeners were PCB-52 and PCB-60, while PCB-8 and PCB-28 were the top congeners of the di- and tri-PCB homologues respectively. PCB-52 was the top congener detected in organic yellow (PY 97) (Jahnke and Hornbuckle, 2019). The detection frequencies of the higher chlorinated PCBs in this sediment system followed the sequence: hexaPCB (88%) > nona-PCBs (76%) > hepta-PCBs (64%) > deca-PCBs (48%) > octa-PCB (48%), whereas in the case of lower chlorinated di- to penta-PCBs, their detection frequencies were 92 to 100%. In this study, sites 1 to 5 and 18 contained elevated levels of PCB-209 (2178–7632 ng g^{-1}) while the concentrations of PCB-209 in other sites varied between not detected (nd) and 148 ng g^{-1}.The prominence of PCB-209 in some of the sediments suggests inadvertent sources of PCBs in the study area which may have arisen from paints and pigments used for coating of surface pipelines and other facilities. PCB-209 can be produced inadvertently during the manufacture of pigments and titanium chlorides or titanium dioxide. There is no clear evidence of pigment or titanium oxide manufacturing in the river basin. However, paints and pigments have been used extensively by the oil industries and those providing anti-corrosion services. In addition, PCB-209 and

Table 2
A comparison of PCB concentrations in sediments of the Escravos River basin with those reported in other regions of the world.

Location	Number of congeners	Concentration range (ng g^{-1} d.w.)	Reference
Africa			
Escravos River Basin, Nigeria	28	226–31,900	This study
Ogun River, Nigeria	19	323–2003	Adeogun et al. (2016)
Ona River, Nigeria	19	589–1360	Adeogun et al. (2016)
New Calabar River, Nigeria	8	210–2160	Ilechukwu et al. (2018)
Forcados River, Nigeria	15	2.7–202	Iwegbue (2016)
River Niger and Nicholas River, Nigeria	27	741–2960	Unyimadu (2017)
Ethiope River, Nigeria	8	0.73–6.7	Ezemonye (2005)
Benin River, Nigeria	8	0.35–15.2	Ezemonye (2005)
Swartkops River and Sundays River Estuary, South Africa	17	70–3800	Olisah et al. (2020)
Msunduzi River, South Africa	8	19,500	Moodley et al. (2016)
Umgeni River, South Africa	8	103–430	Gakuba et al. (2015)
Pangani River and its tributaries, Tanzania	28	0.36–11	Hellar-Kihampa et al., 2013
Awash River Basin, Ethiopia	7	0.85–26.6	Dirbaba et al. (2018)
Congo River Basin, Congo	33	nd–1.4	Verhaert et al. (2013)
Other Regions			
Thames River, England	7	0.12–27.4	Lu et al. (2017)
Ankara Creek, Turkey	7	3.7–743.3	Özyürek et al. (2013)
Missouri River, USA	118	11.0–250	Echols et al. (2008)
Songhua River, China	48	0.59–12.4	Cui et al. (2016)
Yamuna River, India	28	0.21–21.2	Kumar et al. (2013)
Haihe River and Estuary, China	32	0.177–253	Zhao et al. (2010)
Chenab River, Pakistan	24	9.33–144.	Eqani et al. (2012)
Lianjiang River, China	56	4.70–743	Leung et al. (2006)
Belford Harbour, Massachusetts, USA	209	2800–109,000	Subedi et al. (2014)
Northwest Persian Gulf, Iran	7	3400–50,200	Zahed et al. (2009)
Chicago Ship Canal, USA	209	650–500	Peverly et al. (2015)
Seine River Basin, France	13	500–2370	Lorgeoux et al. (2016)

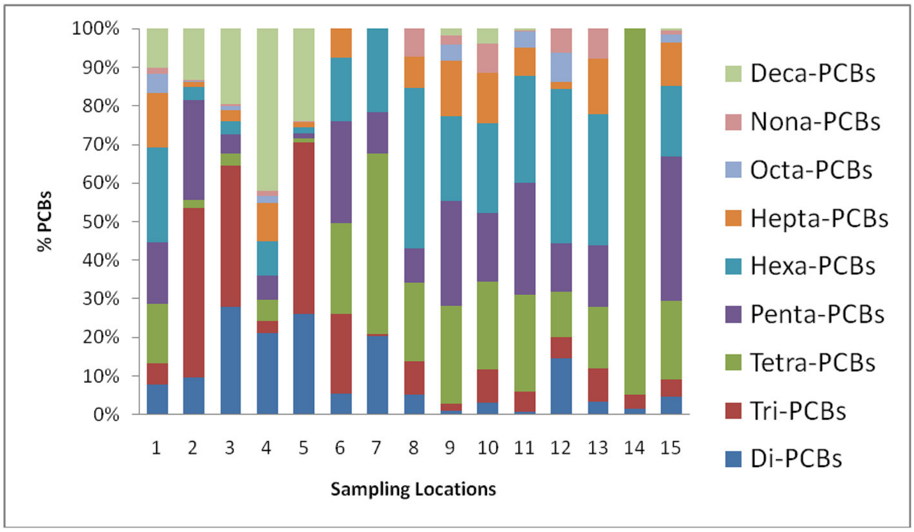
other highly chlorinated PCBs (e.g. PCB-207, PCB-208) have been detected in a popular green pigment "phthalocyanine green" (Hu and Hornbuckle, 2010; Anezaki and Nakano, 2015). PCB-209 was the top ranked among 10 congeners detected in phthalo blue (PB 15:2) (Jahnke and Hornbuckle, 2019). The indicator PCB (*i*-PCBs) concentrations ranged from not detected (nd) to 4930 ng g^{-1} which accounted for 0.0 to 40.8% of the Σ28 PCBs. Sites 1, 16 and 18 contained higher levels of the indicator PCBs than the other sites, while none of the *i*-PCBs were detected in sites 14 and 19. The recommended ecological assessment criteria (EAC) for the *i*-PCBs are set at 1.0 to 10 ng g^{-1} (OSPAR Commission, 2000). The *i*-PCB concentrations in sediments from the Escravos River basin were far above the upper limit of the EAC, except for sites 14 and 19, which suggests their hazardous effects to the ecosystem and humans. The *dl*-PCB concentrations in sediments from this river basin ranged between 42 and 7616 ng g^{-1}, which accounted for 3.0 to 59.4% of the Σ28 PCBs. Sediments from sites 1 to 4, 6, 15, 16 and 18 contained higher concentrations of *dl*-PCBs (> 1000 ng g^{-1}) than other sites. The mono-ortho *dl*-PCB concentrations in these sediments were higher than those of non-ortho *dl*-PCBs except in sites 7, 8, 10, 11, 14 and 21. The high concentrations of non-ortho *dl*-PCBs in sediments from these sites (7, 8, 10, 11, 14 and 21) are of concern because of the similarities in their carcinogenic properties with that of tetrachlorodibenzo-*p*-dioxin (TCDD) (Eqani et al., 2012; Mahmood et al., 2014; Baqar et al., 2017). The median concentrations of non-ortho *dl*-PCBs in sediments from the Escravos River basin followed the sequence: PCB-169 > PCB-77 > PCB-81 > PCB-126, whereas in the case of the mono-ortho *dl*-PCBs, their concentrations followed the sequence: PCB-189 > PCB-157 > PCB-105 > PCB-114 > PCB-123 > PCB-156 > PCB-167. The TOC contents and other sediment physicochemical properties control the sorption and fate of PCBs in sediments. The pH, electrical conductivity, and TOC contents of the sediments ranged from 6.32 to 6.78, 1360 to 7620 μS cm^{-1}, and 1.01 to 5.33% respectively (Supplementary Material Table S3). The TOC and other physicochemical characteristics showed poor correlation with the Σ28 PCB concentrations and those of the individual PCB homologues. The poor correlation between TOC and PCB concentrations suggests continuous fresh input of PCBs into the river basin and that TOC is less important in the fate and distribution of PCBs in sediments of the Escravos River basin.

3.2. Ecological risk of PCBs in sediments from the Escravos River Basin

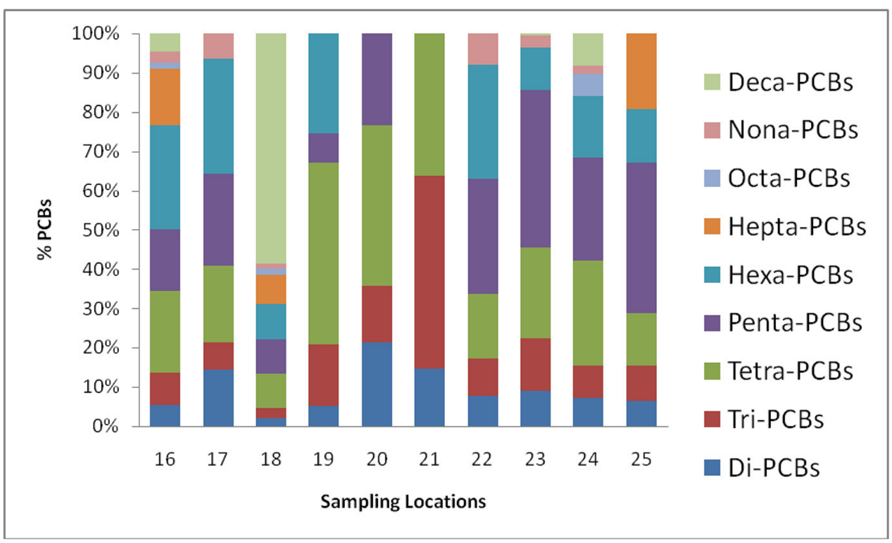
In this study, the ecological significance of PCBs was evaluated by using the SQGs, such as the Interim Sediment Quality Guideline (ISQG), Threshold Effect Level (TEL) (Macdonald et al., 1996), Effect Range Low (ERL), Effect Range Median (ERM) (Long and Morgan, 1990; Long et al., 1995), Probable Effect Level (PEL) (Macdonald et al., 1996), and consensus threshold effect concentrations (TEC) and probable effect concentrations (PEC) (Gómez-Gutiérrez et al., 2007). The PCB concentrations in sediments from the Escravos River basin were above the ISQG, TEL, ERL, ERM, PEL and the consensus TEC and PEC values, which signifies potential adverse effects on benthic organisms. The TEQ values for *dl*-PCBs varied between 4.20 × 10^{-3} and 26.7 ng TEQ g^{-1} (Supplementary Material Table S4). The TEQs of *dl*-PCBs in these sediments exceeded the sediment quality value of 21.5 pg TEQ g^{-1} (see Table 3), which suggests potential risks associated with an organism's exposure to PCBs in sediments from this river basin, especially benthic organisms and filter feeders. PCB-126 and PCB-169 have a major influence on the TEQ values of *dl*-PCBs in sediments from the Escravos River basin. PCB-126 has been established to induce hepatotoxicity and hepatic micronutrient disruption in animals (Klaren et al., 2015). The potential ecological risk of PCBs in sediments from the Escravos River basin ranged from 902 to 128,000 (Fig. 3) which signifies a very high potential ecological risk for exposure of organisms to PCBs in these sediments. The high PERI values of PCBs in sediments from the Escravos River basin suggests the need to put in place clean-up and remediation measures in order to ameliorate the adverse impacts of these compounds on the ecosystem.

3.3. Principal component analysis

The PCA after Varimax rotation for PCBs in sediments of the



a: Compositions of PCBs in surficial sediments from the Escravos River basin (sampling locations 1-15).



b: Compositions of PCBs in surficial sediments from the Escravos River basin (sampling locations 16-25).

Fig. 2. a: Compositions of PCBs in surficial sediments from the Escravos River basin (sampling locations 1–15).
b: Compositions of PCBs in surficial sediments from the Escravos River basin (sampling locations 16–25).

Escravos River basin gave two components with eigen values > 1 which explained 83.14% of the total variability in the data (Supplementary Material Table S5). Factor 1 represents 52.9% of the total variance and has positive loading values in tetra-PCBs, hexaPCBs; hepta-PCBs, octa-PCBs, and nona-PCBs. Factor 1 has a weak positive loading value for penta-PCBs. Apart from the tetra-PCBs, all other homologues in Factor 1 were higher chlorinated PCBs and reflect the homologue types in the technical mixture of Aroclor 1254. The compositions of PCBs in the environment are altered by degradation, leaching, volatilization, transport, solubilization, soil burial and plant uptake. These possibly account for the discrepancies between the compositions of PCBs in the environment and those of the input sources (Liu et al., 2013; Iwegbue et al., 2019). Factor 2 represents 30.2% of the variance and has high positive loading values for di-PCBs, tri-PCBs and deca-PCBs and a weak positive load value for penta-PCBs. The correlation between di-, tri- and deca-PCBs suggests common sources and may have arisen from

Table 3
Ecotoxicological risk of PCBs in sediments from the Escravos River Basin.

	TEL	< ERL	ERL – ERM	> ERM	ERM – PEL	PEL	Consensus TEC	Consensus PEC
SQGs	21.5	22.7	–	180	–	189	29	> 274
Escravos River Basin	25 (100%)	0 (0%)	0 (0%)	25 (100%)	–	25 (100%)	25 (100%)	24 (96%)

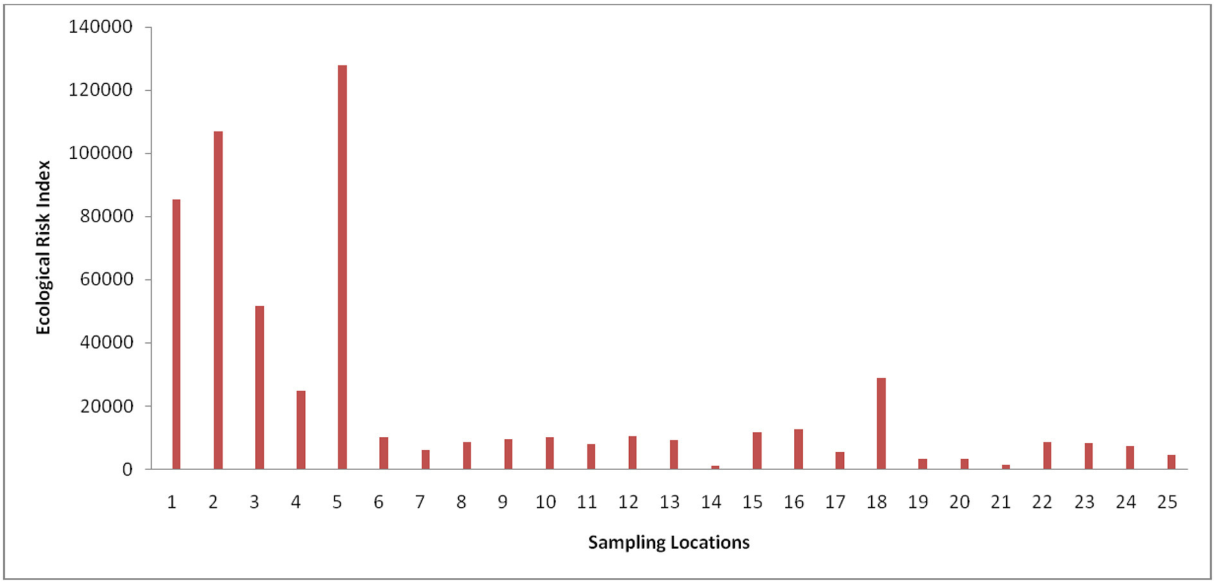


Fig. 3. Ecological risk index of PCBs in sediments of the Escravos River basin.

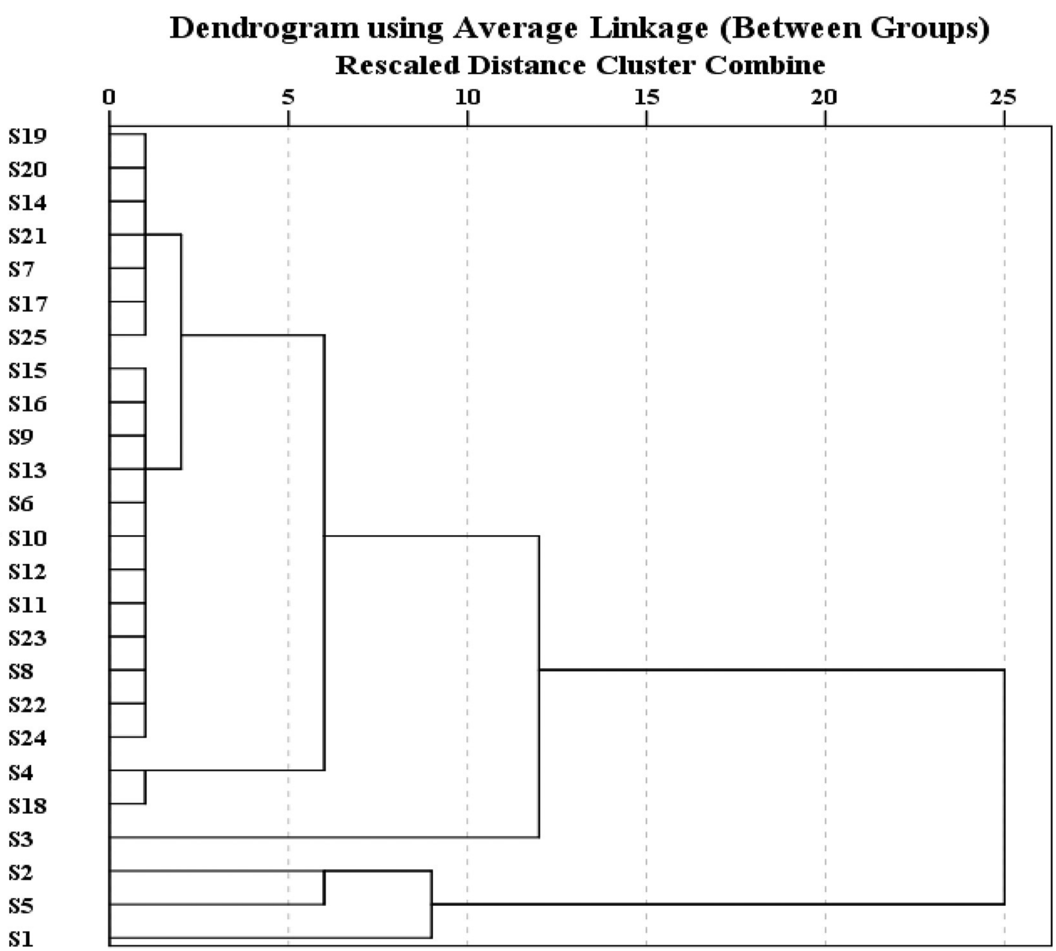


Fig. 4. Hierarchical cluster analysis showing the dendrogram of 25 sampling sites plotted using the average linkage (between groups) and rescaled distance cluster combined.

inadvertent PCB sources such as pigments, silicone products and titanium oxide-based paints (Praipipat et al., 2013; Anezaki and Nakano, 2015). PCB-8 and PCB-18 have been detected in silicone products (Anezaki and Nakano, 2015).

3.4. Cluster analysis

Hierarchical cluster analysis was used to classify the variations in Σ28 PCB concentrations of the investigated sites by using the rescaled distance cluster combine and average linkage methods. The clustering of the sampling sites is summarized in the dendrogram in Fig. 4. The cluster analysis indicated that the investigated sites are clustered into two major groups. The first group consists of sites 1, 2 and 5, which are characterized by very high levels of PCBs (21400–31,900 ng g^{-1}). The second major group was split into two subgroups, the first subgroup consists of site 3 (12,900 ng g^{-1}), while the other subgroup was further split into three other subgroups with sites 4 and 18 (6200–7160 ng g^{-1}) in the first subgroup, sites 6, 8, 9, 10, 11, 12, 13, 15, 16, 22, 23 and 24 (1780–3160 ng g^{-1}) in the second subgroup, while sites 7, 14, 17, 19, 20, 21 and 25 are in the third subgroup (226–1480 ng g^{-1}) - these sites are around residential communities, and are characterized by lower levels of PCBs.

4. Conclusions

This study provided useful data on the concentrations, possible sources, and ecological risks of PCBs in sediments from the Escravos River basin. The results indicated that the PCB concentrations were elevated with significant spatial discrepancies. The lower chlorinated (2-Cl to 5-Cl) PCBs showed dominance over higher chlorinated (6-Cl to 10-Cl) ones. Higher concentrations of Σ28 PCBs were detected in sediments around crude oil production facilities, such as wellheads, flow stations, and truck lines, than around residential communities in the river basin. The homologue distribution in sediments from this river basin followed the sequence: hexaPCBs > penta-PCBs > tetra-PCBs > hepta-PCBs > tri-PCBs > di-PCBs > deca-PCBs > octa-PCBs > nona-PCBs. The homologue distribution pattern reflects those of the Aroclor 1254 composition. The ecological risk assessment suggests very high potential risks for exposure of organisms to PCBs in sediments from the Escravos River basin. The results suggest that sediments from the Escravos River basin require clean-up and remedial actions in order to reduce the adverse effects of PCBs on the ecosystem and humans. It is therefore necessary to institute further studies on the distribution of other halogenated hydrocarbons, including polybrominated diphenyl ethers, dioxins, and organochlorine pesticides, among others, in the sediments, water and biota from the Escravos River basin, and to determine their influence on the macrobenthic community assemblage and structure. This will give a comprehensive account of the impact of halogenated hydrocarbons on the ecosystem.

CRediT authorship contribution statement

Chukwujindu M.A. Iwegbue: Conceptualization, Methodology, Formal analysis, Writing - original draft, Supervision. **Ernest Bebenimibo**: Methodology, Resources, Investigation. **Godswill O. Tesi**: Resources, Visualization, Formal analysis. **Francis E. Egobueze**: Resources, Investigation. **Bice S. Martincigh**: Writing - review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary material to this article can be found online at https://doi.org/10.1016/j.marpolbul.2020.111462.

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