Assessment of Dichlorodiphenyltrichloroethane (DDT) and its Isomers in Water and Sediments: A case study of River Kibos-Nyamasaria, Kisumu County-Kenya

Julius Ochieng Ogola, [1, 2]* Richard Mogwasi[1] Kennedy Olale[1]

[1]Department of Chemistry, School of Pure and Applied Sciences, Kisii University, P.O. Box 408-40200, Kisii, Kenya.

[2]Kenya Industrial Research and Development Institute (KIRDI), Laboratory Services & Research Centre (LSC), P.O. Box 6017-40103, Kisumu, Kenya.

Abstract

This study aimed determining the concentration of banned or restricted DDTs isomers in water and sediments in river Kibos-Nyamasaria during the wet and dry seasons. The isomers were analyzed using gas chromatography with a Mass Spectrophotometer detector. A total of six DDT isomers or metabolites were detected in the water and sediments. The DDT compounds (o, p'- DDT, p, p' - DDT, o, p'- DDD, p .p'- DDD, o, p' - DDE, p, p'- DDE) were detected in all the samples, with p, p'- DDD metabolite recording the highest concentration in both seasons with a concentration of 0.09±0.02 μg/L in wet season and 0.03±0.02 μg/L in the dry season. The DDTs isomers had high concentration in wet season than dry season in water samples and most of DDTs were above WHO maximum residues limits (MRLs) at the swamps or entry point to the Lake. p, p'- DDD recorded the highest concentration of 3.28±0.06 μg/kg in dry season at the swamps or entry point to Lake Victoria in sediments while o, p'- DDE had the least concentration of 0.21±0.08 μg/kg during the wet season. Soil organic carbon, soil organic matter and pH in water samples determined, ranges from 2.14±0.09% to 5.47±0.07%, 3.69±0.17% to 9.43±0.11% and 7.26±0.16 to 7.90±0.02 respectively in both season. The levels of the DDTs increased downstream as the river approached Lake Victoria. Since some of the DDTs metabolites were at levels beyond the recommended limits, frequent monitoring of pesticide residues in the area is necessary for preventing, controlling, and reducing environmental pollution to minimize health risks.

Keywords: DDTs metabolites or isomers, Organochlorine pesticides (OCPs), persistent organic pollutant (POP), river Kibos-Nyamasaria.

1.0 Introduction

Dichlorodiphenyltrichloroethane (DDT) is one of the organochlorine pesticides that has been used frequently in agriculture, buildings and as insecticides to control malaria and other insect-borne diseases in public health. According to UNESCO (2015), approximately 2 million tons of waste (industrial wastes, chemicals, human waste, and agricultural wastes such as fertilizers, pesticides, and pesticide residues) are disposed in water bodies every day. DDT is one of the persistent organic pollutant (POPs) similar to other organochlorine pesticides in the environment hence retains their toxic properties for several years within the environment (Paul *et al*., 2022; Nyaundi *et al.*, 2021; Alengebawy *et al.*, 2021; Alex *et al.*, 2019; Ndunda *et al*., 2018; Jayaraj *et al*., 2016; Syed *et al.*, 2014; Jordan, 2002; Abongo, 2009). DDT is a mixture of six metabolites; p, p′-DDT, o, p′-DDT, p, p′-DDE, and other trace impurities. Its isometric composition is p, p' DDT, 77.1 %; o, p'–DDT, 14.9 %; p, p'-DDD, 0.3%; o, p'–DDD, 0.1 %; p, p' –DDE, 4.0 %; o, p' –DDE, 0.1 % (Syed *et al*., 2014; Saoke, 2005). The p, p'-DDD, a metabolite of dichloro-diphenyl-trichloroethane (DDT) has insecticidal properties and is commercially available as an insecticide (Ssebugere *et al*., 2009; Saoke, 2005). Because of being none biodegradable and bio accumulative in nature in both water and sediments, DDTs can cause adverse effects on aquatic community and on humans. It has been reported cause ill health effects such as cancers, reproductive system deformations, endocrine disruptions, malfunctions in immune system and birth defects (Fosu-Mensah *et al*., 2016; Jayaraj *et al*., 2016; Saoke, 2005).

Globally, the use of DDT was stopped in early 1960s due to international concern of its non-biodegradability and bioaccumulation effects (Fosu-Mensah *et al*., 2016). Even though DDT was banned in many countries, it continues to be used in developing countries like Kenya for restricted public health use (Paul *et al*., 2022;Yive & Knols, 2020). DDT was introduced in Kenya in 1950s when it was used as pesticide against pests and insects until mid-1980 due to its availability at low cost, broad spectrum, long residue effect and low toxicity (Omwenga *et al*., 2016). In 1982, the Kenyan government established a Pest Control Products Board to regulate pesticide manufacturing, distribution and application at the same time prohibited or restricted the use of environmentally persistent organochlorine pesticides (Nyaundi *et al.*, 2021, Ndunda et al., 2018, Omwenga *et al*., 2016). Despite the ban or restriction of DDT, Abong'o *et al*. (2018)and Ndunda et al. 2018 reported their continuous use in Kenya by Farmers and public health officers for managing several plant diseases and spread of mosquitoes which causes

malaria respectively. Some farmers who cannot use the banned pesticides and have them in the stock, dump the DDTs or the used containers into the rivers or in their farms, causing pollution, particularly in surface waters from run-offs (Huang *et al*., 2020; Wei *et al*., 2019). Therefore, many rivers and streams lose their water quality after passing through large agricultural fields and major towns and cities due to downstream pollution (James & Achieng, 2019).

Lake Victoria water catchment areas are not exceptional from pollution. Large sugarcane plantations and smallholder farms are found in the Kibos and Miwani areas in Kisumu City, where farmers frequently use pesticides to increase crop yield by control various agricultural pests. Pesticide residues from run-offs enter the Kibos-Nyamasaria river, which drains its constituents into Lake Victoria which is the world's largest tropical lake and the world's second-largest freshwater Lake after lake superior in North America (FAO, 2017; UNESCO, 2015; UNESCO, 2003; World Water Council, 2000).The communities in lake Victoria catchment areas that depend on stream water for their domestic activities are forced to look for alternative expensive tap waters that most cannot afford, especially the urban poor (Abong'o *et al*., 2018; UNESCO, 2015). Sediment analyses was important in this study as they may act as reservoirs rather than ultimate sinks, allowing absorbed chemicals to remain in the aquatic biota for extended periods (Paul *et al*., 2022; Ochoa & Maestroni, 2018).

No comprehensive study has not been conducted in the area of study on the levels of DDT and its metabolites in the environment and agricultural land near river Kibos-Nyamasaria. Since DDTs have been used in Kenya for a longer time, it is not amazing that the aquatic system has become polluted to a certain extent due to their long-term usage. Therefore, the study aimed at determining the concentration of six DDT metabolites residues in water and sediments of river Kibos-Nyamasaria during the wet and dry and their bioaccumulation in Winam gulf at entry of river to swamps before entry into Lake Victoria.

2.0 Materials and Methods

2.1 Study Area

The study was conducted along river Kibos-Nyamasaria, Nyalenda and Dunga swamps in Kisumu east district, county of Kisumu (Figure 1), with altitudes ranging from 1100 to 1160 meters above sea level and situated between a latitude of 0° 40' 0" south and 34° 49' 0" east, (Kanoti *et al*., 2019; Onyango *et al*., 2013). Kibos-

Nyamasaria river drains its waters at the southern shores of the Winam gulf of Lake Victoria through Nyalenda and Dunga swamps. The river flows through industrial area in Kibos, several informal settlements and agricultural farms numerous kilometers (about 25 km) along Kasule and Nyalunya sub-locations in Central Kolwa location (Kisumu east sub-county) before draining into Lake Victoria as shown in Figure 1.

2.2 Description of sampling points

Samples of river water and sediments were collected from five sampling points during the dry (February - March) and the wet season (April – May) along the river Kibos-Nyamasaria and entry swamps to Lake Victoria. The first sampling point (S1) was near Nyamasaria bridge and the last sampling point (S5) was where the river enters or drains into Lake Victoria through Nyalenda and Dunga swamps while the rest of the sampling points were distributed along the river. Table 1 describes the human activities at the various sampling points, various abbreviations used while doing sampling for DDT and its metabolites for laboratory analysis.
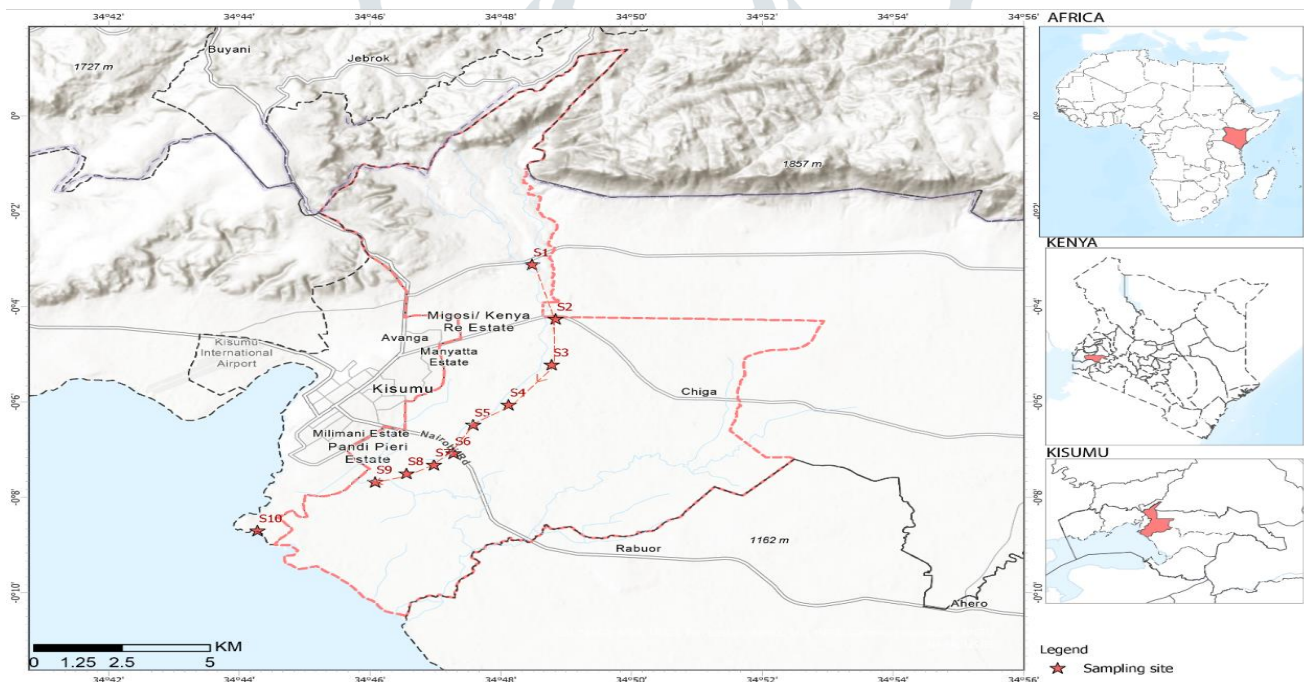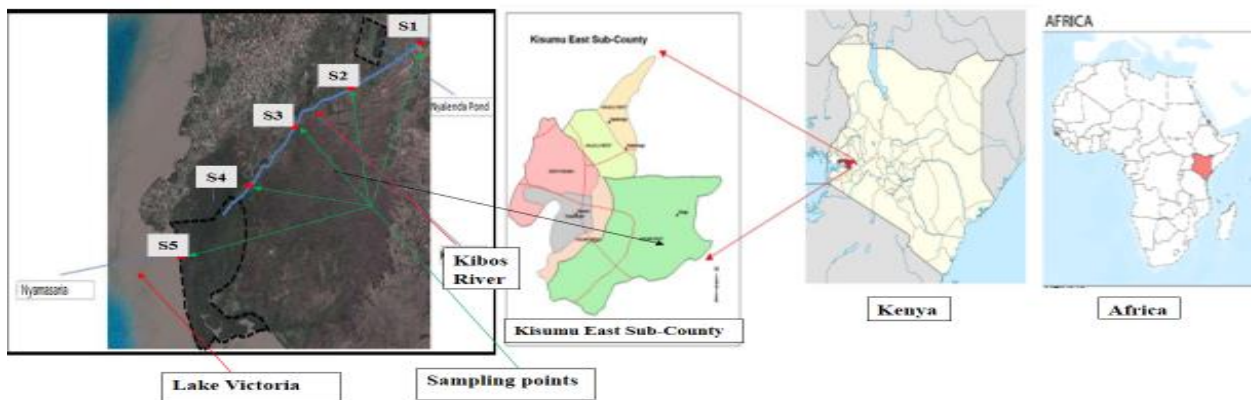
Figure 1: Location of the swamp in which river Kibos-Nyamasaria entered Lake Victoria and some of the sampling points

Table 1: Characteristics of sampling points for Water and sediment along river Kibos-Nyamasaria

Sampling Site	Site intervals (approx.Kms)	Sampling Site descriptions	GPS Coordinates		Human activities around the sampling points
			N(+) /S(-)	E	
S1	(S0-S1)=2	Nyamasaria bridge	-0.118^0	34.788^0	Human settlement, maize, tomatoes, cassava farms on river banks, domestic animals and cattle watering points, sand harvesting, wood selling and treatment point, domestic effluent discharge from Nyamasaria market and estates.
S2	(S1-S2)=2	Behind Nyamasaria Estate	-0.122^0	34.783^0	Human settlement, maize, tomatoes, cassava farms on river banks, domestic animals and cattle watering points, Human water and bathing point, and river sand harvesting.
S3	(S2-S3)=2	Near KIWASCO Nyalenda wastewater treatment plant	-0.125^0	34.776^0	Human settlement, maize, tomatoes, cassava farms on river banks, domestic animals and cattle watering point, Human watering and bathing point, KIWASCO waste discharge point and part of swamps.
S4	(S3-S4)=2	Nyalenda farms	-0.128^0	34.768^0	Human settlement, maize, tomatoes, cassava, etc. farms on river banks, human, domestic animals, and cattle watering points, part of Nyalenda and Dunga swamp.
S5	(S4-5)=4	Point of entry to Lake Victoria	-0.145^0	34.738^0	Nyalenda swamp, Dunga wetland, fishing activities, Human settlement at Nyalenda, Nanga, and Dunga Estates.

2.3 Determination of Physicochemical parameters of water and sediments

Water and sediment samples from the river were collected at different sampling points (Figure 1). The water samples were collected using sterile, 2.5 L ambered glass bottles fitted with screw-cap according to Nyaundi *et al.* (2021) and Ndunda et *al.* (2018) procedures. Distilled water and soap were used to thoroughly clean screw-cap amber glass bottles for collecting samples rinsed with acetone and the respective water samples before collection using the grab sampling method. Sampling bottles were dipped at 20 cm below the water surface, aiming midstream positions, and projecting the container mouth against the flow direction of the river water. 1.0 g mercuric chloride was added to each water sample and mixed thoroughly for 5 minutes to avoid degradation of the pesticides in the water samples by microorganism.

Sediments samples were scooped within a distance of 50 m from the left river bank, midstream and right river bank using a soil auger at a depth of 20 cm in triplicate from the same points from where the water samples were collected along the river bank and swamps. Sediment samples collected from each sampling point were mixed thoroughly on a clean piece of aluminum foil and approximately 200g representative sample taken from the composite selection according to Nyaundi *et al.* (2021) and Fang *et al.* (2017) procedures. The samples were wrapped using aluminum foil well labelled, and placed in a black plastic bag before placing them in a labelled self-sealing zip lock polythene bag and stored temporarily in polyurethane cooler boxes before transportation to the laboratory for further storage, preparation and analysis. The glassware used during sample collection, preparation, and analysis was soaked in 5% nitric acid, rinsed thoroughly with double-distilled de-ionized water after each use then dried overnight in an oven at 105^0 C.

Both samples were treated using recommended methods for river water and sediment sample treatment, before analysis in the laboratory. Water samples were stored at 4^0 C while sediments were stored in aluminum containers at -20^0 C in the laboratory deep-freezer before further sample preparation, extraction, clean-up, and analysis within seven days from collection. DDT residues and its isomers were determined by Gas chromatography (G.C.) equipped with Mass Spectrophotometer (M.S.) as a detector

2.4 Chemicals and Reagents

The chemicals used in the study were of analytical and HPLC grade and were obtained from Germany, Augsburg (Dr. Ehrenstorfer GmbH), Aldrich Chemical Company, British drug houses, BDH (United Kingdom) and Fisher Scientific (USA) through their local suppliers. Organochlorine pesticide reference standard mixture of over 99% pure isodrin was used as an internal standard for identifying and quantifying pesticide residues. Other standards used in the study were EPA CLP organochlorine pesticide mix S.S., 1×1, Tol: Hex (50-50), 2000μg/ml (standard), Decachlorobiphenyl (internal standard), Accustandard Pentachloronitrobenzene, 1.0 mg/ml (internal standard) and Standard reference materials SRM 2261 and SRM 2275.The reagents were purchased from Kobian Ltd through a local supplier in Kenya. Analytical grade anhydrous sodium chloride, sodium hydroxide, sodium sulfate, aluminum oxide, hydrochloric acid, nitric acid, mercury chloride, methanol, and other consumable chemicals required for analysis were obtained from Fisher Scientific (USA) through their local suppliers in Kenya. Diethyl ether and HPLC-grade hexane, were bought at 99% purity and did not require distillation but general-purpose solvents such as n-hexane and acetone were triply distilled before use. The purity of the HPLC grade hexane was recognized by concentrating the solvent and then running it into Gas Chromatogram to determine whether there were any peaks other than those of the solvent according to Paul *et al.* (2022) and Abong'o *et al.*(2018) procedures. Sodium chloride and activated charcoal were dried at 120˚C in a hot air oven for at least two hours or overnight to remove moisture then cooled in desiccators before using them.

Anhydrous sodium sulfate and florisil (magnesium silicate) were activated at 200^0 C and 350^0 C, respectively, in a hot air oven before use for the clean-up process of sample extracts Nthusi, (2017) and Osoro *et al.* (2016)) procedures. The detergents used for cleaning purposes during analysis were bought locally and glassware used were soaked in 5 % chromic or nitric acid for two hours, washed with tap water, rinsed in distilled water, and finally with triply distilled methanol. The apparatus or glassware were then dried in a hot air oven for four hours or overnight at 105^0 C before use according to Osoro *et al.*, (2016) and Abong'o *et al.*(2015) procedures.

2.5 Instrumentation methods

Scion 456-GC Gas chromatography equipped with 8400 autosamplers and MS detector (Scion Instruments premium, Netherlands), Rotary Evaporator manufactured by Bibby Sterilin Ltd U.K. and of model RE 300 Stone Staffordshire (Serial No. R000101238), Soxhlet extractor apparatus fixed on heating mantles of model

WHM12293 manufactured by Daihan Scientific Co. Ltd Wisd 23 from Korea and Analytical balance of model Citizen Scale C.Y. 204-Serial No. 252157/09 manufactured by Citizen Scale CY 204 in Poland were used in this study.

The organochlorine pesticides reference standards were obtained from recommended suppliers stated above (2.4) and then used in the analysis. Working reference standard solutions were prepared appropriately, and each standard solution of 1.0 µL was injected into the Scion 456-GC equipped with an M.S. detector under the following conditions: Scion-5MS High-performance G.C. capillary column or high-resolution Gas chromatography Scion-5MS column of length 30 m and 0.25 mm internal diameter (narrow bore) having a temperature range of -60^0 C to 325^0 C and 0.25µm film: sample size: 1.0 µL split ratio 1:20; detector: M.S. Detector at 300^0 C; column temperature was set at 150^0 C held for 1 minute then programmed to 200^0 C at 4^0 C/min and finally to 300^0 C at 4.5^0 C/min; helium flow pressure inlet was set at 20 Psi (138Kpa) minimum 150psi (1035Kpa) maximum, and injector temperature was held at 250^0 C. Data processing was done using appropriate software installed in Scion 456 GC-MS. The GC-MS linear plots calibration of peak area against the concentration of the standards.

The individual pesticide retention time for identification and peak area for quantification was noted and recorded. The procedure was repeated for the mixed standard solutions, and the retention times and peak areas obtained were used for the calibration of GC-MS. The calibration curves were prepared from stock solutions containing DDT pesticide standards. Detection and identification of DDT residues from samples were based on retention time and external standard method. Prepared samples were analyzed by GC-MS for structural confirmation and levels of concentration of the DDT residues according to modified Paul *et al*. (2022) and Nyaundi *et al.* (2021) procedures.

2.6 Preparation of Standards

100 µg/ml stock solution of organochlorine pesticide mixed standard (EPA CLP organochlorine pesticide mix S.S., 1×1, Tol: Hex (50-50), 2000µg/ml) was prepared in n – hexane and stored in dark flasks at -20 °C in refrigerator until use. 2.5 µg/ml, 5 µg/ml and 10 µg/ml working standard solutions were prepared in n - hexane from the stock solution to be used in instrument calibration daily according to Kelle *et al*. (2022) and EPA (2007) modified methods.

2.7 Quality control, quality assurance and method validation

Accuracy, precision and percentage recoveries were determined by addition of spiking standard of 2 µg/ml of a mixture of standards of DDTs (o, p'-DDT, p, p'-DDT, o, p'-DDE, p, p'-DDE, o, p'-DDD and p, p'-DDD) into the water and sediment samples taken from control site, kept overnight, extracted then analyzed in triplicate according to Paul et al.(2022) and Tribaldo (2007) modified methods. The mean percentage recoveries for water and sediments samples are shown in Table S 1. The percentage recoveries obtained were within the acceptable limits of 70 to 120% which shows good accuracy and precision of the analytical methods used in this study (Paul et al., 2022; Abong'o et al., 2018; Osoro *et al*., 2016; Abong'o, et al., 2015) . The limit of detection, (LOD) was 0.02 µg/ml showing that the method could be used to the determine the pesticide concentration in the water and sediment samples.

2.5 Determination of water and soil physicochemical parameters

Water physicochemical and soil structure tests were done in order to establish their correlation with DDTs residues in water and sediment samples. Water and soil samples pH were measured using a 930-precision pH meter (Biobase). Conductivity, TSS and TDS were measured using the WTW inolab 720 conductivity meter, while turbidity of the waters was measured using Hanna LP 2000 Turbidity meter. Moisture tests of soil were done using the memmert hot air oven method set at $105\,^{0}C$ overnight. Soil organic matter (OM) and soil organic carbon (OC) were determined using muffle furnace while Soil structure test were done using the Mason Jar Test method according to Jeffers, (2019), APHA, (2002) and APHA, (1998) methods.

2.6 Extraction of DDTs residues from water and sediment samples

Modified Onchieku (2019) and Abongo *et al*. (2018) procedures were used for Solvent-phase extraction (SPE) to extract water samples. 50 ml of 0.2 M dipotassium hydrogen phosphate buffer was added to a water sample of 2.0 litres, then transferred into a 2.5L separating funnel in which its pH was adjusted to 7.0 by adding a few drops of 0.1 N sodium hydroxide and 0.1M HCl solutions to neutralize the sample. 100 g of sodium chloride was added to salt out the DDTs residues vfrom the aqueous phase. The pressure generated was released and 60 ml triple distilled dichloromethane (DCM) was added to this solution and shaken for two minutes.

The samples were allowed to settle for 30 minutes to ensure efficient separation of phases. A 250 ml Erlenmeyer flask was used to collect the organic layer, and extraction was repeated twice using 60 ml portions of dichloromethane. After storage in the refrigerator at 4º C, the extracts were combined and cleaned by passing them through an Al_2O_3 chromatographic column topped with anhydrous sodium sulfate. Pesticide residues were repeatedly eluted with 175 ml n-hexane. The elutes obtained were concentrated to 1 ml using a rotary evaporator at 40^0 C after the clean-up procedure and then reconstituted in 0.5 ml HPLC grade isooctane for GC-MS analysis. The analytes were alternatively reconstituted in 0.5 mL 80:20 isooctane: ethanol after clean-up and then transferred to GC-MS autosampler vials for analysis.

The sediment samples were removed from the storage deep freezer (-20^0 C); the wet sediment samples were allowed to thaw for 4 hours in the laboratory. Pebbles, stones, and plant materials were removed from the air-dried samples, crushed and homogenized in mortar and pestle and sieved through a 250 μm mesh sieve size according to Nyaundi *et al.* (2021) and Onchieku, (2019) modified procedures. Before transferring the sediment sample into the Soxhlet thimble, triplicates of 30g portions of sediments were mixed thoroughly with equivalent amounts of anhydrous sodium sulfate to dry the samples before transferring each sample to a pre-extracted Whatman (9.0 cm) filter paper then extracted with 200 ml of hexane to acetone (3:1v/v) in a 250 ml round-bottomed flasks for a minimum of 16 hours using Soxhlet-extractor apparatus.

Other samples were extracted alternatively using the Soxhlet-extractor apparatus for 24 hours in 200 ml of triply distilled acetone: hexane (1:1) mixture in 250 ml round-bottomed flasks. The extracts of each were concentrated at 10 ml using a rotary evaporator at 40° C. After storage in the refrigerator at 4º C, the extracts were combined and thoroughly cleaned by passing them through an Al_2O_3 chromatographic column topped with anhydrous sodium sulfate. Elutes were concentrated to 1ml using a rotary evaporator at 40° C and then reconstituted in 0.5 ml HPLC grade isooctane for GC-MS analyses. The final samples were analyzed by GC-MS Scion Instruments premium, Netherlands model Scion 456-GC-MS under suitable specified conditions.

2.7 Clean-up procedure for river water samples and sediment extracts

The organic phase was cleaned for 10 ml extract of water sample by passing it through a glass column fitted with a tap and packed with 15g of the activated Florisil (magnesium silicate 60-100 mesh size), followed by a drying agent of 4 g of activated anhydrous sodium sulfate and 1.5 g activated charcoal that acted as a decolourizer

according to modified Nthusi (2017) and Abong'o *et al*. (2018)procedures. The pesticide residues were then eluted from the column using 200 ml portions of 6%, 15%, and 50% of diethyl ether in triple distilled hexane in that order at a flow rate of 5 ml/min. The eluents obtained were collected in a 500 ml round-bottom flask and reduced or concentrated to 1 ml (just about dryness) using a rotary evaporator at 40^0 C. Elutes were reconstituted with 0.5 ml HPLC grade hexane or isooctane before l μL of the sample was injected and analyzed by the Gas Chromatography-Mass Spectrophotometer (GC-MS). The analytes, alternatively, were reconstituted in 0.5 mL 80:20 isooctane: ethanol and transferred to G.C. autosampler vials for G.C. analysis.

For sediment samples, l0-ml of the sediment extracts were cleaned up by passing through a 60 cm long x 2 cm (id) glass columns fixed with a tap and packed with 15 g of the activated florisil (magnesium silicate 60-100 mesh size) and topped up with 4 g of activated anhydrous sodium sulfate (drying agent) and 1.5 g of activated charcoal which acted as a decolourizer. Florisil was activated at 350^0 C while anhydrous sodium sulfate activated at 200^0 C before being used for the clean-up process according to modified Onchieku (2019) and Ndunda *et al*. (2018) procedures .

The extracts were then eluted through the columns at a flow rate of 5 ml/ min using 200 ml of 6%, 15%, and 50% diethyl ether HPLC grades in hexane. The three eluents were collected in 500 ml round bottom flasks, then combined and concentrated to near dryness using a rotary evaporator at 40^0 C and then transferred to graduated tubes. The samples were reconstituted in 0.5 ml HPLC grade n-hexane to 1 ml and further reduced to 0.5 ml, then preserved or analyzed using GC-MS. The analytes alternatively, were reconstituted in 0.5 mL 80:20 isooctane: ethanol and transferred to GC autosampler vials for GC-MS analysis.

2.8 Data Analysis

The data collected for the concentration level of six DDTs and its metabolites or isomers were analyzed using statistical packages for social scientists (SPSS), version 23.0 (IBM-SPSS Inc., Chicago, IL, USA) software. A t-test was used to compare DDTs pesticide levels in water and sediment between seasons to establish a significant relationship in group means between DDTs levels in water and sediment samples during both seasons. The Shapiro-Wilk test was used for data normality. Pearson correlation analysis was used to examine the relationship between DDTs pesticide residues in water and sediment with selected soil physicochemical parameters.

3.0 Results and discussion

3.1 Physicochemical properties of water and soil samples from the study area

The physicochemical properties of soil samples from the study sites are summarized in Table 3. The pH of water samples ranged from 7.50±0.17 at Nyamasaria Bridge near Nyamasaria market and estate (S1) to 7.90±0.02 at Nyalenda farms (S4) during the wet season. During the same season, conductivity ranged from 123.56±0.75 (S1) to 139.26±0.86 µs/cm (S5) while total dissolve solid (TDS) and total suspended solids (TSS) ranged from 105.36±0.50 (S1) to 120.10±0.45 (S5) and 83.20±0.90 (S1) to 123.73±0.60 mg/L (S4) respectively. During the dry season, the pH of water samples ranged from 7.26±0.16 (S1) at Nyamasaria Bridge to 7.86±0.05 (S5) at the point of entry to Lake Victoria (S5). Total dissolve solid (TDS) and total suspended solids (TSS) ranged from 101.33±0.25 (S1) to 118.10±0.33 (S5) and 83.20±0.90 (S1) to 126.90±0.70 mg/L (S4) respectively. The soils pH ranged from 6.73±0.07 at Nyamasaria Bridge near Nyamasaria market and estate (S1) to 7.23±0.05 at the point of entry to Lake Victoria (S5) during the dry season. During the wet period, the pH ranged from 6.20±0.05 at the Nyalenda wastewater treatment plant (S3) to 7.25±0.05 at the point of entry to Lake Victoria (S5), indicating that the soils were generally weakly acidic to basic. Soil pH is one factor that influences pesticide bioavailability and transport in soils (Aiyesanmi et al., 2008). Conversion of DDT to DDE requires soil pH levels close to 10 as DDT transformation becomes faster in naturally occurring alkaline soils than in acid soils (Nash *et al*., 1973). Furthermore, during wet season, soil organic carbon ranges from 2.28±0.12 % (S1) to 5.47±0.07 % (S5) while soil organic matter ranges from 3.93±0.22 (S1) to 9.43±0.11 % (S5). During the dry season, soil organic matter ranges from 3.69±0.17 (S1) to 8.75±0.02 % (S5) while soil organic carbon ranges from 2.14±0.09 % (S1) to 5.07±0.01 % (S5). Soil conductivity ranged from 109.5±0.61 (S1) to 230.1±0.30 µs/cm (S5), while clay and silt content during the dry season ranged from 40.74±0.66 (S1) to 45.99±0.19% (S5) and 25.80±0.06 % (S1) to 31.82±0.12% (S5) respectively (Table 3). In addition, during the wet season, Soil conductivity ranged from 112.1±0.2 µs/cm (S1) to 233.63±0.25µs/cm (S5), while clay and silt content ranged from 40.35±0.03 (S1) to 45.51±0.07% (S5) and 26.66±0.03 % (S1) to 30.05±0.03 % (S5) respectively (Table 3). There was an increase in soil and water physicochemical parameters downstream along the river and swamps to Lake Victoria, indicating increased human, industrial and agricultural activities downstream along the river swamps and wetland.

The trend was much more evident during the wet than the dry season; this could be attributed to surface run-off from human settlement and industrial and agricultural activities upstream and downstream to the swamps and point where the river drains into Lake Victoria. Pearson's correlation analysis between selected water physicochemical parameters and DDTs pesticides during the wet and dry seasons were all positive (Table S1), except for the correlation between p, p'- DDD with TDS% and TSS% during the dry season, which was negative and not significant (P>0.01).

Pearson's correlation between conductivity and p, p'- DDD (wet season) and p, p'- DDD, and o, p'-DDE (dry season) were not statistically significant. The correlation between the water pH with all DDTs and its isomers analyzed were significantly positive (P≤0.01) (Table S1) during wet and dry seasons except p, p' -DDT (r = 0.029), which was not significant during the dry season. In addition, the correlation between turbidity with all DDTs were significantly positive except p, p' – DDT, and p, p' – DDD, which were insignificant at (P≤0.01). Correlation between conductivity and p, p'-DDE, were significantly positive (P≤0.05) during the wet season. During the dry season, the correlation between conductivity and p, p'- DDE were significantly positive (P≤0.05) (Table S1).

Furthermore, the correlation between soil pH, conductivity, soil moisture content, organic matter, and organic carbon with all six DDTs pesticide were significantly positive (P≤0.01) during wet and dry seasons except for the correlation between moisture content and o, p' – DDE, clay and p, p'-DDT that was significant at P≤0.05 during wet season. (Table S2).

Table 3: Physicochemical characteristics of water and sediments along river Kibos-Nyamasaria

	Water Samples									
Site	S1		S2		S3		S4		S5	
Parameter	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
pH	7.50±0.17	7.26±0.16	7.61±0.12	7.40±0.21	7.61±0.09	7.45±0.18	7.90±0.02	7.88±0.01	7.89±0.09	7.86±0.05
Conductivity (µs/cm)	123.56±0.75	120.53±0.70	126.00±0.81	130.53±0.87	132.66±0.85	128.53±1.00	137.56±0.97	133.00±0.75	139.26±0.86	137.26±0.36
TDS (mg/L)	105.36±0.50	101.33±0.25	111.40±1.35	107.53±0.86	117.26±1.10	115.46±1.12	115.60±0.88	113.40±0.79	120.10±0.45	118.10±0.33
TSS (mg/L)	89.70±0.10	83.20±0.90	97.60±0.90	111.40±0.00	113.20±0.20	120.30±0.60	123.73±0.60	126.90±0.70	111.50±0.90	110.50±0.41
Turbidity (NTU)	159.10±0.80	139.36±1.15	181.46±1.05	156.13±0.80	173.30±0.91	152.40±0.88	201.46±1.12	177.06±0.61	188.50±1.08	184.30±1.19
					Sediment sample					
Ph	6.90±0.08	6.73±0.07	7.03±0.07	6.92±0.07	6.20±0.05	6.83±0.10	7.26±0.06	7.16±0.15	7.25±0.02	7.23±0.05
Conductivity(µs/cm)	112.10±0.20	109.50±0.61	123.80±0.36	120.50±0.36	142.23±0.35	138.43±0.35	231.20±0.36	226.47±0.40	233.63±0.25	230.10±0.3
Moisture (%)	19.00±0.02	16.82±0.09	19.86±0.10	16.98±0.03	22.10±0.03	17.43±0.02	24.04±0.03	17.70±0.02	26.34±0.03	19.14±0.03
Organic Matter (%)	3.93±0.22	3.69±0.17	4.13±0.02	3.89±0.08	8.23±0.03	6.82±0.16	8.03±0.02	6.89±0.10	9.43±0.11	8.75±0.02
Organic carbon (%)	2.28±0.12	2.14±0.09	2.40±0.01	2.25±0.04	4.77±0.02	3.95±0.09	4.66±0.01	4.00±0.06	5.47±0.07	5.07±0.01
Clay (%)	40.35±0.03	40.74±0.66	44.05±0.09	42.94±0.14	43.28±0.06	42.93±0.21	44.32±0.02	44.77±0.15	45.51±0.07	45.99±0.19
Silt (%)	26.66±0.03	25.80±0.06	28.15±0.15	25.85±0.07	28.80±0.12	31.04±0.02	29.73±0.04	30.11±0.03	30.05±0.03	31.82±0.12
Sand (%)	32.96±0.02	33.14±0.03	30.87±0.06	31.14±0.12	27.57±0.68	26.03±0.02	25.92±0.03	25.10±0.06	22.45±0.22	22.23±0.03

3.2 DDTs pesticide residues in water at various sampling sites

The data on the concentration of the six DDTs pesticides residues in water at different sampling points (S1-S5) during the different seasons are presented in Table 4. p, p'- DDD (0.09±0.02) µg/L had the highest concentration at point S5 during the wet season and that of 0.03±0.02 µg/L during the dry season at sampling points (S1 and S2). All the DDTs isomers had higher concentration in wet season than dry season (Table 4) and were higher at the swamps and the entry point of the river to the Lake Victoria. During the dry season, point (S1) recorded the least concentration of DDTs isomers than all the other sampling points except p, p'- DDD isomer which recorded the highest concentration of 0.03±0.01µg/L. Sampling point (S5) generally recorded the highest concentration of DDTs except p, p'- DDD. Generally, the mean concentration of p, p'- DDD isomer residual levels were higher than all the other DDTs pesticides metabolites detected in water regardless of the sampling season (Table 4).

Physicochemical characteristics of river water and sediments with DDTs pesticides residues

The pH influence the transport and bioavailability of DDTs pesticides residues in water and sediments samples (Aiyesanmi et al., 2008; Drevenkar et al., 1996). Pesticides containing organochlorines like DDTs and its metabolites respond variably in water and soil, depending on their specific properties and the water-soil physicochemical parameters. The significant positive correlation between water/soil pH and DDTs pesticides residues during the wet and dry seasons and the substantial negative correlation between the pH and p, p′-DDD suggest that pH may have increased pesticide adsorption and desorption. The ability of DDTs pesticides to coagulate or sorb ions is influenced by the pH and speciation of dissolved ions. This finding is similar to an earlier work by Fosu-Mensah *et al*. (2016), which reported a significant increase in the concentrations of most organochlorine pesticides with an increase in soil pH. The water and soil pH reported in this study were within WHO allowable pH range between 6.5-8.5 for most natural rivers, streams or Lakes (Rehman *et al*., 2015). The sorption, transport and transformation of DDTs pesticides and its isomers or metabolites are significantly influenced by the organic matter composition of the soil (Tariq *et al*., 2016). In this study, during the wet season, soil organic carbon ranges from 2.28±0.12 % (S1) at Nyamasaria Bridge to 5.47±0.07 % (S5) at swamps and entry point to the Lake while soil organic matter ranges from 3.93±0.22 (S1) to 9.43±0.11 % (S5). During the dry season, soil organic matter varied from 3.69±0.17 (S1) to 8.75±0.02 % (S5) while soil organic carbon ranges

from 2.14±0.09 % (S1) to 5.07±0.01 % (S5) (Table 3). Depending on the type of pesticides and the organic matter, soil with an organic carbon concentration of greater than 5% may facilitate the sorption of DDTs pesticides (Rehman et al., 2015).

Furthermore, a strong positive correlation was observed in both dry and wet seasons between conductivity (both water and soil), organic matter, and organic carbon with DDTs pesticides detected, which shows that the DDTs pesticide residues and its metabolites levels in the soils are linked with high conductivity, organic matter and organic carbon of the soil (Table S1 and S2). This could be attributed to DDTs pesticide molecules having a high tendency to bind to organic matter and organic carbon in the soil, similar to fats, oil, or lipids of animals and plants (Paul et al., 2022; Nyaundi *et al.*, 2021; Nyaundi *et al*., 2020; Alex *et al*., 2019; Abong'o *et al*., 2018; Ndunda *et al*., 2018; Fang *et al*., 2017; Fosu-Mensah *et al*. 2016). The findings from this study are almost similar to a study by Fosu-Mensah *et al*. (2016) and F. Aiyesanmi & A. Idowu, 2012 which reported almost the same trend or significant ($p<0.05$) correlations between organic carbon, organic matter, and total DDTs pesticides residues detected in soil samples. Moreover, even though, organic matter and organic carbon composition are known to be the most critical DDTs sorbent in the soil surface, additional factors such as physicochemical characteristics of DDTs and particle-size characteristics are involved in pesticide retention (Fosu-Mensah *et al*., 2016).

Similarly, the behavior of DDTs pesticides in the soil is influenced by the soil texture (Fosu-Mensah *et al*. ,2016). Clay soils help accumulate DDTs through colloid formation, whereas Sandy soils are known to facilitate the leaching of DDTs pesticides residues. The high negative correlation between the percentage of sand in both dry and wet seasons and nearly all the DDTs pesticides residues detected indicates the influence of sand on extractable pesticides in soils. Therefore, an increase in the percentage of sand resulted in a corresponding decrease in DDTs pesticides detected and vice versa (Table S2). These findings agreed with similar studies conducted by Fosu-Mensah *et al*. (2016) and Aiyesanmi and Idowu (2012).

Moreover, the negative correlation between the percentage of clay soil and p, p'- DDD during the dry season indicates that the percentage clay has a significant influence on the distribution of DDTs pesticides in soils. Hence, an increase in the percentage of clay soils resulted in a corresponding decrease in p, p'- DDD and vice versa. This finding agrees with the study conducted by Fosu-Mensah et al. (2016). The high positive and strong

correlation ($p > 0.05$) between the percentage of silt and almost all the DDTs pesticides detected and identified shows that an increase in the percentage of silt increased the concentrations of almost all DDTs pesticides and its metabolites or isomers detected (Table S2). This finding, however, is also in agreement with the study conducted by Fosu-Mensah *et al*. (2016), which reported the same significant ($p > 0.05$) correlations between percentage silt and DDTs pesticides detected in soil samples.

Table 4: Seasonal variations of DDTs Pesticide residues in water during the wet and dry seasons at various sampling points

	Water Samples (μg/L)									
	Wet season					**Dry season**				
OCPs (μg/l)	**S1**	**S2**	**S3**	**S4**	**S5**	**S1**	**S2**	**S3**	**S4**	**S5**
o, p'- DDT	0.01 ± 0.03^d	0.01 ± 0.02^c	0.02 ± 0.01^b	0.02 ± 0.01^a	0.02 ± 0.02^a	0.00 ± 0.00^c	0.00 ± 0.00^d	0.02 ± 0.01^b	0.02 ± 0.01^b	0.02 ± 0.03^a
p, p' – DDT	0.04 ± 0.01^e	0.05 ± 0.01^d	0.06 ± 0.10^c	0.07 ± 0.02^b	0.07 ± 0.01^a	0.00 ± 0.00^{ef}	0.00 ± 0.00^{ef}	0.01 ± 0.01^d	0.02 ± 0.01^c	0.02 ± 0.03^a
o, p'- DDD	0.01 ± 0.01^c	0.02 ± 0.01^b	0.02 ± 0.03^c	0.02 ± 0.01^b	0.03 ± 0.02^a	0.00 ± 0.00^d	0.00 ± 0.00^d	0.01 ± 0.01^c	0.01 ± 0.01^b	0.02 ± 0.01^a
p, p'- DDD	0.06 ± 0.02^c	0.06 ± 0.01^d	0.06 ± 0.01^c	0.08 ± 0.03^b	0.09 ± 0.02^a	0.03 ± 0.01^a	0.03 ± 0.02^b	0.01 ± 0.01^g	0.01 ± 0.01^f	0.02 ± 0.01^e
o, p'- DDE	0.04 ± 0.03^e	0.05 ± 0.01^d	0.05 ± 0.02^c	0.06 ± 0.02^b	0.06 ± 0.01^a	0.02 ± 0.01^c	0.02 ± 0.01^c	0.02 ± 0.02^c	0.02 ± 0.01^b	0.03 ± 0.02^a
p, p'- DDE	0.01 ± 0.01^d	0.02 ± 0.01^c	0.02 ± 0.02^c	0.02 ± 0.01^b	0.02 ± 0.01^a	0.02 ± 0.01^c	0.02 ± 0.01^d	0.02 ± 0.02^{bc}	0.02 ± 0.01^b	0.02 ± 0.02^a

Means within a row followed by different letters (a, b, c, d, e, f,) are significantly different ($p < 0.05$) with respect to sampling point and DDTs. **S**=Sampling point; bdl=below detectable limit, results are in μg/L.

3.3 Seasonal variation of DDTs residues in sediment samples at various sampling points

The variations in season of DDTs metabolites residue in sediment at different sampling points (S1-S5) both in wet and dry seasons are shown in Table 5. The number of DDTs pesticides found at the sampling points varied greatly in seasons. The levels of DDTs isomers determined in water and sediments were above recommended level of WHO in both seasons. The concentrations of p, p'- DDD isomer were highest among DDTs isomers in both seasons, with the highest mean concentration value of 3.28±0.02 and 3.28±0.06 μg/kg during the dry season at point S4 (swamps) and S5 (entry point to Lake Victoria) respectively. The o, p'- DDE isomer of DDTs pesticides recorded the least concentration of 0.21±0.08 μg/kg at point S3 during the wet season while p, p'- DDD isomer recorded the highest concentration value of 3.28±0.06 μg/kg at point S5 which was at the swamp and entry point of the river to Lake Victoria. Generally. There was an increase in DDTs pesticide residues in sediments downstream (S1-S5) along the river to swamps and eventually to Lake Victoria in both seasons (Table 5). DDTs pesticides residues were more in sediments during the dry season than in the wet season, suggesting solubility and bioaccumulation of pesticides in sediment (Paul *et al*., 2022; Abong'o *et al*., 2018; Osoro *et al*., 2016). However, the expectations were that DDTs pesticide and its metabolites or isomers concentrations would be higher during the rainy season due to increased farming activities and increased volumes of run-offs from the agricultural activities along the river banks but that was not the case from the findings of this study. DDTs pesticides restricted under the Stockholm convention 2004 and 2009 on persistent organic pollutants (POPs) such as; DDTs and its metabolites (o, p'- DDT, p, p' – DDT, o, p'- DDD, p .p'- DDD, o, p' – DDE, p, p'- DDE) were detected in the sediments sample from point (S1-S5) both in wet and dry seasons and they were all above recommended levels of WHO (Table 5) which indicates danger to aquatic community and human health.

Table 5: Seasonal variations in DDTs residues in sediments during wet and dry seasons at various sampling points

OCPs (µg/kg)	Sediments (µg/kg)									
	Wet season					Dry season				
	S1	S2	S3	S4	S5	S1	S2	S3	S4	S5
o, p'- DDT	1.01 ± 0.02^d	1.68 ± 0.01^a	1.37 ± 0.12^c	1.55 ± 0.01^b	1.53 ± 0.03^b	1.05 ± 0.01^f	1.66 ± 0.02^b	1.45 ± 0.02^e	1.65 ± 0.01^c	1.82 ± 0.12^a
p, p'- DDT	1.80 ± 0.13^d	2.18 ± 0.01^{bc}	2.11 ± 0.21^c	2.27 ± 0.02^b	2.95 ± 0.01^a	2.00 ± 0.10^b	2.20 ± 0.03^b	2.23 ± 0.11^b	2.30 ± 0.02^b	3.03 ± 0.58^a
o, p'- DDD	0.30 ± 0.03^c	0.37 ± 0.01^{bc}	0.40 ± 0.05^{bc}	0.49 ± 0.03^{ab}	0.55 ± 0.02^a	0.31 ± 0.03^d	0.35 ± 0.02^d	0.41 ± 0.08^{cd}	0.56 ± 0.06^{bc}	0.61 ± 0.02^b
p .p'- DDD	2.99 ± 0.01^c	3.10 ± 0.02^{bc}	3.11 ± 0.05^{bc}	3.26 ± 0.02^a	3.24 ± 0.06^{ab}	3.01 ± 0.05^d	3.11 ± 0.03^c	3.22 ± 0.08^b	3.28 ± 0.02^a	3.28 ± 0.06^a
o, p'- DDE	0.24 ± 0.01^a	0.24 ± 0.03^a	0.21 ± 0.08^a	0.27 ± 0.05^a	0.32 ± 0.02^a	0.22 ± 0.10^b	0.23 ± 0.13^b	0.24 ± 0.10^{ab}	0.28 ± 0.05^{ab}	0.34 ± 0.08^a
p, p'- DDE	0.26 ± 0.02^{ab}	0.28 ± 0.01^{ab}	1.03 ± 1.15^a	0.38 ± 0.08^{ab}	0.40 ± 0.03^{ab}	0.29 ± 0.01^c	0.30 ± 0.02^c	0.33 ± 0.10^c	0.39 ± 0.02^b	0.43 ± 0.10^b

Means within a row followed by different letters (a, b, c, d, e, f,) are significantly different ($p < 0.05$) with respect to sampling point and OCPs. **S=**Sampling point; bdl=below detectable limit, results are in µg/kg.

3.4 Comparisons of mean DDTs pesticides residues in water and sediments between wet and dry Seasons

The paired t-test, mean and standard deviation of the concentration of DDTs pesticides in water and sediments during the wet and dry seasons are presented in Table 6. The levels of DDTs pesticides residues in water samples were significantly higher during the wet season than in the dry season. In water samples, p, p'- DDD recorded the highest mean of 0.049 ± 0.030 (t (29)= 6.411, p= 0.000) during the wet season while 0.018 ± 0.011 (t (29)= 6.411, p= 0.000) during the dry season which were all statistically significant between the wet and dry seasons (p< 0.005). The o, p'- DDT recorded the least mean concentration value of 0.009 ± 0.008 (t (29) = 4.133, p= 0.000) in water samples during the wet season and during the dry season of 0.004 ± 0.006 (t (29) = 9.175, p= 0.000) and the difference was statistically significant (p< 0.005).

In sediments the concentrations of p, p'–DDT (t (29) = -2.094, p= 0.045) and o, p'- DDD (t (29) = -2.010, p= 0.054 were significantly higher during the dry season as compared to wet season. In addition, p, p'- DDD reported the highest mean of 1.802 ± 1.376 and 1.939 ± 1.302 (t (29) = -1.744, p= 0.092) in sediments, during the wet and dry seasons respectively and was not statistically significant between the dry and wet season (p> 0.05). The o, p'- DDD recorded the least mean concentration value of -0.028 ± 0.766 (t (29) = -2.010, p= 0.054) in sediment samples during the dry season and was not statistically significant between the wet and dry seasons (p> 0.05) (Table 6).

The p, p'- DDD metabolite recorded the highest concentration than other DDTs isomers during the wet season in water samples in this study. High concentrations of p, p'- DDD (0.09 ± 0.02) µg/L were noted at point S5 (wet season) and during the dry season, p, p'- DDD recorded highest concentration of 0.03 ± 0.02 µg/L at sampling points S1 and S2 respectively. All the DDTs isomers

detected recorded the highest concentration in wet season than dry season in water (Table 4) and were higher at the swamps and the entry point of the river to the Lake Victoria. During the dry season, point S1 recorded the least concentration of DDTs isomers than all the other sampling points except p, p'- DDD isomer which recorded the highest concentration of 0.03 ± 0.01 μg/L at sampling point S1. The p, p'- DDD isomer residual levels were generally higher than all the other DDTs pesticides metabolites detected in water regardless of the sampling season (Table 4). Sampling point (S5) also generally recorded the highest concentration of DDTs except p, p'- DDD which recorded 0.02 ± 0.01 μg/L and was not the highest at point (S5). Most of the DDTs pesticide residues detected were above WHO maximum residues limits (MRLs) in both the wet and dry season in water sample. Sampling point S5 at the swamp or near the river mouths at the entry point to the Lake Victoria recorded the highest concentration above WHO maximum residues limits (MRLs) in both the wet and dry season due to bioaccumulation of DDTs, indicating possible danger to aquatic community and human health (Table 4).

Furthermore, in sediment samples, the p, p'- DDD recorded the highest concentrations among DDTs isomers in both seasons, with the highest mean concentration value of 3.28 ± 0.02 and 3.28 ± 0.06 μg/kg during the dry season at point S4 (swamps) and S5 (entry point to Lake Victoria) respectively. The o, p'- DDE isomer of DDTs pesticides detected recorded the least concentration value of 0.21 ± 0.08 μg/kg at point S3 during the wet season while p, p'- DDD isomer detected the highest concentration value of 3.28 ± 0.06 μg/kg at point S5 which was at the swamp and entry point of the river to Lake Victoria (Table 5). The outcome of this study also revealed and confirmed that, in sediment samples, DDTs concentrations were more during the dry season than the wet season while in water samples, DDTs were more during the wet season than the dry season and in both, the concentration of DDTs increased downstream, which is in agreement with the study

conducted by (Nyaundi *et al*., 2021; Nyaundi *et al*., 2020; Alex *et al.,* 2019; Onchieku, 2019; Abong'o *et al*., 2018; Ndunda *et al*., 2018; Fang *et al*., 2017; Nthusi, 2017; Osoro *et al*., 2016; Fosu-Mensah *et al*.,2016; Abong'o *et al*., 2015; Abongo, 2009). In this study, most DDTs pesticides residues detected in sediment were above WHO maximum residues limits (MRLs). The results are similar to previous studies by Nthusi, 2017; Abong'o *et al*., 2015 and Abongo 2009 along the river Nyando, even though, most values of DDTs pesticides in their study were higher than those found in this study. The same trend and similarity of the results of the study were observed in Rusinga Island of Lake Victoria, Kenya (Osoro *et al*., 2016), River Kuja catchment (Onchieku, 2019), and Nyando River catchment of Lake Victoria Kenya (Abong'o *et al*., 2018; Nthusi, 2017; Abong'o *et al*., 2015; Abongo, 2009). Generally, the mean DDTs pesticide residual levels increased downstream from the river source (first sampling point upstream) to where it drains into Lake Victoria, and this is in agreement with the previous studies conducted by Onchieku (2019), Abong'o *et al*. (2018), Nthusi (2017), Osoro *et al*. (2016), Abong'o *et al*. (2015) and Abongo (2009).

High concentrations of DDTs pesticides were reported in sediments compared to river water samples, and this could be attributed to higher solubility, affinity, and bioaccumulation of DDTs pesticides residues in the soils. These compounds are persistent and move longer distances in surface run-off or groundwater. They have a low solubility in water and therefore tend to adsorb onto the sediment particles. The results of our study are in agreement with previous studies which reported high DDTs pesticide residues in sediments as compared to water samples (Nyaundi *et al*., 2021; Nyaundi *et al*., 2020; Alex *et al.,* 2019; Onchieku, 2019; Abong'o *et al*., 2018; Ndunda et al., 2018; Fang *et al*., 2017; Nthusi, 2017; Osoro *et al*., 2016; Abong'o *et al*., 2015; Abongo, 2009). The variations in DDTs pesticide residues observed in this study at different sampling points along

the river at different seasons might have resulted from human or industrial activities along the river. Some of the human activities involving the use of pesticides along the river line include; the treatment of fence lines poles, the foundations of homes and new construction sites, public health to control mosquitoes around the lake region, treatment of woods or timber around Nyamasaria and Kibos area in Kisumu to control termites and ants by wood venders and a dumping of used pesticides containers into the river. Run-off or leaching of DDTs pesticides into the river could have also occurred when too many pesticides were applied or spilled on the surface carelessly, highly water soluble pesticides were used, or too much rainwater or irrigation water which occurred in a short period washed the pesticides to the river (Fosu-Mensah *et al.* 2016). According to a report by the Pest Control Products Board of Kenya (PCPB)in 2008, many of the pesticides under investigation are no longer imported or used because of banned or restriction, however, some are still being used illegally. Several studies, including those by Gitahi et al. (2002) and Onyango et al. (2014), have reported that, these banned or restricted pesticides may have been used illegally by some people, or dumped illegally. The used pesticide containers also may have been dumped illegally into the rivers in Lake Basin region leading to severe pollution. DDT and its isomers or metabolites reported in this study may be explained by the frequent use of agricultural pesticides and human settlements along the malaria-prone area in the Lake region, which has benefited from mosquitoes control initiatives and termite control in the study area accounting for the high levels of the DDT isomers concentration in the water and sediments.

Table 6: Paired t-test for DDTs pesticides residues in water and sediments between wet and dry Seasons

Pesticide	OCPs in water Means ± S.D. (μg/L)					OCPs in sediments Means ± S.D. (μg/kg)				
	Wet season	Dry season	t value	df	p-value	Wet season	Dry season	t value	df	p-value
o, p'- DDT	0.009±0.008	0.007±0.008	4.133	29	0.000	0.835±0.824	0.831±0.962	0.106	29	0.916
p, p'- DDT	0.040±0.021	0.009±0.010	10.267	29	0.000	1.184±1.275	1.372±1.085	-2.094	29	0.045
o, p'- DDD	0.013±0.007	0.004±0.006	9.175	29	0.000	-0.169±0.730	-0.028±0.766	-2.010	29	0.054
p, p'- DDD	0.049±0.030	0.018±0.011	6.411	29	0.000	1.802±1.376	1.939±1.302	-1.744	29	0.092
o, p'- DDE	0.039±0.018	0.014±0.008	12.637	29	0.000	-0.318±0.674	-0.356±0.687	0.778	29	0.443
p, p'- DDE	0.012±0.009	0.009±0.009	3.645	29	0.001	-0.128±0.833	-0.040±0.556	-1.028	29	0.312

5.0 Conclusion

The higher concentrations of some DDTs pesticides residues and its isomers were attributed to agricultural, industrial, settlement, and human activities upstream and downstream of River Kibos- Nyamasaria. The DDTs pesticide residues might have found their way into the soils via spray drift, wash-off from sprayed agricultural land, accidental spillage on the ground, improper disposal of leftover spray solution or dumping of used pesticide containers into the river or nearby, sprayer wash water and pesticide containers as well as overuse or misuse of the pesticide, among others. The presence of DDTs in the soils may pose a potential danger to soil organisms and can seriously contaminate the surrounding water bodies through leaching and surface run-off.

Some of the DDTs pesticides in this study were above the maximum residue limits (MRLs) recommended in drinking water as per WHO and NEMA standards. The restricted DDTs pesticide residues in soil and water samples from the study area indicate that some individuals still use these DDTs illegally. There is a need to control bioaccumulation and pesticide pollution to relieve the aquatic, animal, and human health calamities that might occur. Frequent monitoring of pesticide residues in this study area is necessary for preventing, controlling, and reducing environmental pollution to minimize health risks. Further there is need of the bio availability levels of the DDT isomers in the Lake Victoria basin be determined to assess the actual health effects of the pesticide residues.

Competing interests

The authors declare that there is no competing interest whatsoever.

REFERENCES

Abdel-Rasheed, M. E.-S. (2011). *Ecological Studies on Lake El-Manzalah With Special Reference To Their Water Quality and Sediment Productivity. Al-Azhar University Faculty of Science, Zoology department, Msc Zoology, Thesis.* Page 1-391.

Abong'o, D. A., Wandiga, S. O., & Jumba, I. O. (2018). Occurrence and distribution of organochlorine pesticide residue levels in water, sediment and aquatic weeds in the Nyando River catchment, Lake Victoria, Kenya. *African Journal of Aquatic Science*, *43*(3), 255–270. https://doi.org/10.2989/16085914.2018.1490244

Abong'o, D. A., Wandiga, S. O., Jumba, I. O., Van den Blink, P. J., Nazariwo, B. B., Madadi, V. O., Wafula, G. A., Kylin, H., & Nkedi-kizza, P. (2015). Organochlorine pesticide residue levels in soil from the Nyando

River Catchment, Kenya. *Africa Journal of Physical Sciences*, *2*(21), 18–32.

Abong'o, D. A., Wandiga, S. O., Jumba, I. O., Van den Brink, P. J., Nazariwo, B. B., Madadi, V. O., Wafula, G. A., Kylin, H., & Nkedi-kizza, P. (2015). Organochlorine pesticide residue levels in soil from the Nyando River Catchment, Kenya. *Africa Journal of Physical Sciences*, *2*(21), 18–32.

Abongo, D. (2009). *Ocurrence, distribution and environmental impacts of organochloride pesticide in the lake Victoria Catchment: A case study of River Nyando drainage basin of Winam Gulf in Kenya. University of Nairobi, Department of Chemistry, PhD Thesis.* Page 1-333.

Alex, W., Arvid, F., Faith, M., Bernard, C., Anders, D., & Robinson, M. (2019). Assessment of health risks associated with organochlorine pesticides levels in processed fish products from Lake Victoria. *African Journal of Food Science*, *13*(5), 101–110. https://doi.org/10.5897/ajfs2019.1814

APHA. (1998). APHA, A. P. H. A. : Standard Methods for the Examination of water and Wastewater. *American Physical Education Review*, *24*(9), 481–486.

APHA. (2002). American Public Health Association; American Water Works Association; Water Environment Federation. *Standard Methods for the Examination of Water and Wastewater*, *02*, 1–541.

Atieno Abongo, D. (2009). *Ocurrence, distribution and environmental impacts of organochloride pesticide in the lake Victoria Catchment: A case study of River Nyando drainage basin of Winam Gulf in Kenya. PhD Thesis.* 333.

County Government of Kisumu. (2019). *Kisumu County Environment Policy 2019*. 1–46.

Drevenkar, V., Fingler, S., Fröbe, Z., & Vasilic, Z. (1996). Persistent organochlorine compounds in water and soil environments. *Environmental Management and Health*, *7*(4), 5–8. https://doi.org/10.1108/09566169610123014

EM, O., SO, W., DA, A., V O, M., & J W, M. (2016). Organochlorine Pesticides Residues in Water and Sediment from Rusinga Island, Lake Victoria, Kenya. *IOSR Journal of Applied Chemistry*, *09*(09), 56–63. https://doi.org/10.9790/5736-0909025663

EPA, U. S. E. P. A. (2007). USEPA Method 1699 2007 pesticides in Water, Soil, Sediment, Biosolids, and Tissue by HRGC-HRMS. *U.Epa*, *December*, 1–96. https://www.epa.gov/sites/production/files/2015-10/documents/method_1699_2007.pdf

European Commission. (2000). *SANCO/3103/2000. Quality control procedures for pesticide residues analysis. Guidelines for Residues Monitoring in the European Union. Second edi*, page 1-30.

F. Aiyesanmi, A., & A. Idowu, G. (2012). Organochlorine Pesticides Residues in Soil of Cocoa Farms in Ondo State Central District, Nigeria. *Environment and Natural Resources Research*, *2*(2), 65–73. https://doi.org/10.5539/enrr.v2n2p65

Fang, Y., Nie, Z., Die, Q., Tian, Y., Liu, F., He, J., & Huang, Q. (2017). Organochlorine pesticides in soil, air, and vegetation at and around a contaminated site in southwestern China: Concentration, transmission, and risk evaluation. *Chemosphere*, *178*, 340–349. https://doi.org/10.1016/j.chemosphere.2017.02.151

FAO. (2017). Water for Sustainable Food and Agriculture Water for Sustainable Food and Agriculture. In *A report produced for the G20 Presidency of Germany*. www.fao.org/publications

Fosu-Mensah, B. Y., Okoffo, E. D., Darko, G., & Gordon, C. (2016). Assessment of organochlorine pesticide residues in soils and drinking water sources from cocoa farms in Ghana. *SpringerPlus*, *5*(1). https://doi.org/10.1186/s40064-016-2352-9

George M. Onyango, George G. Wagah, L. A. O. and B. O. O. (2013). Experiences from Kisumu City. *Maseno University Press*, Page 1-99.

Gitahi, S. M., Harper, D. M., Muchiri, S. M., Tole, M. P., & Ng'ang'a, R. N. (2002). Organochlorine and organophosphorus pesticide concentrations in water, sediment, and selected organisms in Lake Naivasha (Kenya). *Hydrobiologia 2002 488:1*, *488*(1), 123–128. https://doi.org/10.1023/A:1023386732731

Hellar-Kihampa, H. (2011). Pesticide residues in four rivers running through an intensive agricultural area, Kilimanjaro, Tanzania. *J. Appl. Sci. Environ. Manage*, *15*(2), 307–316. www.bioline.org.br/ja

Huang, Z., Liu, C., Zhao, X., Dong, J., & Zheng, B. (2020). Risk assessment of heavy metals in the surface sediment at the drinking water source of the Xiangjiang River in South China. *Environmental Sciences Europe*, *32*(1). https://doi.org/10.1186/s12302-020-00305-w

James, O., & Achieng, G. O. (2019). Assessment of water quality of the Nyando River (Muhoroni-Kenya) using the water quality index (WQI) method Quantitation of Nanoformulated Primaquine View project pharmaceutical remediation from aqueous environment View project. *Article in International Research*

Journal of Environmental Sciences, *May*. https://www.researchgate.net/publication/332911928

Jayaraj, R., Megha, P., & Sreedev, P. (2016). Review Article. Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment. *Interdisciplinary Toxicology*, *9*(3–4), 90–100. https://doi.org/10.1515/intox-2016-0012

Jeffers, A. (2019). Soil Texture Analysis "The Jar Test." *Clemson University Home & Garden Information Center*, 2018–2021. https://hgic.clemson.edu/factsheet/soil-texture-analysis-the-jar-test/

Joseph Nyaundi, Albert Getabu, Job Mwamburi, James Onchieku, Zachary Kinaro, George Ogendi, Jared Babu, & Nicholas Gichuru. (2020). Organochlorine Contaminants in Nile Tilapia, Oreochromis niloticus (Linnaeus 1758) in Densely Populated Areas of South-Western Kenya. *Journal of Environmental Science and Engineering B*, *9*(4), 153–161. https://doi.org/10.17265/2162-5263/2020.04.004

Kanoti, J. R., Olago, D., Opiyo, N., & Nyamai, C. (2019). An overview of groundwater and sanitation challenges in Kisumu City, Kenya. *International Journal of Innovative Research and Development*, *8*(4), 1–7. https://doi.org/10.24940/ijird/2019/v8/i4/143592-347932-

Kasozi, G. N., Kiremire, B. T., Bugenyi, F. W. B., Kirsch, N. H., & Nkedi-Kizza, P. (2006). Organochlorine Residues in Fish and Water Samples from Lake Victoria, Uganda. *Journal of Environmental Quality*, *35*(2), 584–589. https://doi.org/10.2134/jeq2005.0222

Kelle, H. I., Ogoko, E. C., Abiola, O. O., Achem, D., & Udeozo, I. P. (2022). Monitoring and health risk assessment of organochlorine pesticide residue in some leafy and fruiting vegetables from Lagos State , Southwestern Nigeria. *Journal of the Kenya Chemical Society*, *1*(June), 3–13.

Kiyuka Nyaundi, J., Getabu, A., Onchieku, J., Kinaro, Z., Bassa, S., Nyamweya, C., Nyaboke, H., & Getenga, Z. (2021). Occurrence and distribution of Organochlorine Pesticide Residues in Water and Sediments of Earthen Fish Ponds in South Western Kenya. *Uganda Journal of Agricultural Sciences*, *19*(2), 47–60. https://doi.org/10.4314/ujas.v19i2.5

Kubatova Research Group. (2008). Determination of LODs (limits of detection) and LOQs (limit of quantification). *University of Notre Dakota Department of Chemistry*, *3*, pg 3. https://arts-sciences.und.edu/chemistry/kubatova-research-group/_files/docs/determination_of_lods_new.pdf

Masimbe, T. (2018). *Impact Of Climate Extremes On Water Quality And Supply In Urban Informal Settlements In Kenya: A Case Study Of Kisumu City*.

Musa, S., Gichuki, J. W., Raburu, P. O., & Aura, C. M. (2011). Risk assessment for organochlorines and organophosphates pesticide residues in water and Sediments from lower Nyando/Sondu-Miriu river within Lake Victoria Basin, Kenya. *Lakes and Reservoirs: Research and Management*, *16*(4), 273–280. https://doi.org/10.1111/j.1440-1770.2011.00486.x

Nash, R. G., Harris, W. G., & Lewis, C. C. (1973). Soil pH and Metallic Amendment Effects on DDT Conversion to DDE. *Journal of Environmental Quality*, *2*(3), 390–394. https://doi.org/10.2134/jeq1973.00472425000200030020x

Ndunda, E. N., Madadi, V. O., & Wandiga, S. O. (2018). Organochlorine pesticide residues in sediment and water from Nairobi River, Kenya: levels, distribution, and ecological risk assessment. *Environmental Science and Pollution Research*, *25*(34), 34510–34518. https://doi.org/10.1007/s11356-018-3398-8

Ngila N., & Gunnlaugsdottir, H. (2008). *Environmental Study and Monitoring of Undesirable Chemical Substances in Fish / Seafood : a Proposal for Lake Victoria, Kenya*. 1–39.

Njogu, P. M. (2011). Assessment of pollution and prediction of environmental risks of organochlorine pesticides residues on aquatic communities, Jomo Kenyatta University of Agriculture and Technology (JKUAT), PhD (Environmental Technology). *Thesis*, 1–226.

Nthusi, V. K. (2017). *Assessment of Polychlorinated Biphenyls and Organochlorine Pesticides Residue Levels in Fish From Nandi-Lower Nyando River Sub-Catchment , Kenya, University of Nairobi, Department of Chemistry, Msc Thesis*. 1–122.

Ochoa, V., & Maestroni, B. (2018). Pesticides in Water, Soil, and Sediments. In *Integrated Analytical Approaches for Pesticide Management* (pp. 133–147). https://doi.org/10.1016/B978-0-12-816155-5.00009-9

Omwenga, I., Kanja, L., Nguta, J., Mbaria, J., & Irungu, P. (2016). Organochlorine pesticide residues in farmed fish in Machakos and Kiambu counties, Kenya. *Cogent Environmental Science*, *2*(1). https://doi.org/10.1080/23311843.2016.1153215

Onchieku, K. J. (2019). Assessment of organochlorine pesticides (OCPs) contamination in relation to physico-

chemical parameters in the Upper River Kuja Catchment, Kenya (East Africa). ~ *172 ~ International Journal of Fisheries and Aquatic Studies*, *7*(1), 172–179. www.fisheriesjournal.com

Onyango, G. M. (2018). Urban public transport in informal settlements: Experiences from Kisumu City, Kenya. *Bulletin of Geography. Socio-Economic Series*, *40*(40), 145–156. https://doi.org/10.2478/bog-2018-0020

Onyango, J., Kreuzinger, N., Yillia, P., & Kitaka, N. (2014). Potential Risks of Pesticide Application in Kenya : Case of Lake Naivasha Catchment. *7th International Young Water Professional Conference*, *December*.

Paul, M., John, W., Proscovia, N., & Emmanuel, N. (2022). Dichlorodiphenyltrichloroethane (DDT) and its metabolites in house dust, soil and selected food crops from indoor residual sprayed areas of Apac and Oyam Districts, Uganda. *African Journal of Pure and Applied Chemistry*, *16*(2), 28–39. https://doi.org/10.5897/ajpac2022.0884

Pinto, M. I., Sontag, G., Bernardino, R. J., & Noronha, J. P. (2010). Pesticides in water and the performance of the liquid-phase microextraction based techniques . A review. *Microchemical Journal*. https://doi.org/10.1016/j.microc.2010.06.010

Rehman, H., Akba, N. U., Quereshi, M., Ahmad, N., & Masab, M. (2015). Physicochemical Analysis of Water and Soil Collected from Dandiidharkhel Lake Karak and its Effects on Fish Breeding. *World Applied Sciences Journal*, *33*(8), 1397–1401. https://doi.org/10.5829/idosi.wasj.2015.33.08.96224

Saoke, P. (2005). *Kenya POPs Situation Report : DDT , Pesticides and Polychlorinated Biphenyls*. *November*, 1–60.

Ssebugere, P., Kiremire, B. T., Kishimba, M., Wandiga, S. O., Nyanzi, S. A., & Wasswa, J. (2009). DDT and metabolites in fish from Lake Edward, Uganda. *Chemosphere*, *76*(2), 212–215. https://doi.org/10.1016/j.chemosphere.2009.03.049

Syed, J. H., Malik, R. N., & Muhammad, A. (2014). Organochlorine pesticides in surface soils and sediments from obsolete pesticides dumping site near Lahore city, Pakistan: Contamination status and their distribution. *Chemistry and Ecology*, *30*(1), 87–96. https://doi.org/10.1080/02757540.2013.829051

Tariq, S. R., Shafiq, M., & Chotana, G. A. (2016). Distribution of Heavy Metals in the Soils Associated with the Commonly Used Pesticides in Cotton Fields. *Scientifica*, *2016*, 2–11. https://doi.org/10.1155/2016/7575239

Tribaldo, E. B. (2007). Analysis of Pesticides in Water. *Handbook of Water Analysis, Second Edition*, 449–490. https://doi.org/10.1201/9781351069663

UNESCO. (2003). duplicateWater for People, Water for Life. *The World Water Development Report*, 36. https://doi.org/10.1017/CBO9781107415324.004

UNESCO. (2015). *A systematic review of emerging pollutants on human health and livelihoods of population living in the Lake Victoria Basin of Kenya. Case study report*. 118.

Wei, J., Duan, M., Li, Y., Nwankwegu, A. S., Ji, Y., & Zhang, J. (2019). Concentration and pollution assessment of heavy metals within surface sediments of the Raohe Basin, China. *Scientific Reports*, *9*(1), 1–7. https://doi.org/10.1038/s41598-019-49724-7

World Water Council. (2000). World Water Vision - Making Water Everybody's Business. *Journal of Chemical Information and Modeling*, *53*(June), 1689–1699. https://doi.org/10.1017/CBO9781107415324.004

Yive, N., & Knols, B. G. J. (2020). *Synthesis Report for the Terminal Evaluation of UNEP DDT Projects*. *July 2020*. https://stg-wedocs.unep.org/handle/20.500.11822/34309%0Ahttps://stg-wedocs.unep.org/bitstream/handle/20.500.11822/34309/01_11_2020_DDT Synthesis Report Final.pdf?sequence=1

Supplementary tables

Table S1: Mean percentage recoveries, Limit of Detection (LOD) and Limit of Quantification (LOQ) for DDT pesticide residue isomers

DDTs residues	% Recovery ± SD	LOD (µg/L)	LOQ (µg/L)
o, p'- DDT	83.14 ± 2.57	0.0013	0.0040
p, p'- DDT	80.25 ± 1.09	0.0019	0.0059
o, p'- DDD	79.91 ± 0.98	0.0017	0.0051
P, p'- DDD	92.13 ± 1.87	0.0019	0.0057
o, p'- DDE	94.01 ± 2.21	0.0018	0.0060
p ,p'- DDE	78.55 ± 0.69	0.0015	0.0045

SD=Standard Deviation, n=3

Table S2: Pearson's correlation analysis between selected water physicochemical parameters and DDTs pesticides during the wet and dry season

Wet season						
Parameters	**1**	**2**	**3**	**4**	**5**	**6**
pH@25	0.897**	0.767**	0.966**	0.992**	0.864**	0.940**
Conductivity (us/cm)	0.662**	0.825**	0.516**	0.315	0.698**	0.468*
TDS (mg/l)	0.808**	0.806**	0.664**	0.562**	0.729**	0.690**
TSS (mg/l)	0.795**	0.827**	0.525**	0.513**	0.744**	0.731**
Turbidity (NTU)	0.914**	0.874**	0.839**	0.825**	0.852**	0.906**
Dry season						
Parameters	**1**	**2**	**3**	**4**	**5**	**6**
pH@25	0.759**	0.029	0.822**	0.419*	0.965**	0.764**
Conductivity (us/cm)	0.807**	0.816**	0.844**	0.023	0.144	0.428*
TDS (mg/l)	0.848**	0.553**	0.849**	-0.012	0.502**	0.579**
TSS (mg/l)	0.802**	0.654**	0.800**	-0.314	0.542**	0.621**
Turbidity (NTU)	0.754**	0.364	0.828**	0.115	0.780**	0.712**

** Correlation was significant at the 0.01 level (2-tailed). * Correlation was significant at the 0.05 level (2-tailed) (1) o, p'- DDT (2) p, p' – DDT (3) o, p'- DDD (4) p. p'- DDD (5) o, p' – DDE (6) p, p'- DDE

Table S3: Pearson's correlation analysis between selected sediment physicochemical parameters and DDTs pesticides during the wet and dry season

Wet season						
Parameters	1	2	3	4	5	6
Soil pH@25	0.882**	0.692**	0.837**	0.903**	0.727**	0.923**
Conductivity (us/cm)	0.966**	0.808**	0.875**	0.913**	0.787**	0.896**
Moisture (%)	0.739**	0.476**	0.639**	0.745**	0.418*	0.692**
Organic matter (%)	0.922**	0.800**	0.670**	0.679**	0.717**	0.744**
Organic carbon (%)	0.922**	0.800**	0.670**	0.679**	0.717**	0.744**
Clay (%)	0.480**	0.408*	0.168	0.134	0.141	0.250
Silt (%)	0.884**	0.828**	0.884**	0.888**	0.912**	0.915**
Sand (%)	-0.867**	-0.751**	-0.619**	-0.592**	-0.610**	-0.664**
Dry season						
Parameters	1	2	3	4	5	6
Soil pH@25	0.624**	0.759**	0.959**	0.559**	0.773**	0.790**
Conductivity (us/cm)	0.785**	0.695**	0.880**	0.754**	0.881**	0.806**
Moisture (%)	0.405*	0.773**	0.832**	0.301	0.718**	0.692**
Organic matter (%)	0.703**	0.456*	0.731**	0.823**	0.956**	0.717**
Organic carbon (%)	0.703**	0.456*	0.731**	0.823**	0.956**	0.717**
Clay (%)	0.024	0.014	0.227	0.149	0.581**	0.197
Silt (%)	0.921**	0.634**	0.906**	0.888**	0.760**	0.727**
Sand (%)	-0.548**	-0.303	-0.599**	-0.696**	-0.922**	-0.560**

** Correlation was significant at the 0.01 level (2-tailed). * Correlation was significant at the 0.05 level (2-tailed). (1) o, p'- DDT (2) p, p' - DDT (3) o, p'- DDD (4) p, p'- DDD (5) o, p' - DDE (6) p, p'- DDE