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Dissipation of environmental DDT and its metabolites in selected rivers of south-western Kenya

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Rivers are the main source of domestic and industrial water supplies in Kenya. In this study, water sampling was done at eight upstream sites in the Kuja River catchment, Kenya, between October 2016 and April 2017, specifically to test for residue levels of the organochlorine pesticide, dichlorodiphenyltrichloroethane (*p,p'*-DDT), and its degradation products, dichlorodiphenyldichloroethylene (*p,p'*-DDE) and dichlorodiphenyldichloroethane (*p,p'*-DDD). The analysis was performed with gas chromatography coupled with electron-capture detection in an autosampler. Concentrations of these residues in the surface water samples ranged from below detection limit (BDL) to 1.1113 µg l^{-1} in the wet season, and from BDL to 2.007 µg l^{-1} in the dry season. Overall, the highest mean residue concentration was for *p,p'*-DDT (0.9669 ± 0.2994 µg l^{-1}). The lowest mean concentration in the dry season was that of *p,p'*-DDE (0.1824 ± 0.0964 µg l^{-1}), and in the wet season it was *p,p'*-DDD (0.0610 ± 0.0038 µg l^{-1}). From our results it is evident that DDT is still in use and detectable in the study area, though the mean levels detected were below the acceptable thresholds for natural water as suggested by the World Health Organization (WHO). Except for a slightly higher mean spatial distribution of the metabolite *p,p'*-DDT, the resides were recorded as below the maximum admissible concentrations of pesticide residues in drinking water, as set out in WHO guidelines and by Kenya's National Environment Management Authority (NEMA). Monitoring organochlorine pesticide contamination levels in Kenya's water resources should be scaled up to leverage potential for a sustainable blue economy and in safeguarding human and environmental health.

Keywords: electron-capture detection, gas chromatography, global standards, Kuja River, natural surface water, organochlorines, seasonal differences

Introduction

The use of pesticides has benefited agriculture, forestry, and the domestic sphere to varying degrees, leading to tremendous economic gains. However, the use of some chemicals has led to bioaccumulation in the environment and negative health impacts for people (Chopra et al. 2011; Saeedi Saravi and Shokrzadeh 2011; Heidari-Beni et al. 2015). For instance, pesticide application in the agricultural sector, including dichlorodiphenyltrichloroethane (DDT) as an insecticide, helped to increase global food production by more than one-third in the last three decades (Liu et al. 2002; FAO 2011; Talebmorad et al. 2020; Muyesaier et al. 2021). Even so, serious health implications to humans and negative impacts on the environment have accrued from the use of organochlorine pesticides (OCPs) such as DDT. Studies conducted locally have shown that DDT use in agriculture and for the prevention of insect-borne diseases is associated with toxic effects in humans, since excessive inhalation and continuous consumption of contaminated foods can seriously disrupt or alter the endocrine system, reproductive organs and hormone production (WHO 2001; Musa et al. 2011; Omenge et al. 2016). DDT and its metabolites pose risks to human health from either occupational or non-occupational exposure, may cause the death of farm animals, and can contaminate and bioaccumulate in aquatic environments (Madadi et al. 2005; Javadinejad et al. 2019; Nyaundi et al. 2019). Furthermore, its negative impacts have slowly outweighed positive benefits, hence the eradication and ban of the use of DDT both in Kenya and internationally, according to the United Nations (UN; 2004) and the Stockholm Convention on Persistent Organic Pollutants of 2001 (Lallas 2001).

Despite national and regional restrictions to control persistent organic pollutants (POPs) that adversely affect human health and the environment, some toxic chemicals continue to be used locally for managing fungal diseases, insect pests, rodents and weeds; for crop disease protection; and for purposes of animal husbandry and public health (Abong'o et al. 2015). DDT has been used in the Lake Victoria catchment to help eradicate insect-borne diseases, such as malaria and sleeping sickness in humans (Getenga et al. 2004; Madadi et al. 2005; Abong'o et al. 2015; Osoro et al. 2016). Studies on the distribution of hexachlorocyclohexane (HCH) and DDT residues in the coastal marine environment of Mumbai, India, and within the Indian sub-basins, indicated the adverse effects of these pesticides to human health, including

disorders of the immune and reproductive systems, spinal cord developmental abnormalities, and cancers (Pandit et al. 2002; Rajendran et al. 2005). Owing to their toxicity in humans and animals, the use of many classes of POPs, especially OCPs, has been banned in most developed countries as well as in numerous developing countries, such as Kenya (Getenga et al. 2004; Ize-Iyamu et al. 2007; Mungai et al. 2019). The International POPs Elimination Project report of 2005 (Di Gangi 2006) notes that Kenya has maintained a ban on the use of DDT in combating malaria or in the context of other public health concerns since 1988. Even so, current enforcement policies have not eliminated its availability and application, and the level of OCP pollution in the environment remains significant (Getenga et al. 2004; Okeniyia et al. 2009; Adeboyejo et al. 2011; Adeyemi et al. 2011; Olatunbosum et al. 2011; Upadhi 2012; Williams 2013; Eslamian et al. 2018). Furthermore, existing data indicate that population growth and industrial and human-related activities (e.g. urbanisation within the Lake Victoria catchment) are importantly contributing to high levels of organic and inorganic contaminants in both aquatic and terrestrial environments (Sitoki et al. 2010; Volschenk et al. 2019).

Several health concerns are related to people's exposure and consumption of pesticide residues, such as DDT-contaminated foods like fish (Nyaundi et al. 2020, 2021). Studies indicate that children and pregnant women constitute more-vulnerable population groups in this regard (US-EPA 2004; Jiang et al. 2005; Heidari-Beni et al. 2015). Moreover, some investigations have emphasised that OCPs persist in the environment since significant trace element concentrations continue to be detected (Jiang et al. 2005; Ezemonye et al. 2009). Chronic exposure over a given period in an organism's lifetime, the contact frequency and the concentration levels of the target OCPs determine the extent of the risks to human health and biota.

According to data presented by the IUPAC (2010), the risks to both human health and aquatic ecosystems from exposure to OCPs can be uncovered through assessments of plant and animal communities and the risks to specific species. Such assessments can expose the toxicity characteristics of OCPs like DDT and its metabolites, and the extent of their bioaccumulation in different matrices (e.g. Pardío et al. 2012). The potential health risk posed by ingestion of pesticide-contaminated crops and aquatic food resources, such as fish, is currently being prioritised by several scientific research groups (Fianko et al. 2011; Gavor et al. 2013; Omenge et al. 2016; Osoro et al. 2016).

Wetland degradation, water pollution, poor practices in semi-intensive agriculture (like cut and burn in subsistence farming) and commercial cash-crop farming in the Lake Victoria catchment have led to rapid habitat changes (Mugenda and Mugenda 2005; Odume et al. 2012; Harmsen 2018). In this study, we investigated residue levels of the organochlorine pesticide, dichlorodiphenyltrichloroethane (*p,p′*-DDT), and its degradation products, dichlorodiphenyldichloroethylene (*p,p′*-DDE) and dichlorodiphenyldichloroethane (*p,p′*-DDD), in the catchment of the upper Kuja River, also known as the Gucha River, which runs through heavily populated counties in south-western Kenya, before it joins the Migori River and flows into Lake Victoria.

Materials and methods

Study area

The study was carried out in streams and rivers connected to the primary stage of the Kuja River, which ultimately joins the Migori River and flows into Lake Victoria. Kuja River has a total catchment area of ~6 600 km^2, and flows through the highly populated counties of Kisii and Nyamira in south-western Kenya. These counties have an estimated population density of about 1 200 persons per square kilometer (KNBS 2019). Stratified and then randomly selected sites in the neighbouring counties of Kericho (upstream) and Migori (downstream) were also sampled (Figure 1). The study area has a semi-Equatorial climate and rainfall pattern and is characterised by loam volcanic soils suitable for subsistence and commercial farming. The sampling sites (34°40′ S, 34°60′ E to 0°24′ S, 0°56′ E) were selected in relation to their proximity to intensive agro-chemical industrial systems and large human settlements (Rusongoza 2003).

Water sampling

Water samples were collected using a Van Don sampler at eight sites (labelled A–H; see Figure 1) situated on randomly selected first-order streams and rivers in the Kuja River catchment, from October 2016 to April 2017. Sampling was carried out bi-monthly in replicates, in the subsequent quarters during the sampling period, and to cover seasonality (rain and dry). *In situ* measurements of water temperature, conductivity, dissolved oxygen (DO) and pH were made using a YSI Multi-parameter meter (Model 35C). A Secchi disk (20-cm diameter) was used to measure turbidity. Total phosphorus and total nitrogen concentrations were determined using spectrophotometric method (APHA 2017).

For determination of OCP residues, surface water samples were collected in 2.5-l amber glass bottles filled to the brim, with 1 ml of 10 ppm extracted for laboratory analysis. A Coleman cooler box was used to temporarily store the water samples before being transported to the laboratory for storage at 4 °C prior to clean-up and extraction.

Water sample extraction and clean-up

Once in the laboratory, particle-associated OCP residues in the water samples were extracted using Soxhlet extraction for 20–25 min using 60 ml of dichloromethane (DCM) mixed with 175 ml of *n*-hexane (Fisher Scientific, USA). The resulting extract was dissolved with *n*-hexane and then re-concentrated to 1–3 ml and eluted (US-EPA 2004; Osoro et al. 2016).

OCPs extraction in water was carried out using liquid-liquid extraction (LLE) method. For the samples, 50 ml of 0.2 M potassium dihydrogen phosphate (buffer) solution was added into a separating funnel containing 2 l of water in order to extract the organic layer from the sample. To neutralise the sample in the funnel, a mixture of 0.1 M HCl and 0.1 N sodium hydroxide was added. Sodium chloride (100 g) was then added to salt out pesticides from the aqueous phase. As pressure was slowly released, 60 ml of triple-distilled DCM was added and shaken for 2 min. This sample was allowed to settle for 30 min, until phase

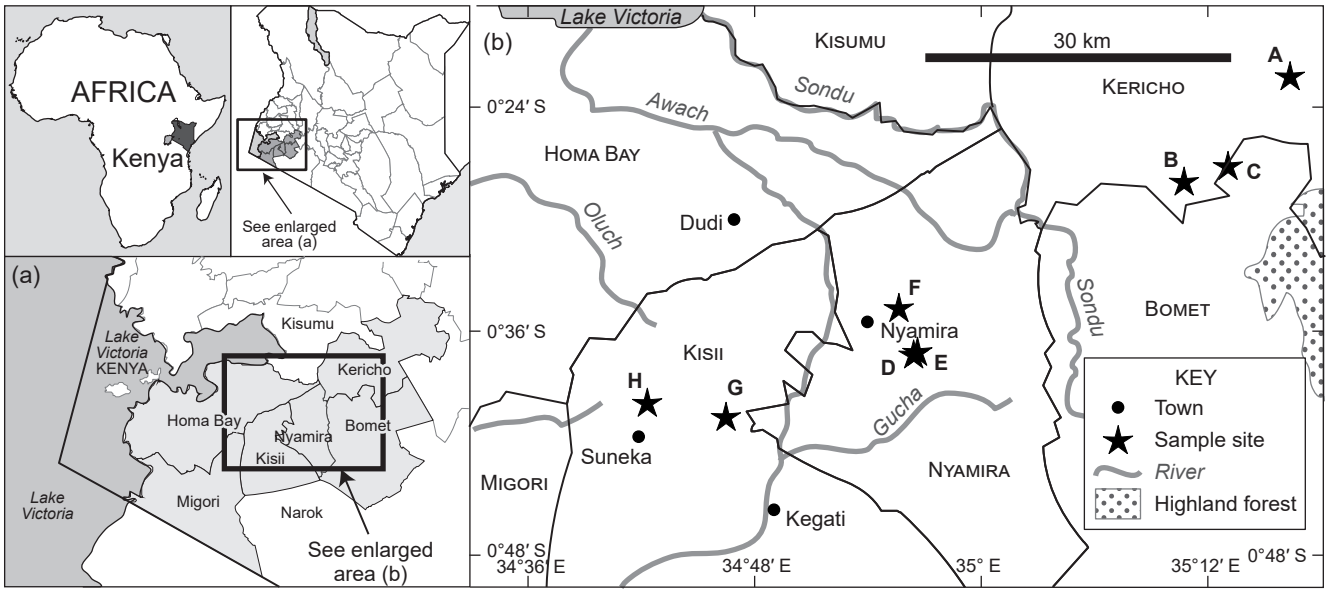

Figure 1: Map of the upper Kuja River catchment in south-western Kenya, indicating the sampling sites in this study (labelled A–H)

separation of the organic layer was achieved. Next, 60 ml of DCM was applied twice in the extraction of the organic layer and drained into a 250-ml Erlenmeyer flask. A chromatographic column of Al_2O_3 containing anhydrous Na_2SO_4 was used in cleaning the extract of the combined mixture which had been kept at 4 °C. In addition, external calibration was employed to determine the amount of unknown DDT residue concentrations; 175 ml samples of *n*-hexane mixed with HPLC-grade isooctane were run to sequentially elute the residues, which were then concentrated to 1 ml each by use of a rotary evaporator at 40 °C, and finally reconstituted to 0.5 ml for gas chromatography.

Quality control and quality assurance of the data handling and analysis involved composite water sampling in three replicates from downstream to upstream (with the water samples temporarily kept in a cooler box). For accuracy and study of the recovery rate, 2 l of spiked distilled water samples with a known amount of pesticide mixture standard was prepared and then concentrated to 0.1 µm l^{-1}. The detection limit of each DDT residue was obtained using known external standards (Dr Ehrenstorfer GmbH, Ausburg, Germany), as well as distilled water as blanks. For determination of machine contamination after a known quantity of samples had been eluted, 0.5 ml of isooctane (Fisher Scientific, USA) was injected before reconstitution and for quality assurance.

Gas chromatographic analysis

Determination of residue levels of *p,p′*-DDT, *p,p′*-DDE and *p,p′*-DDD was carried out using a gas chromatograph, whereby final samples were analysed by an Agilent 6890N GC Model equipped with electron capture detector (GC-ECD) and an auto sampler (Agilent 7683 Series injector). The column and injector temperature was set to between 280–300 °C since it was open programming. The 30-mm DB-5 long column had a 0.25-µm film thickness and 0.25-mm internal diameter for sensitivity. At a constant flow rate of 1 ml min^{-1}, the extracted and cleaned-up liquid mixture sample of 1-µl volume was injected onto the mobile phase containing the inert helium gas whose stationary phase was monitored, while nitrogen gas was applied to improve column sensitivity of the volatile compound. Helium gas was used in the detector. There was no split ratio employed.

Data analysis

Statistical analyses were performed using GraphPad Prism version 5.03. Data normality was confirmed using the D'Agostino–Pearson omnibus K^2 test. Datasets were presented by graphing the means with standard error bars (±SEM). Paired *t*-tests were used in the determination of temporal statistical differences in the DDT residues between the wet and dry seasons, with $p \leq 0.05$ as statistically significant. In addition, repeated measures analysis of variance (ANOVA) with Tukey's *post hoc* method was used to test spatial distributions of the DDT residues between sites over a specified time. Correlation between the concentrations of the OCPs and the physicochemical parameters was assessed using Pearson's product-moment correlation coefficient test. Principal Component Analysis (PCA) was used to correlate the concentrations of *p,p′*-DDT, *p,p′*-DDD and *p,p′*-DDE across the eight sampling sites in the Kuja River catchment.

Results

The mean concentrations of *p,p′*-DDD, *p,p′*-DDE and *p,p′*-DDT residues in the surface water samples collected within the Kuja River catchment area in the wet and dry seasons from October 2016 to April 2017 are presented in Table 1. Only *p,p′*-DDD was below the detection limit (BDL) (at sites B and D), in both the dry and wet seasons, whereas *p,p′*-DDE and *p,p′*-DDT were detectable at all sampled sites. *p,p′*-DDT was detected in the widest range of concentrations (0.0375–1.1113 µg l^{-1}, in the

wet season), and *p,p′*-DDD in the narrowest range (BDL–0.327 µg l^{-1}, in the wet season) (Table 1). The residue with the widest range of concentrations was *p,p′*-DDT (0.0634–2.0071 µg l^{-1}), detected at sites A and H, in the dry season. *p,p′*-DDE was detected in the lowest range of concentrations (0.0038–1.0654 µg l^{-1}) at sites B and H in the wet season. In the dry season, the concentration of *p,p′*-DDE ranged from 0.0302 and 0.8513 µg l^{-1} at sampling sites E and A, respectively (Table 1), and the concentration of *p,p′*-DDD ranged between BDL and 0.9823 µg l^{-1} (detected at sites B, D and E).

Across seasons and among all residues, the highest mean (±SE) concentration was for *p,p′*-DDT in the dry season (0.9669 ± 0.2994 µg l^{-1}), while the lowest mean concentration was for *p,p′*-DDD in the wet season (0.082 ± 0.0964 µg l^{-1}) (Figure 2). There were no significant differences among the detected concentrations of all three residues during the wet season (ANOVA: $p > 0.05$) (Figure 2a); whereas, only *p,p′*-DDT and *p,p′*-DDE were significantly different in the wet season ($p < 0.05$; Figure 2b). Mean concentrations for *p,p′*-DDD did not differ significantly from *p,p′*-DDE and *p,p′*-DDT concentrations in the wet season (ANOVA: $p > 0.05$). Paired *t*-tests of the mean concentrations showed no statistical significant difference between seasons for *p,p′*-DDT and its residues ($p > 0.05$). *P,p′*-DDT exhibited the highest overall concentration in the dry season (Figure 2b), and composed over 75% of the analysed OCPs, achieved from the sum total frequency of occurrence, at sites B, C and G in the wet season and at sites C, D, G and H in the dry season (Table 1).

Positive and negative Pearson's product-moment correlation coefficients were calculated between the water-quality parameters and *p,p*'-DDE, *p,p*'-DDD and *p,p*'-DDT concentrations in both the wet and dry seasons (Table 2). The strongest correlation (*r*) between *p,p′*-DDD and conductivity during the wet season was statistically significant ($r = 0.757$; $p = 0.029$); however, the remaining positive correlations during the wet season were not statistically significant ($p > 0.05$). Other strongly correlated relationships in the wet season exist for *p,p′*-DDD and total phosphorus (TP) ($r = 0.481$; $p = 0.228$) and *p,p′*-DDE and pH ($r = 0.516$; $p = 0.190$). The weakest positive correlation was between *p,p′*-DDT and conductivity ($r = 0.017$; $p = 0.968$). The strongest statistically significant positive correlations in the dry season were between *p,p′*-DDE and pH ($r = 0.749$; $p = 0.032$), followed by *p,p′*-DDT and DO ($r = 0.724$; $p = 0.043$). The weakest positive correlation was between *p,p′*-DDT and conductivity ($r = 0.025$; $p = 0.952$).

Table 1: Mean concentrations (µg l^{-1}) of *p,p*'-DDE, *p,p*'-DDD and *p,p*'-DDT detected in surface waters along the upper Kuja River, Kenya, in the wet and dry seasons (sampled from October 2016 to April 2017). See Figure 1 for locations of the sampling sites. *p,p′*-DDE = dichlorodiphenyldichloroethylene; *p,p′*-DDD = dichlorodiphenyldichloroethane; *p,p′*-DDT = dichlorodiphenyltrichloroethane; BDL = below detection limit

Sampling site	Wet season (µg l^{-1})			Dry season (µg l^{-1})		
	p,p′-DDE	*p,p′*-DDD	*p,p′*-DDT	*p,p′*-DDE	*p,p′*-DDD	*p,p′*-DDT
A	0.0053 ± 0.0001	0.3270 ± 0.005	0.1123 ± 0.050	0.8513 ± 0.230	0.6456 ± 0.011	0.0634 ± 0.004
B	0.0039 ± 0.034	BDL	0.0609 ± 0.005	0.1009 ± 0.020	BDL	0.0842 ± 0.012
C	0.0073 ± 0.0005	0.0007 ± 0.0002	0.8947 ± 0.201	0.0634 ± 0.003	0.0011 ± 0.0001	1.0776 ± 0.351
D	0.8406 ± 0.035	BDL	0.0375 ± 0.005	0.0578 ± 0.002	BDL	1.7515 ± 0.012
E	0.8248 ± 0.005	0.0481 ± 0.013	1.1113 ± 0.505	0.0302 ± 0.003	0.9823 ± 0.312	1.0215 ± 0.001
F	0.8946 ± 0.010	0.0589 ± 0.023	0.0546 ± 0.015	0.1350 ± 0.031	0.0934 ± 0.004	0.1124 ± 0.002
G	0.0283 ± 0.002	0.0254 ± 0.002	0.8912 ± 0.105	0.0987 ± 0.014	0.1218 ± 0.050	1.6174 ± 0.204
H	1.0654 ± 0.313	0.0275 ± 0.013	0.2433 ± 0.002	0.1154 ± 0.002	0.5197 ± 0.054	2.0071 ± 0.505

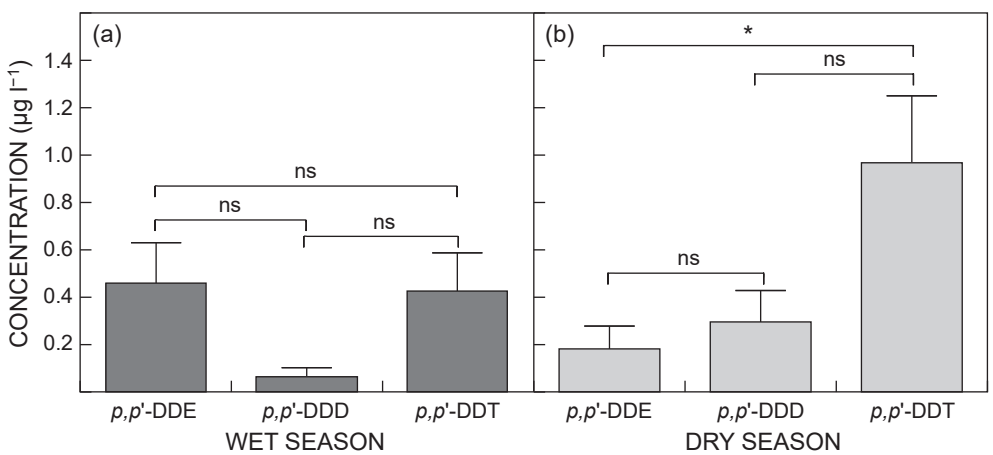

Figure 2: Concentrations of residues of *p,p*'-DDT and its metabolites, *p,p*'-DDD and *p,p*'-DDE, along the upper Kuja River, south-western Kenya, with comparison between the wet and dry seasons. Bars represent mean ± SEM; ns = not statistically significant; $p \leq 0.05$

Table 2: Correlation between the detected *p,p*'-DDE, *p,p*'-DDD and *p,p*'-DDT, and physicochemical parameters at the sampling sites in the upper Kuja River in south-western Kenya during the wet and dry seasons (sampled from October 2016 to April 2017). Bold font signifies significance as determined by a Pearson correlation test; *r* represents the Pearson's product-moment correlation coefficient (−1.0 to ≤1.0). *p,p'*-DDE = dichlorodiphenyldichloroethylene; *p,p'*-DDD = dichlorodiphenyldichloroethane; *p,p'*-DDT= dichlorodiphenyltrichloroethane

		Temp. (°C)	Conductivity	TSS (mg l^{-1})	DO	pH	Turbidity (NTU)	Total P (mg l^{-1})	Total N (mg l^{-1})
Wet season									
p,p'-DDE	*r*	−0.026	−0.272	0.185	0.116	0.516	0.255	0.281	−0.365
	p-value	0.950	0.515	0.661	0.784	0.190	0.542	0.501	0.374
p,p'-DDD	*r*	−0.614	0.757	−0.082	0.162	−0.207	0.368	0.481	0.288
	p-value	0.105	**0.029**	0.847	0.701	0.622	0.369	0.228	0.489
p,p'-DDT	*r*	0.279	0.017	0.173	−0.123	−0.092	0.018	−0.175	−0.252
	p-value	0.504	0.968	0.683	0.772	0.828	0.967	0.679	0.548
Dry season									
p,p'-DDE	*r*	0.120	0.161	0.127	−0.193	0.749	−0.068	0.405	0.303
	p-value	0.776	0.704	0.765	0.647	**0.032**	0.872	0.319	0.466
p,p'-DDD	*r*	−0.045	0.211	−0.582	−0.249	−0.014	−0.232	−0.165	−0.151
	p-value	0.915	0.616	0.131	0.553	0.974	0.579	0.696	0.722
p,p'-DDT	*r*	−0.311	0.025	−0.623	0.724	−0.118	−0.667	−0.779	0.205
	p-value	0.454	0.952	0.099	**0.043**	0.782	0.071	**0.022**	0.626

The overall strongest negative Pearson's product-moment correlation was observed between *p,p*'-DDT and TP during the dry season (r = −0.779; p = 0.022). The strongest negative correlation in the wet season was between *p,p*'-DDD and water temperature (r = −0.614; p = 0.105), whilst the weakest negative correlation was between *p,p*'-DDE and water temperature (r = −0.026; p = 0.950). During the dry season, the weakest negative correlations was observed for *p,p*'-DDD and pH (r = −0.014; p = 0.974).

In the dry season, sites B and F were closely correlated, likewise sites C, D and G were also closely correlated with *p,p*'-DDT (Figure 3), probably because of homogeneity of the areas and similar climate conditions during the study period. In the dry season, sites B and E were closely correlated with each other, while sites C and G were closely correlated with *p,p*'-DDT.

Discussion

Residues of *p,p*'-DDE, *p,p*'-DDD and *p,p*'-DDT in catchment of the upper Kuja River in both the wet and dry seasons were assessed. The mean concentrations of *p,p'*-DDT were slightly below the maximum acceptable concentrations of pesticide residues in natural waters (2.0 µg l^{-1}) according to the guidelines of the World Health Organization (WHO 2008), but above the maximum threshold (0.2 µg l^{-1}) established by the United States Environmental Protection Agency (EPA) (US-EPA 2004), as well as Australia's acceptable threshold (IUPAC 2010). The *p,p'*-DDT concentration were below the maximum acceptable concentrations for the discharge of the organic contaminant into natural waters (1.5 mg l^{-1}) as established by Kenya's National Environment Management Authority (NEMA Kenya 2006). Unlike the results of our study, Njogu et al. (2010) reported relatively higher mean concentrations of *p,p'*-DDD (range: BDL–6.691 µg l^{-1}) and *p,p'*-DDE (range: BDL–27.153 µg l^{-1}) than *p,p'*-DDT (range: BDL–3.082 µg l^{-1}) in waters of Lake Naivasha in Nakuru County (Kenya). This difference of concentrations between DDT and its metabolites could be attributed to high levels of human activities such as horticultural and growing cash crops in the catchments. An investigation of the persistence of pesticides in a large freshwater lake in India described how conditions of high deposition of pesticides accompanied by low dissipation in natural waters may inhibit microbial activity, in turn facilitating high decomposition in bottom sediments leading to anaerobic conditions in lacustrine habitats and riverine ecosystems, generating deoxygenated waters and high levels of hydrogen sulphide, carbon dioxide and methane (Amaraneni 2002). Furthermore, Abong'o et al. (2015) reported concentrations of *p,p'*-DDD in the River Nyando catchment to be below WHO/FAO threshold of 2.0 µg l^{-1} (IUPAC 2010) of global standards in natural waters. In regard to public health drinking water requirements, the mean OCP residue level results in the sampled stream and river surface waters were observed to be generally within global acceptable thresholds, possibly due to duration of use.

Exposure to pesticide residues over a given timeline has a cumulative effect on human health (including chronic common cough, colds, cancer of the kidney, skin, eyes and prostate glands) (Abong'o et al. 2015). The spatial distribution of the detected OCP residues was wider and the concentrations higher in the dry season than in the wet season, although not statistically significantly. For instance, *p,p*'-DDT observed in this study in the dry season was 1.013 µg l^{-1}. Owing to the lipophilic nature of *p,p*'-DDT (and its metabolites), the residues distribute between the organic matter and bottom sediments and, in the dry season, the OCP concentration increases owing to less water volume and higher relative resuspension of sediment particles in the water column, the bottom sediments act as a pollutant sink resulting in the observed differences in detectable concentrations across seasons in our study area (PCPB

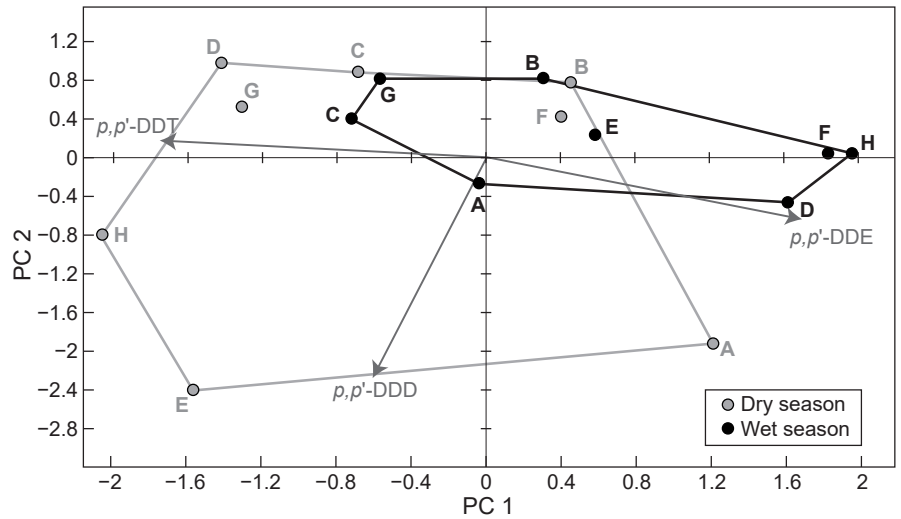

Figure 3: Principal components analysis scatterplot diagram indicating correlation between concentrations of residues of *p,p'*-DDT, *p,p'*-DDD and *p,p'*-DDE in the Kuja River catchment in south-western Kenya, between sites A–H for the study period October 2016–April 2017

2012a; Musa et al. 2011). The observed higher occurrence of *p,p'*-DDT could be attributable to more recent use of the main compound in the study area (Wandiga et al. 2003), whereas lower *p,p'*-DDE and *p,p'*-DDD concentrations could be attributable to applications of *p,p'*-DDT before it was banned, hence the dissipation and breakdown of the main chemical into metabolites in the environment (Abong'o et al. 2015). Additionally, semi-intensive agricultural practices and commercial cash-crop farming in the study area could be a major source of the metabolite residues observed. Importantly, our results reveal that DDT and its metabolites persist in Kenya's aquatic environment despite the pesticide having been banned for decades, other than for limited use in disease vector control (PCPB 2010, 2012b).

In this study, strong correlations were observed in the dry season compared with the wet season, probably as a result of variations in water quality. This could be attributed to water quality parameter changes that may occur as a result of reduced runoffs, hence low water mixing is experienced in the dry season. Water mixing in natural waters is essential for equal dissolved oxygen distribution and is a deterrent to stratification in the water column. Three significant correlations were noted in the dry season, while only one was observed in the wet season. Research has demonstrated the effect of environmental factors on biodegradation and bioaccumulation of given pesticides in different matrices (Osoro et al. 2016). Furthermore, pesticides may attach themselves to organic matter, such as suspended solids in the water column, whereby the availability of active ingredients that support decomposition (such as DO) may dictate their duration in target areas (Nyaundi et al. 2019). In addition, favourable water-quality parameters (especially temperature) and the agricultural use of organic and inorganic manure can increase pesticide residence in given sites (Jayasiri et al. 2022). The principal component analysis scatter diagram (Figure 3) indicates identifiable correlations between the sample sites and detected OCP residues.

Conclusions

This study provides evidence that DDT and its metabolites persist in natural surface water in first-order streams and rivers of the upper Kuja River in Kenya despite the pesticide having been banned for decades. Levels of the residues in the dry season, especially *p,p'*-DDT, were slightly higher than in the wet season due to reduced water levels and increased stratification in the water column. Even though the results presented here revealed that concentrations of the DDT residues were beneath thresholds set by the WHO (2001) and NEMA Kenya (2006), the residue levels in the study area suggest previous application of DDT, a widely banned organochlorine pesticide, which presents a threat to both human and animal health and the environment.

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