
Distribution of Pesticide Residues in Water and Sediment Samples Collected from Lugu Dam in Wurno Irrigation Area, Sokoto State, Nigeria.

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Abstract

This study considered the levels of 12 organochlorine pesticide (OCPs) residues (γ-HCH, aldrin, dieldrin, endrin, endosulfan, alachlor, cypemethrin, atrazine, DDE, DDD, DDT and heptachlor) in water and sediments from Lugu dam located in Wurno, Sokoto State, Nigeria. Sampling was conducted between December, 2015 and September 2016 during the dry and wet seasons to study the effects of seasonal variation on the samples. Water samples were subjected to liquid-liquid extraction using dichloromethane while sediment samples were subjected to cold extraction with petroleum ether/acetone (1:1 v/v) mixture and clean-up on silica gel adsorbents. The water and sediment samples were analysed for the presence of OCPs. The detection and determination of the pesticide residues were performed by gas chromatography coupled with ECD. The result revealed the mean concentration of residues in water to range from heptachlor $0.21 \pm 0.01 \mu\text{g/L}$ to DDE 1.32 ± 0.13 in the heavy rains period and heptachlor $0.22 \pm 0.03 \mu\text{g/L}$ to DDD $1.11 \pm 0.12 \mu\text{g/L}$ during the dry season, while in the sediment the residues concentration ranged from heptachlor $0.61 \pm 0.11 \mu\text{g/g}$ to DDD $2.51 \pm 0.13 \mu\text{g/g}$ in the heavy rains period and heptachlor $0.44 \pm 0.10 \mu\text{g/g}$ to DDD $2.36 \pm 0.16 \mu\text{g/g}$ in the dry season. Higher residue concentrations were observed in the samples during the heavy rains than the dry season. The concentration levels of some of the individual pesticides exceeded the EU limit requirements for drinking water and indicated potential risk to humans and cattle if the water is used without treatment.

Key words: Pesticide residues, organochlorine, sediment, water, seasonal variation, dam.

INTRODUCTION

The use of pesticides in Nigeria has continued to increase, particularly in large-scale commercial farming enterprises due to increases in acreage and need to intensify agricultural production. Recent figures show the doubling in importation of pesticides from

approximately 5,200 tonnes in 1985, with very significant increases in application in rice, cocoa, wheat, maize, sugarcane, horticulture, and fruit and vegetable farming (PCPB, 2005). In particular, the tremendous growth in rice and wheat production with subsequent increases in their exports has been attributed to the use of herbicides. However, with this increase in pesticide usage in agriculture, better management and control of pesticide application will be required in future because of the residue limit requirements as well as the need to safeguard against the potential adverse effects on the local environment and human health (Lalah *et al.* 2001; Schulz, 2004).

In addition to keeping accurate records of pesticide usage in the farms, it is necessary to monitor the distribution, fate, and effects of pesticide residues within the catchments. Monitoring of pesticide residues draining into canals, streams, and rivers within catchments and modeling of their fate and toxicity have become useful global approaches of assessing pesticide efficacy and ecological impact on a given area (Kreuger, 1998; Liess *et al.* 1999; Ewald and Aebisher, 2000; Bach, *et al.* 2001; Muller *et al.* 2002; SETAC, 2003).

The occurrence of pesticides residue, especially organochlorines (OCs) in the environment is a great worry due to their tendency for long-range transport. Also their capacity to bio-accumulate in food chain poses a threat to human health and the environment (Chau, 2005; Zhou *et al.* 2006; Pandit *et al.* 2006; Guo *et al.* 2008). Pesticides enter and pollute any component of the environment in a number of ways, including application, accidental spillage or through the unauthorized dumping of pesticide products or their containers (Cox, 2002). Contamination of water bodies for example is a major concern for fish and other aquatic organisms such as mussels, oysters, prawns and lobsters which are major sources of protein (Esumang and Chokky, 2009).

Organochlorine (OC) pesticides are among the agrochemicals that have been used extensively for long periods. They have been used widely in agriculture, as well as, in mosquito, termite and tsetse fly control programs (Guo *et al.*, 2008). OC pesticides are characterized by low polarity, low aqueous solubility and high lipid solubility (lipophilicity) and as a result they have a potential for bioaccumulation in the food chain posing a great threat to human health and the environment globally (Afful *et al.*, 2010).

Residues and metabolites of many OC pesticides are very stable, with long half lives in the environment (El-Mekkawi *et al.*, 2009). Studies have shown that DDT is still in its highest concentration in biota of some areas. It is a hydrophobic molecule which disrupts ionic channels like $\text{Na}^+ - \text{K}^+$ pumps in nervous cell membrane leading to automatic stimulation of neurons and involuntary contraction of muscles (Esmaili, 2002).

Many other recent works have indicated the presence of OC residues in surface waters, sediments, biota and vegetation (Darko *et al.*, 2008; Dem *et al.*, 2007). The persistent nature of organochlorine residues in the environment may pose the problem of chronic toxicity to animals and humans via air, water and foods intake. Many of these OC and their metabolites have been implicated in a wide range of adverse human and environmental effects including reproduction and birth defects (Edwards, 1987), immune dysfunction, endocrine disruptions and cancer (Adeyemi *et al.*, 2008).

Chlorinated pesticides namely aldrin, dieldrin, endrin, chlordane, dichlorodiphenyltrichloroethane (DDT), heptachlor, mirex, toxaphene and hexachlorobenzene (HCB) are among the twelve chemical substances called "dirty dozen" and defined under the Stockholm Convention. The manufacture and use of some pesticides have been banned or restricted in developed countries. However, some developing countries are still using chlorinated pesticides for agricultural and public health purposes (Xue *et al.*, 2006). They are being used in developing countries including Nigeria due to lack of appropriate regulatory control and management on the production, trade and use of these chemicals and probably due to their low cost and efficacy (Darko and Acquah, 2007).

Chlorinated pesticide residues enter aquatic environment through effluent released, discharges of domestic sewage and industrial wastewater, atmospheric deposition, runoff from agricultural fields, leaching, equipment washing and disposal of empty containers and direct dumping of wastes into the water systems (Yang *et al.*, 2005). Pesticide residues could distribute among the components of an ecosystem, such as water and sediment. Due to their persistence, pesticides in water can be transferred into the food chain and accumulate in aquatic organisms like plankton. Residues of pesticides can be bio-concentrated through biogeochemical processes and can be scavenged from the water through sorption onto suspended material before they get deposited to the bottom substrate. The sediment component of aquatic ecosystems deposits pesticides. Sediment is one of the principal reservoirs of environmental pesticides, representing a source from which residues can be released to the atmosphere, groundwater and living organisms (Xue *et al.*, 2006).

Persistence of these organic pollutants in sediment is possible due to their low solubility and tendency to associate with suspended particulate matter. Due to their low water solubility, chlorinated pesticides have a strong affinity for particulate matter. They are hydrophobic compounds that tend to adsorb to suspended particulate matter and benthic sediments in aquatic ecosystems. Sediments serve as ultimate sinks for them. Indirect exposure to contaminated sediments takes place when fish feeds on benthic invertebrates that are ingesting particulate matter. Direct exposure through the sediment takes place by release of contaminated particulate matter into the water column by both natural and anthropogenic processes. The ill effects from pesticides may result from short or long-term exposure, low or high-level exposure through dermal absorption, inhalation and oral ingestion. Some of the symptoms of pesticides poisoning include irritation, dizziness, tremor, tonic and chronic convulsion (Winter, 1992).

Persistent organic pollutant (POP) contamination is usually monitored by measuring levels either in inorganic ecosystem compartments such as water, air and sediment or in biota. Monitoring in inorganic compartments has the advantage of producing an immediate, geographically localized measure of contamination. Lugu dam in Wurno was established for the sole aim of producing and retaining water for agricultural activities especially during the dry season. Numerous agricultural activities are being carried out in and around the dam since its establishment which necessitates the use of intensive agrochemicals to enhance productivity. The dam is a depository of last resort for a large number of surface runoffs, drainage channels and chemical containers from the surrounding farms. The introduction of deleterious materials into the dam is thus expected. The quality of water from the dam must be constantly monitored. There is a need to monitor concentrations of chlorinated pesticides in water and sediments columns in order to assess compliance with the POPs Convention. Given the potential for contamination by pesticides, this study was undertaken to determine the distribution and concentration of chlorinated pesticide residues in sediments and water from Lugu dam in Wurno irrigation area.

MATERIALS AND METHODS

Site Description

The study area was in Wurno dam located in Wurno Local Govt. Area of Sokoto State. The area is densely populated, rich in agriculture and a major producer of rice, wheat, onions, potatoes etc, for the state Cattle, sheep, goat, poultry, and beehives are also kept. The sampling sites for residue determination were specifically located in Lugu dam in Wurno irrigation area Figure 1 where pesticides are extensively used to control weeds and other pests. Water from the dam is also used by local inhabitants and cattle mostly without any form of treatment.

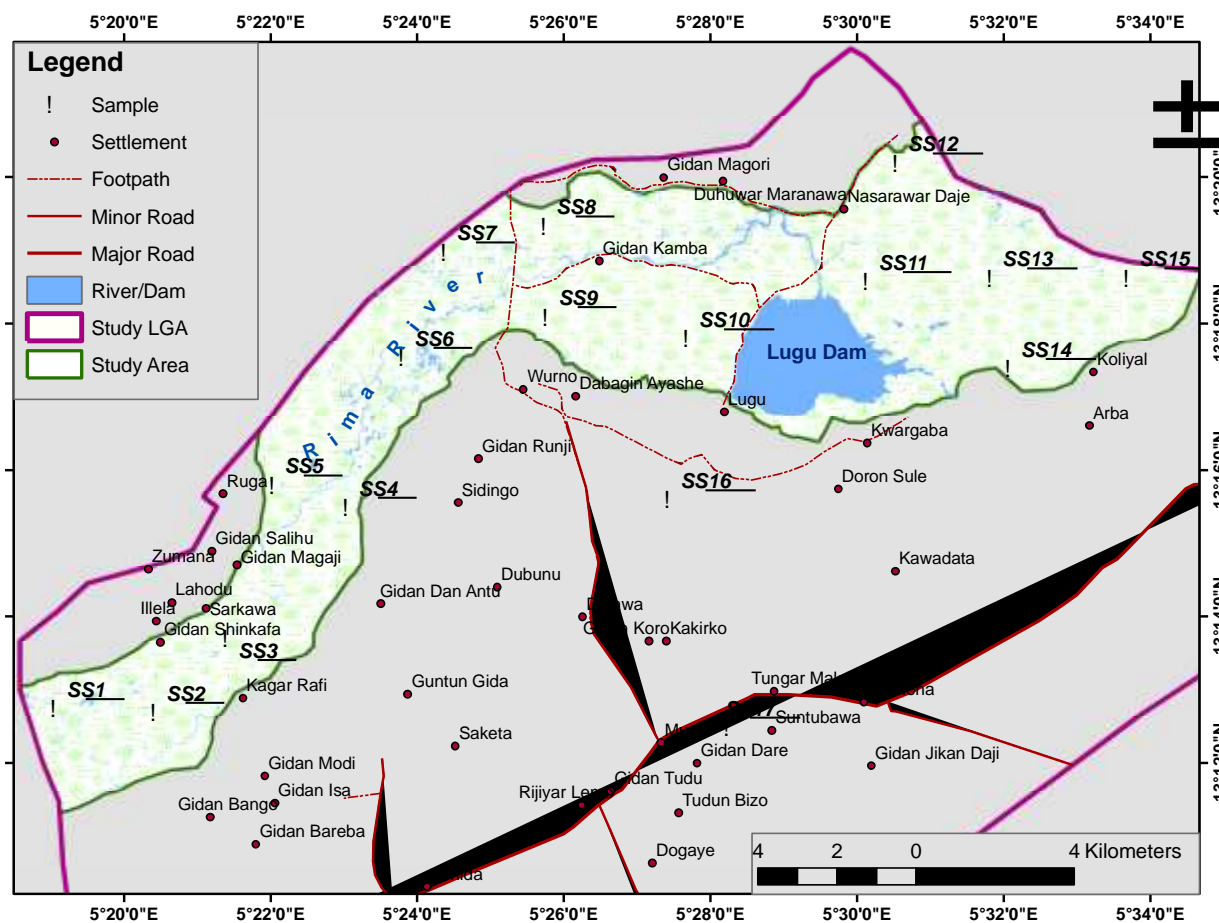


Figure 1: Map of the study area and the sampling site.

Sampling Strategy

Sampling was conducted between December 2015 and September 2016 during the dry and wet seasons to study effects of seasonal variation on the samples. Field investigations were carried out four (4) times at Lugu dam during the dry season months of December 2015 and March, 2016 and the wet season months of July and September, 2016.

Pretreatment of Sampling and Storage Vessels

Prior to sampling, sample tools and glassware were washed with detergent, rinsed with distilled water and pure acetone (99.9%) and then dried in an oven overnight at 100⁰C. Glass containers were used in collecting water samples for chlorinated pesticide residue determination.

Collection of Samples

Samples of water and sediments were collected from the river (Lugu dam). Water samples were taken at five different locations along the course of the river by grab method. At each sampling location four grab samples were taken across the width of the river and pulled together to form a composite sample. The sample was then stored in a pre-cleaned glass bottle. The water samples were acidified by concentrated HNO₃ to pH 2 to prevent alteration of the organic matter. The samples were kept in glass bottle and preserved in a refrigerator prior to analysis.

Sediments samples were taken at five different locations as in the case of water samples using pre-cleaned Ekman grab sampler. The sample was taken into a glass bottle, labeled as represented. The sediment samples were stored in black polythene bags prior to

subsequent analysis.

Treatment of Samples

Water and sediment samples were extracted and cleaned up before identification and determination of chlorinated pesticide residues were carried out.

Extraction of Water Samples

Water samples were subjected to liquid-liquid extraction. 250cm³ aliquot of water sample was introduced into a 500cm³ capacity separating funnel and 30cm³ of HPLC grade of dichloromethane was added. The mixture was well shaken and the stopper removed continuously to release the gas built up in the bottle. The solvent extract was carefully drained into a glass container. The extraction process was repeated with 20cm³ dichloromethane and the solvent extract was again drained out and combined with the first portion (US EPA Method 3510C, 2007).

Extraction of Sediment Samples

5g of wet sediment was homogenized with 5g of anhydrous granulated Na₂SO₄ using a mortar and a pestle. Cold solvent extraction (Steinwandter, 1992) was carried out using 50cm³ HPLC grade petroleum ether/acetone (1:1 v/v) mixtures in a 250cm³ reagent bottle containing the homogenized sediment sample. The mixture was well shaken and the stopper removed continuously to release the gas built up in the reagent bottle. The mixture was allowed to stand for 30 minutes and then filtered with a filter paper into a glass container (US EPA Method 3570C, 2002).

Clean-up of Extracts

Column chromatography was employed to clean-up the extracts (US EPA method 3630B, 1996). The glass separating column (20 cm) was packed with activated silica gel (90% < 45 μm) and washed down with n-hexane to remove any dirt. The extracts were de-moisturized over 1 g of anhydrous granulated Na₂SO₄ and separated into two eluted fractions using mixtures of dichloromethane, hexane and acetonitrile as eluting solvents. For the first fraction, 30cm³ of a dichloromethane/hexane (20/80) mixture was used, while 30cm³ of a dichloromethane/hexane/acetonitrile (50/49.5/0.5) mixture was used for the second fraction in order to ensure that the polar acetonitrile eluted any remaining residue. The fractions were combined, concentrated to 2cm³ using a rotary evaporator and subsequently analyzed.

GC Analysis

A Shimadzu 2010 GC equipped with an ECD was used to analyse the OCP residues. Separation was done on an SGE BPX-5 of 60 m capillary column with 0.25 mm internal diameter and 0.25 μm film thicknesses, equipped with 1 m retention gap. The oven temperature was programmed as follows: initial temperature was set at 90 °C for 3 min and ramped at 30 °C/min to 200 °C for 15 min and then to 265 °C at a rate of 5 °C/min for 5 min then to 275 °C at the rate of 3 °C/min and allowed to stay for 15 min. The injector setting is a pulsed splitless mode with a temperature of 250 °C at a pressure of 1.441 bar. Pulsed pressure was 4.5 bar, pulsed time 1.5 min, purge flow of 55.4 mL/min with a purge time of 1.4 min. The detector temperature was 300 °C. Nitrogen was used as carrier gas at a flow rate of 30 mL/min.

A Varian CP-3800 GC equipped with a Combi PAL Auto sampler was used to measure levels of the OP residues. The column used was a 30 m × 0.25 mm internal diameter fused silica capillary coated with VF-1701 (0.25 μm film). The oven temperature was programmed as follows: initial temperature was set at 70 °C for 2 min and ramped at

25 °C/min to 200 °C for 6 min and then to 250 °C at 20 °C/min and allowed to stay for 19 min. The injector setting is a pulsed splitless mode at a temperature of 270 °C. The detector temperature was 280 °C in “constant makeup flow” mode. Nitrogen gas was used as carrier gas at a flow rate of 2 mL/min.

Quality Assurance and Quality Control

Quality control measures were assured through analysis of solvent blanks, procedure blanks. All reagents used were HPLC grade. Each sample was analyzed in triplicates and mean concentrations were calculated based on the number of samples that tested positive. Recalibration curves were run with each batch of samples to check their correlation coefficient which was kept above 0.98. The results of assurance analysis indicated that pesticide determinations were within accepted levels of accuracy.

RESULTS AND DISCUSSION

Table 1: the concentration of pesticide residues (mean \pm SD) detected in Lugu dam water (μ g/L) and sediments (μ g/g) samples.

OCPs	WS1	WS2	SS1	SS2
Aldrin	0.31 \pm 0.05	0.63 \pm 0.11	1.13 \pm 0.26	1.15 \pm 0.21
Dieldrin	0.66 \pm 0.17	0.59 \pm 0.22	1.22 \pm 0.12	1.32 \pm 0.16
Endrin	0.57 \pm 0.12	0.33 \pm 0.01	1.22 \pm 0.14	1.16 \pm 0.12
Endosulfan	1.12 \pm 0.13	0.96 \pm 0.16	1.89 \pm 0.11	1.82 \pm 0.10
Alachlor	0.61 \pm 0.19	0.37 \pm 0.12	1.35 \pm 0.02	1.21 \pm 0.15
γ -HCH	1.30 \pm 0.17	1.05 \pm 0.14	2.10 \pm 0.17	1.92 \pm 0.11
Cypemethrin	0.32 \pm 0.01	0.35 \pm 0.11	0.68 \pm 0.12	0.71 \pm 0.16
Atrazin	0.77 \pm 0.19	0.51 \pm 0.02	1.55 \pm 0.16	1.16 \pm 0.12
DDE	1.32 \pm 0.13	1.00 \pm 0.15	2.49 \pm 0.11	2.31 \pm 0.13
DDD	1.07 \pm 0.16	1.11 \pm 0.12	2.51 \pm 0.13	2.36 \pm 0.16
DDT	1.13 \pm 0.14	0.97 \pm 0.17	2.50 \pm 0.12	2.30 \pm 0.12
Heptachlor	0.21 \pm 0.01	0.22 \pm 0.03	0.61 \pm 0.11	0.44 \pm 0.10
Σ OCPs	9.39 \pm 1.47	8.09 \pm 1.36	19.30 \pm 1.56	17.86 \pm 1.64

Unfiltered water samples were analysed; WS1= water samples (first sampling), WS2 = water samples (second sampling), SS1 = sediment samples (first sampling), SS2 = sediment samples (second sampling); First sampling; August, 2017 (heavy rains) and second sampling; December, 2016 (Dry season).

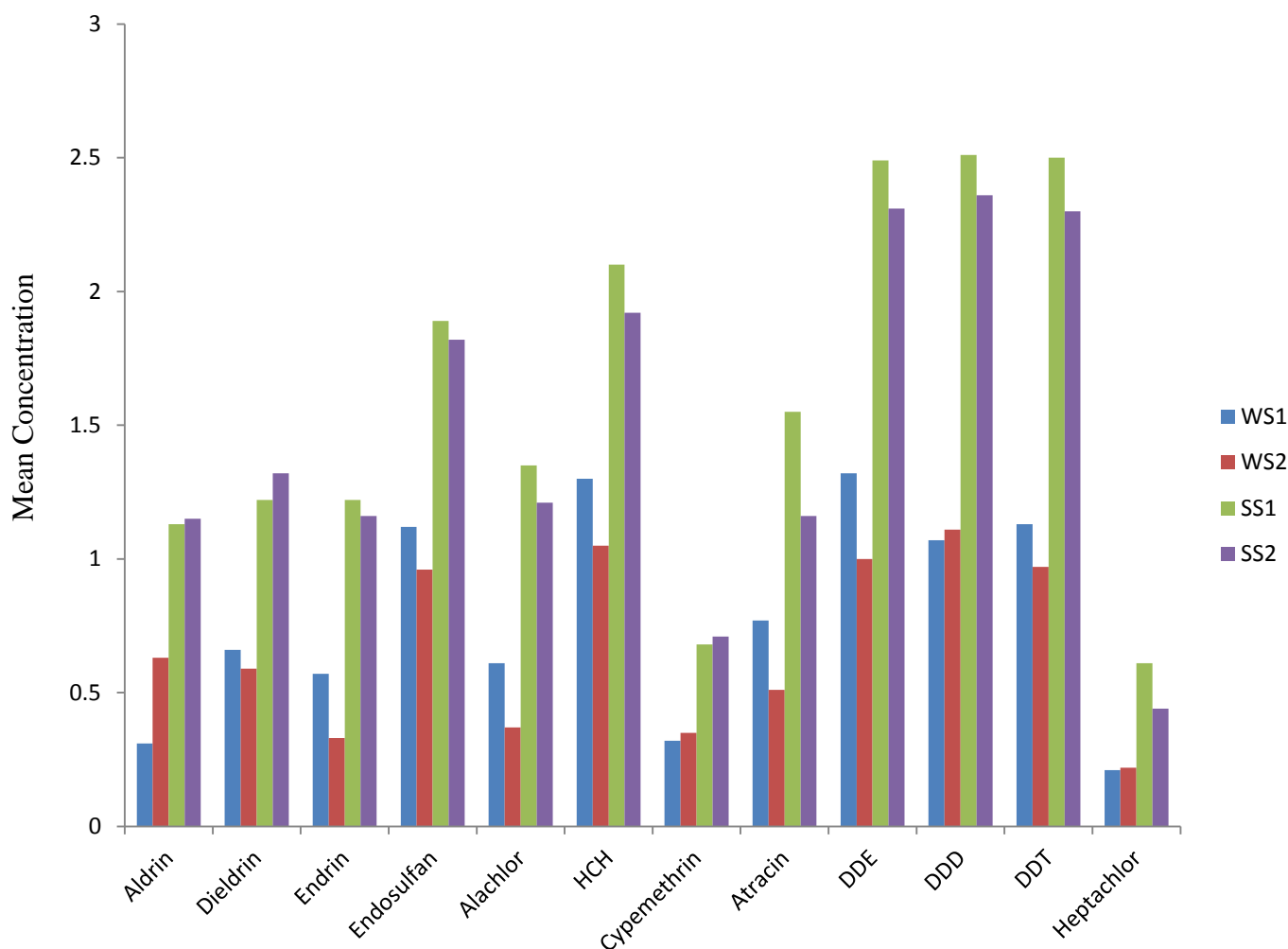


Fig. 2: The mean concentration variation between the two sampling times and between sediment ($\mu\text{g/g}$ dry weight) and water ($\mu\text{g/L}$). Note: WS1= water samples (first sampling), WS2= water samples (second sampling), SS1= sediment samples (first sampling), SS2= sediment samples (second sampling)

DISCUSSION

Table 1 showed the concentration of organochlorine pesticide residues in water and sediment samples. From all the pesticide residues determined, endosulfan, γ -HCH, DDT and its metabolites (DDD and DDE) showed high concentrations when compared with other OCPs present in the water and sediment samples. The mean concentration of OCPs in the water ranged from heptachlor $0.21 \pm 0.01 \mu\text{g/L}$ to DDE $1.32 \pm 0.13 \mu\text{g/L}$ and sediment ranged from heptachlor $0.44 \pm 0.10 \mu\text{g/g}$ to DDD $2.51 \pm 0.13 \mu\text{g/g}$. Concentrations of the OCPs in water samples were much lower when compared to concentrations in sediment samples. This showed that the OCPs molecules were sparingly soluble in water (hydrophobic) and may therefore adsorb on the sediment particles of the river.

The results showed that DDE ($1.32 \mu\text{g/L}$) had the highest mean residue concentration in surface water of Lugu dam during the first sampling (heavy rains) period followed by γ -HCH ($1.30 \mu\text{g/L}$). In general, all the analyzed residues were detected in all water samples taken during both sampling periods. More residues of the pesticides (except aldrin, cypemethrin, DDD and heptachlor) were detected during the first sampling period compared with those detected in the second drier season sampling period and this could be attributed to runoff of residues from the surrounding farmlands where these chemicals are being used

intensively into the river during heavy rains. All these pesticides, except heptachlor, are very hydrophobic and/or have high Kow values. However, the water samples analyzed were unfiltered and therefore most likely the pesticide residues leaching into the river during heavy rains were particulate- and/or sediment-bound resulting in higher levels being detected. The Lugu dam water is used as drinking water without treatment, and therefore these concentrations can be taken in by humans and cattle.

The usage of pesticides, especially herbicides, during the rainy season when planting activities often start and subsequent wash-off, could also explain the higher concentrations of the residues in water and sediment samples taken during the heavy rains period.

Substantial residue levels of organochlorine insecticides including endosulfan, γ -HCH, DDT and its metabolite, and endrin in water and sediment could indicate possible illegal usage in the study area (Wandiga, 2001) and/or their persistence from previous application before they were banned in 1997.

Higher concentrations of the pesticide residues were detected in river sediment compared with those detected in the water column and this is in agreement with studies of organochlorine pesticide residues in water and sediment samples, which have shown that the concentrations of organochlorine pesticide residues in sediment are generally higher than their corresponding concentrations in the water column (Crawford, 2004). The variation in concentrations between the two sampling periods and between water and sediment is shown in Fig. 1. In general, the concentrations of the residues in water in this study were higher (except aldrin in WS1, cypemethrin and heptachlor) than the EU drinking water limits of 0.5 $\mu\text{g/L}$ for individual pesticide and 1.0 $\mu\text{g/L}$ for total pesticide concentration and corresponding levels reported in other agricultural sub-catchment sites in other tropical ecosystems such as in a banana plantation system in Jamaica (USEPA, 1992; Mansingh and Wilson, 1995), showing that the Lugu dam water was contaminated with various pesticide residues, including dieldrin, DDT and its metabolite (DDD and DDE), γ -HCH, endosulfan, cypermethrin, endrin, alachlor, and heptachlor during the first and second sampling periods. The presence of dieldrin and p, p'-DDD and DDE in the water body resulted from transformation of aldrin and p, p'-DDT. DDT metabolizes very slowly to DDD and DDE in human beings and is excreted from the body in the urine. Sunlight and bacteria could change aldrin to dieldrin which in soil and water degrades slowly (ATSDR, 2002). Again, the detection of p,p'-DDE and p,p'-DDD is an indication of photochemical degradation of p,p'-DDT which shows past use of p,p'-DDT within the Wurno irrigation farm catchment. Thus farmers within the irrigation site are probably still using DDT on their farms.

The high concentration presence of γ -HCH, which is still a popular pesticide for seed dressing in the region, in various compartments in this sub-catchment, can be attributed to high usage both in pre-sowing and planting periods (Keng'ara *et al.* 2004). The concentration of lindane in the water samples in this study was within the range reported for the river Ovia in Edo State (Ize-Iyamu *et al.*, 2007). The contamination of the river might be connected with the use of lindane by farmers in the area. For sediment samples taken during sampling periods, concentrations of γ -HCH and DDT and its metabolites in surface sediments did not show much difference. However, concentrations of some of the herbicides such as atrazin in sediment samples collected in the first rainy season sampling were higher than those in the second drier season sampling by at least a factor of two. The increased concentration of this herbicide during the rainy season could be attributed to increased usage to control weeds in the surrounding farms. Heptachlor was quantified in the sediment with a mean concentration of 0.61 $\mu\text{g/g}$ during the rainy season but it was at a lower mean concentration during the drier season (Table 1). The results showed that the mean concentration level of all the pesticide residues detected in the water samples were above the maximum acceptable concentration of 0.1 $\mu\text{g/L}$ value set by the European Union for the protection of the aquatic environment and

drinking water, whilst the levels were very low when compared to the FEPA allowable level of 10 µg/L.

Termites are very destructive in the dry period (Anonymous 2006) and it was likely that aldrin was used for the elimination of termites in the sub-catchment and was later washed away into the river. Sediment samples showed higher residue concentrations in the first rainy season sampling than during the second drier season. This trend could be explained either by the fact that there was a strong washout of pesticide residues from the farms into the river due to heavy rains during the first sampling and also partly by the reduced levels of pesticides usage over the 4 month lapse between the two samplings. A similar seasonal pattern has been reported in sediments from estuarine zones in the banana growing sub-catchment of River Hope in Jamaica, with similar intensive applications of pesticides, where residues were detectable more frequently and at higher concentrations in rainy weather than in the dry period at ranges of 0.03–66.1 and 0.05–1.18 µg/g for endosulfan, and 0.13–3.70 and 0.95–2.33 µg/g for dieldrin, respectively. (Mansingh and Wilson, 1995).

By contrast, sediment samples in coastal regions of North of Vietnam were reported to have higher concentrations of organochlorine residues in the dry season than under rainy conditions with ranges of 0.17–3.48 and 0.012–2.36 µg/kg, respectively, although pesticide application history was not given (Nhan *et al.* 1997). A comparison of the residue concentrations obtained in this study with those of other contaminated environments in other regions such as Kingston Harbour (Mansingh and Wilson, 1995) shows that this Lugu dam in Wurno was relatively more contaminated with residues of pesticides such as endosulfan, γ-HCH and DDT with sediment concentrations being about two, four, and ten times higher, respectively. Alpha BHC, beta-BHC, heptachlor epoxide, aldrin, o,p0-DDT, and p,p0-DDT with residue levels of 1.38, 2.33, 1.39, 2.72, 1.39, and 1.15 µg/g, respectively, have been detected at comparatively high levels in sediment samples from a freshwater system in Turkey (Barlas, 2002). The high concentrations of herbicides detected in water and sediment in Lugu dam imply a potential threat to the ecology of this sub-catchment as has been reported in other studies of herbicides (Kreuger, 1998; Ewald and Aebisher, 2000; Bach *et al.* 2001; Muller *et al.* 2002; SETAC, 2003; De Snoo and van der Poll, 1999; Schulz and Liess, 1999; Berenzen *et al.* 2005).

CONCLUSION

This study shows that the 12 organochlorine pesticides (OCPs) determined were present at detectable levels in all the samples. All the pesticides determined were found to be contaminants of the water and sediment samples. However, the concentration of OCPs in the water was low when compared to the concentration in sediments samples, as evidenced of the hydrophobic nature of the OCPs and their subsequent adsorption to particulate matter in sediment samples. The detection of these OCPs in the samples might be due to previous and probably recent use of these pesticides from the agricultural areas which are the major sources of these contaminants in the river. The OCPs residues may have direct or indirect effects on the build-up of the environment and the health of the people especially people living around the area. The Federal Environmental Protection Agency had published regulations on the control of various types of pesticides within the Nigerian environment. Therefore, there is need to monitor and enforce the existing laws on the production, transportation and use of banned pesticides as stipulated by the Federal Ministry of Environment in Nigeria.

Other rivers and food samples should be studied in details as related to monitoring, assessment, distributional trends, sources identification and ecotoxicological effects of persistent organochlorine pesticides.

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