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Distribution of organochlorine pesticides and polychlorinated biphenyls present in surface sediments of the Sabaki and Tana estuaries, Kenya

Veronica W. Wanjeri[1]*, Eric O. Okuku[1], Boaz O. Ohowa[1]

[1] Kenya Marine and Fisheries Research Institute, PO Box 81651, Mombasa, Kenya

* Corresponding author: wanjeriogolla@yahoo.com

Abstract

Polychlorinated biphenyls (PCBs) and Organochlorine pesticides (OCPs) in the surface sediments of the Sabaki and Tana estuaries were studied to determine distribution as well as their ecological risk. The concentration range of PCBs and OCPs were 0.65-9.29 ng/g dw and 0.47-9.84 ng/g dw, respectively. Sabaki Bridge in the Sabaki River and Tana 4 in the Tana River recorded high levels of both PCBs and OCPs. The calculated values of DDD+DDE/DDT showed that the presence of DDT from both the rivers is a result of historical input. The ecotoxicological impact of sediment pollution by PCBs and OCPs was assessed using sediment quality guidelines specified by the Canadian Council of Ministers of the Environment. The concentration values for PCB, HCB, Heptachlor epoxide, and Chlordane in this study indicate low ecological risk to sediment dwelling organisms. DDT showed an adverse biological effect to sediment dwelling organisms. As a result, there is a need to establish a programme for monitoring persistent organic pollutants in Kenya, so that any elevation in concentration above the environmental quality standards can be detected and appropriate actions taken to minimize potential adverse effects to the environment and public health.

Keywords: estuarine, ecotoxicological risk, surface sediments, polychlorinated biphenyls, organochlorine pesticides

Introduction

OCPs and PCBs are among the group of POPs which have been banned or restricted globally under the Stockholm Convention (UNDP, 2001). These environmental contaminants are of major concern on regional and global scales due to their long-range transportation, high lipophilicity, environmental persistence, and potential toxic biological effects to both humans and wildlife (Dierking *et al*. 2009; Barakat *et al*. 2013).

OCPs were extensively used in agriculture and for mosquito control for several decades (1940s through to 1960s). Even though many of these compounds were banned globally under the Stockholm Convention on POPs (UNDP, 2001), some developing countries continue to use them. Most of the pesticides are developed with the ability to have a wide spectrum of applications, but some are developed with the concept of target organism toxicity, even though quite often non-target species are also adversely affected under the latter conditions. Due to their high toxicity, slow degradation, and bioaccumulation, the use of OCPs can adversely affect environmental health and ecosystem services. Pesticides are reported to cause extinction, behavioral changes, loss of safe habitat, and population decline in several bird species. Their prolonged use has been shown to cause a drastic decrease in birds like the peregrine falcon, sparrow hawk, and bald eagle (Mitra *et al.,* 2011). They are also reported to affect many aquatic and terrestrial species such as microorganisms, invertebrates, plants, and fish (Jayaraj *et al.,* 2016).

PCBs are organochlorine compounds that have been widely deployed industrially in the past few decades in many different products. They have been used for instance as dielectric, coolant, and heat exchange

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fluids in electrical equipment such as transformers and capacitors. They have also been used as additives in pesticides, cutting oils, surface coatings, heat transfer fluids, hydraulic lubricants, sealants, carbonless copy paper, flame retardants, adhesives, and paints (Mohammed *et al.,* 2011; Kassegne *et al.,* 2020). PCBs are introduced into the environment through human activities. In particular, they are derived from the discharged waste of some chemical and electrical industries, mostly through leaks from industrial facilities, evaporation, and inappropriate disposal practices (Pazi *et al.,* 2011; Gakuba *et al.,* 2015; Kassegne *et al.,* 2020).

environments. Lalah *et al.* (2003) determined the concentrations of OCPs (e.g., DDT, DDE, DDD, endrin, lindane, endosulfan) residues in fish, water, and sediment samples from the Tana and Sabaki rivers, while Everaarts *et al*. (1996) reported the presence of low concentrations of OCPs and PCBs residues in sediments and macroinvertebrates from some sites along the Indian Ocean coast of Kenya. This study aimed to determine the distribution of persistent OCPs and PCBs in sediments from the Sabaki and Tana estuarine areas and identify their possible sources and probable environmental risks.

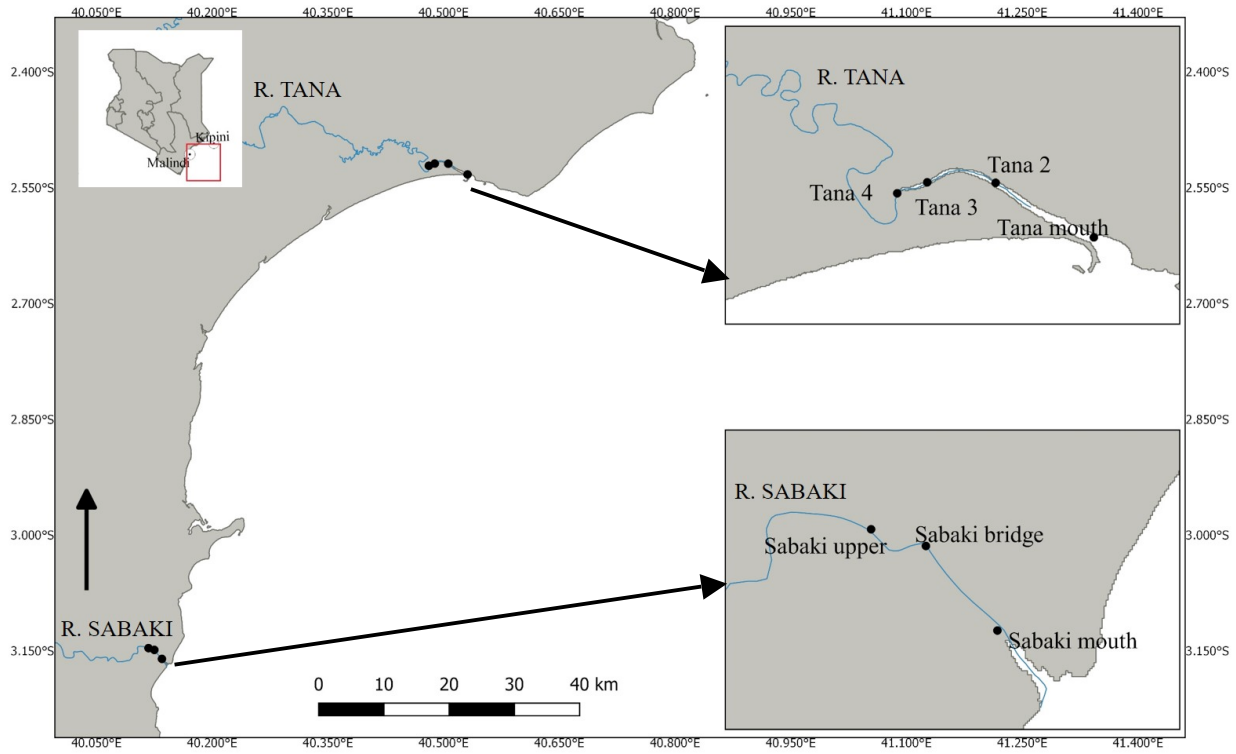

Figure 1. Map showing the selected sampling locations in the Tana and Sabaki estuarine systems.

PCBs are known to possess varying toxicological and physicochemical properties related to their chemical structures, and as such, they elicit adverse effects on humans and ecosystems (UNEP, 2009). They have been classified as probable human carcinogens and associated with cancers of the liver, gall bladder, gastrointestinal tract, breast, brain, and disruption of hormone function (Montuori *et al.,* 2015; Montuori *et al.,* 2020).

Most of the studies on POPs in Kenya have been focused on OCPs and targeted freshwater and river

Materials and methods

Study area

The study was carried out in th3 Tana and Sabaki estuarine systems of Kenya (Fig. 1). Tana River is the largest river in Kenya rising from the Aberdares and Mount Kenya ranges of central Kenya. It runs through the arid and semi-arid lands in the eastern part of the country to enter the Indian Ocean through a roughly triangular-shaped delta, with its apex at Lake Bilisa in the north of Garsen (Okuku *et al.,* 2013). The Athi-Galana-Sabaki River is the second largest river system in Kenya. It originates from the Ngong

hills in central Kenya (as River Athi). It flows mainly through sand and rocks and mining industries for cement and other inorganic products as the Athi River. It further flows through areas with major industries and coffee and tea farms where agrochemicals and fertilizers are used on a large scale before discharging into the Indian Ocean (Okeyo 1998; Lalah *et al.,* 2003).

Sample collection and storage

Sediment samples were collected from selected locations in the Tana and Sabaki estuarine systems (Fig. 1). Surface sediment samples of about 100-200 g were collected using a grab sampler, put in aluminum containers previously cleaned with hexane HPLC grade (sigma Aldrich), and stored in a cool box at a sufficiently low temperature (~4 ˚C) to limit biological and chemical activity. The samples were transported to the Kenya Marine and Fisheries Research Institute laboratory and kept frozen at -20 ˚C before transportation to the Laboratory of Physics and Toxico-Chemistry (LPTC) at the University of Bordeaux 1, France, for analysis.

Analytical procedures

Grain size and carbon analysis

Sediment samples were dried in an oven at 105 ˚C to constant weight. Grain size analysis of samples was performed through sieving (Folk, 1980), while total organic matter was analyzed using the ashing method. Total organic carbon (TOC) content was determined by oxidation with 1 N $K_2Cr_2O_7$ acidified with concentrated H_2SO_4 and titration with 0.5 N $[Fe(NH_4)_2(SO_4)_2]$ (Loring and Rantala, 1992).

Extraction and clean-up

Sediment samples were processed and analyzed in the laboratory as described by Thompson *et al*. (1999). Wet sediment samples of about 100 g were weighed, put in clean pre-weighed aluminum containers, covered with clean aluminum sheets with holes, and freeze-dried for 48 hours using a Heto power dry LL 3000 freeze dryer (Thermo Scientific). After freeze-drying, the samples were weighed to obtain the dry weight, and sieved through a 2 mm mesh-sized metallic sieve to remove any coarse materials. The samples were then stored in clean, well-labeled glass amber bottles awaiting analysis. Prior to extraction, about 3 g of each sample was put in the sample extraction vial and spiked with 30 µL of an internal standard containing a mixture of PCB 30, PCB 103, PCB 155, PCB 198 (Promochem, Dr Ehrenstorfer GmbH, France) and d8 4,4' DDT (Cambridge Isotope Laboratory, France). The added internal standard was used to quantify the recovery of the total extraction procedure. The samples were then extracted for 20 minutes with 30 mL dichloromethane (Pro-labo, Fontenay-sous-Bois, France) using the START E microwave-assisted extraction system (Milestone, Italy). The extracts were mechanically filtered into 25 mL amber glass vials through clean glass funnels stuffed with pre-cleaned glass wool. The filtered extracts were concentrated to about 1 mL using Rapidvap LABCONCO (Serlabo Technologies, France). The concentrated samples were subjected to a clean-up process during which the lipids and sulfur were removed from the extracts using a micro-column containing acidified silica (Silica gel, 0.063 ± 0.2 mm, Merck, Darmstadt, Germany) and activated copper (40 mesh, 99.5 % purity, Aldrich, Saint Quentin Fallavier, France). The PCBs were then purified on the micro-column by eluting 3 x 5 mL with a mixture of n-pentane and dichloromethane (90/10 v/v). The extracts were finally concentrated under nitrogen and transferred to 100 µL isooctane (99 % extra pure, Scharlau, ICS, St Medard en Jalles, France). The solution was further re-concentrated to 100 µL in an injection vial, and 1 µL of the sample was injected for analysis using Gas Chromatography-Mass Spectrometry.

Gas Chromatography-Mass Spectrometry (GC-MS) analyses

Analysis was performed using a Hewlett-Packard 5980 Series II gas chromatograph equipped with a ^{63}Ni electron-capture detector using a HP5 capillary column (60 m × 0.25 mm internal diameter × 0.25 µm film thicknesses). The GC conditions were set by injecting 1 µL through a split-less liner at a temperature of 280 ˚C; detector temperature: 290 ˚C; initial oven temperature: 60 ˚C held for 2 min, heated to 120 ˚C at 6 ˚C/min and held for 5 min, then heated to 280 ˚C at 2 ˚C/min and held for 20 min. Helium gas was used as the carrier gas. The PCB congeners were analyzed individually, whenever possible, though in some cases the concentrations were reported as the sum of overlapping congeners due to co-elution on the GC column. The relative response factors of the different compounds were determined by injecting a standard solution SRM 2262 for PCB (NIST, MD, USA) spiked with the same solution of internal standards (PCB 30, PCB 103, PCB 155, PCB 198, and OCN) and SRM 2261 for OCP spiked with (d8 4,4' DDT and OCN) as that used for spiking the sediments. The response factors were determined after every four samples. Blank injections of isooctane were performed between each injection of a sample to prevent cross-contamination.

Quality control and quality assurance

Laboratory glassware and reagent containers were thoroughly cleaned and dried in an oven for 4 hours at 450 ˚C. All reagents, solvents, and standards were of HPLC quality and tested for suitability before sample analysis. Milli-Q water (organic grade quality) was used for all cleaning throughout the analytical process. A solvent blank and reagent blank were run with each batch under the exact condition of the sample to trace any potential contamination during sample preparation. The average recovery of the internal standards ranged from 82-99 % for OCP and 89-104 % for PCB. The reported values in this study were corrected according to the values found in the blank, Instrumental detection limits (IDLs), and method detection limits (MDLs).

Results and discussion

Sediment physicochemical characterization

The results of surface sediment TOC, organic matter (OM), and particle grain size are presented in Table 1. High levels of TOC (16.3 mg/g), OM (1.45 %) and silt particle size (78.70 %) were reported in samples from Sabaki Bridge. Tana River mouth samples had high levels of TOC (14.2 mg/g) and sand particle size, > 63 µm (95.91%). Tana 2 samples had a high level of organic matter (8.02 %) compared to samples from the other stations. The surface sediments from the Sabaki and Tana rivers had sandy particle size, an indication that the grain size of the sediments with a high percentage of sand tends to have high porosity and high permeability (Kilunga *et al.,* 2017).

Distribution of POPs in surface sediments

The concentration of POPs, namely PCBs and OCPs, in surface sediments of the Sabaki and Tana estuarine systems are illustrated in Figure 2. The POPs concentrations in Sabaki estuary were in the range of 1.37-7.93 ng/g dw, whereas in the Tana estuary, the concentrations were in the range of 1.13-16.99 ng/g, dw. High concentrations of POPs as well as TOC, organic matter and % silt content was observed at Sabaki Bridge. This shows a positive relationship between POPs and TOC confirming that POPs tend to have a high affinity for organic matter (Wu *et al.,* 2015; Wu *et al.,* 2016). Both the Sabaki and Tana river mouths recorded the lowest concentrations of POPs due to continuous flushing of sediment by the sea resulting in sediment with a high sand proportion (94.5 % and 95.9 %, respectively).

PCBs in surface sediment

The total concentrations of PCB (sum of 12 congeners) in the surface sediment samples (Table 2) in Sabaki estuary was low (0.68-3.87, mean: 2.01 ng/g) compared to Tana estuary (0.65-9.29 ng/g, mean 5.59 ng/g). The concentration of PCBs reported in this study was comparable to levels reported by Okuku *et al*. (2019) for Sabaki estuary (0.58-2.40 ng/g) and Tana estuary (4.94-7.99 ng/g). PCB concentrations in the Tana estuary were also similar to those of the Yellow River: 1.4–5.2 ng/g (He *et al.,* 2006), Tonghui River: 0.78-8.47 ng/g (Zhang *et al*., 2004), Jiulong River: 1.0-8.1 ng/g (Wu *et al*., 2016) and Makelele river: 0.9-10.9 ng/g (Kilunga *et al.,* 2017). High concentrations of PCBs have been found in the Awash River Basin, Ethiopia: 0.85-26.56 ng/g (Dirbaba *et al.,* 2018), Umgeni River, South Africa: 102.60-427.80 ng/g (Gakuba *et al.,* 2015), Msunduzi River, South Africa: 214.21-610.45 ng/g (Adeyinka *et al.,* 2018), Haihe River, China: nd–253 ng/g (Zhao *et al.,* 2010), Damietta estuary, Egypt: 0.29 to 377 ng/g (Barakat *et al.,* 2013) and Soan River, Pakistan: 37.4-187 ng/g (Malik *et al.,* 2014).

PCBs in the Sabaki estuary may have resulted from several activities in the catchment area including industrial installations and companies around Athi River

Table 1. TOC concentration (mg/g), organic matter (%) and < 63 µm particles fraction (%) in sediment from the Sabaki and Tana estuaries.

STN	TOC (mg/g)	% Organic matter	% Silt (< 63 µm)	% Sand (> 63 µm)
Sabaki upper	6.64	0.72	35.21	64.79
Sabaki bridge	16.30	1.45	78.65	21.35
Sabaki Mouth	3.45	0.14	5.54	94.46
Tana Mouth 1	14.91	1.02	4.09	95.91
Tana 2	11.92	2.92	41.12	58.88
Tana 3	6.18	8.02	35.93	64.07
Tana 4	13.45	4.67	37.26	62.74

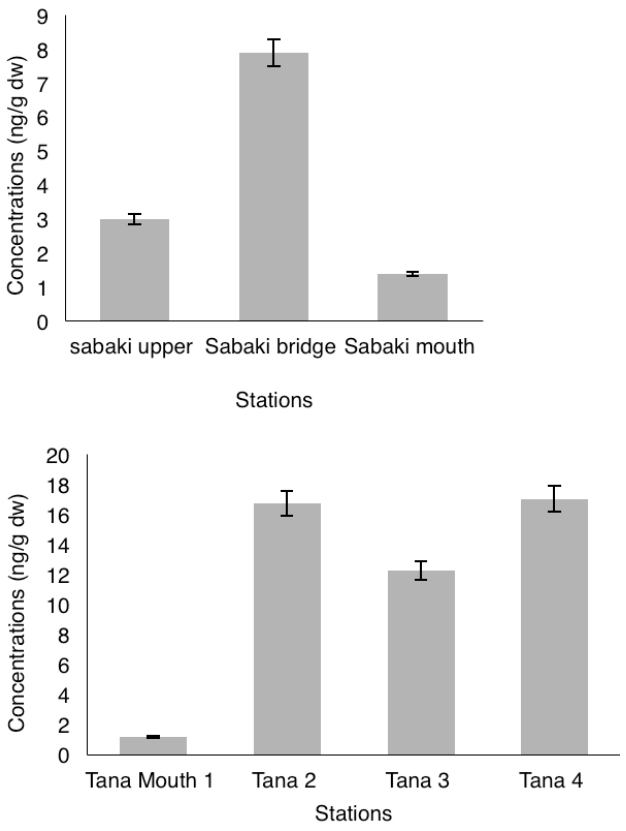

Figure 2. POPs concentration in the Sabaki and Tana estuarine areas.

and Nairobi that discharge their effluent into the river system. Sabaki Bridge had the highest concentration of PCBs in the Sabaki estuarine system which may have been the result of road traffic at the bridge.

PCB concentration in Tana 2 (9.29 ng/g dw) was high compared to the other stations in the estuary, probably due to oil leakage from the boats used by the fishermen given that this is a landing site where most of the boats are anchored. However, the low PCB concentrations at the Tana Mouth station (0.65 ng/g dw) and Sabaki mouth (0.68 ng/g dw) were due to tidal dilutions. High levels of PCBs in the Tana River system could be attributable to the possible leakage or inadvertent disposal of materials used in transformers and capacitors in the Seven Folks electricity-generating dam. Leakage from broken transformers and used electrical equipment has been reported elsewhere to be a major anthropogenic source of PCBs transferred to the environment (Fu *et al.*, 2003; Kassegne *et al.*, 2020). The Tana River holds the Seven Folks Scheme, a serially cascaded dam used for hydroelectricity generation (Masinga, Kamburu, Gitaru, Kiambere, and Kindaruma Dams). Such installations use large transformer and capacitor systems that would apply Aroclor formulations as dielectric and heat retardants in the past, before the ban on PCB production and use by various PCB producing countries following the Stockholm Convention (UNEP, 2009). Even though

Table 2. Descriptive statistics (Sum, mean, and standard deviation values) of PCB concentrations (in ng/g dw) on surface sediment samples from the Sabaki and Tana estuarine systems.

Compounds	Sabaki River			Tana River			
	Sabaki upper	Sabaki bridge	Sabaki mouth	Tana Mouth 1	Tana 2	Tana 3	Tana 4
PCB (ng/g)							
28+50	0.23	0.51	0.10	0.07	0.80	0.47	1.16
44	0.14	0.25	0.05	0.05	0.37	0.17	0.31
101	0.10	0.22	0.05	0.08	0.54	0.21	0.00
87	0.10	0.18	0.05	0.06	1.47	0.71	0.74
118	0.40	1.14	0.17	0.15	2.89	1.80	3.03
153	0.32	1.10	0.13	0.13	1.84	1.18	1.48
138	0.04	0.20	0.04	0.04	0.51	0.23	0.10
128	BDL	BDL	0.02	0.01	BDL	BDL	BDL
187	0.05	0.09	0.03	0.02	0.17	0.11	0.07
180	0.04	0.08	0.02	0.02	0.44	0.20	0.07
170	0.05	0.09	0.03	0.02	0.26	0.17	0.17
206	BDL	BDL	BDL	BDL	BDL	BDL	BDL
∑ PCB congeners	**1.48**	**3.87**	**0.68**	**0.65**	**9.29**	**5.26**	7.15
Mean	0.15	0.39	0.06	0.06	0.93	0.53	0.71
STDEV	0.13	0.41	0.05	0.05	0.87	0.56	0.96

BDL-Below detection limit

Kenya ratified and implemented the Convention, due to the recalcitrance of PCBs, it is expected that residues of these contaminants still exist in various environments, including aquatic systems.

The PCBs with congeners of Penta-Hexa and hepta chlorobiphenyls were the most prominent homologous groups. Heavier PCB congeners dominated due to their adsorption to particulate material resulting in their accumulation and deposition in the sediments (Malik *et al.,* 2014). In the Sabaki and Tana estuarine systems, the most abundant PCB congeners reported were PCB 118 (Sabaki 1.71 ng/g; Tana 7.87 ng/g) followed by PCB 153 (Sabaki 1.55; Tana 4.63 ng/g) (Fig. 3). These are among the most persistent PCB congeners and have a long half-life (Kilunga *et al.,* 2017). As much as commercial use of PCBs has been banned, the presence of the PCBs congeners indicated historical pollution as also reported elsewhere by Kilunga *et al.* (2017). The persistence of PCBs in aquatic sediments is due to their low rate of degradation and vaporization, low water solubility, and partitioning to particles and organic carbon (Aly Salem *et al.,* 2013; Montuori *et al.,* 2020).

OCPs in the surface sediment

The levels of total OCPs, including HCHs, DDT, and its metabolites DDXs, heptachlor, heptachlor *epoxide* chlordane, Nanochlor, and mirex, were detected in the Sabaki and Tana estuarine systems (Table 3). The total OCP concentrations in surface sediments in the Sabaki estuary were in the range of 0.69-4.01 ng/g dw with a mean of 0.12 ng/g dw, while in the Tana estuary, the concentrations were in the range of 0.47-9.84 ng/g dw with a mean of 0.56 ng/g dw. The highest concentrations of OCPs were reported at Sabaki Bridge and Tana 4 with values of 4.01 ng/g dw and 9.84 ng/g dw, respectively. Lalah *et al.* (2003) reported a concentration range of < 0.003 to 108.51 ng/g in the Sabaki estuary (Lalah *et al.*, 2003). This suggests that although OCPs use has been banned in Kenya, there might be an illegal or minor application of OCPs for malaria vector and tsetse fly control (Wandiga *et al.,* 2002). OCPs in the Sabaki and Tana River estuaries showed similar concentrations with Bizerte lagoon, Tunisia, at 1.1-14.0 ng/g (Barhoumi *et al.,* 2014), and the Volturno River, Italy, at 0.52- 9.89 ng/g (Montuori *et al.,* 2020). Higher concentrations of OCPs have been reported by Unyimadu *et al.* (2019) in the Niger River, Nigeria (4672-7009 ng/g), Dirbaba *et al.* (2018) in the Awash River Basin, Ethiopia (6.63–206.13 ng/g) and Kilunga *et al.* (2017) in tropical urban rivers of the Congo (21.6 - 146.8 ng/g).

The concentration of Heptachlors (including heptachlor and its metabolite, heptachlor epoxide) was 0.51 ng/g dw, and Cis chlordane at 0.09 ng/g dw in the Sabaki estuary. In the Tana estuary, Heptachlor was only detected at Tana Mouth due to its use in termite control by the community in the area (Lalah *et al.,* 2003; Zhao *et al.,* 2009), while its metabolite, heptachlor epoxide was present in all the other sites except in Tana Mouth with a concentration of 0.11 ng/g dw.

HCN has been reported to have a total of eight HCN isomers, among which only α, β, ɣ, ε and δ isomers are stable and commonly identified in the environment (Wang *et al.,* 2009). Although HCN is no longer in use, HCN concentrations in Sabaki and Tana estuarine systems in this study were 0.07 ng/g dw and 0.75 ng/g dw, respectively. At the same time, the presence of ɣ- HCN in Sabaki (0.02 ng/g dw) and Tana (0.12 ng/g dw) systems may be as a result of the application of

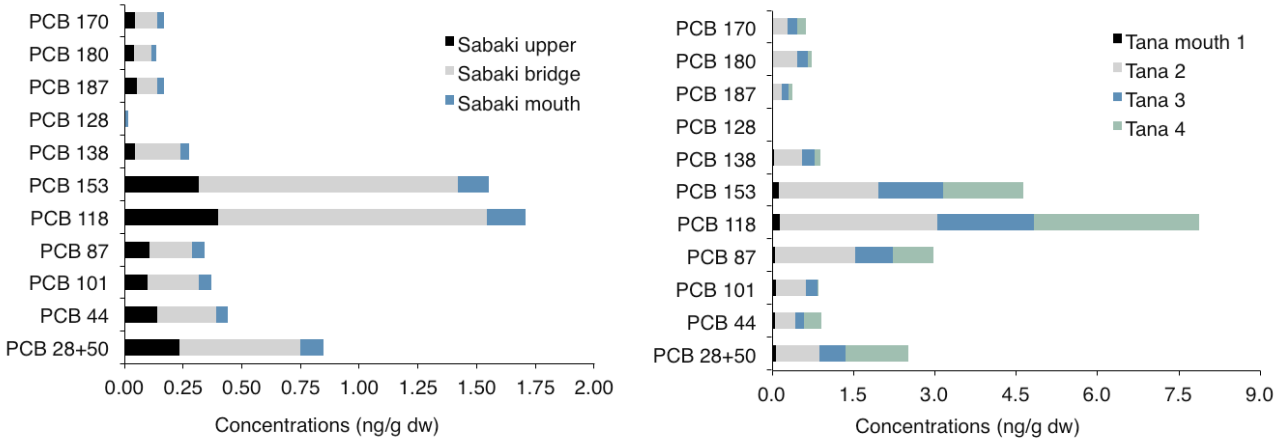

Figure 3. PCB congeners in Sabaki and Tana Rivers estuarine systems.

Table 3. Descriptive statistics (Sum, mean, and standard deviation values) of OCP concentrations (in ng/g dw) on surface sediment samples from the Sabaki and Tana estuarine systems.

Compounds	Sabaki River			Tana River			
	Sabaki upper	Sabaki bridge	Sabaki mouth	Tana Mouth 1	Tana 2	Tana 3	Tana 4
OCP (ng/g)							
HCB	0.04	0.10	0.02	0.03	1.16	0.78	0.54
gamma-HCH	0.00	0.05	0.01	0.00	0.25	BDL	0.10
Heptachlor	0.16	0.11	0.19	0.04	BDL	BDL	BDL
Hep.Hepoxide	0.04	BDL	BDL	BDL	0.18	0.05	0.11
Cis chlordane	0.04	0.08	0.03	BDL	0.30	0.09	0.19
Trans Nonachlor	0.20	0.07	0.02	0.02	0.18	0.09	0.16
o,p' DDE	0.03	0.20	0.02	0.03	0.43	0.33	0.46
p,p'DDE	0.10	0.22	0.03	0.03	0.57	0.31	0.41
o,p' DDD	0.56	1.51	0.21	0.22	BDL	2.38	3.65
p,p' DDD	0.10	0.70	0.05	0.04	1.80	1.29	1.82
o,p' DDT	0.18	0.67	0.07	0.06	1.68	1.14	1.67
p,p' DDT	0.05	0.31	0.01	0.01	0.64	0.45	0.70
Mirex	BDL	BDL	0.02	BDL	0.21	0.01	0.04
∑ OCP	**1.51**	**4.01**	**0.69**	**0.47**	7.40	6.93	9.84
∑ DDT	1.03	3.49	0.41	0.36	4.99	5.67	8.43
Mean	0.13	0.36	0.06	0.05	0.67	0.63	0.82
STDEV	0.15	0.44	0.07	0.06	0.60	0.73	1.07

BDL-Below detection limit

Lindane (ɣ- HCN being an active ingredient) which has been used in Kenya since 1949 for both agriculture and pest vector control purposes (Lalah *et al.,* 2003; Wang *et al.,* 2009; Dirbaba *et al.,* 2018) and is still used under restriction for termite control. Kassegne *et al.* (2020) also detected Lindane (ɣ- HCN) in Akaki River (mean 371.78 ng/g) despite the ban.

DDT and it's metabolites like p,p'DDE, o,p'DDE, o,p'DDD, p,p' DDD, o,p'DDT and p,p'DDT were detected in the surface sediment in both the Sabaki and Tana estuaries (Table 2). The highest concentrations of ∑6 DDTs were recorded at Sabaki Bridge (3.49 ng/g) and Tana 4 (8.43 ng/g) (Fig. 4). Tana estuary samples showed a decrease in the total concentration of DDT from the upper parts towards the Indian Ocean because it passes through areas with a history of organochloride pesticide use (Lalah *et al.*, 2003). The concentration of total DDT in the Tana estuary was comparable to the Volturno River, Italy, at 0.10 to

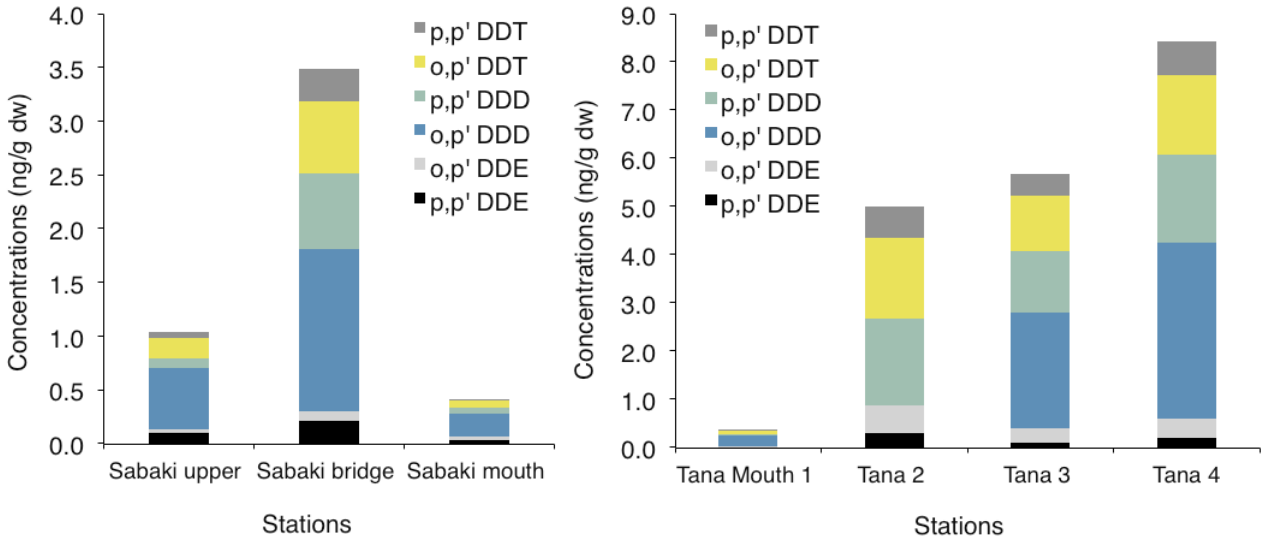

Figure 4. Concentration of DDTs metabolites in the Sabaki and Tana estuarine systems.

5.22 ng/g (Montuori *et al.,* 2020), Bizerte lagoon, Tunisia, at 0.3–11.5 ng/g (Barhoumi *et al.,* 2014) and Jiulong River, Taiwan at 2.3-11.8 ng/g (Wu *et al.,* 2016). A higher concentration of DDT was reported in the Awash River Basin, Ethiopia by Dirbaba *et al.* (2018) ranging from 1.99–139.68 ng/g, in the Niger River, Nigeria by Unyimadu *et al.* (2019) ranging between BDL and 107.6 ng/g, and Barakat *et al.* (2013), in the Damietta estuary, Egypt ,ranging between 0.07 and 81.5 ng/g.

The concentration of DDT isomers were found to be p,p'DDE >o,p'DDD > o,p'DDE > p,p'DDD > o,p'DDT > p,p'DDT in the Sabaki estuariy while in the Tana estuary they were as follows: p,p' DDE >o,p'DDE> o,p'DDD > p,p'DDD > p,p'DDT > o,p'DDT. This was also observed by Zhao *et al. (*2009) when they conducted a study in Taihu Lake, China, as well as by Kilunga *et al*. (2017) on tropical urban rivers in Kinshasa, Democratic Republic of the Congo. However, this was contrary to the findings of Malik *et al.* (2014) on the Soan River, Pakistan.

It has been reported that DDT can be biodegraded under aerobic and anaerobic conditions to DDE and DDD, respectively (Malik *et al.,* 2014; Nguyen *et al.,* 2019). Thus, the ratio of DDE/DDD has been used to denote the DDT degradation status. If the ratio of DDE/DDD is greater than one (> 1), it indicates the anaerobic degradation of DDT into DDD while if it is less than one (< 1), it shows the DDT conversion into DDE via aerobic degradation (Ali *et al.,* 2016). In this study, the Tana estuarine system reported a DDE/DDD ratio < 1, suggesting an aerobic degradation of DDT to DDD via dehydrochlorination and oxidation processes, and further degradation into DDD by reductive dechlorination in the environment (Cheng *et al.,* 2014; Kilunga *et al.,* 2017). Whereas in the Sabaki estuarine system the DDE/DDD ratio was > 1, indicative of anaerobic degradation of DDT into DDD. A similar study on the difference in DDE/DDD ratios in sediment was also reported on the Egyptian Mediterranean coast (Aly Salem *et al.,* 2013). The source of DDT in the environment either as a historic or of recent origin has been determined by applying the DDD+DDE/DDT ratio. If the ratio DDD+DDE/DDT is > 0.5, this indicates historical input, and if <0.5, this indicates recent input (Kilunga *et al.,* 2017; Montuori *et al.,* 2020). In this study, the values of DDD+DDE/DDT in the Sabaki and Tana estuarine systems were 0.57 and 2.73, respectively, suggesting historical input of DDT in both the estuaries due to their capability to remain in the agricultural soil for a long time and re-mobilize through runoffs. A similar observation was reported by Aly Salem *et al*. (2013), and Montuori *et al.* (2020). However, this was contrary to the findings of Zhao *et al.* (2009) which indicated recent DDT input due to illegal input of DDT or usage of other pesticides containing DDT, such as dicofol.

Table 4. Comparison of OCP and PCB concentrations (ng/g dw) in surface sediments in this study with those from various locations in the world.

Location	PCB	OCP	DDT	References
Sabaki estuary, Kenya	0.68-3.87	0.69-4.04	1.03-3.49	This study
Tana estuary, Kenya	0.65-9.29	0.47-9.84	0.36-8.43	This study
Tana estuary, Kenya	4.94–7.99	-	-	(Okuku *et al.,* 2019)
Sabaki estuary, Kenya	0.58–2.40	-	-	(Okuku *et al.,* 2019)
Ramisi Estuary	ND-0.15	-	-	(Okuku *et al.,* 2019)
Awash River Basin, Ethiopia	0.85–26.56	6.63–206.13	1.99–139.68	(Dirbaba *et al.,* 2018)
Bizerte lagoon, Tunisia	0.8–14.6	1.1-14.0	0.3–11.5	(Barhoumi *et al.,* 2014)
Niger River, Nigeria	-	4672-7009	Bdl-107.6	(Unyimadu *et al.,* 2019)
Umgeni River, South Africa	102.60–427.80	-	-	(Gakuba *et al.,* 2015)
Msunduzi River, South Africa	214.21–610.45			(Adeyinka *et al.,* 2018)
Damietta estuary, Egypt	0.29 to 377	0.27–288	0.07-81.5	(Barakat *et al.,* 2013)
Tropical urban rivers, Congo	0.9 - 10.9	21.6 - 146.8	1.23-270.6	(Kilunga *et al.,* 2017)
Taihu Lake, China	-	4.22 - 461	0.25 - 375	(Zhao *et al.,* 2009)
Haihe River, China	nd–253	0.997– 2447	n.d. – 155	(Zhao *et al.,* 2010)
Volturno River,Italy	4.3 to 64.3	0.52 to 9.89	0.10 to 5.22	(Montuori *et al.,* 2020)
Jiulong River, Taiwan	1.0-8.1	5.2 - 551.7	2.3-11.8	(Wu *et al.,* 2016)
Soan River, Pakistan	37.4- 187	NA	6.98–30.1	(Malik *et al.,* 2014)

NA-data is not available, nd-not detected

Table 5. Comparison of OCP and PCB concentrations in sediments of the study area with TEC and PEC values in ng/g dw.

	TEC		PEC		Sabaki estuary (Range ng/g)	Tana estuary (Range ng/g)
	TEL	ER-L	PEL	ER-M		
DDD	3.54	2	8.51	20	0.27-2.21	0.26-5.47
DDE	1.42	2	6.75	15	0.06-0.30	0.03-0.87
DDT	NG	1	NG	7	0.09-0.98	0.07-2.36
Total DDT	7	3	4.45	350	0.41-3.49	0.36-8.43
Heptachlor epoxide	0.6	NG	2.74	NG	BDL-0.04	BDL-0.18
HCB	0.3	NG	1.0	NG	0.02-0.10	0.03-1.16
Chlordane	4.5	0.5	8.9	6	0.02-0.20	0.02-0.18
PCB	34.1	50	277	400	0.68-3.87	0.65-9.29

NG- No guideline

Ecotoxicological assessment

Contaminated sediments can represent potential risks to sediment-dwelling organisms such as benthic and epibenthic species. To evaluate the ecotoxicological significance of sediment pollution by PCBs and OCPs in the Sabaki and Tana estuarine systems, sediment quality guidelines (SQGs) specified by the Canadian Council of Ministers of the Environment (CCME) were applied (CCME 2002). They include threshold effect concentrations (TEC) and probable effect concentrations (PEC). TEC was intended to identify contaminant concentrations below which harmful effects on sediment-dwelling organisms were not expected. PEC was used to identify contaminant concentrations above which harmful effects on sediment-dwelling organisms was expected to frequently occur (MacDonald *et al.,* 2000; Gómez-Gutiérrez *et al.,* 2007). Effects range-low (ER-L) and effects range-median (ER-M) values are used to predict the potential impacts of contaminants in sediments. In addition, the threshold effect level (TEL) and the probable effect level (PEL) was used as the criterion for the prediction of toxicity (Long and Morgan, 1990; MacDonald *et al.,* 2000; CCME, 2002; Gómez-Gutiérrez *et al.,* 2007).

Sediment quality criteria and concentration ranges of major organochlorine contaminants are summarized in Table 4. PCB, HCB, Heptachlor epoxide, and Chlordane concentrations in sediments from the Sabaki and Tana estuarine systems were below ER-M, ER-L, PEL, and TEL values at all the stations, suggesting rather low toxicity to benthic organisms. However, total DDTs values were higher than the threshold effect concentrations (TECs), including TEL and ER-L in both estuarine systems, suggesting that DDT could potentially pose adverse toxic effects to benthic organisms.

Conclusion

This study determined the concentration of various POPs in the sediments from selected locations in Kenya and predicted any potential risk to environmental health. The concentrations of POPs were relatively low suggesting low ecological risk. DDT metabolites were relatively high in the Sabaki and Tana estuaries, indicating potential toxic effects on benthic organisms. This study recommends a need to establish a POPs monitoring programme for continual assessment of potential ecotoxicological risks in Kenya estuaries.

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References

Adeyinka GC, Moodley B, Birung G, Ndungu P (2018) Quantitative analyses of selected polychlorinated biphenyl (PCB) congeners in water, soil, and sediment during winter and spring seasons from Msunduzi River, South Africa. Environmental Monitoring and Assessment 190 (10): 1-13

Ali U, Li J, Zhang G, Mahmood A, Jones KC, Malik RN (2016) Presence, deposition flux and mass burden of persistent organic pollutants (POPs) from Mehmood Booti Drain sediments, Lahore. Ecotoxicology and Environmental Safety 125: 9-15

Aly Salem DMS, Khaled A, El Nemr A (2013) Assessment of pesticides and polychlorinated biphenyls (PCBs) in sediments of the Egyptian Mediterranean coast. The Egyptian Journal of Aquatic Research 39 (3): 141-152

Barakat AO, Mostafa A, Wade TL, Sweet ST, El Sayed NB (2013) Distribution and ecological risk of organochlorine pesticides and polychlorinated biphenyls in sediments from the Mediterranean coastal environment of Egypt. Chemosphere 93 (3): 545-554

Barhoumi B, LeMenach K, Dévier M-H, El megdiche 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. Environmental Science and Pollution Research 21 (10): 6290-6302

CCME (Canadian Council of Ministers of the Environment) (2002) Canadian sediment quality guidelines for the protection of aquatic life. In: Canadian Environmental Quality Guidelines. Canadian Council of Ministers of the Environment, Winnipeg, Manitoba. pp 1-5

Cheng H, Lin T, Zhang G, Liu G, Zhang W, Qi S, Jones KC, Zhang X (2014) DDTs and HCHs in sediment cores from the Tibetan Plateau. Chemosphere 94: 183-189

Dierking J, Wafo E, Schembri T, Lagadec V, Nicolas C, Letourneur Y, Harmelin-Vivien M (2009) Spatial patterns in PCBs, pesticides, mercury and cadmium in the common sole in the NW Mediterranean Sea, and a novel use of contaminants as biomarkers. Marine Pollution Bulletin 58 (11): 1605-1614

Dirbaba NB, Li S, Wu H, Yan X, Wang J (2018) Organochlorine pesticides, polybrominated diphenyl ethers and polychlorinated biphenyls in surficial sediments of the Awash River Basin, Ethiopia. PloS One 13 (10): e0205026

Everaarts JM, Van Weerlee EM, Fischerm CV, Hillebrand TJ (1998) Polychlorinated biphenyls and cyclic pesticides in sediments and macro-invertebrates from the coastal zone and continental slope of Kenya. Marine Pollution Bulletin 36: 492-500

Folk R (1980) Petrology of sedimentary rocks; Syllabus. Hemphill's Publishing Company, Austin, Texas. 190 pp

Fu J, Mai B, Sheng G, Zhang G, Wang X, Peng PA, Xiao X, Ran R, Cheng F, Peng X, Wang Z, Wa Tang U (2003) Persistent organic pollutants in environment of the Pearl River Delta, China: an overview. Chemosphere 52 (9): 1411-1422

Gakuba E, Moodley B, Ndungu P, Birungi G (2015) Occurrence and significance of polychlorinated biphenyls in water, sediment pore water and surface sediments of Umgeni River, KwaZulu-Natal, South Africa. Environmental Monitoring and Assessment 187 (9): 568

Gómez-Gutiérrez A, Garnacho E, Bayona JM, Albaigés J (2007) Screening ecological risk assessment of persistent organic pollutants in Mediterranean sea sediments. Environment International 33 (7): 867-876

He M, Sun Y, Li X, Yang Z (2006) Distribution patterns of nitrobenzenes and polychlorinated biphenyls in water, suspended particulate matter and sediment from mid- and down-stream of the Yellow River (China). Chemosphere 65: 365-374

Jayaraj R, Megha P, Sreedev P (2016) Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment. Interdisciplinary Toxicology 9 (3-4): 90-100

Kassegne AB, Okonkwo JO, Berhanu T, Daso AP, Olukunle OI, Asfaw SL (2020) Ecological risk assessment of organochlorine pesticides and polychlorinated biphenyls in water and surface sediment samples from Akaki River catchment, central Ethiopia. Emerging Contaminants 6: 396-404

Kilunga PI, Sivalingam P, Laffite A, Grandjean D, Mulaji CK, de Alencastro LF, Mpiana PT, Poté J (2017) Accumulation of toxic metals and organic micro-pollutants in sediments from tropical urban rivers, Kinshasa, Democratic Republic of the Congo. Chemosphere 179: 37-48

Lalah JO, Yugi PO, Jumba IO, Wandiga SO (2003) Organochlorine pesticide residues in Tana and Sabaki Rivers in Kenya. Bulletin of Environmental Contamination and Toxicology 71 (2): 298-307

Long ER, Morgan LG (1990) The potential for biological effects of sediments-sorbed contaminants tested in the National Status and Trends Program. National Oceanic and Atmospheric Admininistration. 175 pp

Loring DH, Rantala RTT (1992) Manual for the geochemical analyses of marine sediments and suspended particulate matter. Earth-Science Reviews 32 (4): 235-283

MacDonald DD, Ingersoll CG, Berger TA (2000) Development and evaluation of consensus-based Sediment quality guidelines for freshwater ecosystems. Archives of Environmental Contamination and Toxicology 39 (1): 20-31

Malik RN, Mehboob F, Ali U, Katsoyiannis A, Schuster JK, Moeckel C, Jones KC (2014) Organo-halogenated contaminants (OHCs) in the sediments from the Soan River, Pakistan: OHCs (adsorbed TOC) burial flux, status and risk assessment. Science of the Total Environment 481: 343-351

Mitra A, Chatterjee C, Mandal FB (2011) Synthetic chemical pesticides and their effects on birds. Research Journal of Environmental Toxicology *5* (2): 81-96

Mohammed A, Peterman P, Echols K, Feltz K, Tegerdine G, Manoo A, Maraj D, Agard J, Orazio C (2011) Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in harbor sediments from Sea Lots, Port-of-Spain, Trinidad and Tobago. Marine Pollution Bulletin 62 (6): 1324-1332

Montuori P, Aurino S, Nardone A, Cirillo T, Triassi M (2015) Spatial distribution and partitioning of organophosphates pesticide in water and sediment from Sarno River and Estuary, Southern Italy. Environmental Science and Pollution Research 22 (11): 8629-8642

Montuori P, De Rosa E, Sarnacchiaro P, Di Duca F, Provvisiero DP, Nardone A, Triassi M (2020) Polychlorinated biphenyls and organochlorine pesticides in water and sediment from Volturno River, Southern Italy: occurrence, distribution and risk assessment. Environmental Sciences Europe 32 (1): 1-22

Nguyen TX, Nguyen BT, Tran HTT, Mai H, Duong TT, Bach Q-V (2019) Seasonal, spatial variation, and potential sources of organochlorine pesticides in water and sediment in the lower reaches of the Dong Nai river system in Vietnam. Archives of Environmental Contamination and Toxicology 77 (4): 514-526

Okeyo DO (1998) Updating names, distribution and ecology of riverine fish of Kenya in the Athi-Galana-Sabaki River drainage system. Naga, The ICLARM Quarterly 21 (1): 44-53

Okuku E, Ohowa B, Kiteresi L, Wanjeri V, Okumu S, Ochola O, Ongore C (2013) Screening of potential ecological risk of metal contamination in some Kenyan estuaries. Research Journal of Physical and Applied Science 2 (4): 52-63

Okuku EO, Imbayi KL, Omondi OG, Wayayi WVO, Sezi MC, Maureen KM, Mwangi S, Oduor N (2019) Decadal pollution assessment and monitoring along the Kenya Coast. In: Monitoring of Marine Pollution. IntechOpen

Pazi I, Kucuksezgin F, Gonul L (2011) Distribution and sources of organochlorinated contaminants in sediments from Izmir Bay (Eastern Aegean Sea). Marine Pollution Bulletin 62 (5): 1115-1119

Thompson S, Budzinski H, Garrigues P, Narbonne JF (1999) Comparison of PCB and DDT distribution between water-column and sediment-dwelling bivalves in Arcachon Bay, France. Marine Pollution Bulletin 38 (8): 655-662

UNDP (2001) Human development report 2001: Making new technologies work for human development. United Nations Development Programme. 274 pp

UNEP (2009) Stockholm convention on persistent organic pollutants (POPs). United Nations Environment Programme (UNEP). Geneva, Switzerland. pp 1-64

Unyimadu JP, Osibanjo O, Babayemi JO (2019) Concentration and distribution of organochlorine pesticides in sediments of the Niger River, Nigeria. Journal of Health and Pollution 9 (22): 190606

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

Wang J, Bi Y, Pfister G, Henkelmann B, Zhu K, Schramm K-W (2009) Determination of PAH, PCB, and OCP in water from the Three Gorges Reservoir accumulated by semipermeable membrane devices (SPMD). Chemosphere 75 (8): 1119-1127

Wu Q, Leung JYS, Yuan X, Huang X, Li H, Huang Z, Li Y (2015) Biological risk, source and pollution history of organochlorine pesticides (OCPs) in the sediment in Nansha mangrove, South China. Marine Pollution Bulletin 96 (1): 57-64

Wu Y, Wang X, Ya M, Li Y, Hong H (2016) Distributions of organochlorine compounds in sediments from Jiulong River Estuary and adjacent Western Taiwan Strait: Implications of transport, sources and inventories. Environmental Pollution 219: 519-527

Zhang Z, Huang J, Yu G, Hong H (2004) Occurrence of PAHs, PCBs and organochlorine pesticides in the Tonghui River of Beijing, China. Environmental Pollution 130: 249-261

Zhao Z, Zhang L, Wu J, Fan C (2009) Distribution and bioaccumulation of organochlorine pesticides in surface sediments and benthic organisms from Taihu Lake, China. Chemosphere 77 (9): 1191-1198

Zhao L, Hou H, Zhou Y, Xue N, Li H, Li F (2010) Distribution and ecological risk of polychlorinated biphenyls and organochlorine pesticides in surficial sediments from Haihe River and Haihe Estuary Area, China. Chemosphere 78 (10): 1285-1293