Concentration and Distribution of Organochlorine Pesticides in Sediments of the Niger River, Nigeria

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Introduction

Pollution of aquatic ecosystems is a serious environmental concern, particularly in Africa. The challenge remains a multi-faceted problem due to indiscriminate dumping of waste and illegal use of banned pesticides.1,3 There is a need for constant assessment and monitoring of hazardous substances, particularly in aquatic environments in developing countries, because rivers are media with easy trans-boundary transport of chemical substances.

Several studies have reported the relationships between persistent organic pollutants (POPs) and suspended sediments.4,5 Investigations include POPs transport, variation in suspended-sediment-bound concentrations with flow regimes of rivers; relationships between the concentrations of POPs in suspended sediment and in bed sediment; and the effects of particle type and size of suspended sediment. However, there is little information on the effect of sedimentation regimes on the distribution of POPs in bed sediment. Nichols investigated kepone in suspended bed sediments of the St. James River in Canada, reporting concentrations greater than 200 mg/kg around the source of contamination.

Background. Pollution in aquatic ecosystems is a serious environmental concern. There is a great need for constant assessment and monitoring of hazardous substances, particularly in aquatic environments in developing countries, as rivers are media with easy trans-boundary transport of chemical substances.

Objectives. The present study assessed the occurrence and distribution of organochlorine pesticides (OCPs) in the sediments of the Niger River, Nigeria.

Methods. A total of 120 samples of sediment were collected from 15 locations along the river using Van Veen grab. The Environmental Protection Agency (USEPA) 3570 method with slight modification was used for sample preparation. Organochlorine pesticides were analyzed using Hewlett Packard 5890 series II gas chromatography with electron capture detector. Confirmation of OCPs was performed using a gas chromatograph/mass spectrometer (Shimadzu QP2010) and capillary column type HP1MS (30 m x 0.25 um x 0.25 mm id).

Results. The highest concentration of ΣOCPs in the sediment samples of the River Niger (5023±1596 µg/kg, 4672-7009 µg/kg) was detected in a location at Onitsha, while the lowest concentration (1570±204.5, 1214-1820 µg/kg) was detected in a location at the Nicolas River.

Discussion. High values of ΣOCPs (>2000 µg/kg) were detected in all of the locations except in three locations where lower levels were detected. The ΣOCPs were higher during the dry season compared to the rainy season. This may be because the resident time of the sediment transported was higher during the dry season compared to the rainy season, which is characterized by storms, high current, and bottom scour. The chlordane concentration ranged between 24.4 and 134.1 μg/kg dry weight (dw) in locations Nicolas 14 and Lokoja 5; and the Probable Effect Concentration guidelines were exceeded. Dieldrin was detected at very low levels in most of the locations and ranged from 5.67 to 70.3 μg/kg dw in locations Onitsha 9 and 8; and the Probable Effect Concentration guideline was only exceeded in location Onitsha 8; however, the Toxic Effect Concentration guideline was exceeded at all of the locations. Dichlorodiphenyldichloroethane (DDD) was not detected in location Lokoja 6 or 7, and Onitsha 8 and 9, although the concentration in all other locations exceeded the guidelines. Dichlorodiphenyldichloroethylene (DDE) concentrations exceeded the guidelines except in location Nicolas 13.

Conclusions. Due to the environmental/human risk and potential danger of the elevated levels of OCPs, there is a need for continuous monitoring of the Niger River.

Competing Interests. The authors declare no competing financial interests.

Keywords. Organochlorine pesticides (OCPs), persistent organic pollutants (POPs), sediment, Niger River

Received September 28, 2018. Accepted April 11, 2019

J Health Pollution 22: (190606) 2019
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and 60-200 mg/kg downstream.\(^4\) This implies the possibility of suspended sediment transport and localization in low energy sedimentary environments away from the source of contamination. This may indicate that the accumulation of POPs in fine sediment signals the contamination of water bodies with POPs.\(^4\)

Although there is insufficient data on POPs consumption and use in Nigeria, POPs have been widely used in Nigeria on food and cash crops, as well as vector disease control since World War II.\(^6,7\) Data on long range transport, deposition, persistence, bioaccumulation, and toxicity are available for few chemicals, hampering the identification of chemicals that may meet the POPs criteria.\(^8\) Data on POPs are rare in Nigeria, particularly on trends in POP levels in the Niger River ecosystem. Information on the environmental fate of POPs in the Nigerian aquatic ecosystem is needed for appropriate national policy on the management of POPs. The present study aimed to determine the concentration and distribution of organochlorine pesticides in the sediment of the Niger River.

**Methods**

Sampling locations included the Gurara River (tributary), Lokoja (confluence), Onitsha, Brass, and Nicolas (Figure 1). Three sites were selected from each location, totaling fifteen representative sites (Table 1). Collection of samples was done quarterly for 2 years from 2008 to 2009, with the intervals coinciding with the early and late rainy and dry season. A total of 120 samples of sediment (30 samples quarterly) were collected. The distance between each sampling location was approximately 1 km. Depths in the stations ranged between 1.0 to 7.50 m. A motorized boat was used for grabbing at all locations.

Samples of surface sediments were collected at a depth of 15 cm of the surface sediments using a Van Veen sediment grabber. The collection was immediately lifted to the boat. A stainless-steel scoop pre-cleaned with acetone was used to collect about 100 g of the sediment sample into a pre-cleaned 200 ml amber glass bottle. The sample was preserved in a cooler with ice blocks. Samples were transferred and preserved in a deep freezer as quickly as possible to avoid degradation. Samples were stored for the shortest possible time interval between sampling and extraction/cleanup.

**Reagents**

Analytical grade petroleum spirit, hexane, dichloromethane, acetone, and acetonitrile were purchased from Merck (Germany). They were distilled over a 0.5 m packed column. Anhydrous granulated sodium...
Sulfate and silica gel (100-200 mesh) were also purchased from Merck (Germany). The external and internal standard were purchased from Restek (USA) and constituted of 1000 µg/ml of α-benzene hexachloride (BHC), β-BHC, γ-BHC, δ-BHC, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide, aldrin, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, methoxychlor, α-chlordane, γ-chlordane, dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethylene (DDE), and dichlorodiphenyldichloroethane (DDD).

Sample preparation and extraction

The details of sample preparation method are described in the Environmental Protection Agency (EPA) 3570 method and Standwandter and Shutler. Anhydrous sodium sulfate (10.0 g) with 5 g of fresh wet sediment was homogenized in a pre-cleaned mortar and transferred to a pre-cleaned polytetrafluoro ethylene extraction tube. Glass beads (5 to 10) were added, followed by a mixture of acetone (25 mL) and petroleum spirit (1:1); the extraction tube was tightly capped and allowed to stand for a minimum of 20 minutes. Twenty (20) μg/l was then added of the internal standard decafluorobiphenyl in iso-octane. The tube was shaken vigorously until the slurry was free-flowing. The samples were extracted by rotating end-over-end for at least 30 minutes. The solvent layer was filtered through a small glass funnel containing a layer of anhydrous sodium sulfate over a plug of glass wool. The sediment sample was extracted twice more by adding 15 mL of acetone/petroleum spirit mixture. All of the extracts were combined in a round bottom flask of rotary evaporator and the sample volume reduced to about 1.0 mL. The details of the procedure for extraction, extract concentration and extract cleanup are described in Unyimadu et al.9,12,13

Quality control and data analyses

Quality assurance and quality control analyses detailed in Unyimadu et al. were performed including analysis of procedural blanks. Using the certified reference material from the International Atomic Energy Agency, samples were extracted, cleaned, and analyzed with the same procedure used for the environmental samples.9,12,13

Gas chromatography analysis

The details of the procedure are described in Unyimadu et al. The organochlorine pesticides (OCPs) were analyzed using Hewlett Packard 5890 series II gas chromatography with electron capture detector. The instrument was operated in splitless mode, the oven temperature program started at 90°C (held for 2 minutes) and was raised 130°C at 15°C/min, then to 290°C at 4°C/min (holding time 20 minutes). Injector and detector temperatures were 250 and 300°C, respectively. The flow rate through the column was 3 mL/min. Confirmation of the OCPs was done using a gas chromatograph/mass spectrometer (Shimadzu QP2010) with capillary column type HP1MS (30m x 0.25um x 0.25mm id).

Determination of percent moisture content

The determination of percent moisture content was determined using Equation 1.

\[
MC = \frac{(m_1 - m_2)}{(m_1 - m_a)} \times 100
\]

Percent moisture content, subtracted

Table 1 — Niger River Sampling Sites

| Sediment samples | Longitude | Latitude |
|------------------|-----------|----------|
| Gurara 1         | 007°.00.29 | 09°.14.58 |
| Gurara 2         | 007°.00.20 | 09°.14.55 |
| Gurara 3         | 007°.00.12 | 09°.14.53 |
| Lokoja 4         | 006°.45.24 | 07°.44.51 |
| Lokoja 5         | 006°.45.05 | 07°.46.18 |
| Lokoja 6         | 006°.45.29 | 07°.47.42 |
| Onitsha 7        | 006°.46.81 | 06°.10.69 |
| Onitsha 8        | 006°.45.19 | 06°.08.01 |
| Onitsha 9        | 006°.42.81 | 06°.05.08 |
| Brass 10         | 006°.14.11 | 04°.17.99 |
| Brass 11         | 006°.15.72 | 04°.21.65 |
| Brass 12         | 006°.18.72 | 04°.25.50 |
| Nicolas 13       | 006°.19.88 | 04°.17.99 |
| Nicolas 14       | 006°.19.21 | 04°.21.65 |
| Nicolas 15       | 006°.19.16 | 04°.23.66 |

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from 100, gave the dry weight (dw) of the sediment.

Tared weighing bottles were dried for 2 hours at 105°C, and allowed to cool in a desiccator and the tared bottles were weighed with the lids placed underneath: \( m_a \).

Five (5) g of fresh weight sediment was placed in the tared bottle and the new weight noted: \( m_1 \).

The weighing bottles with their caps placed underneath were placed in a ventilated drying oven for 4 hours at 105°C (the air exit was left open). The bottles were cooled in a desiccator and weighed (all the lids of the series contained in the desiccator were closed to avoid moisture input): \( m_2 \).

The weighing bottles were placed in the drying oven for 1 hour at 105°C and re-weighed under the same conditions until the weight became constant.

**Organic carbon (percent)**

Total organic carbon was determined using the back-titration method and calculated using Equation 2. Ten (10) g sediment sample was weighed and transferred to a wide neck 500 mL Erlenmeyer flask and 10 mL of 1 molar solution of potassium dichromate was added. The content of the flask was gently homogenized. Twenty (20) mL of concentrated sulphuric acid was added with a Teflon dispenser. The flask was agitated by rotation for one minute to homogenize the sample (at approximately 120°C). The flask was placed on an insulating plate and oxidation was allowed to continue for 30 minutes. Two hundred (200) mL of distilled water was added and then 10 mL of phosphoric acid. The flask and its contents were homogenized. Three drops of diphenylamine were added as a titration indicator. The excess dichromate was titrated with 0.5 mol ferrous iron solution (this reagent was freshly prepared each day). The titration was continued until the color changed from purplish blue to a luminous greenish blue. Determination of the end point was facilitated by the addition of 1-2 drops of indicator as soon as the color began to change.

**Equation 2**

\[
\text{Total organic carbon in percent of } 105°C \text{ dried sediment} = 100 \times 3.9 \left(10^{-V}ight) / P
\]

where \( P \) represents the mass in g; \( V \), the volume (mL) of the iron (as Fe\(^{2+}\), ferrous ion) solution at a concentration of 0.5 mol/L.

**Determination of particle size distribution**

The particle size of the sediment samples was determined using the method of Jones et al. The sediment samples were air dried, crushed in a mortar and debris were handpicked. The samples were then weighed. Destruction of organic matter was achieved by treatment of the dried sediment with hydrogen peroxide solution. The destruction of any cement was also carried out by shaking of the sediment with dilute hydrochloric acid.

The soil retained on each sieve was weighed. Each sieve to be used was weighed to 0.1 g. Five hundred (500) g of oven dried sediment was weighed to the nearest 0.1 g. The sediment was sieved through a nest of sieves by handshaking for at least 10 minutes. After shaking, the sieves and the pan were weighed to the nearest 0.1 g with the retained sediment. The weights of sediment retained on each sieve
were determined. The sum of the weights retained was checked against the original sediment weight. The percentage retained on each sieve was calculated using Equation 3.

\[
\text{Equation 3} \quad \frac{(\text{Sediment weight retained on each sieve/original sediment weight}) \times 100}{}
\]

Results

The target compounds were not detected in the blanks. Spiked sediment samples showed satisfactory precision and recoveries (Table 2) and
the detection limit of the equipment was in the range of 0.25 - 0.50 ng/l. To monitor the accuracy of the gas chromatography method, the International Atomic Energy Agency standard reference material sediment homogenate (SRM 417) was analyzed with each sample set and the results, based on the standard deviation, were satisfactory.  

Particle size distribution

The grain size silt percent mean in the Gurara, Lokoja, and Onitsha locations ranged from 6.56-9.89%, 5.85-14.9%, and 6.15-13.0%, respectively; while in the Brass and Nicolas stations, the means ranged from 6.40-31.90% and 50.20-61.90%, respectively, with minima at the Lokoja station and maxima at the Nicolas River location (Table 3). The total organic carbon content followed the same trend with mean range values in the Gurara, Lokoja, and Onitsha locations of 0.24-0.64%, 0.42-0.80% and 0.41-0.99%, respectively; and in the Brass and Nicolas locations, 0.65-4.20% and 3.15-4.03%, respectively.

Hexachlorocyclohexanes

α-hexachlorocyclohexane (HCH), γ-HCH, and δ-HCH were detected in all of the sediment samples analyzed and β-HCH was detected in 96% of the samples (Table 4). The sequence of concentration in the Niger River stations was β-HCH > δ-HCH > γ-HCH > α-HCH. The distribution of the HCHs varied considerably along the different sampling locations.

Chlordanes

The levels of chlordanes in sediment are shown in Table 5. α-chlordane, γ-chlordane, heptachlor epoxide, and methoxychlor were detected in all the sediment samples analyzed and heptachlor was detected in 84% of the samples. The sequence of concentration in the Niger River stations was methoxychlor > heptachlor > heptachlor epoxide > α-chlordane > γ-chlordane. The distribution of the chlordanes varied markedly along the different locations.

Endosulfans

The concentration of endosulfan in sediment is shown in Table 6. Endosulfan consists of endosulfan I and II isomers. While endosulfan sulfate and the diol are susceptible to photo degradation, endosulfan I and II are resistant. The sequence of occurrence of endosulfan in this study was endosulfan II > endosulfan sulfate > endosulfan I. Endosulfan I was detected in all the samples analyzed, while endosulfan II and endosulfan sulfate were detected in 86% and 81% of the sediment samples, respectively. The concentration of endosulfan II was higher than that of endosulfan I and II.

### Table 4 — Concentrations (µg/kg) of Hexachlorocyclohexane Pesticides in Sediments

| Sample Code | α-HCH | β-HCH | γ-HCH | δ-HCH |
|-------------|-------|-------|-------|-------|
| Gurara 1    | 52.8±37.1 | 37.8±37.8 | 78.9±33.4 | 119.5±47.0 |
|             | (13.9-100.2) | (BDL-84.2) | (12.1-115.1) | (64.4-185.2) |
| Gurara 2    | 27.4±4.75 | 39.5±18.7 | 52.8±25.5 | 29.9±10.5 |
|             | (20.2-35.8) | (18.5-64.7) | (24.2-86.9) | (17.2-44.9) |
| Gurara 3    | 28.2±10.3 | 119.8±42.1 | 53.6±34.4 | 63.0±20.0 |
|             | (15.9-42.8) | (69.1-180.3) | (17.1-97.8) | (45.8-103.2) |
| Lokoja 4    | 62.6±12.5 | 112.2±22.4 | 22.3±4.45 | 13.1±2.62 |
|             | (42.9-78.7) | (76.8-140.8) | (15.3-28.0) | (8.99-16.5) |
| Lokoja 5    | 32.6±6.52 | 65.2±13.0 | 15.7±3.15 | 112.1±22.5 |
|             | (22.4-41.0) | (10.8-82.0) | (10.8-19.8) | (76.8-141.2) |
| Lokoja 6    | 65.9±13.2 | 68.2±13.6 | 18.6±3.73 | 109.4±21.8 |
|             | (45.2-82.9) | (46.8-85.7) | (12.8-23.4) | (75.0-137.5) |
| Onitsha 7   | 39.7±5.01 | 114.6±17.4 | 8.09±1.22 | 42.0±12.1 |
|             | (28.8-48.1) | (83.4-139.0) | (5.89-9.82) | (25.7-66.5) |
| Onitsha 8   | 35.9±8.44 | 137.5±15.3 | 69.1±29.6 | 56.9±11.4 |
|             | (21.9-48.1) | (107.0-161.1) | (69.6-104) | (48.2-72.3) |
| Onitsha 9   | 41.9±6.35 | 52.1±7.88 | 18.7±2.82 | 85.8±13.0 |
|             | (30.5-50.8) | (37.9-63.1) | (13.5-22.6) | (62.4-104.0) |
| Brass 10    | 18.6±6.33 | 42.2±22.9 | 14.2±5.66 | 97.9±35.1 |
|             | (10.9-29.9) | (16.9-68.2) | (7.69-20.8) | (55.7-136) |
| Brass 11    | 18.5±1.82 | 113.9±34.1 | 18.1±2.43 | 42.7±8.51 |
|             | (16.1-21.5) | (70.9-150.0) | (13.9-21.6) | (33.2-56.9) |
| Brass 12    | 22.3±1.49 | 118.9±35.6 | 22.3±1.72 | 53.3±9.99 |
|             | (19.8-24.8) | (74.1-156) | (19.6±24.6) | (42.3-70.4) |
| Nicolas 13  | 14.7±1.92 | 71.0±9.27 | 12.9±1.70 | 81.6±10.6 |
|             | (11.4-17.0) | (54.9-82.4) | (10.0-15.1) | (63.0-94.6) |
| Nicolas 14  | 3.00±0.39 | 17.4±2.27 | 3.90±0.51 | 63.1±8.22 |
|             | (2.32-3.48) | (13.5-20.2) | (3.02-4.52) | (48.8-73.1) |
| Nicolas 15  | 20.9±2.74 | 89.6±11.8 | 13.1±1.71 | 47.2±6.16 |
|             | (16.2-24.3) | (69.1-104.1) | (10.1-15.2) | (36.5-54.7) |
I, which can be explained by greater degradation of endodulfan I in the sediment.\textsuperscript{18} Endosulfan sulfate, which is a major degradation product of endosulfan, is known to be as toxic as the parent compound.

**Table 5 — Concentration (µg/kg) of Chlordane Pesticides in Sediments**

| Sample Code | \(\gamma\)-chlordane | \(\alpha\)-chlordane | Heptachlor | Heptachlor epoxide | Methoxychlor |
|-------------|-----------------------|----------------------|------------|-------------------|--------------|
| Gurara 1    | \(36.1\pm23.4\)       | \(72.9\pm54.1\)     | \(158.7\pm158.7\) | \(134.9\pm35.1\) | \(194.0\pm119.9\) |
|             | \((11.3-66.1)\)       | \((16.7-141.1)\)    | \((BDL-353.1)\)   | \((88.8-189)\)   | \((65.8-349.0)\) |
| Gurara 2    | \(36.1\pm23.7\)       | \(63.2\pm33.1\)     | \(66.2\pm17.3\)   | \(165.3\pm43.8\) | \(87.9\pm34.6\)  |
|             | \((11.0-66.38)\)      | \((26.8-107.1)\)    | \((43.3-93.0)\)   | \((108.8-232.0)\) | \((47.4-136.0)\) |
| Gurara 3    | \(39.2\pm22.5\)       | \(47.9\pm39.4\)     | \(85.0\pm85.0\)   | \(149.9\pm15.0\) | \(121.9\pm16.6\) |
|             | \((14.9-68.6)\)       | \((7.57-97.1)\)     | \((BDL-189)\)     | \((131.0-179.0)\) | \((93.6-154.0)\) |
| Lokoja 4    | \(80.4\pm16.1\)       | \(42.6\pm8.51\)     | \(254.6\pm50.9\)  | \(104.1\pm125\)  | \(224.0\pm4.00\) |
|             | \((55.1-101.1)\)      | \((29.2-53.5)\)     | \((174.6-320.1)\) | \((71.4-130.9)\) | \((153.6-281.6)\) |
| Lokoja 5    | \(43.2\pm8.64\)       | \(90.9\pm18.1\)     | \(389.5\pm78.0\)  | \(105.8\pm21.2\) | \(319.5\pm64.0\) |
|             | \((29.6-54.3)\)       | \((62.4-114.0)\)    | \((267.0-490.0)\) | \((72.6-133)\)   | \((219.0-402.0)\) |
| Lokoja 6    | \(49.0\pm9.81\)       | \(33.4\pm6.68\)     | \(340.3\pm68.1\)  | \(121.6\pm24.3\) | \(323.8\pm64.8\) |
|             | \((33.62-6414.4)\)    | \((22.9-41.9)\)     | \((233.4-427.9)\) | \((83.4-152.9)\) | \((222.0-407.0)\) |
| Onitsa 7    | \(30.0\pm4.55\)       | \(56.8\pm8.60\)     | \(441.5\pm67.0\)  | \(132.9\pm20.1\) | \(91.6\pm13.9\)  |
|             | \((21.8-36.4)\)       | \((41.3-68.8)\)     | \((321.0-535.0)\) | \((96.9-161.0)\) | \((66.6-111.0)\) |
| Onitsa 8    | \(23.6\pm6.41\)       | \(36.3\pm16.2\)     | \(249.5\pm142.7\) | \(76.6\pm42.2\)  | \(683.3\pm286.1\)|
|             | \((15.1-36.4)\)       | \((19.9-68.9)\)     | \((121-535)\)     | \((37.9-161.0)\) | \((684.0-1026)\) |
| Onitsa 9    | \(39.2\pm5.94\)       | \(60.6\pm9.18\)     | \(306.3\pm46.3\)  | \(92.5\pm14.1\)  | \(195.5\pm29.5\) |
|             | \((28.4-52.56)\)      | \((44.6-83.58)\)    | \((46.5-620.0)\)  | \((67.8-123.4)\) | \((142.1-210.6)\) |
| Brass 10    | \(38.7\pm17.3\)       | \(33.3\pm22.99\)    | \(126.3\pm126.3\) | \(117.8\pm11.1\) | \(226.0\pm31.5\) |
|             | \((18.9-61.0)\)       | \((9.19-60.2)\)     | \((BDL-254.0)\)   | \((109.0-140.0)\) | \((173.0-260.0)\) |
| Brass 11    | \(47.9\pm28.4\)       | \(50.0\pm13.7\)     | \(199.5\pm30.5\)  | \(148.5\pm33.5\) | \(150.0\pm22.0\) |
|             | \((17.4-77.4)\)       | \((33.3-70.8)\)     | \((150.0-232.0)\) | \((102.0-183)\)  | \((127.0-191.0)\) |
| Brass 12    | \(56.4\pm25.8\)       | \(55.6\pm12.2\)     | \(211.3\pm38.3\)  | \(170.5\pm25.5\) | \(166.0\pm24.0\) |
|             | \((27.2-83.2)\)       | \((42.8-75.3)\)     | \((154.0-250.0)\) | \((128.0-198.0)\) | \((140.0-211.0)\) |
| Nicolas 13  | \(13.5\pm1.77\)       | \(41.6\pm5.42\)     | \(82.8\pm10.8\)   | \(112.1\pm14.9\) | \(653.0\pm85.0\) |
|             | \((10.5-15.7)\)       | \((32.1-48.2)\)     | \((64.0-96.0)\)   | \((86.4-130.0)\) | \((505.0-757.0)\) |
| Nicolas 14  | \(8.09\pm1.05\)       | \(16.32\pm2.13\)    | \(110.2\pm13.9\)  | \(67.1\pm8.76\)  | \(87.3\pm11.20\) |
|             | \((6.26-9.38)\)       | \((12.6-18.9)\)     | \((85.6-127.0)\)  | \((51.8-77.81)\) | \((67.6-101.0)\) |
| Nicolas 15  | \(11.6\pm1.52\)       | \(21.2\pm2.77\)     | \(187.3\pm24.3\)  | \(119.0\pm15.5\) | \(188.3\pm24.3\) |
|             | \((9.02-13.52)\)      | \((16.4-24.6)\)     | \((145.0-217)\)   | \((92.0-138.0)\) | \((146.0-218.0)\) |

Dichlorodiphenyltrichloroethanes

DDT, DDE, and DDD were detected in 76%, 100%, and 60% of the sediment samples, respectively (Table 6). The sequence in the concentration of the metabolites was DDD>DDE>DDT.

Endrin, aldrin and dieldrin

The concentration of endrin in the sediment samples was in the order of endrin ketone > endrin aldehyde > endrin (Table 7). Endrine and endrine ketone were detected in 100% of the
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Table 6 — Concentrations (µg/kg) of Endosulfan and DDTs in Sediments

| Sample Code | Endosulfan 1 | Endosulfan 11 | Endosulfan Sulfate | DDE      | DDD      | DDT      |
|-------------|-------------|--------------|--------------------|----------|----------|----------|
| Gurara 1    | 63.8±33.4   | 124.0±65.0   | 269.0±187.5        | 59.8±45.5| 38.8±38.8| 47.3±47.3|
|             | (27.0±108)  | (52.5±210)   | (72.4±507)         | (12.7±117)| (BDL-86.1)| (BDL-105) |
| Gurara 2    | 50.9±23.9   | 411.3±212.2  | 240.3±113.3        | 103.8±35.7| 299.7±147.7| 236.1±180.4|
|             | (24.0±83.1) | (117.0±693)  | (113.0±393.0)      | (60.5±155)| (135.0±497.0)| (49.5±463.0)|
| Gurara 3    | 34.3±6.40   | 482.8±248.8  | 71.5±71.5          | 61.0±25.9 | 455.2±438.2| 221.3±20.88|
|             | (24.8±45.2) | (208.0±813.0)| (BDL-159)          | (31.2±96.6)| (15.1±993.0)| (202.0±263.0)|
| Lokoja 4    | 33.5±6.28   | BDL          | 26.4±5.29          | 71.2±14.25| 533.8±106.2| 54.13±10.8 |
|             | (22.9±42.2) |             | (18.1±33.2)        | (48.8±89.4)| (366.0±671.0)| (37.1±68.0) |
| Lokoja 5    | 71.3±14.3   | 317.6±63.5   | BDL                | 68.9±13.8 | 317.6±63.5 | BDL      |
|             | (48.9±89.6) | (217.8±399.0)|             | (47.3±86.6)| (BDL-399.0)| BDL      |
| Lokoja 6    | 27.4±5.48   | BDL          | 422.6±84.5         | 66.5±13.3 | BDL      | 107.6±21.5|
|             | (18.5±34.5) |             | (289.8±531.3)      | (65.6±83.6)| (BDL-353.0)| (73.8±153.5)|
| Onitsha 7   | 84.2±12.8   | 101.6±15.5   | 30.9±4.70          | 117.3±17.7| BDL      | 33.1±4.99 |
|             | (61.2±102)  | (73.8±123.0) | (22.5±37.6)        | (85.2±142.0)| BDL      | (24.1±40.1)|
| Onitsha 8   | 52.0±24.9   | 180.3±840.1  | 9.39±14.1          | 81.4±37.8 | BDL      | 10.0±15.0 |
|             | (26.9±102)  | (1850±2774)  | (BDL-37.6)         | (37.4±142)| BDL      | (BDL-40.1) |
| Onitsha 9   | 57.7±8.74   | 78.9±11.9    | BDL                | 57.3±8.69 | BDL      | BDL      |
|             | (41.9±70.0) | (57.4±95.7)  |             | (41.7±69.5)| BDL      | BDL      |
| Brass 10    | 43.1±21.0   | 43.6±7.70    | 115.7±115.7        | 51.1±17.5 | 147.0±147.0| 9.31±9.31|
|             | (19.7±69.1) | (32.0±56.3)  | (BDL-257.0)        | (29.9±70.6)| (BDL-300.0)| (BDL-20.68)|
| Brass 11    | 98.5±46.5   | 142.6±53.3   | 149.3±9.25         | 38.9±19.5 | 287.2±234.3| 37.2±14.9 |
|             | (46.2±147.0)| (86.9±218)   | (132.0±165.0)      | (17.3±60.9)| (46.9±524.0)| (21.8±58.0)|
| Brass 12    | 101.3±46.2  | 149.7±50.3   | 167.0±10.5         | 44.3±17.6 | 334.5±226.5| 37.9±21.9 |
|             | (49.1±149.0)| (96.8±222.0) | (150.0±188.0)      | (23.8±63.4)| (96.0±567.0)| (13.7±66.6)|
| Nicolas 13  | 21.9±2.83   | 148.0±14.5   | 352.0±46.0         | 22.2±2.90 | 97.3±12.7 | BDL      |
|             | (16.8±25.14)| (133.0±177.0)| (272.0±408.0)      | (17.2±25.8)| (75.2±113)| BDL      |
| Nicolas 14  | 31.6±4.11   | 103.5±13.5   | 394.3±51.3         | 43.9±10.2 | 105.5±13.6| BDL      |
|             | (24.4±36.6) | (80.0±120.0) | (305.0±457.0)      | (28.2±59.0)| (81.6±122.0)| BDL      |
| Nicolas 15  | 21.8±2.84   | 42.9±5.59    | 445.0±58.0         | 65.9±14.8 | 61.6±8.03 | BDL      |
|             | (16.8±25.2) | (33.1±49.7)  | (344.0±516.0)      | (45.5±93.3)| (47.6±71.4)| BDL      |
samples, while endrine aldehyde was detected in 76% of the samples analysed. Aldrin was detected in all the samples, while dieldrin was detected in 96% of the samples. The sequence of concentration in the Niger River stations was, aldrin < dieldrin in all of the stations.

**Total organochlorine pesticides in sediments**

The concentration of the sums of OCPs is shown in Table 8. The order in the summation of concentration of the different pesticides in this study was \( \Sigma \text{Endrine} > \Sigma \text{Chlordane} > \Sigma \text{Endosulfan} > \Sigma \text{DDT} > \Sigma \text{HCH} > \Sigma \text{Dieldrin}. \) The dieldrins (aldrin + dieldrin) occurred at the lowest concentration in the sediment samples analyzed. The highest concentration of \( \Sigma \text{OCPs} \) in the sediment samples of the Niger River (5023±1596 µg/kg, range 4672-7009 µg/kg) was detected in station 8 at Onitsha location, while the lowest concentration (1570±204.5, range 1214-1820 µg/kg) was detected at station 14 at Nicolas River. High
# Research

## Organochlorine Pesticides in Sediments of the Niger River, Nigeria

**Table 8 — Concentration (µg/kg) of Total Organochlorine Pesticides in Sediments**

| Sample Code | HCH | Chlor dane | Endrin | Endosulfan | DDT | Dieldrin | OCPS |
|-------------|-----|------------|--------|------------|-----|----------|-------|
| Gurara 1    | 267.3±29.8 (155.0-400) | 596.5±391.5 (182.0-1098.0) | 497.9±419.0 (70.17-1019) | 456.8±156.2 (267.0-681) | 145.9±40.0 (93.6-207.0) | 216.0±56.0 (142.0-302.0) | 2181±962.5 (1083-3492) |
| Gurara 2    | 150.5±22.5 (114.0-192.0) | 418.5±65.0 (314.0-537.0) | 389.8±226.8 (145.0-685.0) | 502.5±333.3 (135.0-1169) | 640±292.5 (309.0-1036) | 182.8±50.3 (118.0-259.0) | 2482±905.3 (1402-3764) |
| Gurara 3    | 197.5±22.0 (166.0-231.0) | 433.8±185.3 (221.0-688.0) | 1477.5±689.0 (701.0-2407) | 588.5±171.0 (371.0-844.0) | 737.5±479.5 (256.0-1352) | 351.8±110.8 (214.0-514.0) | 3804±1658 (1907-6070) |
| Lokoja 4    | 210.0±121.7 (144.0-264.0) | 706.1±141.2 (484.2-887.7) | 245.0±120.0 (168.0-308.0) | 59.9±11.9 (41.9-75.3) | 658.9±131.7 (451.8-828.3) | 300.1±60.0 (205.8-377.3) | 2513±505.7 (1723-3159) |
| Lokoja 5    | 225.8±45.20 (154.8-284.0) | 918.8±183.8 (630.0-1155) | 1908.8±381.7 (1308.6-2399) | 71.9±14.3 (48.88-89.62) | 386.7±77.3 (265.2-486.2) | 134.6±26.85 (92.4-169.0) | 3675±735 (2520-4620) |
| Lokoja 6    | 262.5±52.5 (180.0-330.0) | 819.0±163.8 (561.0-1029.6) | 428.8±85.8 (294.0-539.0) | 449.8±89.9 (304.8-564.5) | 174.1±34.8 (119.4-218.9) | 271.3±54.3 (186.0-341.0) | 2456±491 (1684-3088) |
| Onitsha 7   | 198.0±30.0 (144.0-240.0) | 752.3±113.8 (547.0-912) | 400.8±60.8 (291.0-486.0) | 217.3±33.3 (158.0-263.0) | 109.0±182.0 | 80.7±12.3 (58.7-97.86) | 1800±272.8 (1309-2182) |
| Onitsha 8   | 297.0±53.5 (47.0-371.0) | 1069.0±174.0 (878.0-1316) | 1552±625.5 (1367-2532) | 1864±800 (1877-2815) | 374±498 (148.0-429.0) | 350.2±76.8 (249.0-392.0) | 5023±1596 (4672-7009) |
| Onitsha 9   | 198.0±30.0 (144.0-240.0) | 674.0±102.0 (490.0-817.0) | 819.8±376.9 (66.0-1190) | 136.9±20.6 (99.9-166.0) | 55.9±10.1 (41.7-69.5) | 78.0±11.8 (56.7-94.5) | 2146±325 (1561-2601) |
| Brass 10    | 172.8±70.2 (91.2-249.0) | 481.0±129.0 (313.0-726.0) | 547.3±313.3 (206.0-1132) | 325.0±146.0 (105.0-617.0) | 207.4±155.1 (46.5-371) | 174.0±49.0 (1113-2484) | 1997±745.3 (1113-2816) |
| Brass 11    | 194.0±26.50 (149.0-226.0) | 596.3±58.1 (480.0-661) | 434.3±272.3 (161.0-785) | 390.8±25.3 (353.0-441.0) | 363.3±239.3 (110.0-608.0) | 156.5±11.3 (143.0-179.0) | 2127±132.0 (1863-2329) |
| Brass 12    | 216.8±25.8 (170.0-245.0) | 624.3±52.6 (519.0-699.0) | 464.8±239.3 (171.0-842.0) | 418.0±26.5 (377.0-471.0) | 416.8±222.3 (173.0-649.0) | 115.5±22.3 (165.0-233) | 2329±147.1 (2098-2623) |
| Nicolas 13  | 180.3±23.8 (139.0-209.0) | 407.8±53.3 (315.0-473.0) | 692.5±90.5 (355.0-803.0) | 557.0±73.0 (430.0-646.0) | 557.0±73.0 (430.0-646.0) | 123.3±16.2 (95.2-143.0) | 2081±271.3 (1609-2413) |
| Nicolas 14  | 87.7±11.2 (67.6-101.1) | 289.8±37.8 (224.0-336.0) | 383.0±50.0 (296.0-444.0) | 528.8±68.7 (409.0-613.0) | 120.9±15.6 (93.6-140.0) | 1570±204.5 (1214-1820) |
| Nicolas 15  | 170.8±22.3 (132.0-198.0) | 338.3±43.8 (262.0-392.0) | 869.5±113.5 (672.0-1008) | 509.3±60.9 (394.0-590.0) | 120.5±15.6 (93.8-139.0) | 101.8±13.17 (78.8-118.0) | 2298±299.8 (1777-2665) |

Abbreviations: HCH, α-HCH+β-HCH+γ-HCH+δ-HCH; Chlor dane, cis-chlordane+trans-chlordane+heptachlor epoxide + methoxychlor; DDT, p,p’-DDT+p,p’-DDE+p,p’-DDD; Endosulfan, endosulfan 1+endosulfan 2+endosulfan sulfate; Dieldrin, aldrin+dieldrin; OCPS, HCH+Chlordane+DDT+Endosulfan+Dieldrin.
values of \( \Sigma OCPs >2000 \mu g/kg \) were also detected in all of the other stations except for stations 7 (Onitsha), 10 (Brass), and 13 (Nicolas 13), where lower levels were detected.

**Discussion**

Previous studies showed relationships between bound concentrations of PCBs and kepone and tidal cycle.\(^4\)\(^9\) Nichols found a positive correlation between suspended-sediment-bound concentrations and the suspended-sediment organic-C content.\(^9\) Abarnou et al. further observed that bound concentrations varied with depths in the water column. Moreover, relationships between total loads of suspended sediment and mean PCB concentrations have been reported.\(^9\) This may suggest differences in the distribution of sediment grain size.

**Hexachlorocyclohexanes**

The \( \alpha/\gamma \) ratio has been used for identification of the possible sources of HCH. The ratio of \( \alpha-HCH \) to \( \gamma-HCH > 3 \) is an indication of an input of technical HCH and long range atmospheric transport and deposition.\(^20\) However, a ratio close

| Location / Compounds | Dry Season Range | Dry Season Mean | Rainy Season Range | Rainy Season Mean |
|-----------------------|------------------|-----------------|--------------------|------------------|
| Gurara Location       |                  |                 |                    |                  |
| \( \Sigma HCH \)       | 154.0-400.0      | 240.0±80.0      | 114.0-231.0        | 170.1±33.7       |
| \( \Sigma Chlordane \) | 430.0-1098       | 696.8±194.1     | 182.0-393.0        | 269.0±58.67      |
| \( \Sigma Endrin \)    | 548.0-2407       | 1233±622.1      | 70.7-876.0         | 343.4±296.6      |
| \( \Sigma Endosulfan \)| 135.0-1169       | 674.8±223.2     | 267.0-464.0        | 357.0±52.0       |
| \( \Sigma DDT \)       | 93.6-1352        | 751.6±430.9     | 166.2-386.2        | 264.2±55.6       |
| \( \Sigma Dieldrin \)  | 118.0-514.0      | 251.6±140.6     | 207.2-302.4        | 248.6±27.6       |
| \( \Sigma OCPs \)      | 2795-6070        | 3998±976.6      | 1083-2384          | 1647±367.3       |
| Lokoja Location        |                  |                 |                    |                  |
| \( \Sigma HCH \)       | 136.5-360.4      | 222.8±72.0      | 104.7-222.9        | 165.1±23.2       |
| \( \Sigma Chlordane \) | 390.4-1003       | 580.3±294.1     | 172.5-373.6        | 259.8±38.6       |
| \( \Sigma Endrin \)    | 501.2-2001       | 1136±522.1      | 60.7-734.5         | 320.4±296.6      |
| \( \Sigma Endosulfan \)| 125.6-1112       | 654.8±200.2     | 227.5-462.2        | 327.8±42.0       |
| \( \Sigma DDT \)       | 91.6-1222        | 631.6±400.9     | 136.0-340.6        | 244.8±35.6       |
| \( \Sigma Dieldrin \)  | 108.9-414.0      | 221.6±140.6     | 199.8-360.4        | 227.6±7.64       |
| \( \Sigma OCPs \)      | 1354-6112        | 3444±976.6      | 903.8-2256         | 1542±367.3       |
| Onitsha Location       |                  |                 |                    |                  |
| \( \Sigma HCH \)       | 216.3-412.6      | 282.5±72.6      | 144.2-330.8        | 208.1±53.5       |
| \( \Sigma Chlordane \) | 735.8-1463       | 1010±252        | 490-1170           | 744.8±186.1      |
| \( \Sigma Endrin \)    | 437.3-2552       | 1332±715        | 66.0-1823          | 814.6±566        |
| \( \Sigma Endosulfan \)| 149.0-2116       | 1126±1230       | 99.6-2502          | 829.9±906.3      |
| \( \Sigma DDT \)       | 56.1-182.5       | 99.4±49.6       | 37.4-4988          | 895±1364         |
| \( \Sigma Dieldrin \)  | 85.5-436.2       | 198.9±143.4     | 56.7-262           | 130.6±83.6       |
| \( \Sigma OCPs \)      | 1964-7788        | 3980±2278       | 1309-6230          | 2933±1678        |

Abbreviations: \( \Sigma HCH \), \( \alpha-HCH+\beta-HCH+\gamma-HCH+\delta-HCH \); \( \Sigma Chlordane \), cis-chlordane+trans-chlordane+heptachlor epoxide + methoxychlor; \( \Sigma DDT \), \( p'p'-DDT+p'p'-DDD+\gamma'-p'p'-DDE \); \( \Sigma Endosulfan \), endosulfan 1+endosulfan 11+endosulfan sulfate; \( \Sigma Dieldrin \), aldrin+dieldrin; \( \Sigma OCPs \), \( \Sigma HCH+\Sigma Chlordane+\Sigma DDT+\Sigma Endosulfan+\Sigma Dieldrin \).

**Table 9 — Seasonal Variation (Mean and Range) of Persistent Organic Pollutants (µg/kg) in the Sediment of Gurara, Lokoja and Onitsha locations of the Niger River**
to or <1 is characteristic of lindane sources. In the present study, the α/γ-HCH mean ratio of close to 1, with ranges in parenthesis, were observed in the following locations: Gurara 1, 0.77±0.38, (0.14-1.44); Gurara 2, 0.62±0.21, (0.41-0.83); Gurara 3, 0.68±0.24, (0.43-0.93); Lokoja 5, 1.34±1.44; Lokoja 6, 0.99±0.13, (0.83-1.23); Lokoja 11, 1.00±0.03 (0.93-1.06); Nicolas 13, 0.95±0.19, (0.76-1.13); Nicolas 14, 1.18±0.42, (0.76-1.13); Nicolas 15, 0.82±0.34, (0.14-1.13), and are indicative of a lindane source. The following locations, Lokoja 4, 2.80±0.03, (2.79-2.81); Lokoja 5, 2.07±0.02 (2.07-2.07); Onitsha 8, 1.49±1.68, (0.32-4.89); Onitsha 9, 2.24±0.02, (2.19-2.25); Brass 10, 1.33±0.13, (1.06-1.44) had α/γ-HCH mean ratio less than 3. A ratio greater than 3 was obtained only in location Lokoja 6, 3.54±0.0, (3.54-3.54), and Onitsha 7, 4.89±0.01, (4.89-4.90); which reflects the use of technical HCH in this area. Iwata et al. reported α/γ ratios of 4.8-9.6 in the Bay of Bengal and the Arabian Sea, and 0.65-2.40 for the Eastern Indian Ocean. In other studies in India, the overall ratios ranged between 0.09 to 6.41 with a mean value of 1.96, which reflects the regular usage of technical HCH and lindane (γ-HCH) in these areas. Additionally, there is the possibility of transformation of α- and γ-HCH to β-HCH in the environment. Furthermore, the special arrangement of chlorine atoms in the molecular structure of β-HCH makes microbial degradation more difficult than the other isomers, which may lead to the accumulation of β-HCH in sediment. Lower levels of γ-HCH have been reported in marine sediments by Klonova et al., who investigated sediments of James Rose Island and detected levels of 0.20-0.30 µg/kg dw. In the African environment, previous studies also detected lower HCH levels compared to the present study. Sunday detected low levels of α and γ-HCH in Ogunpa, Ona and Oniyere Rivers in Nigeria, the α-HCH concentrations were ND-0.20, ND-0.90, and ND-0.40 µg/kg dw, respectively, while the concentration of γ-HCH in the river sediments were ND-1.20, ND, and ND-2.00 µg/kg dw, respectively. Ojo detected low levels in the Lekki lagoon: α-HCH concentration was ND-116.0 µg/kg dw and γ-HCH was

| Location | Chlordane | Dieldrin | DDE | DDT | DDT | Endrin | Heptaepoxide | Lindane |
|----------|-----------|----------|-----|-----|-----|--------|-------------|--------|
| Gurara 1 | 108.2     | 26.7     | 38.8| 59.8| 47.3| 145.9  | 62.8        | 134.9  |
| Gurara 2 | 99.3      | 9.83     | 299.7| 103.8| 236| 640    | 58.8        | 165.3  |
| Gurara 3 | 87.1      | 58.6     | 455.2| 61  | 221| 737.5  | 33.1        | 149.9  |
| Lokoja 5 | 123       | 10.8     | 533.8| 71.2| 54.1| 658.9  | 13.6        | 104.1  |
| Lokoja 6 | 82.4      | 55.7     | 317.6| 68.9| BDL | 386.7  | 43.7        | 105.8  |
| Lokoja 11| 86.8      | 28.9     | BDL | 117.3| 33.1| 150.2  | 44          | 132.9  |
| Onitsha 8| 59.9      | 70.3     | BDL | 81.4 | 9 | 91.4   | 99          | 76.6   |
| Onitsha 9| 99.8      | 5.67     | BDL | 57.3 | BDL| 55.9   | 33.8        | 92.5   |
| Brass 10 | 72        | 39.9     | 147 | 51.1| 9.31| 207.4  | 42          | 117.8  |
| Lokoja 4 | 97.9      | 12.8     | 287.2| 38.9| 37.2| 363.3  | 19.2        | 148.5  |
| Lokoja 5 | 112       | 19.1     | 334.5| 44.3| 37.9| 416.8  | 28.3        | 170.5  |
| Lokoja 6 | 24.4      | 25.6     | 105.5| 43.9| BDL | 528.8  | 44.8        | 67.1   |
| Brass 11 | 32.8      | 23.6     | 61.6 | 65.9| BDL | 120.5  | 40.2        | 119    |
| Brass 12 | 3.24      | 1.90     | 4.88 | 3.16| 4.16| 5.28   | 2.22        | 2.47   |
| Nicolas 13| 17.6   | 61.8     | 28.0 | 31.3| 62.9| 572    | 207         | 16.0   |

*Source: MacDonald et al.*

**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.

**Table 10 — Comparison with Consensus-based Sediment Quality Guidelines µg/kg dw**
Marchand and Martin and Kaba detected low levels of α and γ-HCH in Ebrie Lagoon, Côte d’Ivoire with concentrations of 0.01-13.40 and 0.07-19.8 µg/kg dw, respectively. Additional studies have detected low levels of the same compounds in Lake Nyumba, Tanzania, Mcllwaine, Zimbabwe, and Abu-Qir Bay, Egypt. Kumar and Mukherjee observed low levels of α and γ-HCH, 0.10-26.53 and 0.12-25.3 µg/kg dw, respectively, in the sediment of Sundarban mangrove ecosystem in Bay of Bengal, India. Echols et al. detected low levels of γ-HCH (lindane) <0.31-2.60 µg/kg, in sediment sample from the lower Missouri River, USA.

**Chlordanes**

Out of the 15 locations, the ratio of cis-chlordane/trans-chlordane was less than 1 in 13, indicating recent use of chlordane in the study area. In Lokoja 4 and 6 the ratio was greater than 1, with values of 1.90±1.76; (1.89-1.96) and 1.48±1.22; (2.10-1.08), respectively. This indicates that chlordane from the Lokoja area remained from previous “older” usage. The concentration of heptachlor was higher than the epoxide in 12 out of the 15 locations, which implies fresh input of chlordanes into the Niger River environment.

Literature on the levels of chlordanes in environmental sediments is scarce. Sunday did not detect heptachlor in the Nigerian rivers; however, Ojo detected relatively high levels of heptachlor, ND-184.5 µg/kg dw in Lekki Lagoon sediment samples. Kaba also reported low heptachlor levels, ND-6.80 µg/kg dw in Ebrie Lagoon, Côte d’Ivoire. Echols et al. detected low levels of chlordane downstream of Kansas City, 3.00 µg/kg, in sediment sample from the lower Missouri River.

**Endosulfan**

Endosulfan I and II in technical endosulfan account for 70% and 30%, respectively, and the ratio of endosulfan I/endosulfan II in the technical product is about 2.33. Because endosulfan I decomposes more rapidly than endosulfan II in sediment, the ratio of endosulfan I-/endosulfan II <2.33 is used to judge the age of their residues in sediment. The endosulfan I-/ endosulfan II isomer ratios in this study ranged from 0.02 to 0.99 in 12 of the 15 locations in which endosulfan I and endosulfan II were simultaneously detected, indicating that there is no recent application of technical endosulfan in the investigated area from Niger River sediments. Sunday detected low endosulfan levels of ND-14.0 µg/kg dw in the sediment of Ona River.

**Dichlorodiphenyltrichloroethanes**

The possible sources of DDT in the aquatic environment may be identified using the ratios of the parent compound of DDT to DDD or DDE (that is, its metabolites). If the ratio (DDT/DDD+DDE) is much greater than 1, this may be an indication of fresh use of DDT, while historical application of DDT may be indicated by a smaller ratio (Ma et al.). In the present study the ratio of DDT/DDD+DDE in the sampling locations Nicolas 13, Nicolas 14, Nicolas 15, Onitsha 9, and Lokoja 5 were zero as there was no detection of DDT in those locations. The ratios in the other locations were Gurara 1, 0.51±0.51, (below detection limit (BDL) -1.02); Gurara 2, 0.50±0.31, (0.19-0.80); Lokoja 4, 0.08±0.01, (0.08-0.09); Onitsha 7, 0.28±0.00, (0.28-0.28) and Onitsha 8, 0.07±0.11, (BDL-0.28). This indicates that there was no recent input of DDT into the Niger River sediment. However, in stations Gurara 3 and Lokoja 6, the ratio 1 was exceeded with the values of 1.68±1.44, (0.24-3.48) and 1.36±0.38 (0.61-1.62), respectively.

The ratio of parent DDT to its metabolite, DDE, can be used to estimate the recent input of technical DDT. A ratio of < 1 may indicate aged mixture, while a ratio >1 may be an indication of the presence of DDT in the last 5 years. In Gurara locations 1, 2, and 3, the p, p’-DDT / p, p’-DDE ratio were 3.30±3.30, (BDL-6.62), 3.25±2.85, (0.40-6.12), and 4.34±1.61, (2.72-6.72), respectively, indicating recent DDT input into the ecosystem at these locations.

DDE is an aerobic degradation product of DDT; while DDD is an anaerobic product. Therefore, the ratio of DDD to DDE may be used to understand the degradation pathways of DDT. A ratio of DDD/DDE less than one (<1) shows aerobic degradation, and higher than 1 (>1) shows anaerobic degradation (Doong et al., Hiller et al.). In the location where DDD and DDE were simultaneously detected, the DDD/DDE ratio in the locations Gurara 1, 2, 3, and Lokoja 4, 5, ratios were 2.72±2.72, (BDL-5.43); 3.87±2.71, (1.09-6.58); 5.37±4.90, (0.48-10.28); 7.50±0.06, (7.47-7.53); and 4.62±0.02, (4.60-4.65), respectively. In the brackish water locations of Brass 10, 11, 12, and Nicolas 13, 14, the ratios were 2.14±2.14, (BDL-4.32); 5.84±3.12, (2.72-9.29); 6.55±2.51, (4.04-9.18); 4.24±0.21, (3.82-4.38) and 2.58±0.76, (2.07-4.10), respectively. These results are indications that the degradation pathways in the Niger River environment were anaerobic. However, at the Nicolas 15 location, the degradation pathway was aerobic with a ratio of 0.96±0.12, (0.72-1.05).

Lower levels of DDT have been reported in marine sediments by Klonova et al. They investigated sediments of James Rose Island and detected levels of 0.30-0.60 µg/kg dw. Hong et al. detected relatively high
levels of DDTs, 0.31-274.0 µg/kg dw in sediment from coastal areas of Vietnam. Low levels of DDTs were reported in most Asian rivers. Liu et al. detected levels of 0.90-33.1 µg/kg dw in the Yangtze Estuary, China; Yang et al. found 0.32-80.18 µg/kg dw in Haihe River, China; and Wurl and Obbard also detected low levels of DDTs in coastal areas of Singapore. Kumar and Mukherjee observed low levels of DDT, DDD and DDE concentrations, 0.02-15.7, 0.02-9.62 and 0.07-16.33 µg/kg dw, respectively, in the sediment of Sundarban mangrove ecosystem in Bay of Bengal, India. Echoles et al. detected low levels of p, p'-DDE (6.40 µg/kg); p, p'-DDD (1.20 µg/kg); and DDD (1.10 µg/kg) in sediment sample from the lower Missouri River. Olutunbosu et al. reported moderately high levels of total OCPs in Niger Delta sediments: Calabar River, 57.9 µg/kg dw; Bakassi, 140.0±57.9 µg/kg dw; and Uzere, 102 57.9 µg/kg dw. Low p, p’-DDE, p, p’-DDD and p, p’-DDE were reported by Sunday; while Ojo reported high levels of p, p’-DDE of 263 (11.0-555) µg/kg dw in the Lekki Lagoon. Marchand and Martins reported high maximum levels of p, p’-DDE, p, p’-DDD, p, p’-DDE, and ΣDDT of 7.40 (0.10-149.0), 28.1 (0.20-803.0), 15.70 (0.20-354.0), and 17.1 (1.10-997.0) µg/kd, respectively, in some locations of the Ebríe Lagoon. Kaba also reported relatively high levels of ΣDDT, 46.2 (2.50-242.0) µg/kg in Ebríe Lagoon. Matthiesen and Griechus reported high maximum levels of ΣDDT in some locations of Lake Kariba, Zimbabwe, 57.0 (40.0-740.3) µg/kg dw; and in Voelviei Dam in South Africa, 130.0 (13.0-740.0) µg/kg dw.

Most of the results from Africa and other parts of the world are still lower than the levels of ΣDDT obtained in the present study. Low levels of ΣDDT were detected in most Asian river sediments compared to the present study: Maskaoui et al. reported a ΣDDT range of 0.01 to 0.43 µg/kg dw; another study identified low levels in Chinese estuarine systems; and a range of 7.40 to 80.5 µg/kg was reported in sediments in Vietnam. Pereira et al. reported concentrations of up to 30212 µg/kg around San Francisco, California. Unyimadu, Osibanjo, Babayemi

Table 9

| Location               | DDTs (µg/kg) | DDD (µg/kg) | DDE (µg/kg) |
|------------------------|--------------|-------------|-------------|
| Lekki Lagoon           | 263 (11.0-555) | 140.0±57.9  | 102 57.9    |
| Calabar River          | 57.9         |             |             |
| Bakassi                | 140.0±57.9   |             |             |
| Uzere                  | 102 57.9     |             |             |

Endrin, aldrin and dieldrin in sediments

Echoles et al. detected low levels of dieldrin and endrin concentrations of 4.80 µg/kg and 3.0 µg/kg, respectively, in sediment sample from the lower Missouri River. Most environmental conditions via biotic or abiotic mechanisms favor the conversion of aldrin to a more persistent product, dieldrin. In most surface water, the presence of aldrin/dieldrin is attributed to particulate surface run-off. The distribution of the aldrins and dieldrins varied markedly along the different study locations. Sunday did not detect aldrin in the river sediments, but low levels of dieldrin were detected in the Ogunpa River (ND-1.80), Ona River (ND-0.50), and Onyere River (ND-6.0 µg/kg dw). Ojo detected high levels of both aldrin and dieldrin in Lekki Lagoon with concentrations of ND-347, and 190-8460 µg/kg dw, respectively. These levels are higher than the levels detected in the present study. Kaba detected low levels of aldrin and dieldrin in Ebríe Lagoon, with concentrations of 0.07-62.1 and ND-125.0 µg/kg dw, respectively.

Total organochlorine pesticides in sediments

Hong et al. detected relatively high levels of DDTs (0.31-274.0 µg/kg dw) in sediment from coastal areas of Vietnam. However, low levels of DDTs were reported in most Asian rivers. Liu et al. detected levels of (0.90-33.1 µg/kg dw) in the Yangtze estuary. Additionally, low levels of HCHs were reported in most Asian rivers. Liu et al. detected levels of 0.50-17.5 µg/kg dw in the Yangtze estuary. Fillman et al., Barakat et al., and Sapozhnikova et al. detected low levels DDTs and HCHs in the Black Sea, Romania, Alexandria Harbor, Egypt and the Salton Sea, California, respectively.

Distribution pattern and seasonal variation

Endrin, chlordane, endosulfan and metabolites were very prominent, compared to DDT, HCH, dieldrin, and isomers which occurred at very low concentrations. The sequence was Σendrin > Σchlordane > Σendosulfan > ΣDDT > ΣHCH > ΣDieldrin. Seasonal variation (Table 9) of POPs in the Gurara River and Lokoja location showed marked differences between the rainy season and the dry season. The ΣOCPs were higher during the dry season compared to the rainy season period. This may be because the resident time of the sediment transported was higher during the dry season compared to the rainy season, which is characterized by storms, high current, and bottom scour. The temporal distribution of POPs in the Onitsha location was different from the other locations. In this location, total OCPs were higher during the rainy season compared to the dry season.

Sources of persistent organic pollutants and environmental/human health implications

In Nigeria, OCPs were largely used in agriculture until the 1990s, and OCPS are still being used in some countries against certain insects. Some of these pesticides may be persistent in the environment for decades. This persistence may be a result of resistance to physical, chemical, and biological forces of degradation. For instance, the chemistry of β-HCH makes microbial degradation more difficult than the
other isomers, which may result in the accumulation of β-HCH in sediment and aquatic organisms, including fish. Marine waters and sediments may be contaminated with OCPs through surface run-off and inflow from rivers. There may also be significant contribution from anthropogenic activities surrounding the river. For example, the River Niger at Onitsha is located in a densely populated area with likely input sources, such as the chemical industry, agriculture, and sewage.

Humans may be exposed to OCPs through domestic application of contaminated water and consumption of fish from the river. From the Warri to the Onitsha segments of the Niger River, smoked fish and palm oil/kernel production are common. Organochlorine pesticides pose problems of human/animal toxicity, slow degradation, fat solubility, and bioaccumulation. Globally, up to 200,000 deaths a year are a result of pesticide poisoning, with developing countries representing a larger share of these deaths. Biochemical effects of major OCPs in humans have been largely documented and include neurotoxicity, reproductive and developmental disorder, genotoxicity, tumorigenic effects, nausea and vomiting (aldrin and dieldrin); convulsions, tremor and incoordination (chlordane); itching, psoriasis, eczema, leucoderma and skin rashes (BHC/DDE); nausea, dizziness, incoordination, vomiting, anorexia, anemia, muscular weakness, hyperexcitability, and nervous tension (DDT). Numerous toxic effects on aquatic organisms have also been reported.

**Conclusions**

The analyses of sediment from the longitudinal section of the Niger River to the Delta revealed a wide spectrum of persistent organic pollutants. The sources of most of the pollutants could be attributed to agricultural and industrial activities, waste water from slaughter houses, and storm water run-off. These compounds consist of agricultural, industrial sewage and waste derived particularly from slaughter houses along the banks of the River. Their ubiquitous occurrence has been confirmed by other authors in other Niger Rivers.

In the sampled sediment, endrin, chlordane, endosulfan, and DDTs were dominant compared to HCHs and dieldrin. The consensus-based sediment quality guidelines were exceeded in all locations (Table 10) for dieldrin, chlordane, DDD, DDE, DDT, heptachlor epoxide, and lindane, sometimes 5- to 10-fold. The ∑OCPs were higher during the dry season compared to the rainy season period. This may be because the resident time of the sediment transported is higher during the dry season compared to the rainy season, which is characterized by storms, high current, and bottom scour.

The OCP load in the Niger River sediment was also higher than global averages. The POP load in the water and sediment decreased downstream, with maximum loads at Onitsha. The concentrations of organochlorine pesticides in sediment of the Niger River exceeded permissible limits; this presents a potential danger for humans, animal health, and the environment. Due to the environmental/human risk and potential danger this presents, there is a need for continuous monitoring of this water body.

**Acknowledgements**

This study was funded as part of employment.

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