

## Research Article

# Evaluation of Contamination of River Niger by Persistent Organic Pollutants (POPs) using Sediment Quality Guidelines (SQGs)

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## Abstract

The consensus-based Sediment Quality Guidelines (SQGs) were critically evaluated to determine if they would provide effective tools for assessing sediment quality conditions in fresh and brackish water ecosystems in River Niger, Nigeria, contaminated with Persistent Organic Pollutants (POPs). Sediment Quality Guidelines have been used in numerous applications, including designing monitoring programmes, interpreting historical data, evaluating the need for comprehensive sediment quality assessment and ecological risk assessments.

Fifteen representative sites along River Niger, three each from Gurara River (tributary) in Niger State, Lokoja (confluence) in Kogi State, Onitsha in Anambra State, Brass and Nicolas River (brackish tributaries) in Bayelsa were purposefully selected for sampling over a 24-month period. The samples were analyzed using a gas chromatograph, HP 5890 series 11 with dual column and ECD detector. Sediment toxicity should be observed only rarely below the threshold effect concentration (TEC) and should be observed more frequently above the probable effect concentration (PEC).

The mean Polychlorinated Biphenyl  $\Sigma$ PCB range of 688-2964  $\mu\text{g}/\text{kg}$  dry wt. exceeded the TEC and PEC sediment quality guidelines of 59.8 and 676  $\mu\text{g}/\text{kg}$  dry wt. in all the locations. For organochlorine pesticides the  $\Sigma$ OCPs range between 1997-5023  $\mu\text{g}/\text{kg}$  dw, which was very high and SQGs were exceeded in all locations for chlordane (cis and trans chlordane), dichlorodiphenyldichloroethylene (DDE) and Lindane, sometimes 3-5 folds. The exceedance of screening values is an indicator of potential toxicity of River Niger sediments to benthic fauna. The results of this evaluation have provided reliable bases for classifying the entire sediment of River Niger as toxic. More site-specific monitoring and intensive evaluation of benthic health risk in this River should be conducted.

## Introduction

Persistent Organic Pollutants (POPs) are lipophilic, semi-volatile chemical substances that persist in the environment, bioaccumulate through the food web, and poses a risk of causing adverse effects to human health and the environment [1]. There has been international concern in recent times based on scientific and toxicological evidence about the dangers to human health and the environment by persistent toxic chemicals and their wastes [2]. The River Niger, the most important river in Nigeria, draining 60 % of Nigerian landmass, is being subjected to increasing human interference and receives considerable amount of pollutants from industrial, domestic sewage, storm water channels, agricultural activities and petroleum exploration and associated pollution in the Delta area. The river has a variety of physical modifications, such as dams, (Shiroro and Kianji), impoundments, channels for irrigation and dredging, which are capable of degrading water quality and contaminate sediments due to their many uses [3]. These physical and chemical impairments may affect biological organisms, in the river, causing health and reproductive problems in fish [4,5].

There have been a number of field studies investigating aspects of the relationships between POPs and suspended sediments [6-11]. These have looked at transport, suspended-sediment-bound concentrations under different flow regimes in rivers, correlations between suspended-sediment POPs concentrations and bed sediment and freely-dissolved concentrations, and the effects of suspended-sediment particle type and size. Publications comparing POPs concentration and sediment quality guidelines are scarce.

Numerical sediment quality guidelines, (SQGs; including sediment quality criteria, sediment quality objectives and sediment

quality standards) have been developed by various federal, state, and provincial agencies in North America for both fresh water and marine ecosystems. Such SQGs have been used in numerous applications, including designing monitoring programs, interpreting historical data, evaluating the need for detailed sediment quality assessment, assessing the quality of prospective dredged materials, conducting remedial investigations and ecological risk assessment and developing sediment quality remediation objectives [10]. Numerical SQGs have been used by scientists and managers to identify contaminants of concern in aquatic ecosystems and to rank areas of concern on regional or national basis [12]. It is obvious therefore that numerical SQGs when used in combination with other tools, such as sediment toxicity tests, represent a useful approach for assessing the quality of fresh water and marine sediments [12-17]. These SQGs have been developed to protect sediment-dwelling organisms, wildlife and humans.

The SQGs for the protection of sediment-dwelling organisms were grouped into two categories including TECs (threshold effect

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concentration) and PECs (probable effect concentration). The TECs were intended to identify contaminant concentrations below which harmful effects on sediment dwelling organisms were not expected. The PECs were intended to identify contaminant concentrations above which harmful effects on sediment dwelling organisms were expected to occur frequently [18]. Consensus PECs and TECs were investigated in the following compounds of interest, total PCBs, chlordane, dieldrin, DDD, DDE, DDT, total DDT, endrin, heptachlor epoxide,  $\gamma$ -HCH (Lindane) and total PAH [18].

This study therefore aims at obtaining information on the concentration of organochlorine pesticides and chlorinated biphenyls contaminants in sediments of the River Niger, their distribution in space, and provide scientific data for use in risk-based approach for the development and application of national environmental standards and guidelines, for POPs contaminants in such aquatic environment by comparing the levels with international sediment quality guidelines.

## Description of the Study Area

The River Niger 4,160 km long, is the 12<sup>th</sup> longest river in the world and the third longest in Africa, after Nile-Kagara 6500 Km, and Congo 4288 km [19].

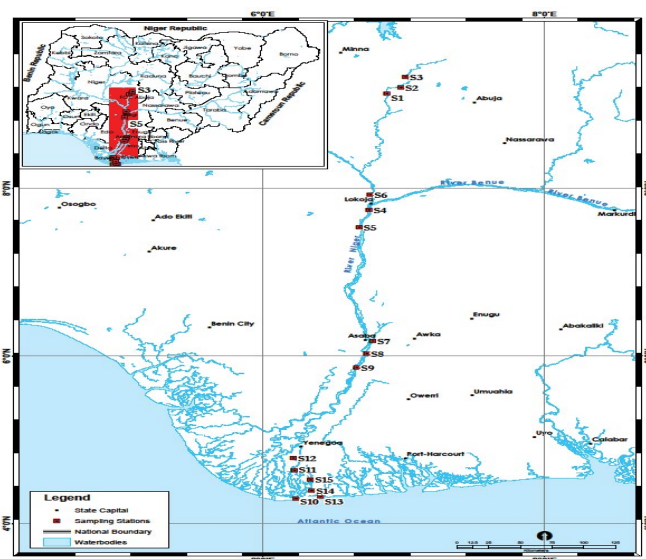
The Niger rises from the mountain of Sierra Leone on the Futa Jalon highlands, entering Nigeria, from North-West, the lower Niger Flows for 1271 km, reaching the sea via a number of tributaries. The Niger has a coastal delta which covers 36,260 km<sup>2</sup>, most of which is heavily forested, and also a coastal fringe of saline mangrove swamps, estuaries and freshwaters [20].

## Hydrology

The highest discharge rate of the River Niger in the rainy season is 14,000 m<sup>3</sup>/s and lowest discharge rate in the dry season is 1,500 m<sup>3</sup>/s. This maximum discharge is at Onitsha during October period of the rainy season. The Kaingi Dam is the major man-made feature on the river Niger. The Dam serves not only as major control of flow, it also acts as a major sediment trap for sediments transported from the upper reaches of the river. The drainage area of the Niger amounts to 260,000 km<sup>2</sup> and is drained by many affluents. The Benue river which is by far the largest tributary of the River Niger rises in the Cameroon on the Adamawa Plateau very high above sea level. At Lokoja, the Niger is joined from the east by its largest tributary, the Benue River, which about doubles the annual discharge of the Niger. The total drainage area of the Niger and Benue within the territory of Nigeria is approximately 140, 000 km<sup>2</sup> and covers about 60% of the Nigeria's total area. They form the main artery of the country [20]. Figure 1.

## Climate

Locally the seasonal pattern and amount of rainfall depend on the latitude and the position of ITCZ (intertropical convergence zone) which migrate from 5 N (December to March) to 20 N (July-August). According to Nriagu, [21] four main climatic areas are visited by the River Niger: i) a tropical transitional zone at the top of the Niger basin and its affluent, with a rainy season which is 8 months long from April to November and annual precipitations higher than 1,500 mm, ii) a sudanian zone gathering both from the north of Guinea and Côte d'Ivoire to the south of Mali as the west course of the river leading to the north of Nigeria which forms the east course of the river. Annual precipitations range from 750 to 1,500 mm with a 5 to 7 months rainy season, iii) a sahelian/sub-desert zone gathering the Central delta and the river downstream in Mali and Niger. Precipitations are ranging from 250 to 750 mm with one rainy season 3 to 4 months long. (iv) An equatorial zone in south Nigeria (marine delta) characterized by two rainy seasons, two dry seasons and very high precipitations (4,000 mm).



**Figure 1:** Map of the River Niger showing the sampling stations and the drainage basin.

## Water Chemistry

The lower Niger is predominantly fresh water with zero salinity, and very high turbidity. Along the river as a rule, the range between the lower water levels and the average high-water levels increase when going downstream, to a point which is called the apex of the Niger Delta, where the range starts to decrease, until it reaches the tidal range of the sea into which the river debouches. The apex of the Niger Delta is situated near the village Aboh in Delta State [21]. During the wet season (May-October), salinities fall to almost zero throughout the delta. River flow in the dry season (November-March) is still sufficient to keep the maximum salinity at the mouth to 28 ‰. Detailed studies of the Bonny estuary, part of the delta have been carried out (Dublin-Green, 1990) and results showed that salinity, conductivity, pH, dissolved oxygen and alkalinity exhibited spatial and temporal variations. Minimum salinities of 14-24 ‰ and maxima of 19-31 ‰ were detected in the late wet season and late dry season respectively, in both the upper and lower reaches of the estuary.

## Methodology

River Niger traverses different ecological zones in its journey from Kebbi State to the Niger Delta Region. In this regard, the influence of population density, agricultural and industrial activities on the environmental fate may be determinant factors on the levels and fate of POPs. Consequently, the project design is as follows:

Fifteen representative sites along River Niger; three each from Gurara River (tributary) in Niger State, Lokoja (confluence) in Kogi State, Onitsha in Anambra State, Brass and Nicolas rivers (tributaries) in Bayelsa State were purposefully selected for sampling over a 24-month period (Fig. 1). The locations were properly coded and georeferenced. The frequency of sampling was quarterly between 2008 and 2009 to be able to capture the early and late rainy seasons, with the associated storm water runoff into the river and also capture the early and late dry season, sometimes associated with sudden point source discharges (Table 1).

## Sediment Sampling

A total of 120 sediment samples were collected from the Niger, Brass and Nicolas Rivers quarterly between February and December 2008 to 2009, using Van Veen grab sampler. Five sampling locations along these rivers were selected and three samples from each location were collected. The distance between each sampling location was approximately 1 km Water which is covered by moving the boat to

**Table 1:** River Niger Nigeria sampling sites, coordinates, samples collected and comments.

Code Sediment	Code Water	Long.	Lat.	Dates Sampled	Comment
NGSD1	NGSW1	007.00.29	09.14.58	31/03/08-09	Surface and Bottom water collected by wadding. Sediment collected by grabbing. Discharge mainly agricultural runoff. Water released from Shiroro dam in December. Fish samples also collected.
NGSD2	NGSW2	007.00.20	09.14.55	01/06/08-09	
NGSD3	NGSW3	007.00.12	09.14.53	01/08/08-09	
NLSD4	NLSW4	006.45.24	07.44.51	15/12/08-09	Samples collected by motorized boat. Highly polluted area, dairy industry, timber processing, sand mining/quarrying, slaughter house, agricultural runoff. Fish samples also collected.
NLSD5	NLSW5	006.45.05	07.46.18	01/04/08-09	
NLSD6	NLSW6	006.45.29	07.47.42	02/06/08-09	
NONSD7	NONSW7	006.46.81	06.10.69	02/08/08-09	
NONSD8	NONSW8	006.45.19	06.08.01	16/12/08-09	
NONSD9	NONSW9	006.42.81	06.05.08	10/03/08-09	
NBRSD10	NBRSW10	006.14.11	04.17.99	14/05/08-09	Samples collected by motorized boat. Highly polluted area, dairy industry, timber processing, sand mining/quarrying, slaughter house, no agricultural activity, heavy industrialization. Fish samples also collected.
NBRSD11	NBRSW11	006.15.72	04.21.65	18/07/08-09	
NBRSD12	NBRSW12	006.18.72	04.25.50	08/12/08-09	
NNCSD13	NNCSW13	006.19.88	04.17.99	08/03/08-09	High and low tide water samples collected with motorized boat. No agricultural activity. High presence of petroleum exploration. No industry. Fish samples collected
NNCSD14	NNCSW14	006.19.21	04.21.65	10/05/08-09	
NNCSD15	NNCSW15	006.19.16	04.23.66	15/07/08-09	
				06/12/08-09	

the next station. Depths in the stations ranged between 1.0 to 7.50 m. Motorized boat was used for grabbing at all the locations except Gurara River.

Immediately the grab is lifted to the boat a stainless-steel scoop pre-cleaned with acetone was used to collect about 100g of the sediment sample into a pre-cleaned 200 ml amber glass bottled. The sample was preserved in a cooler with ice blocks. Immediately on land the sampled were preserved in a deep freezer to avoid degradation. Samples were stored for the shortest possible time interval between sampling and extraction/cleanup.

## Experimental

### Chemicals

All solvents analytical grade (Hexane, acetone, Dichloromethane, Petroleum spirit, acetonitrile) were purchased from Merck, Germany, and distilled over 0.5 m packed column (reflux ratio approximately 1:25) [22]. The solvent purity was tested by gas chromatographic analyses. Anhydrous granulated sodium sulfate and silica gel 100-200 mesh (Merck, Germany) which are part of the analytical procedure were cleaned with pure n-hexane by distillation. The external and internal standard, were purchased from Restek USA. and was constituted of 1000 µg/ml of the following 20 organochlorine compounds, α-BHC, β-BHC, γ-BHC, δ-BHC, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide, Adrin, Dieldrin, endosulfane 1, endosulfane 11, endosulfane sulfate, methoxychlor, α-chlordane, γ-chlordane, DDE, DDT and DDT. The PCB external standard consisting of 27 congeners was also purchased from Restek USA. The congener IUPAC numbers were 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, and 206.

### Sediment Sample Preparation

The procedures EPA3570, and Steindwandter and Shutler [23] with slight modifications were used. Approximately 10.0 grams of anhydrous sodium sulfate was added to a pre-cleaned mortar and 5grams of fresh wet sediment was added to the mortar and homogenized to a complete mixture with a pistle. The mixture was carefully transferred to a pre-cleaned polytetrafluoro ethylene (PTFE) extraction tube which has a PTFE screw cap. 5 to 10 pre-cleaned glass beads were added. 25 mL of a mixture of acetone and petroleum spirit (1:1) was added to the 100 ml PTFE extraction tube; the extraction tube was tightly capped and allowed to stand for minimum of 20 minutes. This allows complete permeation of solvent to the matrix. 20 µg/l of the internal standard decaflourobiphenyl in iso-octane directly was added to the sediment and sodium sulphate mixture. The tube was shaken

vigorously until the slurry is free-flowing. Any chunks were broken manually with the glass rod, working quickly but gently. The cap was replaced immediately after the breaking of the chunks. More sodium sulfate was added and manually mixed as necessary to produce free-flowing, finely divided slurry. The samples were extracted by rotating end-over-end for at least 30 minutes. Care was taken to release pressure by opening and closing the flasks at intervals.

The solids were allowed to settle for one to two minutes. The solvent layer was filtered through a small glass funnel containing a layer of anhydrous sodium sulfate over a plug of glass wool into a receiving cornical flask. The sodium sulfate was thoroughly pre-wetted with acetone before sample filtration. The sodium sulfate was rinsed with 2 to 3 mL of acetone assoon as the surface is exposed. The top of the sodium sulfate layer was not allowed to go dry. The sediment sample was extracted twice more by adding approximately 15 mL of acetone/petroleum spirit mixture to the sample, capping the extraction tube tightly, and shaking vigorously by hand for 2 minutes. All the extracts are combined and poured into the round bottom flask of the rotary evaporator.

The round bottom flask of the rotary evaporator was placed in a constant temperature hot water bath so that the concentrator flask is partially, but not completely, immersed. The temperature of the bath was adjusted and the position of the apparatus so that, the solvent heat evenly. The sample volume was reduced to approximately 1.0 mL.

### Cleanup for Sediment

A 600 mm x 19 mm id cleanup column was prepared by blocking the hole with glass wool and adding 3g of activated silica gel (60 to 100 mesh, calcined at 650°C for 24 hrs in a murfle furnace, and then stored at 130°C until use. Before use the silica gel was deactivated with 1 ml distilled water. The column was topped with 1 cm of preheated Na2S04 previously heated at 650°C for 8 hrs in a furnace and stored in a clean bottle in a dessicator. The column was rinsed by eluting with 20 ml hexane twice and discarded (Appendix 90). The concentrated extract in iso-octane was transferred to the column and eluted with 50 ml of 20 + 80 DCM/hexane (v/v ratio). The eluent was collected in a 100 ml round bottom flask. This fraction (referred as eluent 1) contains PCBs and about 14 OCs [24].

The elusion was continued with another 50 ml of 50 + 49.65 + 0.35 DCM/hexane/acetonitrile mixture and the eluate collected in another 100 ml round bottom flask. This fraction called eluate 2 contains endosulfan, dieldrin, endrin, and methoxychlor. The eluates are reduced by volume with rotary evaporator to 3 ml and solvent exchanged to iso-octane and the volume is further reduced to 1 ml in

a stream of nitrogen [24].

### Quality Control and Data Analysis

Certified reference standards from Accustandards USA was used for the instrument calibration and quantification of PCB congeners and OCPs. The PCB congeners and the OCPs were identified in the sample extracts by comparing the accurate retention time from the standard mixture and quantified using response factors from five level calibration curves of the standards. Appropriate quality assurance and quality control (QA/QC) analysis was performed including analysis of procedural blanks (analyte concentration were <MDL 'method detection limit') to check for purity of reagents, potential laboratory contamination and inferences. Random duplicate samples were analysed (standard deviation <5) to check the precision of the instrument. Five calibration curves with r<sup>2</sup> value of 0.999 was used for the quantification of the OCPs and the PCBs. Calculated concentrations were reported as less than the limit of detection if the peak area did not exceed the specified threshold (three times the noise). Concentrations below the limit of detection (BDL) were assigned zero values for the statistical analysis. The PCBs were denoted by their International Union of Pure and Applied Chemistry (IUPAC) numbers. The Certified Reference Material (CRM) from IAEA was extracted, cleaned up and analysed using the same procedure used for the environmental samples. All the results were expressed in wet weight bases and were not corrected for recoveries.

## Results and Discussion

### Quality Control and Quality Assurance

All data were subjected to strict quality control procedures, including the analysis of procedural blanks and spiked samples with each set of samples analysed. Five-point standard curve method was used with r<sup>2</sup>=0.999. None of the target compounds were detected in the procedural blanks for water and sediment. Spiked water and sediment samples were determined with good precision and high recoveries (Table 4.2). The recoveries for the OCPs ranged between 78±2.20 % to 92±2.10 % and for the PCBs ranged between 80±2.10 to 93±2.80. In addition, the errors involved in sampling were assessed by carrying out triplicate sampling of water at the same site and the analysis of sample extracts.

The results (Table. 2) showed that the precision was generally satisfactory. The standard deviation for the 20 OCPs determined ranged from 0.05 to 5.76, with mean standard deviation of 1.50. Finally, internal standards were used to compensate for losses involved in the sample extraction and work-up, to further improve the analytical quality. The detection limit of the equipment used ranged from 0.25 to 0.50 ng/L for OCPs and 0.05 to 0.30 ng/l for PCBs.

To monitor the accuracy of the GC method, an International Atomic Energy Agency (IAEA) Standard Reference Material sediment homogenate (SRM 417) and fish tissue homogenate (IAEA SRM 406) were analyzed with each sample set and the results, based on the standard deviation was satisfactory (Table 2).

### Concentration of OCPs

The highest concentration of ΣOCPs in the sediment samples of the River Niger, 5023±1596 µg/kg, with range 4672-7009 µg/kg was detected in station NONSD8 at Onitsha location, while the lowest concentration of ΣOCPs, 1570±204.5, with range 1214-1820 µg/kg was detected at station NNCS14 (Table 3), at Nicolas River. High values of ΣOCPs >2000 µg/kg were also detected in all the other stations except stations, NONSD7, NBRSD10, and NNCS1, where lower levels were detected. The concentration of the summation of the OCP compounds varied markedly along the different locations of the River Niger with high concentration of the different isomers

**Table 2:** Analysis of Standard Reference Material (SRM 417 from IAEA).

Compound	SRM	Sediment homogenate	
	SRM Value	This Study	SD
α-HCH	0.28	0.19	0.05
β-HCH	2.80	2.50	0.15
γ-HCH	0.54	0.49	0.03
p'p'-DDT	19.0	17.5	0.50
p'p'-DDE	14.0	13.3	0.35
p'p'-DDD	21.0	20.58	0.21
Heptachlor	2.0	1.75	0.13
Heptachlor epoxid	4.80	3.39	0.71
Aldrin	1.60	1.20	0.20
Dieldrin	2.30	2.41	0.06
Endrin	7.10	7.40	0.15
Endosulfan 1	14.0	13.10	0.45
Endosulfan 11	5.10	4.80	0.15
Endo. sulfate	8.40	7.50	0.45
α-Chlordane	1.80	1.68	0.06
γ-Chlordane	1.20	1.11	0.05
PCB-18	-	-	-
PCB-28	5.70	5.46	0.12
PCB-44	9.70	8.99	0.35
PCB-52	17.0	16.40	0.30
PCB-101	42.0	41.2	0.30
PCB-105	22.0	18.0	0.50
PCB-118	-	-	-
PCB-128	12.0	10.99	0.30
PCB-138	45.0	42.0	0.50
PCB-156	5.90	5.40	0.20
PCB-170	8.10	7.75	0.20
PCB-195	1.20	0.98	0.10
PCB-206	1.80	1.45	0.12

**Table 3:** Concentration of POPs in the sampled locations µg/kg (fw).

Sample Location	ΣOCPs	ΣPCBs (27 congeners)
NGSD1	2181±962.5 (1083-3492)	2679±309.1 (2126-3298)
NGSD2	2482±905.3 (1402-3764)	2093±443.3 (1466-2818)
NGSD3	3804±1658 (1907-6070)	2601±289.0 (2148-3096)
NLSD4	2513±505.7 (1723-3159)	1499±333.2 (999.6-1999)
NLSD5	3675±735 (2520-4620)	2039±453.2 (1359-2719)
NLSD6	2456±491 (1684-3088)	740.7±164.6 (493.8-987.6)
NONSD7	1800±272.8 (1309-2182)	1405±312.4 (937.2-1874)
NONSD8	5023±1596 (4672-7009)	2830±629.0 (1887-3774)
NONSD9	2146±325 (1561-2601)	535.8±152.2 (328.8-828.0)
NBRSD10	1997±745.3 (1113-2816)	1517±733.3 (743.0-2369)
NBRSD11	2127±132.0 (1863-2329)	1061±120.3 (892.0-1244)
NBRSD12	2329±147.1 (2098-2623)	919.8±48.3 (847.0-995.0)
NNCS13	2081±271.3 (1609-2413)	687.8±98.3 (524.0-786.0)
NNCS14	1570±204.5 (1214-1820)	2032±290.3 (1549-2323)
NNCS15	2298±299.8 (1777-2665)	2964±423.8 (2258-3388)

\*Mean values, range in parenthesis

identified in different locations but the lowest concentration most times detected at the Nicolas River location NNSD14.

Hong et al., [25], detected relatively high levels of DDTs, 0.31-274.0 µg/kg dry weight in sediment from coastal areas of Vietnam.

However, low levels of DDTs were reported in most Asian Rivers. Liu et al., [26] detected levels of 0.90-33.1,  $\mu\text{g}/\text{kg}$  dry weight in Yangtze Estuary, China, Yang, et al., [27], 0.32-80.18  $\mu\text{g}/\text{kg}$  dry weight, in Haihe River, China, and Wurl and Obbard, [28] also detected low levels of DDTs in coastal areas of Singapore. Hong et al., [25], detected low levels of HCHs, ND-1.00  $\mu\text{g}/\text{kg}$  dry weight in sediment from coastal areas of Vietnam. Also low levels of HCHs were reported in most Asian Rivers. Liu et al., [26] detected levels of 0.50-17.5,  $\mu\text{g}/\text{kg}$  dry weight in Yangtze Estuary, China, Yang, et al., [27], 1.88-18.8  $\mu\text{g}/\text{kg}$  dry weight, in Haihe River, China, and Wurl and Obbard, [28] also detected low levels of HCHs in coastal areas of Singapore, 3.40-46.1  $\mu\text{g}/\text{kg}$  dry weight. Fillman et al., [29], Barakat et al., [30] and Sapozhnikova et al., [31] detected low levels DDTs and HCHs in Black sea Romania, Alexandria harbor Egypt and Salton Sea California respectively. The levels of DDTs and HCHs were 0.60-72.0; 0.20-40.0, <0.25-885; 0.25-6.00, 6.80-40.2; and ND respectively.

### Concentration of PCBs

The total PCBs in sediment was very high in all the locations of the River Niger (Table 3). The sum PCB concentration sequence in the locations is as follows Nicolas>Gurara>Onitsha>>Lokoja>Brass. The highest sum PCB concentration, 2964 $\pm$ 423.8  $\mu\text{g}/\text{kg}$ , range 2258-3388  $\mu\text{g}/\text{kg}$  fw was surprisingly detected at Nicolas River location NNCS15, followed by 2830 $\pm$ 629.0, (1887-3774)  $\mu\text{g}/\text{kg}$  detected at NONSD8 at Onitsha (Table 3). The sum PCB concentration at NGSD1, NGSD2, and NGSD3 were 2679.0 $\pm$ 309.1, (2126-3298)  $\mu\text{g}/\text{kg}$ , 2093 $\pm$ 443.3, (1466-2818)  $\mu\text{g}/\text{kg}$ , 2601 $\pm$ 289.0  $\mu\text{g}/\text{kg}$  (2148-3096  $\mu\text{g}/\text{kg}$  respectively. Lower levels were detected at NNCS13, NNCS14, NNCS15, 687.8 $\pm$ 98.3, (524.0-786.0)  $\mu\text{g}/\text{kg}$ , 2032 $\pm$ 290.3  $\mu\text{g}/\text{kg}$ , (1549-2323)  $\mu\text{g}/\text{kg}$ , 2964 $\pm$ 423.8  $\mu\text{g}/\text{kg}$ , and (2258-3388)  $\mu\text{g}/\text{kg}$  respectively. The third highest levels were detected midstream at Onitsha location NONSD7, NONSD8, and NONSD9, 1405 $\pm$ 312.4  $\mu\text{g}/\text{kg}$  (397.2-1874)  $\mu\text{g}/\text{kg}$ , 2830 $\pm$ 629.0, (1887-3774)  $\mu\text{g}/\text{kg}$ , 535.8 $\pm$ 152.2,  $\mu\text{g}/\text{kg}$  (328.8-828.0 respectively. The sum PCBs at the Lokoja location, NLS4, NLS5, NLS6 were, 1499 $\pm$ 333.2, (999.6-1999),  $\mu\text{g}/\text{kg}$  2039 $\pm$ 453.2, (1359-2719)  $\mu\text{g}/\text{kg}$ , and 740.7 $\pm$ 164.6, (493.8-987.60)  $\mu\text{g}/\text{kg}$  respectively (Table 4.22, Fig. 4.25). Lastly the lowest levels of sum PCBs were observed at the Brass River locations, NBRSD10, NBRSD11, and NBRSD12, with values 1517 $\pm$ 733.3, (743.0-2369)  $\mu\text{g}/\text{kg}$ , 1061 $\pm$ 120.3, (892.0-1244),  $\mu\text{g}/\text{kg}$  and 919.8 $\pm$ 48.3, 847.0-995.0)  $\mu\text{g}/\text{kg}$  respectively. The lowest  $\Sigma\text{PCB}$  concentration 535.8 $\pm$ 152.2,  $\mu\text{g}/\text{kg}$  (328.8-828.0) was observed at location NONSD9 in Onitsha (Table 3). This location is constantly flushed by fresh water from Anambra River.

Spatial variations in suspended- sediment-bound concentrations can also reflect source differences [10]. There is also likely to be a dilution of suspended sediments carrying contaminants by clean suspended material as the distance away from the source increases [6]. Temporal variations in non-tidal stretches of rivers usually result from changes in flow levels into and through the river, often varying with season [10].

The sum PCBs decreased downstream. However, high values were obtained at NNCS15 location. Such observations indicate that local points of high contamination are not necessarily restricted to near-source zones; instead contamination can be localized in low energy sedimentary environments far from source by suspended-sediment transport. Nicholls [7] suggests that the monitoring of fine-sediment accumulation zones could provide an early-warning system for POPs contamination of water bodies.

Echols et al., [32], detected low levels of sum PCBs downstream, 60.0 $\pm$ 70.0  $\mu\text{g}/\text{kg}$ , and upstream, 19.0 $\pm$ 6.00  $\mu\text{g}/\text{kg}$ , in sediment sample from lower Missouri River. Sediments from upper Mississippi River were generally comparable to those in the lower Missouri, most within

the range between 10.0 and 100.0  $\mu\text{g}/\text{kg}$  dw, but a few sediments from the upper Mississippi (US Geological Survey 2007) contained concentrations of total PCBs in sediments between 1000 and 3300  $\mu\text{g}/\text{kg}$ , which are close to the values obtained at mid-stream the River Niger in this study. PCBs from sediments from+ Hudson River, with known point sources of PCBs had a median concentration of 2700  $\mu\text{g}/\text{kg}$  dw for over 5100 samples collected in 2002 by the US EPA [14]. Almost 30 % of the sediment samples from this EPA program had total PCB concentrations above 20,000  $\mu\text{g}/\text{kg}$  dw which is about 10 times higher than concentrations found in the lower River Niger. Only Kaba, [1991], reported high maximum levels of  $\Sigma\text{PCBs}$  335.0 (8.50-1014)  $\mu\text{g}/\text{kg}$  dw in some locations of the Ebrie Lagoon. All the others, Sunday [33], Ojo [34], reported very low levels compared to the present study.

The reports of Maldonado et al., [35], in Cities in India, Nhan et al., [36], in cities in Thailand, Japan and Australia, showed concentrations of 4.80-1000, 63.0-240, 11.00-520, and 0.50-790  $\mu\text{g}/\text{kg}$  dw which are also lower than the levels detected in this study. Eisenreich et al., [37] reported gradual decrease in the concentration of  $\Sigma\text{PCBs}$  in the 1960s to 1980s from 470-880  $\mu\text{g}/\text{kg}$  dw to 250-290  $\mu\text{g}/\text{kg}$  dw, in Lake Ontario sediment cores. Oliver et al., [38] reported the sequence in concentration of the PCB homologues as Tetra>Penta>Hexa, in surficial sediments of Lake Ontario with concentrations 77.0-200>76.0-180.0>41.0-93.0  $\mu\text{g}/\text{kg}$  dw (Table 2.6). His findings also support the gradual decrease of PCBs in Lake Ontario surficial sediments over the years. The concentrations are lower than the present study and also the sequence disagrees with the present study where the sequence Penta>Hexa>Tetra dominates. The sequence of the homologues in Hamilton and Wheatney harbor sediments and oligocheats agree with the sequence in this study, where penta homologue dominates. Chapman et al., [39], and NOAA, [40] reported very high sum PCB levels, >20,000  $\mu\text{g}/\text{kg}$  dw, in long beach California, Santiago bay, Connecticut River, New Jersey, Raritan Bay, Virginia, Elizabeth River and St Andrews Bay, all in the United States. These locations had PCB manufacturing plants close to them before the ban. Burgess et al., [41], detected high PCB level, 3,800  $\mu\text{g}/\text{kg}$  dw in New Bedford harbor USA. This result agrees with the highest PCB concentration in this study, 2964  $\mu\text{g}/\text{kg}$  fw detected in location NNCS15 at Nicolas. Very low levels of PCBs have been detected in marine sediments. Montine et al., (2001) reported low levels of PCBs, 0.47-2.47  $\mu\text{g}/\text{kg}$  dw in marine sediment from Admiralty Bay. Negri et al., [42] detected low levels of PCBs, <5.0-40.0, 220-373, and <5.0  $\mu\text{g}/\text{kg}$  in Scot Base, McMurdo and Turtle Rock Base respectively. However, Crooket and White, [43] reported PCB levels of 220-4300  $\mu\text{g}/\text{kg}$  in Winter Quarters Bay. Klonova, et al, [44], detected low PCB levels, 0.50-2.0, and 0.40-0.80  $\mu\text{g}/\text{kg}$  dry weight. Marine sediments are contaminated by POPs through inflow from rivers.

### Consensus based sediment guidelines

The consensus-based sediment quality guideless (SQGs) were critically evaluated to determine if they would provide effective tools for assessing sediment quality conditions in fresh water ecosystems in River Niger. Sediment toxicity should be observed only rarely below the TEC (threshold effect concentration) and should be observed frequently above the PEC (probable effect concentration).

The table above (Table 4) shows the concentration of POPs in sediment in all the locations of the River Niger compared to the TEC and PEC sediment guidelines [18]. The mean  $\Sigma\text{PCBs}$  in the locations ranged between 536.0 to 2964  $\mu\text{g}/\text{kg}$  dry weight detected in locations NONSD9 and NNCS15. The  $\Sigma\text{PCBs}$  exceeded the guideline PEC 676  $\mu\text{g}/\text{kg}$  and TEC 59.8  $\mu\text{g}/\text{kg}$  in all the locations except location NONSD9. The chlordane concentration ( $\gamma$ -chlordane+  $\alpha$ -chlordane) ranged between 24.4 to 134.1  $\mu\text{g}/\text{kg}$  dry weight in locations NNCS14 and NLS5. The guideline limits were also exceeded in this case [45-



**Table 4:** Consensus-Based Sediment Quality Guidelines ( $\mu\text{g}/\text{kg}$  dw).

Location	$\Sigma\text{PCBs}$	Chlordane	Dieldrin	DDD	DDE	DDT	$\Sigma\text{DDT}$	Endrin	Hepta epoxide	Lindane
NGSD1	2679	108.2	26.7	38.8	59.8	47.3	145.9	62.8	134.9	78.9
NGSD2	2093	99.3	9.83	299.7	103.8	236	640	58.8	165.3	52.8
NGSD3	2601	87.1	58.6	455.2	61	221	737.5	33.1	149.9	53.6
NLSD4	1499	123	10.8	533.8	71.2	54.1	658.9	13.6	104.1	22.3
NLSD5	2039	134.1	52.7	317.6	68.9	BDL	386.7	43.7	105.8	15.7
NLSD6	741	82.4	55.7	BDL	66.5	107.6	174.1	64.9	121.6	18.6
NONSD7	1405	86.8	28.9	BDL	117.3	33.1	150.2	44	132.9	8.09
NONSD8	2830	59.9	70.3	BDL	81.4	10	91.4	99	76.6	69.1
NONSD9	536	99.8	5.67	BDL	57.3	BDL	55.9	33.8	92.5	18.7
NBRSD10	1517	72	39.9	147	51.1	9.31	207.4	42	117.8	14.2
NBRSD11	1061	97.9	12.8	287.2	38.9	37.2	363.3	19.2	148.5	18.1
NBRSD12	920	112	19.1	334.5	44.3	37.9	416.8	28.3	170.5	22.3
NNCSD13	688	55.1	41.2	97.3	22.2	BDL	557	38.9	112.1	12.9
NNCSD14	2032	24.4	25.6	105.5	43.9	BDL	528.8	44.8	67.1	3.9
NNCSD15	2964	32.8	23.6	61.6	65.9	BDL	120.5	40.2	119	13.1
TEC	59.8	3.24	1.90	4.88	3.16	4.16	5.28	2.22	2.47	2.37
PEC	676	17.6	61.8	28.0	31.3	62.9	572	207	16.0	4.99

MacDonald et al., (2000)  $\mu\text{g}/\text{kg}$  dry weight.

\*TEC= threshold effect concentration, below which harmful effects are unlikely to be observed in sediments

\*PEC= probable effect concentration, above which harmful effects are likely to be observed.

49]. The situation is different when dieldrin is considered. Dieldrin was detected at very low levels in most of the locations and ranged between 5.67 to 70.3  $\mu\text{g}/\text{kg}$  dry weight in locations NONSD9 and NONSD8.

The PEC guideline was only exceeded in location NONSD8 with reference to Dieldrin; however, the TEC guideline was exceeded in all the locations. In the case of DDD, which was not detected in locations NLSD6, NLSD7, NONSD8 and NONSD9, the concentration in all the other locations exceeded the guidelines, while DDE concentrations exceeded the guidelines except in location NNCSD13 (Table 4). DDT was not detected in most locations, and when detected, the levels were low, except in locations NLSD6 and NGSD2 where the concentrations exceeded the guidelines.  $\Sigma\text{DDT}$  guideline was exceeded only in locations NGSD2, NGSD3, and NLSD4. The PEC guideline was not exceeded in any location for endrin; however, heptachlor epoxide and lindane guidelines were exceeded in all locations.

## Conclusion

This exceedance of screening value is an indication of potential toxicity to benthic fauna, more site-specific monitoring and or intensive evaluation of benthic health risk should be conducted. The results of the evaluation of the TEC and PECs of the sediments, has provided a reliable basis for classifying the entire sediment of the River Niger as toxic. All the sediment locations in the Niger are hotspots because most of the time the guidelines are exceeded 5 to 10-fold. Constant monitoring of this River sediment and remediation is recommended.

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