RESEARCH ARTICLE

CrossMark

Organochlorine pesticide residues in sediment and water from Nairobi River, Kenya: levels, distribution, and ecological risk assessment

Elizabeth N. Ndunda [1,2] · Vincent O. Madadi [1] · Shem O. Wandiga [1]

Abstract
Production and use of most organochlorine pesticides (OCPs) was banned through the Stockholm Convention on persistent organic pollutants. However, appreciable amounts are still detected in the environment due to their persistence, illegal use, and releases from contaminated soils and obsolete stocks. The present study investigated the levels of OCP residues in Nairobi River. Sediment and water samples were collected from three sites along the river and screened for 17 OCPs using gas chromatography electron capture detector (GC-ECD). Mean pesticide residues ranged from 0.01 to 41.9 µg kg^{-1} in sediment and below detection limit to 39.7 ng L^{-1} in water. In sediment α-HCH, β-HCH, γ-HCH, heptachlor epoxide, and p,p'-DDD were detected in all samples, while α-HCH, γ-HCH, δ-HCH, heptachlor epoxide, endosulfan I, and endrin were detected in all water samples. Levels of OCPs in water were below the WHO maximum allowable limits for surface water. However, values higher than the sediment quality guidelines for sediment samples in Racecourse Road Bridge and Outering Road Bridge were reported, thus confirming the toxicity to aquatic organisms. Consequently, as these compounds are known to bio-accumulate in fatty tissues, continued use of the river water poses a health risk to animals and humans.

Keywords Nairobi River · Organochlorine pesticides · Persistent organic pollutants · Gas chromatography electron capture detector · Residues

Introduction

Pesticides use in Kenya spans over 10 decades. Sodium arsenate was the first pesticide to be introduced for tick control in 1912, followed by organochlorine pesticides (OCPs) such as technical HCH in 1949, toxaphene in 1950, DDT in 1956, and dieldrin in 1961 (Wandiga 2001). Consequently, use of OCPs resulted in to environmental contamination, with the earliest work by Williams et al. (1997) on OCPs in inshore sediments and waters from Mombasa reporting levels up to 460 µg kg^{-1} dry weight for DDT and less than 100 µg kg^{-1} for the other

pesticides. Later, Everaarts et al. (1998) reported levels ranging from bdl to 2.6 µg kg^{-1} dry weight of the investigated pesticides in sediments along the Kenyan coast. Similar works reported OCP residues in the range of 0.5–9.0 ng L^{-1} in water and 0.6–59 µg kg^{-1} in sediments along the Indian ocean (Wandiga et al. 2002), 25–484 ng L^{-1} in water from Tana river, and 18.0–58.0 ng L^{-1} and bdl–108.5 µg kg^{-1} in water and sediments, respectively from Sabaki River (Lalah et al. 2003). A separate study carried out in Lake Victoria also detected OCPs in the range of bdl–360 ng L^{-1} and bdl–69.6 µg kg^{-1} in water and sediment, respectively (Wandiga and Madadi 2009) and 1.0 × 10^3–1.24 × 10^6 ng L^{-1} in water from River Nyando basin (Getenga et al. 2004). These reports are a clear evidence of the trail of contamination left behind through the use of OCPs.

Since 2004, due to evidence of adverse health effects, coupled with properties of long-range transport, persistence, and bioaccumulation, a global action to ban the production and use of most OCPs took place through the adoption of the Stockholm convention on persistent organic pollutants (POPs) (UNEP 2004). As a result, most of the OCPs are no longer in use while others are restricted for use. Despite these efforts, appreciable amounts continue to be detected in the

Responsible editor: Ester Heath

✉ Elizabeth N. Ndunda
elizabeth.ndunda@mksu.ac.ke

1 Department of Chemistry, School of Physical Sciences, University of Nairobi, P.O. Box 30197-00100, Nairobi, Kenya

2 Department of Physical Sciences, School of Pure and Applied Sciences, Machakos University, P.O. Box 136-90100, Machakos, Kenya

environment due to their persistence, illegal use, and releases from obsolete stocks. There is therefore a great need for continued monitoring of these compounds to track the progress toward their complete elimination from the environment, which also provides a mechanism for detecting any illegal use.

Monitoring of these compounds in urban aquatic environments is of particular importance because these waters are exposed to all kinds of pollutants. One important aquatic system, which has received minimal attention as far as monitoring of OCPs is concerned, is the Nairobi River, which passes through Nairobi, the capital city of Kenya. In the last five decades, rapid urbanization and industrialization of the city without proper environmental pollution controls have disrupted the river ecology through discharge of municipal and industrial effluents, storm water, and agricultural runoff (Kithiia and Wambua 2010; Muniafu and Otiato 2010; Mwinyihija 2012; Wang et al. 2012). So far, past studies on the extent of contamination have focused on physico-chemical parameters and heavy metals (Dulo 2008; Karanja et al. 2010; Musyoki et al. 2013; Mutune et al. 2014), with no reports on levels of contamination with OCPs. Therefore, the present study contributes to knowledge on state of contamination of the river with OCPs and serves as a guide in policy formulation toward restoration of the river.

Materials and methods

Chemicals and reagents

Dichloromethane (DCM), *n*-hexane, acetone, analytical grade anhydrous sodium sulfate, copper powder, disodium hydrogen phosphate, aluminum oxide 90 (70–230 mesh, Merck), and hydrochloric acid were purchased from Scielab Chemical Suppliers, Nairobi. HPLC grade isooctane and methanol were purchased from Fischer Scientific Kenya Ltd. Sodium sulfate was purified by baking at 200 °C for 12 h, while alumina was activated for 12 h at 200 °C followed by deactivation with 8% HPLC water.

Collection of water and sediment samples

Sampling was done over a period of 6 months, i.e., from February to July 2009 to capture two major seasons experienced in Nairobi (i.e., the dry season from December to February and wet season from March to May). Three sites were chosen to cover the river profile and included: James Gichuru Bridge—upstream (01°16′02 S, 036°46′29 E), Racecourse Road Bridge—midstream (01°16′58 S, 036°50′01 E), and Outering Road Bridge—downstream (01°15′52 S, 036°52′46 E) (Fig. 1). A total of 54 sediments and 54 water samples were collected for analysis. Water was collected by grab method into 2.5 L amber glass bottles, while sediments were collected using a stainless steel shovel from three different spots within a radius of 2 m around the sampling site and homogenized on an aluminum foil. A representative sample of 500 g was wrapped using aluminum foil and put in a zip lock sealing bag, then transported to the laboratory in Colman cooler boxes containing ice cubes. Sediment samples were stored in a freezer at − 20 °C and water samples in a refrigerator at 4 °C.

Extraction of OCPs from the samples

Water was extracted by liquid-liquid partitioning using DCM. One liter was transferred into a 2-L separatory funnel and spiked with 100 ng of PCB 155 as a recovery standard. The pH of the water was adjusted to 7, when applicable, using a phosphate buffer. Hundred grams of NaCl was added to salt out organic compounds into organic phase then 60 mL of DCM was added and the mixture was shaken thoroughly with continuous venting to release excess pressure. The organic phase was collected in Erlenmeyer flask and extraction was repeated twice with 60-mL portions of DCM. The combined extracts were dried using anhydrous Na_2SO_4 and 2 mL isooctane was added to the extract as a keeper, after which the extract was reduced to approximately 1 mL using LABCONCO rotary evaporator.

For sediments, frozen samples were removed from the freezer and allowed to thaw overnight. Twenty grams was weighed in triplicates, and each portion was mixed with 60 g of anhydrous Na_2SO_4, then ground in a mortar and pestle so as to homogenize. The dried samples were transferred into Soxhlet thimbles, and spiked with 100 μL of PCB 155 as a recovery standard. Extraction was carried out using 130 mL of *n*-hexane: acetone (3:1 *v/v*) for 16 h, after which 2 mL of isooctane was added as a keeper and the extract concentrated to 1 mL.

Clean up of extracts and sulfur removal

Extracts were cleaned by eluting through a chromatographic column packed with 15 g of deactivated aluminum oxide and eluted with 167 mL of *n*-hexane. Two milliliters of isooctane was added to the hexane and reduced to 1 mL. Sediment extracts were taken through an additional step of sulfur removal using copper. Before use, copper was activated using dilute hydrochloric acid (1:3), rinsed three times with methanol, dried and stored in an airtight glass vial. Approximately 250 mg of activated copper powder was added to the 1-mL extract and allowed to equilibrate until all the sulfur had reacted with copper as confirmed by the formation of black copper sulfide. To remove the copper sulfide, the extract was passed through anhydrous Na_2SO_4 packed in Pasteur pipette, and the eluate reduced to 1 mL then transferred into 1.5-mL autosampler vials. All the extracts were further reduced to 500 μL under a
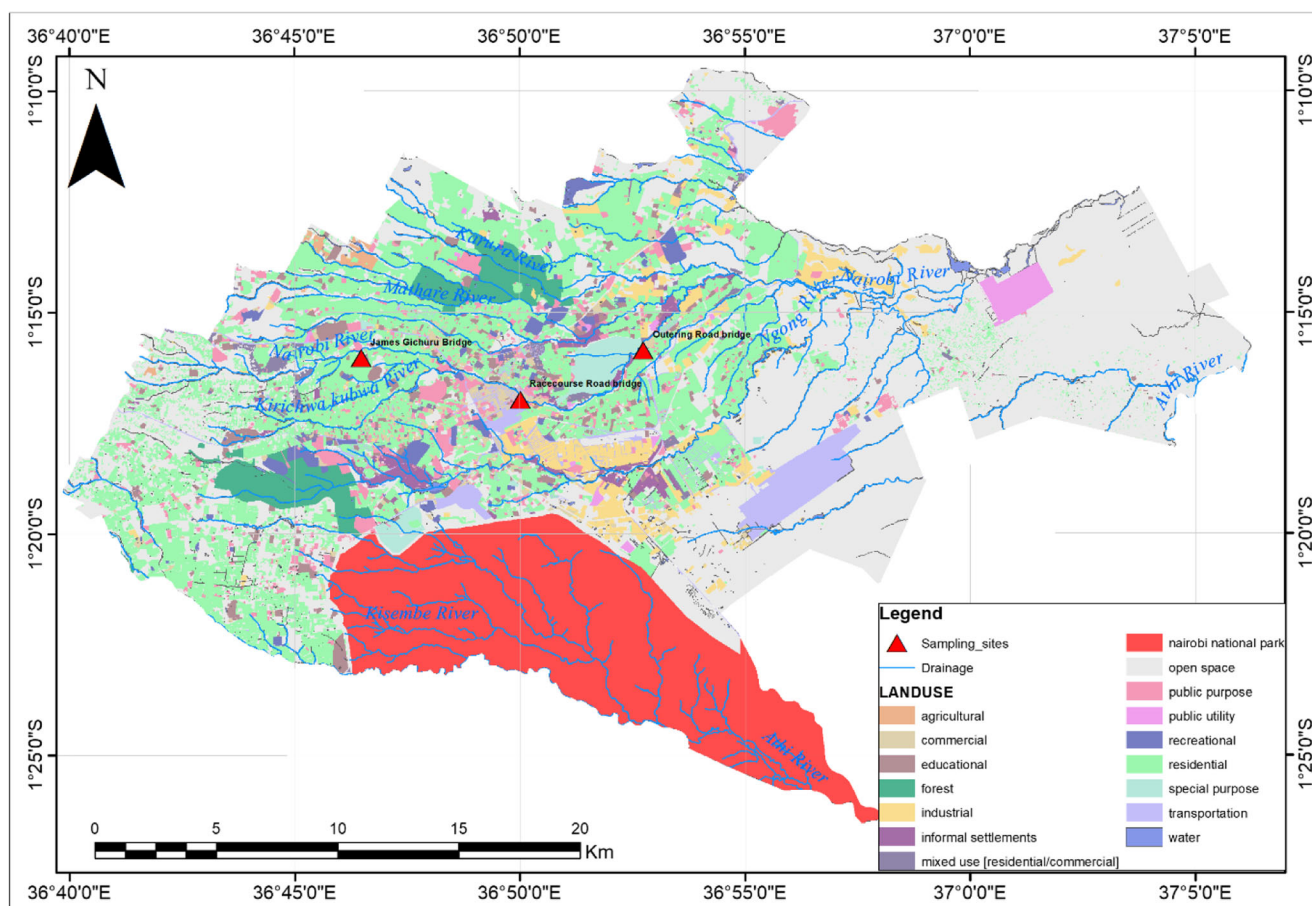
Fig. 1 Map of the study area showing the three sampling sites along Nairobi River, i.e., James Gichuru Bridge, Racecourse Road Bridge and Outering Road Bridge

gentle stream of white spot nitrogen. Finally, 100 ng of PCB 198 was added to each extract in the autosampler vial as syringe standard before GC-ECD analysis.

Quality assurance and quality control

Quality control measures taken included the following: matrix spike with a surrogate recovery standard prior to extraction to check extraction efficiency, analysis of replicate samples, and use of field blanks. Field blanks consisted of distilled water and anhydrous Na_2SO_4 which were carried along during every field trip. They were subjected to the entire analytical procedure as the samples. PCB 155 was used as surrogate standard, whereas PCB 198 was used as the syringe standard to monitor the sensitivity and fluctuations of the ECD detector.

Quantification of OCPs

Analysis of sample extracts and standards was performed using Varian CP 3800 gas chromatograph equipped with electron capture detector (ECD) and fitted with BPX 5 capillary column of dimensions 30 m × 0.25 mm i.d × 0.25-μm film

thickness and confirmatory test done using a second column of different polarity BPX 50 of dimensions 60 m × 0.25 mm × 0.25 μm from SGE Analytical Sciences.

Helium (99.9995% purity) and white spot nitrogen from BOC Kenya Ltd. were used as the carrier and the make-up gas, respectively. The oven temperature was initially set at 90 °C (hold time 3 min), ramped from 90 °C to 190 °C at 8 °C min^{-1} (hold time 10 min), ramped from 190 °C to 220 °C at 4 °C min^{-1} (hold time 10 min), and finally ramped from 220 °C to 275 °C at 5 °C min^{-1} (hold time 16 min). A constant carrier gas flow rate of 1.0 mL min^{-1} was maintained throughout the temperature program while the injector and detector temperatures were set at 250 °C and 300 °C, respectively. Injection volume of 1 μL was used for both the samples and standards following a splitless injection mode. Identification of the compounds was achieved by comparing the retention times of the samples with those of the individual organochlorine pesticides standards, while quantitative analysis was based on multilevel calibration curves prepared by plotting normalized peak areas against the concentrations of respective pesticide standards; resulting into curves with correlation coefficients (r^2) greater than 0.998 (Table 1).

Table 1 Analytical figures of merit

Pesticide	Linearity (R^2)	LOD (pg)	LOQ (pg)	Accuracy (%)		Sensitivity (%)	Precision (%)	Confirmatory studies of OCP levels using a second column
				Water	Sediments			
α-HCH	0.9980	2.1	6.9	70.5	73.1	4.2	1.7	0.3 ± 0.0
β-HCH	0.9983	1.0	3.3	83.2	74.2	5.5	0.5	2.6 ± 1.0
γ-HCH	0.9998	1.2	4.0	77.2	75.4	9.3	2.7	0.4 ± 0.2
δ-HCH	0.9983	1.4	4.6	82.1	72.2	5.0	3.1	0.2 ± 0.1
Heptachlor	0.9986	1.6	5.3	70.3	70.1	10.0	2.2	1.4 ± 1.2
Heptachlor epoxide	0.9980	2.0	6.6	70.9	74.6	8.6	4.3	0.7 ± 0.2
Aldrin	0.9995	2.2	7.3	69.7	71.4	2.3	0.6	0.2 ± 0.0
Dieldrin	0.9991	2.5	8.3	83.9	78.7	8.0	3.5	0.5 ± 0.1
Endrin	0.9996	3.1	10.2	84.6	79.1	5.5	0.8	12.1 ± 8.5
Endrin aldehyde	0.9980	1.6	5.3	70.2	79.2	2.5	2.5	2.6 ± 1.7
Endosulfan I	0.9983	1.8	5.9	75.5	70.1	3.6	1.5	0.4 ± 0.1
Endosulfan II	0.9991	2.0	6.6	77.9	77.9	4.8	2.1	0.2 ± 0.0
Endosulfan sulfate	0.9999	2.7	8.9	74.5	76.5	11.2	0.6	3.0 ± 0.1
p,p′-DDE	0.9987	2.9	9.6	72.6	73.3	8.1	2.1	8.3 ± 2.3
p,p′-DDD	0.9993	3.0	9.9	83.3	76.3	5.3	3.2	0.4 ± 0.2
p,p′-DDT	0.9995	2.8	9.2	79.1	79.1	8.2	1.2	0.3 ± 0.1
Methoxychlor	0.9957	2.5	8.3	80.1	74.9	5.2	2.1	0.2 ± 0.0

Results and discussion

Level of OCPs in sediment

Analysis of blank samples showed no peaks for the analytes of interest, thus eliminating any possibility of cross contamination from the field and glassware used. PCB 155 surrogate standard recoveries ranged from 69.7 to 84.6% for water and 70.1 to 79.2% for sediment (Table 1), which was within the recommended range of 70–120% (Webster et al. 2013). The limit of detection (LOD) ranged from 1.1 to 3.1 pg, and OCP levels below the LOD were reported as below detection limit (bdl), while limit of quantification (LOQ) ranged from 3.3 to 10.2 pg (Table 1). Precision expressed as relative standard deviation (RSD) was in the range of 0.5–4.3% (Table 1).

Sampling sites covered upstream, midstream, and downstream of the river so as to track any possible input of contaminants as the river flows along informal settlements, the central business district of Nairobi City, and numerous light industries downstream. Sediments were selected as matrices of interest for assessment since they acts as sinks for most hydrophobic organic contaminants, which strongly bind to the particulate matter owing to their high octanol-water partition coefficient (K_{ow}) (Hiller et al. 2011; Floehr et al. 2013). The 17 OCPs screened in sediment samples had concentrations range from bdl to 68.1 μg kg^{-1} (Table 2), with α-HCH, β-HCH, γ-HCH, heptachlor epoxide, and p,p′-DDD being most frequent with detection frequency of 100%. Endrin aldehyde recorded the

highest mean concentration of 41.9 ± 29.0 μg kg^{-1} followed by endrin, p,p′-DDE, and β-HCH.

Among the HCH isomers analyzed, β-HCH was the highest in all the sites, which was attributed to its high environmental stability and low volatility (Wu et al. 1997; Kinyamu et al. 1998). There is also a possibility of α-HCH and γ-HCH transforming to β-HCH isomer, therefore making it the most predominant contaminant (Willet and Ulrich 1998). A similar trend for β-HCH has also been reported by Doong et al. (2008) and Salem et al. (2013). The low levels of lindane (γ-HCH) were attributed to its restricted use, and transformation to β-HCH, with its presence also signifying past use of the pesticide. α-HCH gave the lowest concentration among the isomers probably due to its high vapor pressure and Henry's law constant and therefore readily lost through volatilization (Hong et al. 2003).

Among the DDT metabolites, p,p′-DDE recorded the highest concentration, which was attributed to its abundance and persistence in the environment (CCME 1999). The main contributors to ∑DDTs were p,p′-DDE and p,p′-DDD, where the same phenomenon was observed by Covaci et al. (2005). To ascertain whether the reported levels of DDT in the present study were due to current or past application, the ratio of p,p′-DDT to its metabolites, i.e., p,p′-DDE and p,p′-DDD was applied. A ratio greater than 0.5 is an indication of recent DDT application (Wasswa et al. 2011). In the present study, the ratio was 0.04, 0.16, and 0.10 for James Gichuru Bridge, Racecourse Road Bridge, and Outering Road Bridge,

Table 2 Range and mean concentration of OCP residues in sediment ($\mu g\ kg^{-1}$ dry weight); $n = 3$

Pesticide/sampling site	James Gichuru Bridge		Racecourse Road Bridge		Outering Road Bridge		Detection frequency %
	Range	Mean ± SD[a]	Range	Mean ± SD	Range	Mean ± SD	
α-HCH	0.1–0.9	0.2 ± 0.0	0.1–2.0	0.7 ± 0.2	0.1–0.5	0.2 ± 0.1	100
β-HCH	1.7–3.8	2.7 ± 1.0	0.7–10.0	8.3 ± 3.3	4.7–12.2	8.7 ± 2.6	100
γ-HCH	0.2–1.3	0.4 ± 0.2	0.2–2.5	1.0 ± 0.9	0.5–1.5	0.9 ± 0.5	100
δ-HCH	0.1–0.4	0.2 ± 0.1	bdl[b]–2.7	1.5 ± 0.4	0.1–1.2	0.4 ± 0.2	83
Heptachlor	bdl–2.9	1.4 ± 1.2	0.4–0.8	0.5 ± 0.3	bdl–2.6	1.3 ± 1.1	67
Heptachlor epoxide	0.4–0.9	0.7 ± 0.2	0.4–0.8	0.6 ± 0.2	0.5–1.1	0.7 ± 0.2	100
Aldrin	bdl–1.0	0.2 ± 0.0	bdl–0.4	0.2 ± 0.1	bdl–6.4	4.2 ± 2.6	50
Dieldrin	bdl–1.7	0.6 ± 0.2	bdl–1.0	0.5 ± 0.3	0.2–2.0	0.8 ± 0.7	67
Endrin	4.2–29.5	12.1 ± 9.4	bdl–34.7	21.1 ± 12.9	13.9–59.9	30.1 ± 16.7	83
Endrin aldehyde	bdl–4.8	2.6 ± 1.7	0.02–5.7	2.3 ± 1.6	0.3–68.1	41.9 ± 29.0	83
Endosulfan I	0.1–0.4	0.2 ± 0.1	bdl–1.2	0.4 ± 0.1	0.2–3.6	1.9 ± 1.3	83
Endosulfan II	bdl–0.1	0.01 ± 0.00	bdl–6.4	1.2 ± 0.5	1.3–6.2	2.8 ± 1.8	67
Endosulfan sulfate	bdl–6.8	2.0 ± 0.0	bdl–3.6	1.0 ± 0.6	bdl–11.4	6.3 ± 5.1	50
p,p'-DDE	4.5–11.2	8.3 ± 2.3	bdl–30.6	10.3 ± 5.2	9.9–65.3	27.3 ± 21.0	87
p,p'-DDD	0.1–1.4	0.4 ± 0.2	0.1–14.4	4.8 ± 1.7	0.1–14.4	4.6 ± 2.6	100
p,p'-DDT	bdl–0.7	0.3 ± 0.1	bdl–3.4	2.2 ± 1.7	bdl–6.1	3.1 ± 2.2	50
Methoxychlor	bdl–1.0	0.2 ± 0.0	bdl–0.3	0.10 ± 0.06	bdl–4.5	1.6 ± 0.7	50

[a] *SD*, standard deviation

[b] *bdl*, below detection limit

respectively suggesting that the recorded levels of p,p'-DDT were due to previous use of DDT rather than recent application.

Pesticide levels in sediments in the present study were within what has been reported before in Indian Ocean and Lake Victoria (Wandiga et al. 2002; Wandiga and Madadi 2009), but lower than reported levels in Tana River and Nyando drainage basins (Lalah et al. 2003; Getenga et al. 2004). Compared to other parts of the world, pesticide levels were comparable except for the highly polluted Tonghui River, Beijing (Table 3). Generally, it can be concluded that use of OCPs has declined considerably mainly due to the ban in usage, and subsequent shift to less persistent organophosphorus, carbamates, and pyrethoid pesticides.

To determine the ecotoxicological risks posed by OCPs on benthic organisms, we compared the level of OCPs in the present study against the commonly used sediment quality guidelines (SQGs), i.e., effect range-low (ERL) and effect range-median (ERM) (Long et al. 1995) as well as the threshold effect level (TEL) and the probable effect level (PEL) (CCME 1999). TEL and ERL represents the sediment contamination below which adverse effects on sediment-dwelling organisms are expected to rarely occur, while PEL and ERM represents the guideline concentration above which adverse effects are expected to occur frequently. These guidelines are based on chronic and long-term effects of contaminant concentrations on benthic organisms. Outering Road Bridge and

Racecourse Road Bridge had the maximum concentration of p,p'-DDE exceeding all the limits suggesting a high ecological risk to benthic organisms. For Endrin, Outering Road Bridge had the maximum concentration exceeding ERM suggesting probability for occurrence of adverse health effects. James Gichuru Bridge had values of the pesticides detected being lower than the available limits except for p,p'-DDE, which gave maximum concentration values exceeding PEL, ERL, and TEL (Fig. 2). The fact that the reported levels of some pesticide exceeded the available SQGs serves as a further proof that the water is not fit for any use since humans and animals are at a higher risk of exposure with subsequent adverse health effects.

Levels of OCPs in water

Pesticide levels in water ranged from bdl to 86.7 ng L^{-1} (Table 4) with heptachlor recording the highest mean concentration followed by β-HCH, aldrin, and heptachlor epoxide. OCPs are hydrophobic and have low water solubility, thus partition in sediment in aquatic systems and low concentrations are expected on the water column as was the case in the present study. The most frequent OCPs in water were α-HCH, γ-HCH, δ-HCH, heptachlor epoxide, endosulfan I, and endrin with detection frequency of 100%. p,p'-DDT and methoxychlor had levels below detection limit in all the sampling sites. While p,p'-DDT was not detected in water samples, its

Table 3 Levels of OCPs in surface sediment and water from different parts of the world

Region	Sediment (µg kg^{-1} dry wt)	Water (ng L^{-1})	Reference
Babitonga bay, Brazil	bdl–122 ($\sum$DDTs)[a]		Rizzi et al. ([2017])
Bizerte lagoon, Tunisia	1.1–14.0 ($\sum^4$OCPs)[b]		Barhoumi et al. ([2014])
Mediterranean Coast, Egypt	0.09–14.11[c]		Salem et al. ([2013])
Lake Victoria, Uganda	bdl–15.96[d]		Wasswa et al. ([2011])
Densu River basin, Ghana	bdl–10.98[e]	bdl–185	Kuranchie-Mensah et al. ([2012])
Gao-ping River, Taiwan	0.47–47.4 (Σ^{15}OCPs)[f]		Doong et al. ([2008])
Tonghui River, Beijing, China	1.79–13.98	134.9–3788 (Σ^{18}OCPs)[g]	Zhang et al. ([2003])
Scheldt River, Belgium	6.6–27.6 ($\sum$DDTs) [h]		Covaci et al. ([2005])

[a] $\sum$DDTs = DDT, DDE, and DDD

[b] Sum of HCB, *p,p'*-DDT, *p,p'*-DDE, *p,p*-DDD

[c] Mean of OCP pesticides analyzed, i.e., α-HCH, β-HCH, γ-HCH, δ-HCH, *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, aldrin, dieldrin, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide, methoxychlor, γ-chlordane, α-endosulfan, β-endosulfan, endosulfan sulfate. *bdl*, below detection limit

[d] OCPs analyzed are as follows: α-HCH, β-HCH, γ-HCH, *p,p'*-DDT, *o,p'*-DDT *p,p'*-DDD, *p,p'*-DDE, *o,p'*-DDE, aldrin, dieldrin, chlordane, α-endosulfan, β-endosulfan, endosulfan sulfate, heptachlor, heptachlor epoxide

[e] OCPs analyzed are as follows: γ-HCH, δ-HCH, heptachlor, aldrin, dieldrin, γ-chlordane, α-endosulfan, endosulfan sulfate, *p,p'*-DDT, *p,p'*-DDE, endrin, endrin aldehyde, endrin ketone, methoxychlor

[f] Sum of α-HCH, β-HCH, γ-HCH, δ-HCH, heptachlor, aldrin, dieldrin, endrin, endosulfan I, endosulfan II, endosulfan sulfate, *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, methoxychlor

[g] Sum of α-HCH, β-HCH, γ-HCH, δ-HCH, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin aldehyde, endrin ketone, *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, methoxychlor

[h] $\sum$DDTs = DDT, DDE, and DDD

metabolites were detected, suggesting contamination due to the past application regimes in the region. As was in the case for sediments, β-HCH was the most dominant of all the HCH isomers. OCP levels in the present study were compared to WHO set limits for drinking water, which are 1000 ng L^{-1} for DDT, 30 ng L^{-1} for aldrin and dieldrin (combined), 600 ng L^{-1} for endrin and 20,000 ng L^{-1} for methoxychlor (WHO [2011]). The mean values were all below the guideline values. However, this does not mean that the water is safe for

consumption and precaution on use of the water needs to be taken since the compounds are known to bio-accumulate in living organisms leading to adverse health effects.

Statistical analysis using SPSS revealed a significant negative correlation ($p < 0.01$, $r = -0.934$) between pesticide residues in sediments and water. This confirms the strong interaction between sediments and water where the sediments act as the secondary source of contaminants by releasing the bound OCPs into the water column under favorable
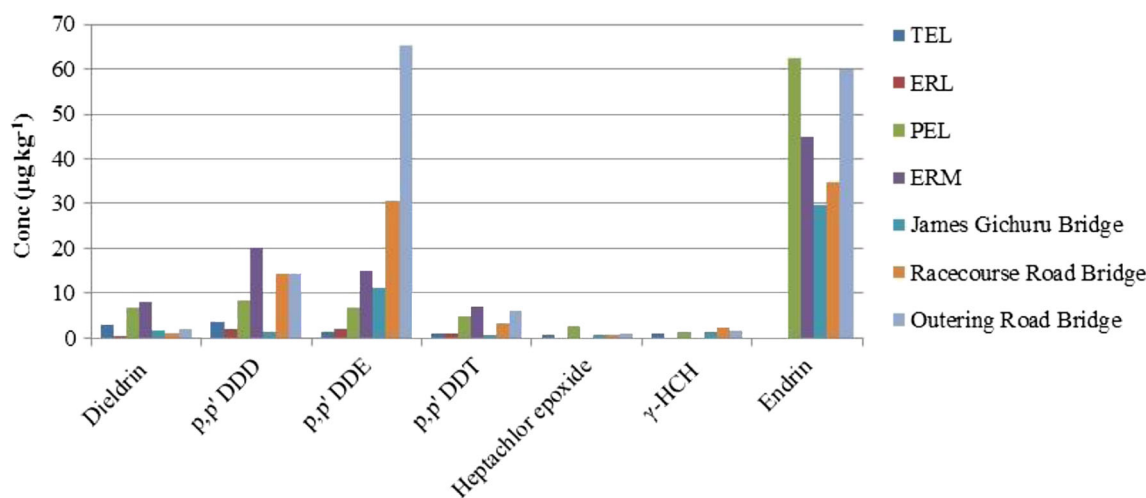

Fig. 2 OCP levels compared to TEL, ERL, PEL, ERM sediment quality guidelines

Table 4 Range and mean concentration of OCP residues in water (ng L^{-1}); $n = 3$

Pesticide/sampling site	James Gichuru Bridge		Racecourse Road Bridge		Outering Road Bridge		Detection frequency %
	Range	Mean ± SD[a]	Range	Mean ± SD	Range	Mean ± SD	
α-HCH	0.8–6.1	2.5 ± 2.1	0.6–4.0	1.5 ± 1.3	0.7–10.4	3.2 ± 1.1	100
β-HCH	bdl–18.9	10.5 ± 6.6	4.3–32.7	18.9 ± 11.5	4.3–86.7	24.9 ± 10.1	87
γ-HCH	1.4–4.6	2.3 ± 1.3	1.8–5.6	3.0 ± 1.45	2.4–33.8	10.3 ± 5.2	100
δ-HCH	0.7–5.9	2.9 ± 2.1	0.9–14.1	3.8 ± 2.1	1.4–12.3	4.8 ± 2.1	100
Heptachlor	bdl[b]	bdl	bdl–43.2	39.7 ± 24.5	bdl–28.8	7.7 ± 2.6	33
Heptachlor epoxide	3.7–10.3	5.6 ± 2.5	4.1–22.8	8.5 ± 3.9	4.1–12.8	6.7 ± 3.1	100
Aldrin	bdl–10.6	4.8 ± 0.4	bdl–69.8	15.3 ± 7.3	bdl–9.4	2.9 ± 1.5	50
Dieldrin	3.3–5.6	4.3 ± 1.0	bdl–7.5	3.6 ± 2.4	3.4–5.0	3.9 ± 0.8	87
Endrin	2.0–8.6	3.8 ± 2.6	2.8–17.9	7.0 ± 3.6	2.1–18.1	9.3 ± 6.6	100
Endrin aldehyde	0.13–0.16	0.1 ± 0.0	0.1–2.3	1.1 ± 0.9	bdl–8.6	2.9 ± 1.3	87
Endosulfan I	0.2–1.0	1.1 ± 0.2	0.9–2.1	1.3 ± 0.4	0.9–2.0	1.3 ± 0.5	100
Endosulfan II	bdl–23.0	3.8 ± 0.0	bdl	bdl	bdl–19.0	3.2 ± 1.7	33
Endosulfan sulfate	bdl–6.8	1.1 ± 0.0	bdl–8.2	3.4 ± 1.4	bdl–10.5	4.8 ± 2.3	50
p,p'-DDE	0.2–2.4	0.9 ± 0.0	0.2–9.9	2.3 ± 1.8	bdl–10.2	5.3 ± 3.9	87
p,p'-DDD	1.1–3.9	1.4 ± 0.5	0.9–1.7	1.1 ± 0.3	bdl–1.5	0.9 ± 0.5	87
p,p'-DDT	bdl	bdl	bdl	bdl	bdl	bdl	0
Methoxychlor	bdl	bdl	bdl	bdl	bdl	bdl	0

[a] *SD*, standard deviation

[b] *bdl*, below detection limit

conditions. Through this interaction between sediments and water, transfer of OCPs to organisms is facilitated qualifying it as a major route of exposure to organisms (Salem et al. 2013).

Spatial and seasonal variation of OCP levels

Outering Road Bridge, located downstream of the river, was the most contaminated of the three sites studied, which was attributed to cumulative effect of contaminants down the river, and may be additional input from agricultural activities taking place downstream of the river. The sampling period covered the dry and rain seasons experienced in Nairobi, whereby February, June, and July fall within the dry season while March, April, and May are within the long rains season. April and May which fall within the rainy season recorded the highest mean concentration OCPs in sediments, but declined in June and July which fall within the dry season (Fig. 3).

On the other hand, OCPs in water were highest during the months of February and March which marks the onset of rainy season, which was attributed to runoff from agricultural areas, as well as wet deposition (Fig. 4).

Fig. 3 Mean concentration of 17 OCPs in sediments across the sampling period
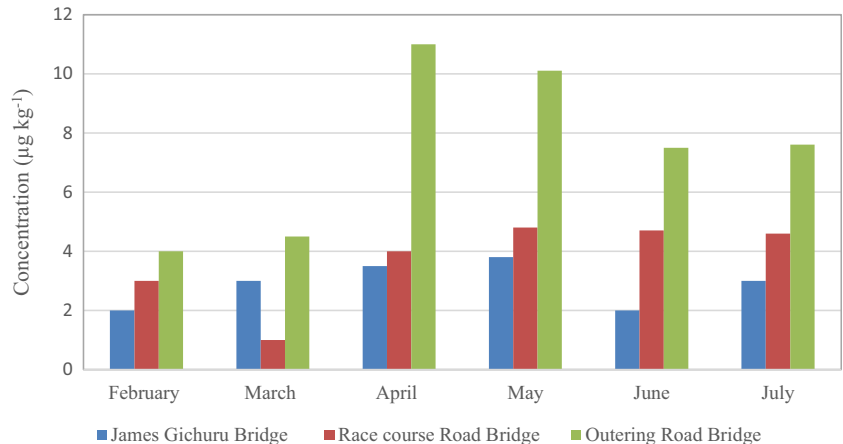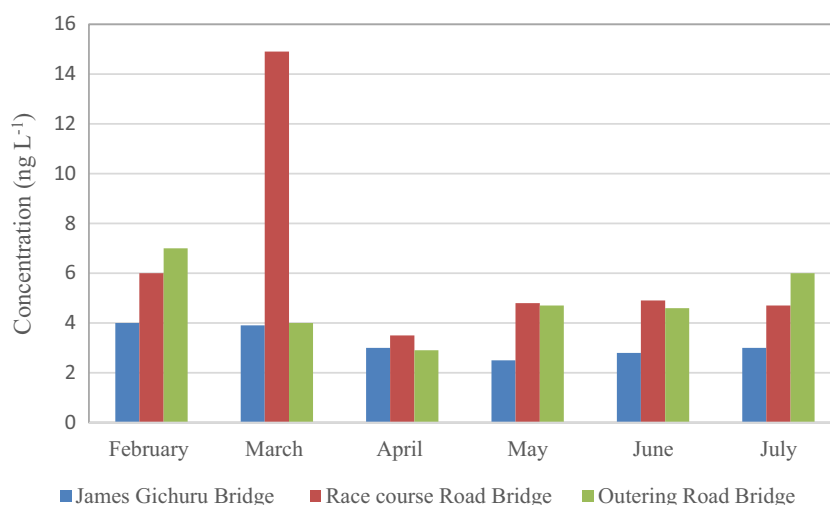
Fig. 4 Mean concentration of 17 OCPs in water across the sampling period

Conclusions

The present study forms a baseline data on contamination of Nairobi River with OCPs. Pesticide levels increased down the river, giving an impression that increasing human activities were contributing immensely to the pollution of the river. Ecotoxicological assessment using sediment quality guidelines showed levels of some pesticides exceeding what is recommended as safe for benthic organisms, meaning that continued pollution of the river may completely interfere with the river ecology.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

Barhoumi B, LeMenach K, Dévier M, El Y, Hammami B, Ameur WB, Hassine SB, Cachot J, Budzinski H, Driss MR (2014) Distribution and ecological risk of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in surface sediments from the Bizerte lagoon, Tunisia. Environ Sci Pollut Res 21:6290–6302

Canadian Council of Ministers of the Environment (CCME) (1999) Canadian soil quality guidelines for the protection of environmental and human health. CCME, Winnipeg

Covaci A, Gheorghe A, Voorspoels S, Maervoet J, Steen Redeker E, Blust R, Schepens P (2005) Polybrominated diphenyl ethers, polychlorinated biphenyls and organochlorine pesticides in sediment cores from the Western Scheldt river (Belgium): analytical aspects and depth profiles. Environ Int 31:367–375

Doong R, Lee S, Lee C, Sun Y, Wu S (2008) Characterization and composition of heavy metals and persistent organic pollutants in water and estuarine sediments from Gao-ping River, Taiwan. Mar Pollut Bull 57:846–857

Dulo SO (2008) Determination of some physico-chemical parameters of the Nairobi River, Kenya. J Appl Sci Environ Manag 12(1):57–62

Everaarts JM, Van Weerlee EM, Fischer CV, Hillebrand TJ (1998) Polychlorinated biphenyls and cyclic pesticides in sediments and macro-invertebrates from the coastal zone and continental slope of Kenya. Mar Pollut Bull 36(6):492–500

Floehr T, Xiao H, Scholz-Starke B, Wu L, Hou J, Yin D, Zhang X, Ji R, Yuan X, Ottermanns R, Roß-Nickoll N, Schäffer A, Hollert H (2013) Solution by dilution? A review on the pollution status of the Yangtze River. Environ Sci Pollut Res 20:6934–6971

Getenga ZM, Keng'ara FO, Wandiga SO (2004) Determination of organochlorine pesticides in soil and water from river Nyando Drainage System within Lake Victoria Basin, Kenya. Bull Environ Contam 72(2):335–343

Hiller E, Zemanová L, Sirotiak M, Jurkovič L (2011) Concentrations, distributions, and sources of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in bed sediments of the water reservoirs in Slovakia. Environ Monit Assess 173:883–897

Hong SH, Yim UH, Shim WJ, Oh JR, Lee ES (2003) Horizontal and vertical distribution of PCBs and chlorinated pesticides in sediments from Masan Bay, Korea. Mar Pollut Bull 46:244–253

Karanja N, Mutua KG, Ayuke F, Njenga M, Prain G, Kimenju J (2010) Dynamics of soil nematodes and earthworms in urban vegetable irrigated with wastewater in the Nairobi River basin, Kenya. Trop Subtrop Agroecosyst 12:521–530

Kinyamu JK, Kanja LW, Skaare JU, Maitho TE (1998) Organochlorine pesticides residues in milk of urban mothers in Kenya. Bull Environ Contam Toxicol 60:732–738

Kithiia MS, Wambua NB (2010) Temporal changes of sediment dynamics within the Nairobi River sub-basins between 1998–2006 time scale, Kenya. Land Reclam 42(1):17–22

Kuranchie-Mensah H, Atiemo SM, Palm LN, Blankson-Arthur S, Tutu AO, Fosu P (2012) Determination of organochlorine pesticide residue in sediment and water from the Densu river basin, Ghana. Chemosphere 86:286–292

Lalah JO, Yugi PO, Jumba IO, Wandiga SO (2003) Organochlorine pesticide residues in Tana and Sabaki Rivers in Kenya. Bull Environ Contam Toxicol 71:298–307

Long ER, Bin C, Smith SL, Calder FD (1995) Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ Manag 19(1):81–97

Muniafu M, Otiato E (2010) Solid Waste Management in Nairobi, Kenya. A case for emerging economies. J Lang Technol Enterpreneursh Africa 2(1):1998–1279

Musyoki MA, Suleiman AM, Mbithi NJ, Maingi MJ (2013) Water-borne bacterial pathogens in surface waters of Nairobi River and health implication on communities downstream Athi River. Int J Life Sci Pharma Res 3(1):1–10

Mutune AN, Makobe MA, Abukutsa-Onyango MOO (2014) Heavy metal content of selected African leafy vegetables planted in urban and peri-urban Nairobi, Kenya. Afr J Environ Sci Technol 8(1):66–74

Mwinyihija M (2012) Pollution control and remediation of the tanning effluent. The Open Environmental Pollution & Toxicology Journal 3:55–64

Rizzi J, Taniguchi S, Martins CC (2017) Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in sediments from an urban- and industrial-impacted subtropical estuary (Babitonga Bay, Brazil). Mar Pollut Bull 119:390–395. https://doi.org/10.1016/j.marpolbul.2017.03.032

Salem MS, Khaled A, Nemr AE (2013) Assessment of pesticides and polychlorinated biphenyls in sediments of the Egyptian Mediterranean coast. Egypt J Aquat Res 39:141–152

UNEP (2004) Stockholm convention on persistent organic pollutants (POPs). United Nations Environmental Programme: Geneva, Switzerland

Wandiga SO (2001) Use and distribution of organochlorine pesticides. The future in Africa. Pure Appl Chem 73(7):1147–1155

Wandiga SO, Madadi VO (2009) Water quality issues in East Africa. In: Ahuja S (ed) Handbook of water purity and quality. Academic Press Elsevier, London, pp 39–65

Wandiga SO, Yugi PO, Barasa MW, Jumba IO, Lalah JO (2002) The distribution of organochlorine pesticides in marine samples along the Indian Ocean coast of Kenya. Environ Technol 23(11):1235–1246

Wang H, Omosa BI, Keller AA, Li F (2012) Ecosystem protection, integrated management and infrastructure are vital for improving water quality in Africa. Environ Sci Technol 46:4699–4700

Wasswa J, Kiremire BT, Nkedi-Kizza T, Mbabazi J, Ssebugere P (2011) Organochlorine pesticides residues in sediments from the Uganda side of Lake Victoria. Chemosphere 82:130–136

Webster L, Roose P, Bersuder B, Kotterman M, Haarich M, Vorkamp K (2013) Determinations of polychlorinated biphenyls (PCBs) in sediments and biota. ICES Tech Mar Environ 53:1–19

Willet KL, Ulrich RA (1998) Differential toxicity and environmental fates of hexachlorocyclohexane isomers. Environ Sci Technol 32(15):2197–2207

Williams TM, Rees JG, Ferguson A, Herd RA, Kairu KK, Yobe AC (1997) Metals, petroleum hydrocarbons and organochlorines in inshore sediments and waters of Mombasa, Kenya. Mar Pollut Bull 34(7):570–577

World Health Organisation (WHO) (2011) Guidelines for drinking water quality, 4th Edition. Geneva, Switzerland: World Health Organization

Wu WZ, Xu Y, Schramm KW, Kettrup A (1997) A study of sorption, biodegradation and isomerization of HCH in stimulated sediment/water system. Chemosphere 35(9):1887–1894

Zhang Z, Huang J, Yu G, Hong H (2003) Occurrence of PAHs, PCBs and organochlorine pesticides in the Tonghui River of Beijing, China. Environ Pollut 130(2):249–261