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Selected persistent organic pollutants (POPs) in water of River Niger: occurrence and distribution

J. P. Unyimadu · O. Osibanjo · J. O Babayemi

Abstract This study assessed the levels and distribution of selected persistent organic pollutants (POPs) in water of River Niger. The selected POPs of interest were organochlorine pesticides (OCPs). 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 selected for sampling quarterly over a 24-month period. A total of 240 surface and bottom water samples were collected using Van Dorn water sampler in the eight quarters of 2008–2009. At the Delta locations where tidal effects take place, high- and low-tide water samples were taken as compared to surface and bottom at the River Niger locations. For sample extraction, EPA method 3510c was employed with slight modifications. Certified reference standards from Accustandards USA was used for the instrument calibration and quantification of OCPs. The extracted samples were subjected to gas chromatography (GC/ECD) for identification/quantification. And Shimadzu GCMS QP2010 was used for confirmation.

Chlordane, endosulfan, endrin and DDT metabolites were very prominent in the water samples, compared to HCH, dieldrin, and isomers which occurred at lower concentrations. The sequence in the concentration of the organochlorine pesticides were ∑chlordane > ∑DDT > ∑endosulfan > ∑endrine > ∑dieldrin > ∑HCH. The highest concentration of ∑OCPs in water samples of River Niger, 1138.0 ± 246.7 ng/L, with range 560.8–1629 ng/L was detected at Onitsha location, while the lowest concentration, 292.6 ± 74.9, with range 181–443.0 ng/L was detected at Nicolas River. Levels of OCPs in a larger percentage of the samples exceeded guidelines and therefore hold potential harmful effects on benthic fauna, fish, and man. Abstraction of water from the River for drinking water treatment should be discouraged. Because of the potential danger, this presents, continuous monitoring of the water body and if possible remediation, determination of the sources of the POPs is therefore very necessary.

Keywords Persistent organic pollutants ·
Organochlorine pesticides · River Niger

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Introduction

There is an increasing concern on pollution of rivers globally and in developing countries in particular. Many hazardous substances have been identified as main pollutants of water bodies in Nigeria; however, with scanty information on persistent organic pollutants (POPs) (Babayemi et al. 2016b). Assessment of

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contaminants in rivers has unique importance because of the potential for long-range transport of the contaminants. In addition, abstraction of water from rivers to be treated for human consumption and consumption of aquatic organisms is a common practice in Africa and Nigeria in particular. Rivers in the country, particularly River Niger, therefore requires assessment for quality.

The River Niger, the most important river in Nigeria, draining 60% of Nigerian landmass, is being subjected to increasing human interference and receives a 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 Kanji), impoundments, and channels for irrigation and dredging, which are capable of degrading water quality and contaminate sediments due to their many uses (Galat et al. 2005). These physical and chemical impairments may affect biological organisms, in the river, causing health and reproductive problems in fish (Hinck et al. 2004, 2006; Schmitt 2002).

Large urban areas like Onitsha might contribute to an increase in some chemical contaminants in the river, which have been identified as a possible cause for declines in benthic macro invertebrate's diversity and density downstream. Previous reports on the River Niger discussed only heavy metals and hydrocarbons. A lot of uncertainty, therefore, exists about the orders of magnitude in which these ecologically important chemicals (POPs) are present. There is a dearth of reports on the composition and characterization of POPs and organochlorine pesticides including DDTs, BHCs, endosulfan and isomers, aldrin, endrin and isomers, dieldrin, chlordane (α, and γ) and methoxychlor in the water body. The development of risk-based acceptance criteria for organochlorines requires information on the background concentration of these contaminants in the environment (Keith and Telliard 1979) and water, in humans, and on exposure pathways.

Also, major constraints to high production in aquaculture and capture fisheries in Nigerian coastal waters include over exploitation, and environmental degradation resulting from domestic, agricultural, industrial waste and other anthropogenic activities (Nwokedi and Obodo 1993). The data available for the levels and distribution of organochlorine compounds in coastal waters in Nigeria is limited to few rivers, lagoons, and estuaries (Babayemi 2016).

There is paucity of data on POPs in Nigeria in general and the River Niger ecosystem in particular. The available reports on POPs in the country are mainly the levels in products (Babayemi et al. 2014, 2016a; Sindiku et al. 2014, 2015). Data gaps on POPs in the Nigerian water bodies need to be filled if Nigeria must fulfill its obligation in implementing the Stockholm Convention on Persistent Organic Pollutants. There is the need to understand the environmental fate of POPs in the River Niger ecosystem towards the development of appropriate national policy on sound management of POPs. This study, therefore, aims at obtaining information on the concentration of organochlorine pesticides in water of the River Niger and to determine their distribution in time and space.

Materials and methods

Study area and sampling method

The River Niger, 4160 km long, is the 12th longest river in the world and the third longest in Africa. With total drainage basin of 440,000 km^2, the River Niger occupies the seventh position in the world (Golterman, 1988).The River Niger rises from the mountains of Sierra Leone on the Fouta Djallon highlands, entering Nigeria, from North-West; the lower Niger, flows for 1271 km, reaching the sea via a number of tributaries (Fig. 1). The River Niger has coastal fringe, estuaries, fresh waters and coastal delta; the surface area of the coastal delta is 36,260 km^2, largely forested (Wellcome 1986). The River Niger flows in the North-South direction until it joins apex of the Niger Delta at Aboh.

A sampling programme was implemented between 2008 and 2009 to collect surface and bottom water samples quarterly from three stations each in Gurara River, Lokoja and Onitsha sites on the River Niger. At the Brass and Nicolas Rivers in the Delta, low-tide and high-tide water samples were collected. There was a need to establish if the distribution in water was random, uniform (homogenous) patchy, stratified (homogeneous within sub areas), or present as a gradient. Stratified sampling was employed, which is the most common approach to sampling (Dean 2003).

Three sites from each of five main locations (making a total of 15 sites) were selected along River Niger for sampling quarterly over a period of 24 months (Table 1). The five main locations were Brass and Nicolas Rivers
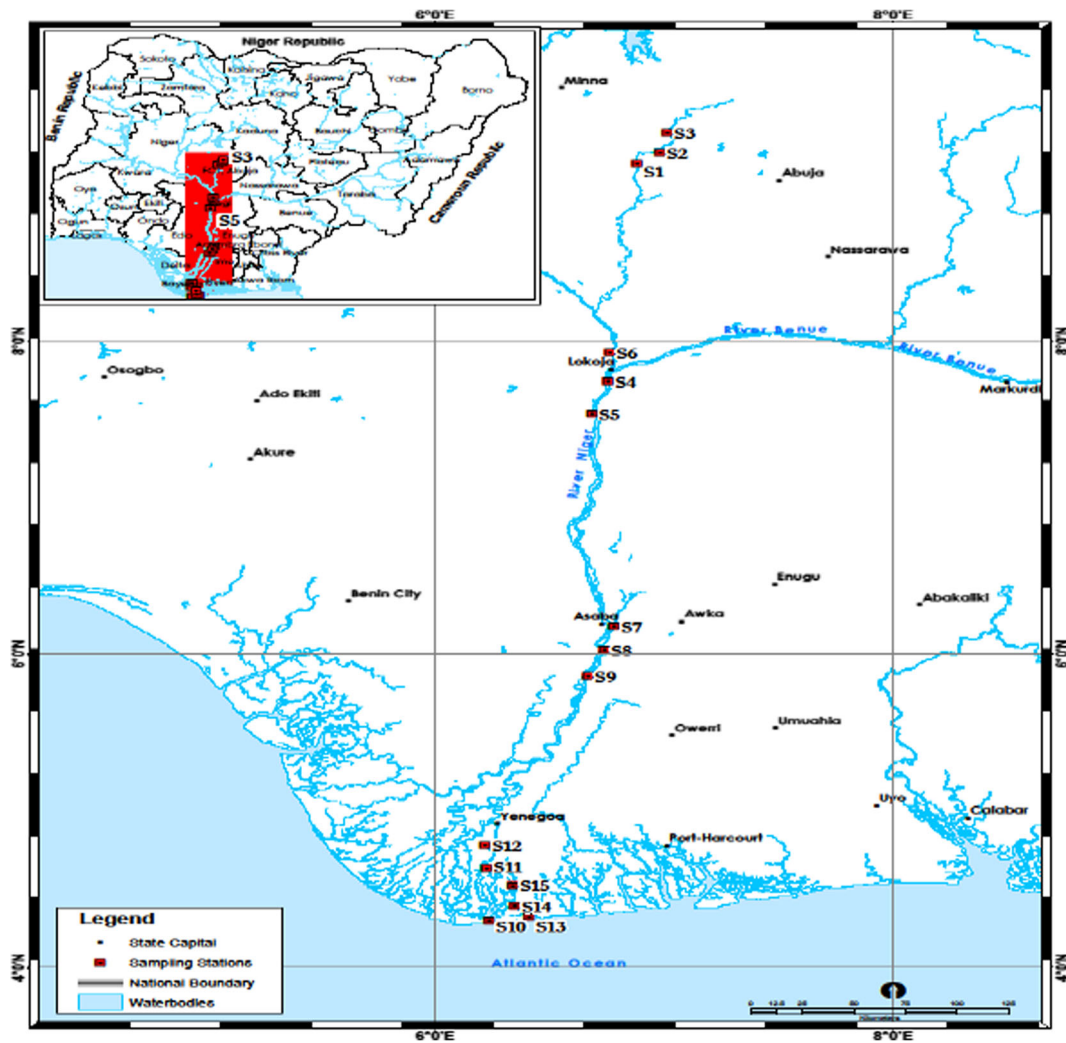
Fig. 1 Map of the River Niger showing the sampling stations and the drainage basin

(tributary) in Bayelsa State, Gurara River (tributary) in Niger State, Onitsha in Anambra State and Lokoja (confluence) in Kogi State. The sampling intervals were selected to coincide with early and late rainy and dry season to be able to capture heavy storm runoff and possible point source pollution.

A total of 240 surface and bottom water samples were collected using Van Dorn water sampler in the eight quarters of 2008–2009, making a total of 60 water samples per quarter. At the Delta locations where tidal effects take place, high- and low-tide water samples were taken as compared to surface and bottom at the River Niger locations. The profiling sampling method was adopted. The Van Dorn sampler used was manually operated and have open tubes of known volume (typically 1 to 3 L) fitted with a closure mechanism at each

end. The sampling device was lowered on a calibrated line to the specific sampling depth; the sample was taken and the top and bottom lids were closed.

Amber glass bottles (500 ml) were used for the collection of surface and bottom water samples to eliminate the effect of light, and were completely decontaminated by washing with detergent to remove any solid residues, soaked for 24 h in an acid bath (chromic acid wash; 100 ml of concentrated H_2SO_4 slowly and with constant stirring to a solution of 5 g of sodium dichromate in 5 ml of water). The bottles were rinsed with deionized distilled water twice to remove all contaminants that can interfere with the analytical results and allowed to dry in an oven over night. The bottles were rinsed twice with analytical grade hexane.

Each quarterly sample was obtained as a series of six grabs, of surface and bottom in each sub location, a total of 3 L of river water sampled into six amber glass bottles of 500 mL each. The water samples were treated in situ with 2 ml of concentrated H_2SO_4, to retard, biological action, hydrolysis, volatility of compounds and reduce adsorption effects. The sample bottle was filled completely to avoid sample oxidation.

They were immediately preserved in coolers with ice blocks. Following collection, each sample was given a unique identification code, each bottle labeled, a custody seal fixed over the screw cap and placed in a polyethene bag. Simultaneous with the collection of primary water samples, a series of quality control samples consisting of field blanks and blind duplicates were also collected.

At the Gurara location, sampling points were assessed by wading, while in the other locations motorized boats were used. Samples were taken with the water sampler facing the upstream.

Reagents

In order to minimize sample contamination, only glass, metal and Teflon container apparatus were used in the laboratory. Glassware was cleaned by agitation in detergent solution and rinsed with running tap water, then distilled water and high-purity acetone and n-hexane

Table 1 River Niger sampling sites, coordinates and samples collected

Sample code	Long.	Lat.
NGSW1	007°.00.29	09°.14.58
NGSW2	007°.00.20	09°.14.55
NGSW3	007°.00.12	09°.14.53
NLSW4	006°.45.24	07°.44.51
NLSW5	006°.45.05	07°.46.18
NLSW6	006°.45.29	07°.47.42
NONSW7	006°.46.81	06°.10.69
NONSW8	006°.45.19	06°.08.01
NONSW9	006°.42.81	06°.05.08
NBRSW10	006°.14.11	04°.17.99
NBRSW11	006°.15.72	04°.21.65
NBRSW12	006°.18.72	04°.25.50
NNCSW13	006°.19.88	04°.17.99
NNCSW14	006°.19.21	04°.21.65
NNCSW15	006°.19.16	04°.23.66

prior to the extraction procedure. 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). Purity of solvents was tested by gas chromatography (GC). Anhydrous granulated sodium sulfate and silica gel 100–200 mesh (Merck, Germany) were cleaned with pure n-hexane by distillation. The external and internal standard was 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, aldrin, dieldrin, endosulfan 1, endosulfan 11, endosulfan sulfate, methoxychlor, α-chlordane, γ-chlordane, DDE, DDD and DDT.

Frequent execution of blank analyses confirmed continuously the absence of laboratory derived contamination at concentration levels above the limit of detection (LOD) and quantification (LOQ) of the analytes being studied.

Sample extraction and cleanup

The method employed was EPA method 3510c with slight modifications. A 25 mL of dichloromethane was added to 250 mL of water sample (unfiltered) in its original sample bottle. The bottle was closed tightly with an aluminum lined cap. A 20 µg/L of internal standard, decafluorobiphenyl was added. The bottle was shaken manually for 15 min so that the vortex formed at the surface reaches almost to the bottom of the bottle. The contents of the bottle were transferred to 500 mL separatory funnel. Ten minutes was allowed for the aqueous and the organic phase to separate. The organic layer was transferred to 250-mL separatory funnel and the aqueous layer was returned to the sample bottle. The 500-mL separatory funnel was rinsed twice with dichloromethane; 10 mL at first and then 15 mL, transferring the solvent to the sample bottle after each rinsing.

The shaking, separation and rinsing procedure was repeated twice. After the third separation, the organic layer was transferred to the 250 separatory funnel and the sample discarded. The 500-mL separatory funnel was rinsed again and the contents added to the 250-ml separatory funnel. The 250-ml separatory funnel was shaken for 2 min and allowed to stand for 10 min (Dean 2003).

A 1 g of anhydrous sodium sulfate was placed in a 125-mL sintered glass funnel and set up to drain into a 250-mL round bottom flask. The organic layer in the 250-mL separatory funnel was drained into the filtration column. A 15 mL of dichloromethane was added to the aqueous layer remaining in the separatory funnel and shaken for 2 min and then allowed to stand for 10 min. The organic layer was drained again through the sodium sulfate filter column and the remaining aqueous layer phase discarded. The 250-mL separatory funnel was rinsed twice with 10 mL of dichloromethane and passed through the sodium sulfate column. The sodium sulfate column was washed with 10 mL of dichloromethane. The combined sample extracts were evaporated under vacuum using a rotary evaporator at 30–35 °C to 5 or 6 mL. The concentrate was transferred with 4×1 mL rinsing to a 15 mL graduated glass tube with a conical bottom. The evaporation was finished to 3 mL under a gentle stream of nitrogen at 50 to 60 °C (water bath) at atmospheric pressure. The extract was solvent exchanged to iso-octane.

A 600 mm × 19 mm id cleanup column was prepared by blocking the hole with glass wool and adding 3 g of activated silica gel (60 to 100 mesh, calcined at 650 °C for 24 h in a muffle furnace, and then stored at 130 °C until use (Unyimadu et al. 2017). Before using the silica gel was deactivated with 1 mL distilled water. The column was topped with 1 cm of preheated Na_2SO_4 previously heated at 650 °C for 8 h in a furnace and stored in a clean bottle in a desiccator. The column was rinsed by eluting with 20 mL hexane twice and discarded. 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 about 14 OCs (Dean 2003).

The elution 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 a 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 (Dean 2003).

Quality control and quality assurance

Certified reference standards from AccuStandard, USA were used for the instrument calibration and quantification of OCPs. 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 were 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 an r^2 value of 0.999 were used for the quantification of the OCPs. 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 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 basis and were not corrected for recoveries.

Determination of instrument detection limits (IDLs) and retention times (R_T)

The instrument detection limits (IDL) is the lowest detectable amount of each analyte that the instrument can detect and record. The IDL was computed using the method described by Miller and Miller (1998).

$$IDL = Yb + 3Sb \qquad (1)$$

where:

Yb   blank value
Sb   standard error of the regression line

The noise and thresholds were set during column background run so as to eliminate noise spikes from being registered as peaks. Each standard was injected into the GC to determine its retention time.

Gas chromatography–electron capture detector/mass spectrometry analysis

Twenty organochlorine pesticides, namely, α-BHC, β-BHC, γ-BHC, δ-BHC, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide, aldrin, dieldrin,

endosulfan 1, endosulfan 11, endosulfan sulfate, methoxychlor, α-chlordane, γ-chlordane, DDE, DDD and DDT were screened in the water samples. The analytical standards (> 98% purity) were used to prepare fortification and standard solutions. The extracted samples were subjected to GC for identification/quantification. The compounds were analysed using Agilent Hewlett Packard GC 5890 series 11 with electron capture detector. The column used was HP 608, 30 m × 530 μm × 0.5 μm. The instrument was operated in a splitless mode, (closed for 1.5 min) and the oven temperature program started at 90 °C (held for 2 min) to 130 °C at 15 °C/min, then to 290 °C at 4 °C /min (holding time 20 min). Injector and detector temperatures were 250 and 300 °C, respectively. Helium was used as carrier gas, 20 cm/s, 2.2 psi at 90 °C with electronic pressure control (EPC), with a flow rate of 2.4 mL min^{-1}. Calibration curve was performed for each compound to be quantified.

GC type used in the confirmation study was Shimadzu GCMS QP2010 and capillary column type: HP1MS (30 m × 0.25 μm × 0.25 mm id). The GC was checked to ensure that it is in good condition. Thereafter, it was flushed with the carrier gas. Calibration was done using reference standards as follows: 0.063, 0.125, 0.25, 0.5 and 1.0 ppm. These standards were run six times, to calculate the mean, range and then the standard deviation, and also peak column performance, peak height and resolutions. The gas used was helium because of its inertness. The column used in the study was the HP1 column which is of high quality and low bleed capacity (the stationary phase coated or adsorbed to the column does not wear off easily) 60 and 80 °C for OCPs.

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 $r^2 = 0.999$. None of the target compounds were detected in the procedural blanks. Spiked water samples were determined with good precision and high recoveries. The recoveries for the OCPs ranged between 78 ± 2.20% to 92 ± 2.10%. In addition, the errors involved in sampling were assessed by carrying out a 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 between 0.05 and 5.76 with a mean standard deviation of 1.50. Internal standards were used to compensate for losses involved in the sample extraction and workup, to further improve the analytical quality. The detection limit of the equipment used ranged between 0.25 and 0.50 ng/l for OCPs.

Occurrence of OCPs

HCHs

Technical HCH has been used as a broad spectrum pesticide for an agricultural purpose which has been banned in Nigeria since 1992. It consists of four isomers: α-HCH (60–70%), β-HCH (5–12%), γ-HCH (10–15%) and δ-HCH (6–10%); while lindane contains > 90% of γ-HCH (Qui et al. 2004; Zhou et al. 2006; Macwan et al. 2012). α-HCH, γ-HCH and δ-HCH were not detected in 96, 84, 60 and 80%, respectively. The sequence of concentration in the River Niger stations were δ-HCH > β-HCH > γ-HCH > α-HCH. The δ-HCH displaced β-HCH in prominence (Table 3). The highest mean concentration of δ-HCH, 61.1 ± 47.1 ng/L and range 2.76–140.4 ng/L, was detected at location NONSW7 at Onitsha and the lowest mean concentration, 5.24 ± 4.47 ng/L, and range 0.97–13.0 ng/L were detected at location NLSW5 at Lokoja. The highest mean concentration of β-HCH, 42.5 ± 23.3 ng/L and range 17.8–87.4 ng/L, was detected at location NONSW7 at Onitsha and the lowest mean concentration, 6.96 ± 4.61 ng/L and range BDL–24.7 ng/L were detected at location NNCSW14 at Brass River. The highest mean concentration of γ-HCH, lindane, 28.7 ± 8.03 ng/L and range 15.4–46.8 ng/L, was detected at location NONSW8 at Onitsha and the lowest mean concentration, 2.05 ± 2.38 ng/L and range BDL–6.47 ng/L, was detected at location NBRSW11 at Brass River. The highest mean concentration of α-HCH, 11.1 ± 4.01 ng/L and range 5.16–19.5 ng/L, was detected at location NONSW8 at Onitsha and the lowest mean concentration, 3.54 ± 2.02 ng/L and range BDL–6.38 ng/L were detected at location NNCSW14 at Nicolas River.

The distribution of the HCHs in water varied markedly along the different location of the River Niger with a high concentration of the different isomers identified

in different locations but the lowest concentration most times detected at the Nicolas River location NNSW14 downstream. The isomer α-HCH was the lowest concentration in most of the locations signifying no recent input of technical HCH into the environment. The concentration of the HCHs decreased downstream. High levels of α-HCH, 150 (1.0–302) ng/L were reported by Osibanjo (2002), at Ibadan streams indicating technical HCH input into the environment. Also, high levels of γ-HCH, 100 (7.0–297.0) in Ibadan streams and 182 (16.0–634.0) in the Lagos Lagoon was also reported. However, the levels of γ-HCH in Ero Dam, Rivers Ero, Osse and Opomu were low ranging from 2.00 to 6.40 ng/L.

Kumar et al. (2012) detected concentration of ∑HCH in the range between less than 0.10 and 285 ng/L, mean and median 151 and 161 ng/L, respectively, in Yamuna River in India, which is similar to the levels of range 22.6 to 119 ng/L obtained in this study. Lindane concentration of 285 ng/L, have been reported in water samples from Northern Nigeria (Okeniyia et al. 2009). There are reports of ∑HCH 4.05–20.59 ng/L in surface water from the Baiyangdian Lake, Northern China (Dai et al. 2011), 6.0–234 ng/L HCHs in water samples from Egypt (Essumang et al. 2001). Even higher values of chlorinated pesticides have been reported in the literature such as ∑OCPs, 631–1540 ng/L, for the Juskei River in Gauteng, South Africa (Sibali et al. 2008).

Aldrin and dieldrin

Aldrin and dieldrin were detected in 98 and 94% of the water samples, respectively; however, the sequence in the concentration of the metabolites were aldrin > > dieldrin (Table 3). The highest mean concentration of aldrin, 124.4 ± 33.3 ng/L and range 67.9–200.4 ng/L, was detected at location NONSW9 at Onitsha and the lowest concentration, 23.5 ng/L with range BDL– 64.2 ng/L, was detected at location NGSW3 at Gurara River. The highest mean concentration of dieldrin, 42.3 ± 30.2 ng/L and range BDL–80.9 ng/L, was detected at location NLSW4 at Lokoja and the lowest mean concentration, 5.45 ± 3.28 ng/L and range BDL–11.9 ng/L were detected at location NGSW3 at Gurara River. The

Table 2 Analytical quality control data

Organochlorines	Triplicate analyses of 3 water samples with the standard deviation				Detection limit (200 ml) (ng/L)	Mean recovery (%) ± standard deviation (%)
	1st	2nd	3rd	SD		
α-BHC	3.2	3.29	3.24	0.05	0.25	82 ± 2.1
β-BHC	7.52	7.98	7.61	0.24	0.25	78 ± 2.2
γ-BHC (lindane)	17.36	16.94	17.57	0.32	0.25	81 ± 3.4
σ-BHC	15.28	14	15.47	0.80	0.25	85 ± 2.2
Hepthachlor	34.32	28.63	34.74	3.41	0.25	86 ± 3.8
Aldrin	1.68	0.77	1.70	0.53	0.25	90 ± 4.4
Heptachlor epoxide	79.2	72.38	80.19	4.25	0.25	78 ± 2.8
γ-Chlordane	–	–	–	–	0.50	88 ± 2.5
Endosufan 1	4.64	8.33	4.69	2.12	0.50	86 ± 3.2
α-Chlordane	1.92	1.61	1.94	0.18	0.50	92 ± 2.8
p,p′-DDE	2.16	2.38	2.18	0.12	0.50	91 ± 2.2
Dieldrin	3.36	3.64	3.40	0.15	0.50	88 ± 2.3
Endrin	5.52	12.74	5.58	4.15	0.50	87 ± 2.5
Endosulfan 11	10.24	18.13	10.36	4.52	0.50	82 ± 2.8
4,4′-DDD	5.52	5.74	5.58	0.11	0.50	83 ± 2.6
Endrin aldehyde	10.56	10.43	10.69	0.13	0.25	81 ± 2.6
p,p′-DDT	–	–	–	–	0.50	80 ± 3.4
Endosulfan sulfate	61.76	72.1	62.53	5.76	0.25	83 ± 2.8
Methoxychlor	1.76	1.54	1.78	0.13	0.25	82 ± 3.2
Endrin ketone	610	618.	617	3.13	0.50	80 ± 3.3

Table 3 Concentration of HCH, aldrin and dieldrin in water samples

Sample code	α-HCH	β-HCH	γ-HCH	δ-HCH	Aldrin	Dieldrin
NGSW1	4.51 ± 1.42 (0.63–6.26)	19.0 ± 10.6 (5.37–33.86)	4.60 ± 1.99 (1.05–8.00)	13.8 ± 9.03 (2.64–30.1)	86.6 ± 45.3 (21.4–155.0)	8.23 ± 1.83 (5.81–12.3)
NGSW2	7.08 ± 2.57 (2.17–11.8)	13.1 ± 7.01 (3.11–36.06)	3.62 ± 3.08 (BDL–10.7)	11.4 ± 3.15 (4.51–18.3)	59.9 ± 38.1 (13.3–162.0)	9.85 ± 4.88 (BDL–18.2)
NGSW3	5.95 ± 3.16 (0.20–15.4)	18.5 ± 10.6 (6.93–37.54)	4.21 ± 1.35 (BDL–6.82)	14.6 ± 7.10 (BDL–24.1)	23.6 ± 19.4 (BDL–64.2)	5.45 ± 3.28 (BDL–11.9)
NLSW4	7.34 ± 3.79 (3.01–13.2)	17.0 ± 14.8 (BDL–50.8)	5.22 ± 5.22 (BDL–15.2)	18.9 ± 9.27 (8.26–34.1)	44.3 ± 35.6 (BDL–118.4)	42.3 ± 30.2 (BDL–80.9)
NLSW5	9.70 ± 6.86 (1.89–19.96)	15.5 ± 10.4 (0.97–40.1)	5.64 ± 3.83 (0.19–16.7)	5.24 ± 4.47 (0.97–13.0)	(30.5 ± 31.4 (3.64–84.7)	40.2 ± 33.4 (3.87–98.5)
NLSW6	5.20 ± 1.47 (2.18–8.19)	11.0 ± 7.10 (2.13–21.8)	4.96 ± 2.76 (2.63–11.6)	5.07 ± 3.54 (0.70–12.9)	44.1 ± 31.0 (11.1–111.7)	11.5 ± 6.68 (2.60–22.4)
NONSW7	9.17 ± 4.16 (3.61–16.8)	42.5 ± 23.4 (17.8–87.4)	6.03 ± 6.03 (BDL–15.4)	61.1 ± 47.1 (2.76–140.4)	61.3 ± 14.8 (29.7–90.2)	16.1 ± 9.49 (2.38–33.3)
NONSW8	11.1 ± 4.01 (5.16–19.5)	31.7 ± 6.79 (19.6–47.0)	28.7 ± 8.03 (15.4–46.8)	12.5 ± 8.68 (2.76–27.5)	87.4 ± 20.6 (51.3–134.4)	11.4 ± 8.13 (2.38–25.37)
NONSW9	6.74 ± 1.28 (4.82–8.80)	35.4 ± 19.7 (11.3–71.5)	18.9 ± 11.8 (5.14–39.9)	54.5 ± 10.3 (37.0–74.7)	124.3 ± 33.3 (67.9–200.4)	7.46 ± 2.16 (3.93–12.3)
NBRSW10	3.94 ± 2.54 (BDL–9.19)	14.8 ± 8.47 (3.42–32.0)	3.50 ± 3.82 (BDL–31.4)	12.5 ± 7.11 (BDL–31.4)	58.5 ± 35.3 (15.5–109.0)	6.58 ± 2.94 (2.73–12.1)
NBRSW11	3.54 ± 2.94 (BDL–12.0)	12.1 ± 8.37 (2.46–30.4)	2.05 ± 2.38 (BDL–6.47)	10.0 ± 7.05 (BDL–25.9)	34.8 ± 26.6 (6.32–91.9)	6.33 ± 5.37 (0.86–16.5)
NBRSW12	4.78 ± 3.14 (0.61–9.27)	10.3 ± 8.03 (2.45–36.1)	3.30 ± 3.44 (BDL–11.5)	14.9 ± 10.9 (3.35–39.1)	35.7 ± 26.1 (5.88–87.7)	5.58 ± 4.97 (BDL–15.0)
NNCSW13	5.93 ± 2.66 (1.27–11.0)	9.02 ± 6.74 (4.04–36.0)	3.86 ± 3.53 (BDL–16.0)	22.9 ± 15.5 (7.38–66.7)	25.4 ± 14.6 (8.48–59.2)	7.19 ± 5.56 (BDL–18.5)
NNCSW14	3.54 ± 2.02 (BDL–6.38)	6.96 ± 4.61 (BDL–24.7)	2.54 ± 2.15 (BDL–7.80)	10.6 ± 6.73 (2.50–15.2)	33.1 ± 19.1 (7.07–61.9)	7.44 ± 5.71 (BDL–15.4)
NNCW15	4.56 ± 2.31 (1.97–10.5)	8.24 ± 5.11 (1.56–21.3)	2.92 ± 1.98 (0.80–7.21)	9.40 ± 7.94 (3.26–27.0)	25.1 ± 12.9 (3.80–43.8)	10.7 ± 5.75 (1.15–19.4)

The ranges are in parenthesis

levels decreased downstream. Higher levels of dieldrin have been reported in the literature. In Ibadan streams, River Ero Dam, River Ero Ondo, River Osse Ondo, 250.0, 560, 740 and 2150 ng/L of dieldrin were detected, respectively (Osibanjo 2002). According to these authors, high levels were detected in River Owesse (1120 ng/L) and River Opomu Ondo (1380 ng/L); low levels (8.0 ng/L) similar to the levels in the present study were detected in the Lagos lagoon.

Low levels of aldrin and dieldrin compared to this study were detected elsewhere; for instance, aldrin level of 0.220 μg/L in surface waters of Konya Closed Basin, Turkey (Aydin et al., 2013). Janiot et al. (1994), GEMS website, Tabucanon et al. (1992) and Giesy et al. (1994) detected ND–6.30, ND–2.24, 1.80–27.0, 1.00–32.5, ND–22.0, ND–24.0, 0.35–1.30 and 8.80–46.0 ng/L in Argentina River, Egypt irrigation, Michigan, USA, above and below Dams, respectively. However, higher levels of aldrin and dieldrin compared to the present study were also obtained elsewhere. GEMS website, Nair and Pillai (1992) and Tabucanon et al. (1992) detected < 1.0.88, < 1.0–3020, 500–50,000, 100–100,000, 1.0–960 and 8.0–890 ng/L in Belgium, Indian Rivers and UK drainage water, respectively.

In Gomti River water samples, aldrin ranged from BDL–77.93 ng/L. The aldrin levels reported for the Beijing Guanting reservoir, 0.60–115 ng/L (Xue et al. 2006) and for Chao Phraya River, Thailand, 0.09–7.7 ng/L (Boonyatumanod et al. 1997). Residue levels of dieldrin in the River Niger water were BDL–22.45 ng/L; for Gomti River, Pearl River estuary, 0.74–34.23 ng/L for dieldrin and 2.11–33.26 ng/L for endrin, as reported by Zhang et al. (2002). The levels of aldrin and dieldrin in the present study were higher than all the levels reported in the literature reference above. The higher mean and detection of aldrin as compared to dieldrin in water samples is in agreement with literature reports (Malik et al. 2008). This suggests the high persistence of aldrin in the environment.

Chlordane

Technical chlordane was generally used as an insecticide, herbicide, and germicide and still being used in some countries against termites (Xue et al. 2006). It is a mixture of over 140 components and among them, trans-chlordane (α-chlordane) 13%, cis-chlordane (γ-chlordane) 11% and heptachlor 5%, are the most abundant components.

Heptachlor epoxide and methoxychlor were detected in all the water samples analyzed while α-chlordane, γ-chlordane, heptachlor, were detected in 86, 96 and 92% of the samples, respectively. The sequence of concentration in the River Niger stations was heptachlor > heptachlor epoxide > methoxychlor >γ-chlordane > α-chlordane (Table 4). The highest mean concentration of heptachlor, 110.8 ± 38.9 ng/L and range 29.9–193.2 ng/L was observed in samples from location NONSW7 at Onitsha and the lowest mean concentration, $19.7. \pm 10.7$ ng/L and range BDL–53.9 ng/L at location NNCSW14 at Nicolas River. The highest mean concentration of heptachlor epoxide, 61.3 ± 14.9 ng/L and range 29.7–90.2 ng/L was recoded at location NONSW7 at Onitsha and the lowest mean concentration, 15.3 ± 8.38 ng/L and range 6.00–34.6 ng/L, was detected at location NNCSW14 at Nicolas River downstream. The highest mean concentration of methoxychlor, 77.3 ± 31.8 ng/L and range 36.9–141.6 ng/L, was detected at location NONSW7 at Onitsha and the lowest mean concentration, 14.6 ± 7.51 ng/L and range 7.28–31.0 ng/L were detected at location NNCSW14 at Nicolas River downstream. The highest mean concentration of γ-chlordane, 39.6 ± 21.9 ng/L and range 16.1–81.7 ng/L, was detected at location NONSW7 at Onitsha and the lowest mean concentration, 5.03 ± 2.77 μg/kg and range 1.36–12.3 ng/L, was detected at location NBRSW12 at Brass River. The highest mean concentration of α-chlordane, 16.5 ± 4.26 ng/L and range 9.14–26.3 ng/L, was detected at location NONSW9 at Onitsha and the lowest mean concentration, 2.94 ± 2.94 ng/L and range BDL–6.54 ng/L, was detected at location NNCSW14 at Nicolas River.

The distribution of the chlordane varied markedly along the different locations of the River Niger with a high concentration of the different isomers identified in different locations upstream but the lowest concentration most times detected at the Nicolas River location NNSW14 downstream.

Literature shows that the ratio of cis-chlordane/trans-chlordane in the technical mixture is about 0.77 (Sovocool et al., 1997). Previous studies showed that trans-chlordane is easier to degrade than cis-chlordane in the environment (Eitzer et al. 2001), and a ratio of cis-chlordane/trans-chlordane >1 is indicative of aged chlordane (Bidleman et al. 2000). The ratio of cis-chlordane/trans-chlordane was more than 1 in 10 out of the 15 locations indicating no recent use of chlordane in most River Niger environment. The concentration of

heptachlor was higher than the epoxide in 6 out of the 15 stations signifying no input of heptachlor into the River Niger environment. In comparison with this study, lower levels of heptachlor were reported in Ibadan streams, River Ogun, Imo River and Kanji Lake with ranges from ND to 72.0 ng/L, (Osibanjo and Jinadu 2002). Very low concentrations (ng/L) of heptachlor, 0.25 (ND–0.80), 4.0 (ND–11.40) and 2.0 (ND–8.60) were detected in River Ogun, River Imo and Cross River, respectively. Also, very low concentrations (ng/L) of heptachlor, 0.47 (ND–3.84), 3.30, 5.0, 1.60 and 4.60 were detected in Kanji Lake, River Ero Dam Ondo, River Osse Ondo, River Owesse and River Opomu Ondo, respectively (Osibanjo and Jinadu 2002).

Imo et al. (2007) reported concentrations of heptachlor epoxide and methoxychlor: ND–60 and ND–56 ng/L respectively, in some rivers in Japan. Malik et al. (2008) also reported concentrations of ∑chlordane (sum of alpha and beta chlordane) ND–28.77 ng/L. These levels were 2–3 magnitudes less than the levels obtained in the present study.

Endrin

Endrin was very well metabolised also in the River Niger to endrin aldehyde and to endrin ketone. The sequence of concentration in the water samples was endrin ketone > endrin aldehyde > endrin (Table 5). Endrine and endrin aldehyde were detected in 78 and 72% of the samples, while endrin ketone was detected in 100% of the samples analysed. High levels of endrin ketone were detected in locations NONSW7, NONSW8, NONSW9, NBRSW11 and NNCSW13. The highest mean concentration of endrin ketone, 189.1 ± 57.7 ng/L and range 44.4–310.0 ng/L, was recorded at location NONSW7 at Onitsha; this was followed by concentration of 100.2 ± 67.4 ng/L and range 18.5–227.0 ng/L in location NNCSW13 in Nicolas River, then concentration of 90.5 ± 110.4 ng/L at location NBRSW11 and the lowest mean concentration, $29.9.1 \pm 17.1$ ng/L with range of 7.47–68.2 ng/L, was detected at location NGSW1 at Gurara location. The highest mean concentration of endrin aldehyde, 91.6 ± 91.6 ng/L, with range BDL–237.6 ng/L, was detected at location NONSW8, followed by NONSW7, 55.1 ± 55.1 ng/L, with range BDL–142.8 ng/L, both at Onitsha; and lowest concentration of 3.59 ± 4.48 ng/L was detected at NNCSW14. The highest mean concentration of endrin, 34.7 ± 6.63 ng/L,

and range 23.0–40.8 ng/L, was detected at location NONSW8 at Onitsha and the lowest mean concentration, 2.95 ± 4.24 ng/L, was detected at locations NNCSW14 downstream. The distribution of the endrin varied markedly along the different locations of the River Niger with high concentrations of the different isomers at the Onitsha location but the lowest concentrations most times detected at the Nicolas locations NNCSW14 to NNCSW15. The endrin isomers increased from upstream to downstream in the River Niger water samples.

The literature on the contamination of global rivers by endrin and the metabolites are scarce. Endrin is an alicyclic chlorinated hydrocarbon and is rapidly converted to the epoxide forms (endrin aldehyde and endrin ketone). Low levels of endrin and isomers compared to this study have been detected in Arctic regions (AMAP 1998), in surface waters from El-Rahawy contaminated area, Egypt, (El-Bouraie et al. 2011), and in Qiantang River, East China (Zhou et al. 2006).

Endosulfan

Endosulfan was very well metabolised also in the River Niger to endosulfan 11 and endosulfan sulfate. The results are shown in Table 6. The sequence of concentration in the water samples was endofulfan 11 > endosulfan sulfate > endosulfan 1. Endosulfan 1 was detected in 100% of the samples, while endosulfan 11 and endosulfan sulfate were detected in 70 and 80% of the samples, respectively. High levels of endosulfan 11 were detected in locations NONSW8, NGSW1, NGSW2 and NGSW3. The highest mean concentration of endosulfan 11, 148.1 ± 122.4 ng/L and range BDL–384.0 ng/L, was detected at location NONSW8 at Onitsha; this was followed by concentration of $92.5.2 \pm 99.2$ ng/L and range BDL–430.0.0 ng/L in location NGSW1 in Gurara, then followed by concentration of 67.4 ± 59.0 ng/L at location NGSW2 and the lowest mean concentration, 9.11 ± 11.4 ng/L with range of BDL–35.4 ng/L, was detected at location NNCSW14 at Nicolas River location. The highest mean concentration of endosulfan sulfate 114.1 ± 91.2 ng/L was detected at location NONSW7, followed by NGW1, 51.2 ± 32.2 N ng/L, with range BDL–114.0 ng/L; and lowest concentration of 13.2 ± 15.3 ng/L detected at NBRSW11 downstream. The highest mean concentration of endosulfan 1, 59.2 ± 45.5 ng/L and range 9.80–135.6 ng/L, was detected at location NONSW8 at Onitsha and the lowest mean

Table 4 Concentrations (ng/L) of chlordane pesticides in water samples

Sample code	γ-chlordane	α-chlordane	Heptachlor	Heptachlor epoxide	Methoxychlor
NGSW1	9.63 ± 2.84 (4.25–15.2)	11.8 ± 6.07 (BDL–22.40)	46.1 ± 20.1 (10.1–77.4)	55.4 ± 25.7 (1.33–112)	17.8 ± 6.19 (4.86–27.8)
NGSW2	7.62 ± 2.32 (5.07–13.2)	7.69 ± 5.55 (BDL–17.9)	30.8 ± 11.5 (11.4–56.5)	46.4 ± 23.3 (10.3–100.0)	30.3 ± 21.6 (4.66–80.2)
NGSW3	6.69 ± 4.55 (2.79–22.6)	7.86 ± 1.66 (5.76–13.5)	27.5 ± 12.7 (8.10–70.86)	56.5 ± 33.8 (11.5–140.0)	27.0 ± 11.9 (4.84–66.7)
NLSW4	7.22 ± 2.41 (2.61–11.3)	4.25 ± 4.50 (BDL–14.5)	21.7 ± 7.45 (6.74–32.7)	43.8 ± 32.4 (11.2–118.4)	40.6 ± 46.5 (0.71–145.8)
NLSW5	6.70 ± 4.31 (0.66–17.2)	3.62 ± 1.38 (2.14–7.71)	23.1 ± 15.3 (2.07–56.3)	48.6 ± 19.7 (21.1–77.3)	11.1 ± 9.87 (0.89–28.3)
NLSW6	4.05 ± 3.20 (0.52–11.4)	2.99 ± 2.99 (BDL–9.41)	27.9 ± 20.1 (7.33–74.5)	44.1 ± 31.0 (11.2–111.8)	17.6 ± 13.9 (3.97–49.7)
NONSW7	39.6 ± 21.9 (16.1–81.7)	14.6 ± 7.13 (5.39–28.2)	110.8 ± 38.9 (29.9–193.2)	61.3 ± 14.9 (29.7–90.2)	77.3 ± 31.8 (36.9–141.6)
NONSW8	29.0 ± 5.49 (20.6–38.2)	15.98 ± 3.26 (10.1–23.2)	30.1 ± 7.38 (24.9–53.9)	58.7 ± 18.5 (29.7–98.9)	45.8 ± 9.30 (29.1–66.5)
NONSW9	32.48 ± 7.37 (19.5–49.2)	16.5 ± 4.26 (9.14–26.3)	86.9 ± 28.78 (42.7–148.8)	25.9 ± 17.1 (5.96–55.8)	48.9 ± 10.9 (29.6–73.7)
NBRSW10	6.75 ± 4.56 (2.48–16.3)	4.17 ± 4.08 (BDL–14.9)	33.7 ± 22.6 (BDL–90.0)	22.6 ± 17.4 (6.24–64.5)	12.5 ± 8.83 (3.33–37.4)
NBRSW11	5.57 ± 2.95 (1.70–15.5)	4.17 ± 3.24 (BDL–14.3)	33.2 ± 28.3 (BDL–85.6)	21.0 ± 15.8 (2.43–52.3)	21.6 ± 23.5 (3.17–104.0)
NBRSW12	5.03 ± 2.77 (1.36–12.3)	6.82 ± 6.26 (BDL–23.2)	21.2 ± 11.6 (5.43–47.6)	30.9 ± 25.6 (4.33–74.7)	16.3 ± 12.9 (3.52–45.5)
NNCSW13	5.50 ± 3.72 (BDL–14.5)	6.91 ± 4.76 (BDL–23.0)	27.0 ± 12.7 (BDL–76.0)	17.6 ± 8.09 (9.05–34.5)	28.7 ± 17.9 (8.19–74.0)
NNCSW14	5.91 ± 3.46 (1.97–12.1)	2.94 ± 2.94 (BDL–6.54)	19.7 ± 10.7 (BDL–53.9)	15.3 ± 8.38 (6.00–34.6)	14.6 ± 7.51 (7.28–31.0)
NNCSW15	5.51 ± 1.94 (1.86–8.42)	4.01 ± 3.85 (BDL–10.6)	25.9 ± 11.2 (7.90–50.4)	18.9 ± 10.8 (2.44–38.76)	17.0 ± 7.56 (7.00–33.6)

The ranges are in parenthesis

Table 5 Concentrations (ng/L) of endrin pesticides in water samples

Sample code	Endrin	Endrin aldehyde	Endrin ketone
NGSW1	7.80 ± 6.68 (BDL–18.7)	6.17 ± 8.82 (BDL–22.1)	29.9 ± 17.1 (7.47–68.18)
NGSW2	8.98 ± 9.02 (BDL–45.03)	10.5 ± 11.3 (BDL–30.6)	31.2 ± 13.7 (12.1–52.1)
NGSW3	3.92 ± 3.36 (BDL–7.60)	6.13 ± 7.00 (BDL–19.2)	60.3 ± 47.3 (14.8–156.0)
NLSW4	BDL BDL	4.62 ± 6.92 (BDL–20.2)	33.7 ± 13.1 (13.1–53.8)
NLSW5	7.92 ± 5.27 (1.35–17.3)	BDL BDL	32.2 ± 17.6 (12.7–55.1)
NLSW6	13.2 ± 16.0 (1.04–49.3)	12.7 ± 9.19 (BDL–24.7)	43.5 ± 35.4 (9.35–124.8)
NONSW7	17.5 ± 5.20 (9.64–27.1)	55.1 ± 55.1 (BDL–142.8)	189.1 ± 57.8 (44.4–310.0)
NONSW8	34.7 ± 6.63 (23.0–40.8)	91.6 ± 91.6 (BDL–237.6)	88.1 ± 27.8 (44.4–148.8)
NONSW9	15.01 ± 9.04 (4.30–31.2)	49.9 ± 25.8 (17.4–98.3)	73.5 ± 16.1 (43.8–104.7)
NBRSW10	4.78 ± 4.78 (BDL–11.8)	10.5 ± 10.5 (BDL–52.4)	49.9 ± 50.1 (11.00–250.0)
NBRSW11	4.31 ± 6.16 (BDL–20.6)	6.81 ± 4.69 (BDL–19.86)	90.5 ± 110.4 (13.8–477.0)
NBRSW12	3.92 ± 4.58 (BDL–15.9)	17.7 ± 15.8 (BDL–47.7)	58.5 ± 62.4 (13.4–277)
NNCSW13	6.42 ± 7.80 (BDL–23.0)	16.3 ± 18.2 (BDL–86.0)	100.2 ± 67.4 (18.5–227.0)
NNCSW14	2.95 ± 4.24 (BDL–15.5)	3.59 ± 4.48 (BDL–11.1)	34.4 ± 16.7 (15.9–85.4)
NNCSW15	5.33 ± 5.14 (BDL–16.89)	4.05 ± 5.06 (BDL–22.4)	38.8 ± 15.4 (5.59–78.2)

The ranges are in parenthesis

BDL below detection limit

concentration, 4.18 ± 1.01 ng/L, was detected at locations NNCSW15.

The distribution of the endosulfan varied markedly along the different locations of the River Niger with high concentrations of the different isomers at the Onitsha location but the lowest concentrations mainly detected at the Nicolas River locations NNCSW14. The endosulfan and isomers decreased from upstream to downstream in the River Niger water samples. The ratio of endosulfan 1 to endosulfan 11 and endosulfan sulfate in most of the water samples was less than 1, signifying no recent input of endosulfan into the environment. High levels of endosulfan have been reported in Ibadan streams and Ogun River with mean values of 98.0 and 116.0, respectively (Osibanjo and Jinadu 2002); the authors also reported low levels in Cross River, Awba Dam Ibadan and Lagos Lagoon and not detected in samples from Kaiji lake, R. Ero Dam Ondo, R. Osse and River Opumu Ondo. Malik et al. (2008) reported concentrations of ∑endosulfan (sum 1, 11 and sulphate) ND–94.67 ng/L in Gomti River water, India.

DDTs

The results of concentrations of DDT and its metabolites are shown in Table 6. DDT, DDE and DDD were detected in 78, 80 and 82% of the water samples, respectively; the sequence in the concentration of the metabolites was DDD > DDT > DDE. The highest mean concentration of DDD, 251 ± 47.6 ng/L and range 174.4–337.2 ng/L, was recoded at location NONSW8 at Onitsha and the lowest concentration, 23.5 ng/L with range BDL–48.2 ng/L, was detected at location NBRSW11 at Brass River downstream. The highest mean concentration of DDE, 40.2 ± 33.4 ng/L and range 3.87–98.4 ng/L, was detected at location NLSW5 at Lokoja and the lowest mean concentration, 5.62 ± 4.08 ng/L and range BDL–12.8 ng/L, was detected at location NGW1 at Gurara River. The highest mean concentration of DDT, 71.7 ± 61.5 ng/L and range 7.32–172.8 µg/kg, was detected at location NONSW8 and the lowest mean concentration, 4.19 ± 2.91 ng/L with range BDL–10.8 ng/L was detected at locations NNCSW14 downstream.

The ratios between the parent compound DDT and its metabolites (DDD and DDE) can be used to identify the possible sources in the aquatic environment (Guo et al. 2009).After DDT applications, much of the DDT is slowly converted to DDE and DDD under aerobic and anaerobic conditions, respectively (Baxter 1990; Aislabie et al. 1997); hence, the ratio between the DDT and DDE and DDD is often used as an indication

Table 6 Concentrations (ng/L) of endosulfan and DDT pesticides in water samples (ng/L)

Sample code	Endosulfan 1	Endosulfan11	Endosulfan sulfate	DDE	DDD	DDT
NGSW1	20.5 ± 7.36 (2.94–32.0)	92.5 ± 99.2 (BDL–430.0)	51.2 ± 32.9 (BDL–114)	5.62 ± 4.08 (BDL–12.8)	76.8 ± 78.0 (BDL–230)	18.7 ± 17.6 (BDL–80.43)
NGSW2	10.7 ± 5.38 (2.72–23.29)	67.4 ± 57.4 (BDL–251.0)	20.7 ± 10.6 (2.60–34.8)	10.2 ± 8.42 (BDL–29.5)	22.6 ± 24.4 (BDL–64.31)	30.6 ± 14.8 (2.52–54.9)
NGSW3	11.6 ± 7.39 (3.04–31.3)	64.9 ± 59.8 (BDL–239)	43.5 ± 36.2 (7.16–113.0)	6.47 ± 4.24 (BDL–15.2)	89.9 ± 87.7 (26.6–397.0)	15.1 ± 12.5 (BDL–32.5)
NLSW4	11.2 ± 7.49 (1.63–24.4)	48.4 ± 72.6 (BDL–211.2)	21.3 ± 15.8 (4.65–56.7)	42.3 ± 30.2 (BDL–80.9)	161.7 ± 137.9 (BDL–465.6)	11.9 ± 6.85 (2.23–22.9)
NLSW5	15.6 ± 9.54 (5.40–30.8)	29.9 ± 29.7 (BDL–81.3)	20.2 ± 11.3 (5.65–43.4)	40.2 ± 33.4 (3.87–98.4)	72.2 ± 36.3 (24.5–161.6)	24.5 ± 14.2 (8.71–49.1)
NLSW6	10.1 ± 7.35 (2.26–26.3)	27.8 ± 41.7 (BDL–121.2)	6.91 ± 2.51 (2.03–11.3)	5.04 ± 3.29 (BDL–12.84)	64.3 ± 44.6 (BDL–170.4)	6.60 ± 5.56 (1.41–19.4)
NONSW7	24.0 ± 13.1 (9.69–75.6)	39.3 ± 12.3 (BDL–60.8)	114.1 ± 91.2 (13.9–266.4)	36.1 ± 11.9 (15.8–60.6)	115.8 ± 115.8 (BDL–292.8)	60.9 ± 74.3 (BDL–189.6)
NONSW8	59.2 ± 45.5 (9.83–135.6)	148.1 ± 148.1 (BDL–384)	28.7 ± 28.7 (BDL–74.4)	31.7 ± 10.2 (15.8–53.7)	251.0 ± 47.6 (174.4–337.2)	71.7 ± 61.5 (7.32–172.8)
NONSW9	11.8 ± 2.69 (7.06–17.9)	28.2 ± 28.2 (BDL–73.2)	38.4 ± 29.5 (6.40–88.1)	35.1 ± 6.64 (23.8–48.2)	158.2 ± 38.4 (91.2–246.0)	16.49 ± 5.47 (8.09–28.2)
NBRSW10	6.38 ± 4.01 (2.34–14.6)	24.4 ± 31.9 (BDL–147.0)	15.1 ± 11.5 (2.38–48.7)	8.76 ± 3.77 (2.81–17.1)	35.3 ± 14.2 (3.93–54.1)	17.2 ± 14.9 (2.54–65.9)
NBRSW11	6.20 ± 4.60 (1.26–16.6)	35.6 ± 40.4 (BDL–177.0)	13.2 ± 15.3 (BDL–60.3)	6.98 ± 3.17 (BDL–17.2)	23.5 ± 17.3 (BDL–48.2)	18.6 ± 21.9 (1.32–88.4)
NBRSW12	7.17 ± 4.80 (2.06–17.03)	27.8 ± 29.9 (BDL–118.0)	15.1 ± 14.1 (0.70–54.4)	12.5 ± 6.91 (4.64–27.6)	17.9 ± 13.9 (BDL–45.9)	22.6 ± 23.6 (0.75–71.9)
NNCSW13	14.1 ± 14.2 (2.70–71.0)	26.3 ± 16.6 (BDL–67.6)	22.9 ± 28.6 (BDL–132)	16.6 ± 7.09 (6.89–39.0)	73.6 ± 63.5 (BDL–191)	22.2 ± 27.2 (BDL–131)
NNCSW14	4.74 ± 0.81 (3.27–5.67)	9.11 ± 11.4 (BDL–35.4)	27.5 ± 25.8 (BDL–113.0)	13.7 ± 4.56 (7.35–28.4)	70.9 ± 54.2 (BDL–159.0)	4.19 ± 2.91 (BDL–10.8)
NNCW15	4.18 ± 1.01 (2.64–6.36)	9.50 ± 10.7 (BDL–32.8)	31.4 ± 30.8 (2.20–130.0)	11.3 ± 4.94 (1.01–18.2)	38.2 ± 31.9 (7.88–166.0)	6.33 ± 3.73 (BDL–16.6)

The ranges are in parenthesis

BDL below detection limit

of age (recent or historic) and biotransformation of the DDT (Qian et al. 2006). The fresh use of DDT is usually indicated by a ratio (DDT   DDD + DDE) much greater than 1; while historical applications are usually indicated when the ratio is smaller (Ma et al. 2008). The levels in this study confirmed that the DDT was of historic application. The prominent DDD levels indicate anaerobic metabolism of DDT. The DDT levels decreased slightly from upstream to downstream.

Levels of DDT and metabolites are low globally compared to this study. Tabucanon et al. (1992) and Pereira et al. (1996) detected low levels of p,p′-DDT, ND–29.0, ND–2.0, 0.03–9.0 and 19.0–23 ng/L; p,p′-DDE, ND–18, ND–19, 0.02–3.20, 19.0–23 ng/L; and p,p′-DDT, ND–18.0, ND–3.5, 0.23–11.0, 67–87 ng/L in 32 sites in Thailand River; 4 sites in California River; 7 sites in Vietnam and 2 sites in Serbia.

Total OCPs

The sequence in the concentration of the summation of the different pesticides investigated in this study varied from location to location. Chlordane, endosulfan, endrin and DDT metabolites were very prominent in the water samples, compared to HCH, dieldrin and isomers which occurred at lower concentrations. The sequence in the concentration of the organochlorine pesticides was ∑chlordane > ∑DDT > ∑Endosulfan > ∑Endrine > ∑Dieldrin >∑HCH (Fig. 2). The highest concentration of ∑OCPs in the water samples of the River Niger, 1138.0 ± 246.7 ng/L, with range 560.8–1629 ng/L, was detected in station NONSW7 at Onitsha location, while the lowest concentration, 292.6 ± 74.9, with range 181–443.0 ng/L was detected at station NNCSW14, at Nicolas River.

Sibali et al. (2008) obtained higher levels compared to this study in pore water, and water of Jukskei River catchment in Gauteng in South Africa. The levels of OCPs obtained in unfiltered environmental water samples ranged from 0.63 ± 0.03 ng/L (γ-HCH) to 1540 ± 0.19 ng/L (p,p′-DDT), while levels in filtered water samples ranged from 0.89 ± 0.01 ng/L (γ-HCH) to 9089 ± 0.01 ng/L (p,p′-DDT). Xue et al. (2006) studied 21 OCPs in surface water and sediments from Beijing Gaunting reservoir. The Total OCPs were reported and ranged from 16.7 to 791 ng/L, 275–1600 ng/L in water and pore water, and 5250 to 33,400 ng/kg in water, pore water and sediment. Kishimba et al. (2004) carried out a study to assess the levels of OCPs in water, sediment, soil and biota from different parts of Tanzania. Levels of

Fig. 2 Concentration of total organochlorine pesticides in water
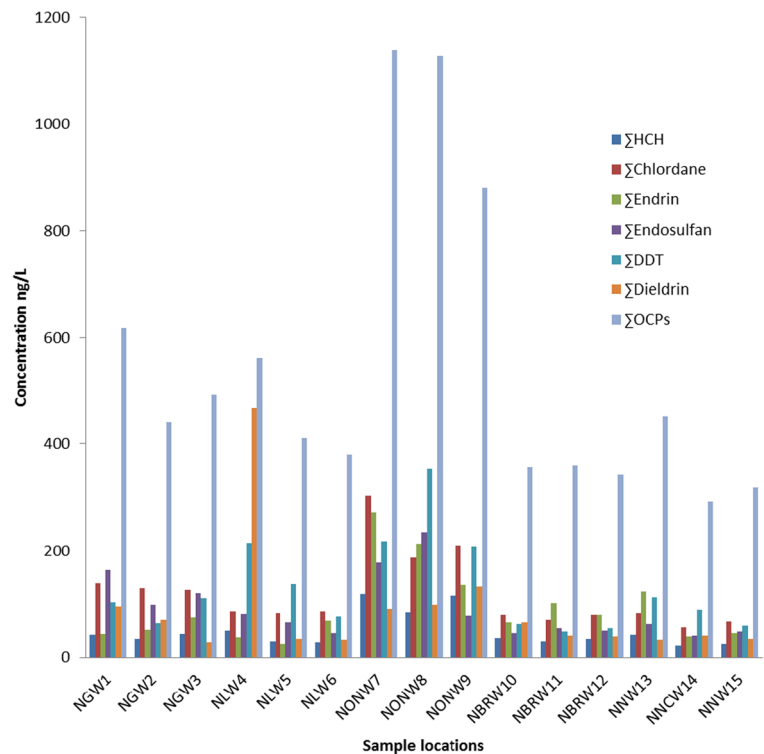
residues found in areas with agricultural pesticide use were low, compared with levels in the former storage areas, which were substantially high. They found that DDT and HCH were dominant in all the areas studied. ∑DDT in water sediment and soil were 2000 ng/L, 700 μg/kg and 500 μg/kg, respectively, while ∑HCH were up to 200 ng/L, 132 μg/kg and 60 μg/kg, respectively.

Fatoki and Awofulu (2003) and Awofulu and Fatoki (2003) studied water and sediment samples from marine and fresh water sediment samples in the Eastern Cape Province of South Africa that receive run off from agricultural lands and effluents from industries. The levels of OCPs they reported ranged from 5.5 (p,p′-DDD) to 450 ± 0.10 ng/L (β-HCH) in water, and 6.0 (aldrin and p,p′-DDD) to 184 ± 0.12 μg/kg (β-HCH) in sediments. Low levels of α-HCH were reported by Jantumen et al. (2004) and Lakaschus et al. (2002) in a cruise to South Africa base and cruise across Atlantic. They detected levels of 5.1–19.0, 2.0–689.0 pg/L in surface water and 3.50–35.0 pg/L in deep (23–25 m) sea water, respectively.

Lakaschus et al.(2002) also reported 1.40–230 pg/L in sea water from Atlantic sea and Booij et al. (2007) reported p,p′-DDE, < 0.30–1.40 ng/L in the cruise from Texel, Netherlands to South Africa in 2001.

The seasonal variations (Table 7) of the POPs in the Gurara River water showed marked differences between the rainy season and the dry season. The ∑OCPs was slightly higher during the dry season than the rainy season with concentrations and ranges, 474.4 ± 336.9; 33.5–1035 and 473.0 ± 67.8; 354.0–652.0 ng/L, respectively, while the individual compounds ∑HCH, ∑chlordane, ∑endrin and ∑endosulfan were higher during the rainy season as compared to ∑DDT and ∑dieldrin that were higher during the dry season.

In the Lokoja location, the total OCPs are higher during the rainy season compared to the dry season, with mean concentrations and ranges 505.6 ± 67.7, 217.6–859.8 ng/L and 391.2 ± 336.9, 18.9–1393 ng/L. All the individual pesticides were higher during the rainy season compared to the dry season except sum DDT.

Table 7 Seasonal variation of POPs (ng/L) in water of Gurara, Lokoja and Onitsha along River Niger

Location	Compounds	Dry season		Rainy season	
		Range	Mean	Range	Mean
Gurara	∑HCH	2.55–62.4	29.9 ± 19.4	17.19–71.7	43.71 ± 14.8
	∑chlordane	4.80–265	114.9 ± 90.33	87.24–186	127.2 ± 23.3
	∑endrin	3.21–90.4	39.9 ± 29.6	23.9–199.0	63.9 ± 37.8
	∑endosulfan	2.63–460.0	115.0 ± 117.8	57.54–164.0	117.2 ± 25.2
	∑DDT	7.67–411.0	115.5 ± 90.9	12.7–96.3	54.4 ± 18.9
	∑dieldrin	5.06–180.0	66.6 ± 46.2	13.7–130.0	54.2 ± 34.9
	∑OCPs	33.35–1035	475.42 ± 336.9	354.0–652.0	473.0 ± 67.7
Lokoja	∑HCH	1.56–52.10	22.45 ± 11.4	14.12–61.32	36.1 ± 11.5
	∑chlordane	3.40–240.2	111.6 ± 77.3	57.4–162.0	118.2 ± 3.56
	∑endrin	2.31–70.14	32.3 ± 24.63	22.9–179	56.57 ± 17.1
	∑endosulfan	2.54–420	112.0 ± 115.8	67.54–145.4	127.2 ± 5.82
	∑DDT	5.98–421.3	112.5 ± 70.49	12.19–186.30	94.14 ± 8.49
	∑dieldrin	3.16–190.4	56.22 ± 26.80	43.47–126.8	74.12 ± 24.49
	∑OCPs	18.9–1393	391.22 ± 336.9	217.6–859.8	505.6 ± 67.76
Onitsha	∑HCH	48.7–125.1	84.7 ± 18.8	73.9–180.2	127.7 ± 22.6
	∑chlordane	127.2–324.3	186.4 ± 47.92	191.3–466.8	281.1 ± 63.9
	∑endrin	71.5–333.3	163.0 ± 80.7	107.1–480.3	245.1 ± 113.7
	∑endosulfan	13.2–279.2	135.9 ± 66.8	19.8–402.1	191.5 ± 103.4
	∑DDT	21.9–377.5	205.3 ± 87.0	32.8–566.4	316.1 ± 138.9
	∑dieldrin	43.2–144.1	87.6 ± 24.3	51.9–207.6	126.2 ± 37.9
	∑OCPs	560.8–1332	840.2 ± 200.1	841.4–1917	1258 ± 267.3

The temporal distribution of POPs in the Onitsha location was different from the other locations. In the Onitsha location, the total OCPs are higher during the rainy season compared to the dry season, with mean concentrations and ranges 1258 ± 267.3, 841.4–1917 ng/L and 840.2 ± 200.1, 560.8–1332 ng/L. All the individual pesticides were higher during the rainy season compared to the dry season.

Seasonal variation

Surface runoff from fields occurs when the amount of water falling on the land exceeds the soil infiltration capacity and then the rainfall intensity and duration of the event determines the loss of pesticide from the land (Rawn et al. 1999). Seasonal variations of pesticide detections in surface water according to the timing of herbicide application relates to sampling intervals, and pesticide detections tend to be more frequent and more concentrated during late spring and early summer (Goolsby et al. 1991). When rainfall is below the normal level in sampling stations, there is reduced runoff from pesticides applied to the fields, thereby reducing the level of pesticide detections. Goolsby et al. (1991) further observed that the largest number of detections in samples collected during spring (51 detections) and summer (53 detections) of 1991 was probably due to greater rainfall, particularly during April where the 28–48 cm of rainfall represented a 17–34 cm departure above the normal rainfall in the Mississippi River area. They concluded that rainfall amounts prior to sample collection were consistent with more pesticide detections at sampling periods.

Conclusions

The levels of OCPs reported in this study exceeded guidelines; this is of considerable concern with respect to possible harmful effects to benthic fauna, fish and man. It is therefore obvious that the water of River Niger is not good for human consumption, and the abstraction of water from the River for drinking water treatment should be discouraged.

River Niger is a very important River in Nigeria. It drains 60% of the Nigerian land area. There is a scarcity of data and information concerning this very important river. The development of risk-based acceptance criteria for organochlorines requires information on the background concentration of these contaminants in the river, which this study has comprehensively investigated. Because of the potential danger this presents, continuous monitoring of this water body and if possible identify the sources of these POPs is therefore very necessary.

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