Emerging Contaminants 6 (2020) 396–404

Contents lists available at ScienceDirect

Emerging Contaminants

journal homepage: http://www.keaipublishing.com/en/journals/emerging-contaminants/

Ecological risk assessment of organochlorine pesticides and polychlorinated biphenyls in water and surface sediment samples from Akaki River catchment, central Ethiopia

Alemnew Berhanu Kassegne [a, b, *], Jonathan O. Okonkwo [c], Tarekegn Berhanu [d], Adegbenro P. Daso [c], Olubiyi I. Olukunle [e], Seyoum Leta Asfaw [b]

[a] Department of Chemistry, Debre Berhan University, P.O.Box 455, Debre Berhan, Ethiopia
[b] Center for Environmental Science, Addis Ababa University, P.O.Box 1176, Addis Ababa, Ethiopia
[c] Department of Environmental, Water & Earth Sciences, Tshwane University of Technology, 175 Nelson Mandela Drive, Private Bag X680, Arcadia, Pretoria, South Africa
[d] Central Research Laboratory, Addis Ababa Science and Technology University, P.O.Box 16417, Addis Ababa, Ethiopia
[e] School of Public and Environmental Affairs, Indiana University, Bloomington, IN, 47405, USA

ARTICLE INFO

Article history:
Received 21 July 2020
Received in revised form
4 November 2020
Accepted 15 November 2020

Keywords:
Akaki river
Organochlorine pesticides
Polychlorinated biphenyls
Sediment
Water

ABSTRACT

The current status of persistent organic pollutants in Ethiopian environment is not well monitored despite the existing pollution potential from a number of sources. Water and sediment samples collected from Akaki River catchment and Aba Samuel Reservoir, Central Ethiopia were analyzed to assess the concentrations, distribution, possible sources and potential ecological risk of eight organochlorine pesticides (OCPs) and seven polychlorinated biphenyls (PCBs). Water and sediment samples were extracted by liquid-liquid and Soxhlet extraction respectively, and analyzed using gas chromatography-mass spectroscopy (GC-MS). The detectable OCPs and PCBs in water samples were DDT, DDE, DDD, lindane and dieldrin and PCB-28, PCB-101 and PCB-118, respectively in the rainy season. Analyzed sediment samples showed the presence of lindane in the dry and p, p'-DDT, p, p'-DDE, p, p'-DDD, α, β-endosulfan, heptachlor epoxide (B), and dieldrin in the rainy seasons. Among the indicator PCBs analyzed, sediment samples showed the presence of PCB-52, PCB-101 and PCB-118 in the dry and all indicator PCBs in the rainy seasons. Sources analysis showed that PCBs and detected OCPs were mainly from the historical input of commercial products, but there were recent discharge of DDT and lindane into the river system. Ecological risk assessment of the analyzed OCPs and PCBs using water and sediment quality guidelines indicated that lindane in the dry and p'-DDT, p, p'-DDE, p, p'-DDD, heptachlore epoxide and dieldrin in the rainy seasons in the sediment samples from Akaki river and Aba Samuel reservoir were above the limit at most of the sites. This suggests there is greater possibility of higher ecological hazards in these residues. However, the levels of total PCB concentrations and other OCPs at all sites were below the limit and thus their potential ecotoxicological risks were rather low.

1. Introduction

Persistent organic pollutants (POPs) are chemicals with high chemical stability, lipophilicity and persistency [1] that enables them causing to cause serious health and eco-toxicological concerns [2,3]. Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are among the most important synthetic POPs and are ubiquitous pollutants in the aquatic environment [4,5]. OCPs were widely used around the world as agricultural and disease controlling chemicals. PCBs, with extremely stable physicochemical properties and excellent electric insulation and thermal stability, were mainly applied to electronic production [6]. The pathways through which these contaminants enter the aquatic environment are well documented [7] and their eco-toxicological risks are

* Corresponding author. Department of Chemistry, Debre Berhan University, P.O.Box 455, Debre Berhan, Ethiopia.
E-mail address: alexbk2010@gmail.com (A.B. Kassegne).
Peer review under responsibility of KeAi Communications Co., Ltd.

https://doi.org/10.1016/j.emcon.2020.11.004

extensively studied [8]. For instance, due to their low solubility in water, these organohalogenated compounds quickly become associated with particulate matter and accumulate in sediments. Sediments are composed of small particles comprising organic and inorganic particles and detritus which are relatively heterogeneous in terms of biological, physical and chemical characteristics. Sediment particles show higher adsorption capacities for organic compounds due to their large surface area [9]. Contaminated sediments may constitute a particular threat to associated biota and even for other organisms throughout the food chain. Due to the possible bioavailability of these contaminants in water and sediments, the research on water and sediment is a critical step in sketching possible exposure pathways to a variety of aquatic organisms [10]. However, while there is a great deal of information from the developed world, data from the developing region is still scarce.

In Ethiopia, OCPs were extensively used to control insect pests in agriculture and public health purposes [11,12]. According to the obsolete pesticide inventory report of the Food and Agriculture Organization, Ethiopia is one of the many African countries burdened with the problem of obsolete pesticide stocks. Most dangerous pesticides are found in these dumpsites. Furthermore, pesticide residues will leak into the surrounding environment around Addis Ababa from agricultural and public health uses [11,12]. PCBs have been used in the country, mainly as oil additives and hydraulic fluids for transformers and electric equipment for many years, until it was stopped in the 2000s. However, PCB containing transformers, capacitors and other devices still exist in the country, some are still in use and others are stored in unprotected stores. A 2004 PCB inventory estimated the presence of large quantities of PCB containing transformers and capacitors throughout the country, and among the suspected contaminated sites were the central region of the Ethiopian Electric power corporation, around Addis Ababa [13]. Thus, despite the official ban of PCB containing materials in the country, the actual release of the chemicals into the environment is not likely to cease for some time. There is a high probability of leakage of these contaminants to nearby water bodies and thereby into aquatic organisms. Generally, studies that investigated the occurrence, level and distribution of OCPs and PCBs in Ethiopian aquatic environments are just a few and those available are concentrated at the Ethiopian Rift Valley lakes [11,14–16].

The Akaki Rivers with their tributaries, located in the central part of Ethiopia, drain into the Addis Ababa city from north to south [17]. Addis Ababa, the capital city of Ethiopia, is one of the fast expanding cities in Africa. It has uncontrolled urbanization and industrialization, poor sanitation, and uncontrolled waste disposal activities, which makes the city's environment susceptible to pollution. It hosts large numbers of industries, but only a few of them treat their wastes to some degree [17,18]. Furthermore, untreated or partially treated domestic and agricultural wastes are released into the nearby water bodies [18,19]. There are two dominant rivers of the Akaki River system: namely, Little Akaki River (LAR) and the Great Akaki River (GAR) that drains Addis Ababa city. Many tributaries join the rivers at different localities. The rivers are the convergence points of all streams crossing the city from different directions. Most industries are concentrated along the Little Akaki River and its major tributaries. Great Akaki River flows through the eastern part of the city. The river consists of many tributaries flowing southwards across the residential and commercial centers of Addis Ababa. The two major rivers join at the Aba Samuel Reservoir, 37 km South-West of Addis Ababa. The Reservoir acts as a pollutant sink from upstream Addis Ababa and nearby agrochemicals from small and large scale agricultural activities (irrigation farms and floriculture). In addition, some pollutants can emanate from natural sources [19]. OCPs and PCBs in the Akaki River system might come from obsolete pesticide sites, public health and agricultural uses and at old transformer and capacitor sites in Gofa, Mexico Square and Kotebe in the premises of the Ethiopian Electric Power Corporation (EEPCO), respectively [13,20,21].

Though Ethiopia is signatory to the Stockholm Convention and agreed to support research on POPs, only limited data is available for such compounds in different media. To the best of our knowledge, there is no study carried out on the levels of OCPs and PCBs and their potential impacts on the ecology. Therefore, the aims of the present study were to determine the concentrations, distributions and seasonal variations, and estimate the potential ecotoxicological risks of OCPs and PCBs in Akaki River catchment, Central Ethiopia.

2. Materials and methods

2.1. Sampling sites

After a detailed preliminary survey of the Akaki River catchment, sampling was conducted at twelve (12) sampling sites. The selection of each sampling site was based on anthropogenic activities in the catchment. The site locations were marked using a GPS (Global Positioning System, Garmin). Among these sites, three (3) sampling sites, including S1, control site1 (GAR at Entoto Kidanemihiret monastery), S2 (GAR at Tirunesh Beijing Hospital), S3 (GAR below Akaki Town) are located on the Greater Akaki River in the residential area. Kotebe maintenance center, where decommissioned transformers and capacitors are stored, is situated between S1 and S2. Another four (4) sites: S4, control site 2 (LAR above Geferesa Reservoir), S12 (LAR at German square, Gofa), S5 (LAR at Lafto Bridge) and S6 (LAR at Jugan Kebele, boundary of Addis Ababa and Oromia Special Zone) are located in Little Akaki River, where a large number of industrial effluents drain into the river. Mexico square, where old transformers and capacitots are deposited, is located between S4 and S12; where as Gofa site is between S12 and S5. Sampling sites S7 (Aba Samuel Reservoir below the confluence point of GAR and LAR), S8 (Aba Samuel Reservoir at the midpoint) and S9 (Aba Samuel Reservoir above the dam) are on the reservoir. Additional two sampling stations were also selected downstream to the reservoir (S10 and S11) (Fig. 1).

2.2. Sampling procedures

Water samples were collected from eleven sampling stations (S1–S11) in August 2016 representing the rainy season. Water samples collected during the dry season could not be processed, because of financial and other logistics limitations. From each sampling site, 1500 mL of water sample was collected by lowering pre-cleaned amber glass into the upper surface of the river, 30–50 cm deep, and allowing them to overflow before withdrawing. Before sampling, bottles were rinsed three times with the river water to be collected. The filtered samples were stored in a refrigerator at 4 °C until further pre-treatment and analyses.

Twenty four (24) sediment samples were collected in August 2016 and January 2017 representing the rainy and dry seasons, respectively. Approximately 500 g of the top few centimeters of the sediment were collected using a stainless steel Ekman bottom Grab sampler. Composite samples were collected at all the sampling stations. Four samples were taken from each sampling site, pooled, homogenized, placed in clean dark-polyethylene bags, labeled, stored on the ice-cooled container and transported to the laboratory. In the laboratory, coarse particles, leaves or large material was removed. Subsequently, sediment samples were air-dried in the

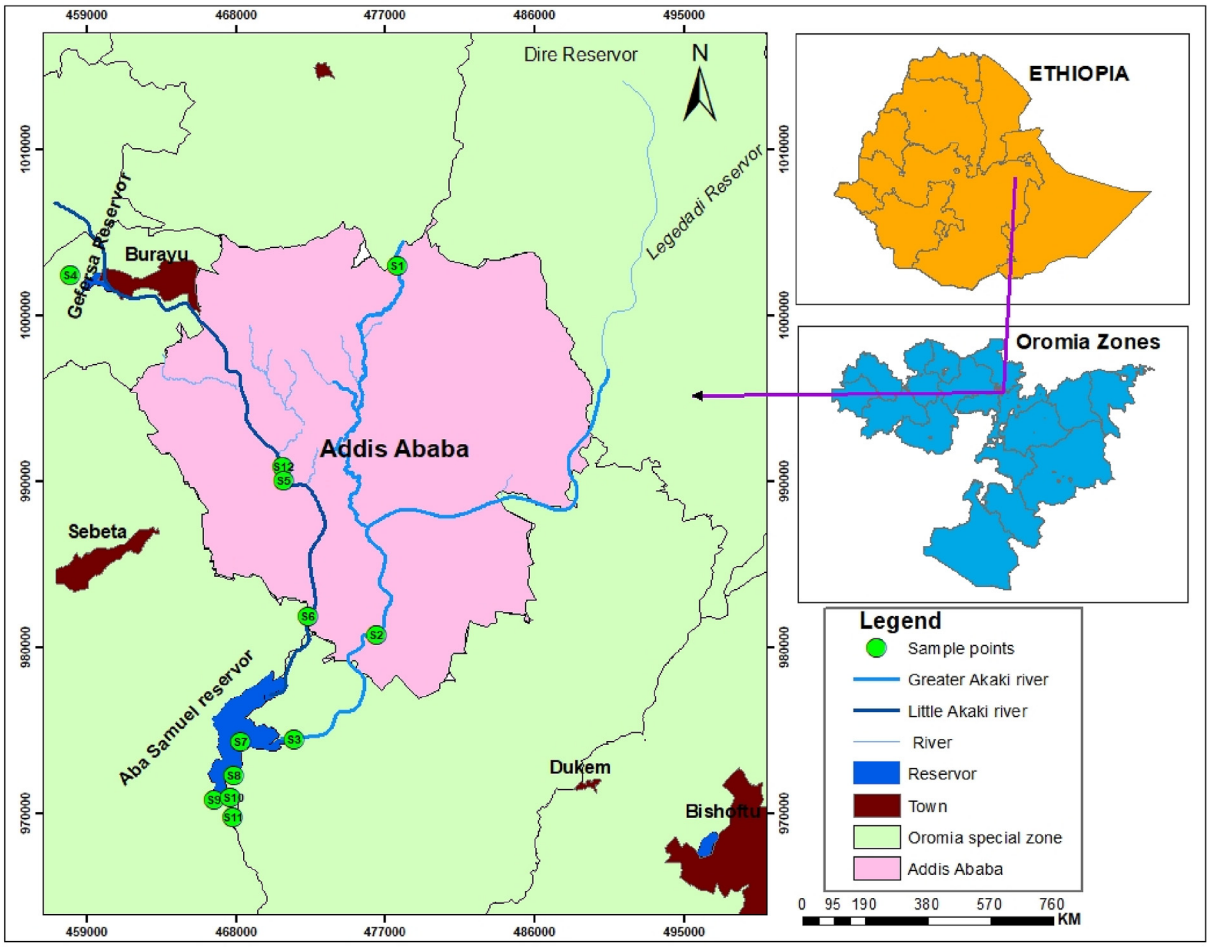

Fig. 1. Map of Ethiopia (top right), Oromia regional state (middle right) and Addis Ababa, Oromia special zone, Aba Samuel Reservoir, Little Akaki and Great Akaki Rivers (left) showing the sampling sites.

shade at ambient temperature, ground, homogenized and, sub-sampled and passed through a stainless steel sieves of different sizes (500-150 μm) and stored until further treatment. Finally, the water and sediment samples were transported to the laboratory in the Department of Environmental, Water and Earth Sciences, Tshwane University of Technology, Pretoria, South Africa for extraction and analyses.

2.3. Extraction and cleanup

2.3.1. Liquid-liquid extraction and clean up of water samples

One liter of filtered water was measured, poured into a separatory funnel and spiked with 200 ppb of 2,4,5,6-tetrachloro-m-xylene (TCMX) as the surrogate standard. The water sample was extracted three times with 40 mL of dichloromethane for each extraction by shaking the separatory funnel vigorously for 2–3 min with intermittent release of pressure. The layers were allowed to separate for 10 min. The three extracts were combined in 250 mL round bottomed flask, dried over anhydrous sodium sulfate and then concentrated to 1–2 mL with a rotary evaporator. To control the effectiveness of sample processing, procedural blanks were prepared similar to the main sample. Prior to instrumental analysis, the extract was spiked with known amounts of the internal standard, PCB-155 and finally injected into the GC-MS system.

2.3.2. Soxhlet extraction and cleanup of sediment samples

The analytical procedure for extraction and cleanup of the sediment samples were based on the previously established method with some modification [22]. Approximately, 10 g of dried, homogenized, powdered and sieved (150 μm) sediment samples were placed in a hexane prewashed cellulose thimble. It was then spiked with 200 ppb of surrogate standard, TCMX, and Soxhlet extracted with 180 mL of hexane: acetone (2:1 v/v) for 16 h. After extraction, the samples were subjected to volume reduction using rotary vapor and 1.0 g of activated copper powder was added for desulfurization. After 3 h, the extract was transferred to a glass column packed with 8 g of acidic silica (40% H_2SO_4) and 0.5 g activated anhydrous Na_2SO_4. The column was conditioned with 10 mL hexane and the sample was transferred into the column using a pipette bulb. The OCPs and PCBs were eluted with 15 mL of hexane and 10 mL of dichloromethane. Finally, the extract was rotary evaporated to 2–3 mL followed by volume reduction by N_2 gas. To control the effectiveness of sample processing, procedural blanks were prepared similar to the main sample. The final extract was re-solubilized in a solution containing internal standard (PCB-155) prior to the analysis.

2.4. Instrumental analysis

The cleaned extracts were analyzed using a Shimadzu GC-MS Model 2010 plus gas chromatograph equipped with a QP 2010 Ultra mass spectrometer (Kyoto, Japan) using electron ionization (EI). The samples were automatically injected by a Shimadzu A0C-20i autosampler. Separation of the individual OCPs and PCBs was

achieved using a fused silica capillary column DB5 (30 m × 0.25 mm i.d. x 0.10 μm film thickness; manufactured by Agilent Technologies INC., USA). The carrier gas used was helium (99.999% purity) at a constant flow rate and linear velocity of 1.5 mL/min and 44.9 cm/s, respectively. The oven temperature program was: 70 °C raised to 140 °C (25 °C/min), a second ramp at 15 °C/min to 210 °C and a final ramp at 10 °C/min to 300 °C, using the splitless injection mode. The ion source and interface temperatures were set at 250 °C and 300 °C, respectively. The fragmented ions were monitored using selected ion monitoring (SIM) mode. Linearity was substantiated by a 7-point calibration levels ranging from 1 to 500 μg/L prepared as a mixture in isooctane. The identification was established on the retention times of injected samples with those of individual standards and monitoring of the reference and target ions. OCPs and PCBs were quantified using the internal standard method, using PCB-155 as an internal standard. The samples were analyzed for 8 OCPs (lindane, p, p'-DDE, p, p'-DDD, p, p'-DDT, heptachlor epoxide (B), dieldrin, α,β -endosulfan and endosulfan sulfate) and 7 indicator PCBs (28, 52, 101, 118, 138, 153 and 180). We perform the injection and selection of *m/z* of OCPs and PCBs with individual standards as well as the time group for the acquisition data with a mixture of standards by GC-MS analyses with SIM mode until achieving the best sensitivities of all OCPs and PCBs peak.

2.5. Quality assurance& quality control (QA/QC)

Chemicals (solvents, reagents, adsorbents) used for OCPs and PCBs analyses were of analytical grade. The glasswares used were carefully cleaned with a laboratory soap solution, rinsed with distilled water and acetone before drying. During extraction, the Soxhlet apparatus was covered with foil to prevent possible degradation of the analytes by UV-light. The rainy season samples were digested and analyzed in duplicate, and the mean ± % difference was reported. To ensure accuracy and monitor procedural performance, surrogate standard (TCMX) was added to each sample before extraction and clean up procedures. The average recovery of the surrogate was satisfactory with the value of 92.40%. As a result, the reported concentrations of target compounds were not recovery corrected [23]. The limits of detection (LOD) and quantification (LOQ) were calculated from the relationship between the standard deviation of the intercept of the calibration curve (SD) and its slope (*S*). The LOD and LOQ were calculated from the following equations: LOD = (3.3 x *SD* of intercept/S) and LOQ = (10 x *SD* of intercept/S). Where the standard deviation of the intercept (SD) is the product of standard error (SE) of intercept and $\sqrt{N}$ (where, N is the number of tests, in our case N = 7) and S the slope of linearity plot. The standard error (SE) of the intercept was generated from regression analyses of the data set [24]. The instrumental LODs ranged from 0.07 to 0.31 μg/kg and LOQs ranged from 0.21 to 0.95 μg/kg.

2.6. Ecological risk assessment

In order to assess whether PCBs and OCPs in the Akaki River catchment and Aba Samuel Reservoir are at concentrations that may cause adverse effects, we compared the PCB and OCP levels in water and sediment against international guidelines [25,26]. A contaminant value below the limit suggests that adverse effects would be rarely observed, whereas a level above the limit suggests adverse effects would frequently occur.

3. Results and discussion

3.1. OCPs and PCBs in water

3.1.1. Concentrations of OCPs and PCBs in water

In this study, 8 OCPs and 7 PCB congeners were analyzed in 11 water samples in the Akaki River system and Aba Samuel Reservoir. The water samples contained detectable concentrations of DDT and its metabolites (DDE and DDD), lindane and dieldrin and three indicator PCBs (PCB-28, PCB-101 and PCB-118). All other OCPs and PCBs were below the detection limit of the instrument used. The concentrations of DDT and its metabolites, lindane and dieldrin in water samples from Akaki River catchment is presented in Table 1. As can be seen from the Table 1, DDT and its metabolites are the abundant pollutants detected in the study area. The possible reasons for the presence of high levels of DDTs may be attributed to the run-off and deposition of DDT, which is used for agricultural and public health purposes. This dominance of DDTs among the analyzed OCPs in water has also been documented in other studies [10,27]. Mean concentrations of ΣDDTs were in the range of 5.33–30.58 ngl^{-1} (mean 11.39 ngl^{-1}). The composition distinction of DDT and its metabolites are useful for identifying the source of DDTs [28]. When (DDE + DDD)/ΣDDTs is more than 0.5, it suggests historical accumulation of DDTs, which may have gone through a long-term weathering [10]. In this study, p,p'-DDT, p,p'-DDE and p,p'-DDD were found in 8 sampling stations of the Akaki River system. Except S5 (ratio = 0.17), the ratios of (DDE + DDD)/ΣDDTs in water from Akaki River catchment (0.66–0.84) were greater than 0.5. These results indicated that DDTs in water from the study area derived from historical DDT sources, while the level at S5 suggests recent discharge. Lindane was detected only at S2 and S10 with concentrations 15.4 ± 0.25 ngl^{-1} and 1.01 ± 0.002 ngl^{-1}, respectively. On the other hand, dieldrin is detected only at S5 with concentration 4.85 ± 0.007 ngl^{-1} [29]. reported lindane levels of 8 ngl^{-1} and this value is similar to what was observed at Akaki River in this study with mean concentrations of 8.2 ngl^{-1}. Meanwhile,

Table 1
Concentrations of OCPs (mean ±% difference, ngl^{-1}) in water samples collected from Akaki river catchment and Aba Samuel reservoir in August 2016 (Rainy season).

No.	Sample Name	p,p'-DDT	p,p'-DDE	p,p'-DDD	ΣDDTs	Lindane	Dieldrin
S1	GAR at Entoto Kidanemihiret Monastery	nd	nd	nd	nd	nd	nd
S2	GAR at Tirunesh Beijing Hospital	nd	nd	nd	nd	15.4 ± 0.25	nd
S3	GAR before mixing the Reservoir	10.2 ± 1.13	5.2 ± 1.2	14.5 ± 6.4	29.9	nd	nd
S4	LAR above Gefersa Reservoir	nd	nd	nd	nd	nd	nd
S5	LAR at Lafto Bridge	76 ± 33.94	4.65 ± 1.3	11.1 ± 4.1	91.75	nd	4.85 ± 0.01
S6	LAR at Jugan kebele	8.2 ± 0.28	4.35 ± 0.07	12.0 ± 2.8	24.55	nd	nd
S7	Aba Samuel Reservoir below the confluence point of GAR and LAR	7.0 ± 1.4	2.95 ± 0.2	32.5 ± 24.7	42.45	nd	nd
S8	Aba Samuel Reservoir at the midpoint	4.35 ± 1.2	6.0 ± 0.42	7.5 ± 3.5	17.85	nd	nd
S9	Aba Samuel Reservoir above the Dam	10.15 ± 1.5	7.0 ± 0.4	14.5 ± 7.8	31.65	nd	nd
S10	Outlet of the Reservoir	4.2 ± 0.7	2.95 ± 0.07	12.0 ± 2.9	19.15	1.01 ± 0.002	nd
S11	About 1000 m downstream to the Reservoir	4.85 ± 0.64	1.65 ± 0.07	9.5 ± 0.7	16	nd	nd

ND = not detected.

work done by Ref. [30] from the Bosomtwi lake reported lindane level of 71 ngl^{-1} much higher that what was observed in the current study.

In the present study, PCB-28, PCB-101 and PCB-118 were detected at some sampling sites. PCB-28 was detected at S5 (0.3 ± 0.07 ngl-1) and at S9 (0.85 ± 0.07 ngl-1). PCB-101 was detected at S2 (5.75 ± 1.8 ngl-1), S3 (7.0 ± 0.07 ngl-1) and S7 (6.8 ± 0.07 ngl-1), while PCB-118 was detected only at S2 (3.8 ± 0.28 ngl-1).

3.1.2. Eco-toxicological risk assessment of water samples

Exposure of residues of OCPs and PCBs to humans could be through water, food and air. The Akaki River is the tributary (upper part) of the most productive Awash River in Ethiopia [17]. Thus, it is important to assess the potential risk of consumption of water drawn from the river. In Ethiopia, there is no established maximum pesticide residue limit for drinking water except DDT. The levels of the OCPs recorded in this study were, however, compared to standard limits set by the World Health Organization (WHO) and that of Australia [25]. The average levels of all pesticide residue concentrations in water samples analyzed were lower than the organochliprine pesticides set limit (Table 2). These results indicated that the residues of DDT, DDE, lindane and dieldrin detected in the water samples from Akaki River system did not pose any ecological risks.

To estimate the potential eco-toxicological risk of PCBs in Akaki River system, the maximum contaminant level (MCL) of PCBs in drinking water set by the United States Environmental Protection Agency (US EPA 2009) (500 ngl^{-1}) was taken into account. Σ_7PCBs in all water samples from Akaki river catchment (0.30–9.55 ngl^{-1}) were well below the MCL of US EPA, which suggested that the potential risks caused by PCBs are rather low.

3.2. OCPs and PCBs in sediment

3.2.1. Concentrations and seasonal variations of OCPs in sediment

Tables 3 and 4 show the concentrations of OCPs in the analyzed surface sediments from the 12 sampling stations from Akaki River catchment and Aba Samuel Reservoir in the dry and rainy seasons expressed in terms of dry weight. As can be seen from Tables, only lindane was detected in the dry season, while p,p'-DDT, p, p'-DDE, p, p'-DDD, α,β-endosulfan, heptachlor epoxide (B) and dieldrin were detected in the rainy seasons.

In the dry season, lindane was detected in all the sampling sites except at one of the control sites (S1). The concentration of lindane ranged from nd-1161.20 μg/kg dry weight with a mean concentration of 371.78 μg/kg. The three highest lindane concentrations 742.4, 850.87, and 1161.20 μg/kg dw were recorded at LAR at the Jugan Kebele, at the outlet of the Reservoir and at about 1000 m downstream to Aba Samuel Reservoir (S6, S10, and S11), respectively. Due to lack of sampling boat, sediment samples were collected on the shores of the Reservoir and this might underestimate the actual levels of pollutants, including lindane in the Reservoir. S6 is the site located at Little Akaki River before joining Aba Samuel reservoir. The predominance of lindane in this study indicates the recent input of lindane in the region and the level varies depending on the sampling site indicating variable sources in different locations. Lindane pollution in the study area might be from the obsolete pesticide accumulation, as it is one of the recorded obsolete pesticides in different regions of the country, particularly in Addis Ababa [31] and wastes of different pharmaceutical products like lotions. Lindane (γ- HCH) was commonly used in most countries for seed dressing to protect crops against ants, but it is currently under restricted pesticides list due to its persistence and toxicity [32]. Lindane is also used against ectoparasites in veterinary and pharmaceutical products (for the treatment of lice and scabies). It is also used for the control of disease vectors, including mosquitoes, lice, and fleas [33]. In this study, higher concentrations of lindane were detected in sediment samples from LAR (mean, 310.86 μ/kg dw) than that of GAR (229.36 μ/kg dw), which could have originated from obsolete pesticide stores and municipal wastes (mainly pharmaceuticals) found near LAR. Lindane concentrations downstream to Aba Samuel reservoir (mean, 1006.04 μ/kg dw) were higher than the values obtained at the reservoir (48.66 μ/kg dw).This might be due to reservoir samples were collected at the shore, that could underestimate the result. To the best of our knowledge, no investigations have been carried out on the distribution of lindane in sediment samples in the study area. Thus, the comparison was carried out in other localities in Ethiopia and Africa.

Table 3
Concentrations of OCPs mainly lindane (μg/kg, dry mass) in sediment samples collected from Akaki river catchment and Aba Samuel reservoir in dry season.

No.	Sample Name	Lindane
S1	GAR at Entoto Kidanemihiret Monastery	nd
S2	GAR at Tirunesh Beijing Hospital	412.56
S3	GAR before mixing the Reservoir	275.51
S4	LAR above Gefersa Reservoir	1.29
S5	LAR at Lafto Bridge	350.48
S6	LAR at Jugan kebele	742.40
S7	Aba Samuel Reservoir below the confluence point of GAR and LAR	120.51
S8	Aba Samuel Reservoir at the midpoint	2.60
S9	Aba Samuel Reservoir above the Dam	22.88
S10	Outlet of the Reservoir	850.87
S11	About 1000 m downstream to the Reservoir	1161.20
S12	LAR at German square, Gofa	149.25

nd: not detected.

The mean concentration of lindane in sediment in this study (371.78 μg/kg dw in the dry season) seems to be higher than the result reported in Tekeze Dam, Northern Ethiopia (6.920 μg/kg dw) [34]. However, our result is much less than the values obtained from sediment samples of Warri River of the Niger Delta, Nigeria (9,190 μg/kg dw at Ovwian, 3,540 μg/kg dw at Ekakpamre, and 470 μg/kg dw at Ovu site) [35].

In the rainy season, the DDTs were the predominant pesticides detected and found in all the twelve sampling stations, including the control sites followed by α, β-endosulfan, heptachlor epoxide (B) and dieldrin. The total concentrations of DDTs in surface sediments were found in the range of 1.91–1076.73 μg/kg with a mean concentration of 112.38 μg/kg. The concentration was in the range of 0.86–482.03 μg/kg for DDT, 0.52–161.80 μg/kg for DDE and 0.53–432.90 μg/kg for DDD (Table 4). The high concentration of

Table 2
Comparison of levels of OCPs in water with guideline values of World Health Organization (WHO), Australia and Ethiopia.

Pesticide	Mean concentration (ngl^{-1}) at Akaki River	WHO guideline value(ngl^{-1})	Australia guideline value (ngl^{-1})	Ethiopian guideline value (ngl^{-1})
P,p'-DDT	15.6	2000	60	30
P,p'-DDE	4.3	2000	60	–
Gamma-HCH (Lindane)	8.2	2000	50	–
Dieldrin	4.8	30	10	–

Table 4
Concentrations of OCPs (mean ±% difference, μg/kg dw) in sediment samples collected from Akaki river catchment and Aba Samuel reservoir in rainy season.

No.	Sample Name	p, p'-DDT	p, p'-DDE	p, p'-DDD	ΣDDTs	α,β-endosulfan	heptachlor epoxide	dieldrin
S1	GAR at Entoto Kidanemihiret Monastery	2.51 ± 0.04	1.79 ± 0.21	2.54 ± 0.32	6.84	nd	nd	nd
S2	GAR at Before Akaki town	1.96 ± 0.08	3.52 ± 0.03	1.81 ± 0.02	7.27	nd	nd	nd
S3	GAR before mixing the Reservoir	6.16 ± 0.12	5.52 ± 0.02	3.81 ± 0.18	15.49	nd	nd	nd
S4	LAR above Gefersa Reservoir	2.78 ± 0.01	1.24 ± 0.14	2.57 ± 0.01	6.59	nd	nd	nd
S5	LAR at Lafto Bridge	12.84 ± 0.08	17.73 ± 0.13	7.49 ± 0.05	38.06	nd	nd	nd
S6	LAR at Jugan kebele	4.21 ± .20	5.88 ± 0.16	3.35 ± 0.30	13.44	nd	nd	nd
S7	Below the confluence point of GAR and LAR	482.03± 0.04	161.80± 0.02	432.90± 0.02	1076.73	127.78± 0.01	12.65± 0.01	78.56± 0.14
S8	Reservoir at the midpoint	28.09 ± 0.03	14.61 ± 0.03	25.05 ± 0.06	67.75	nd	nd	nd
S9	Reservoir above the Dam	28.28 ± 0.03	9.64 ± 0.05	27.54 ± 0.05	65.46	nd	1.27± 0.17	nd
S10	Outlet of the Reservoir	0.86 ± 0.03	0.52 ± 0.15	0.53 ± 0.34	1.91	nd	nd	nd
S11	1000 m downstream to the Reservoir	6.60 ± 0.10	7.52 ± 0.09	5.93 ± 0.31	20.05	nd	nd	nd
S12	LAR at German square	11.58 ± 0.17	7.95 ± 0.30	9.46 ± 0.01	28.99	nd	nd	nd

nd: not detected.

DDT and relatively lower concentrations of DDE and DDD show recent use of the pesticide as explained below. DDT was legally used for public health purposes until recently. The reason for the prevalence of DDTs in all the sampling sites in this season might be due to the higher surface runoff bringing residues from different sources. DDT was used in agriculture during the rainy months from June to October. In addition to this, Ethiopia is one of the many African countries burdened with the problem of obsolete pesticides [31] and DDT is still used for agricultural and public health programs [36,37].

Residual levels of DDTs varied depending on sampling sites indicating variable sources in different locations. Site S7 is a sampling site at Aba Samuel Reservoir below the confluence point of GAR and LAR. At this site, six of the eight analyzed organochlorine pesticides were detected. This site is close to industrial establishments at Little Akaki River and peri-urban agricultural farms. All the detected pesticides were at higher concentrations. Thus, runoffs from the peri-urban areas and waste discharge from the capital city could be the major sources of these pollutants. The highest levels of DDT were found in the samples taken from Aba Samuel Reservoir (S7, S8, and S9), S5 and S12 with values of 482.03 μg/kg, 28.09 μg/kg, 28.28 μg/kg, 12.84 μg/kg and 11.58 μg/kg, respectively. These high values of DDT were observed at Aba Samuel Reservoir and downstream areas, located in a peripheral zone of the capital city (Addis Ababa) where vegetable farms and solid waste dump exist and near the vicinity of the inflow of Little Akaki River (S5 and S12).

It is well known that DDT can be biodegraded to DDE and DDD under aerobic and anaerobic conditions, respectively [38]. The ratio of p, p' DDT and its major degradation product p, p'-DDE can be used to understand the chronology of DDT residues in the environment. Strandberg et al., 1998 [39] suggested that p, p'-DDT/p, p'-DDE ratio lower than 0.3 could be the result of the aged mixtures in the environment, and those higher than 0.5 might indicate recent use of DDT. All the results indicate that the ratio of p, p'-DDT/p, p'-DDE is greater than 0.5 which is indicative of recent inputs of DDTs in all sampling sites. This most likely happened due to the illegal use of DDT for agricultural purposes and for controlling vector-borne diseases in the region. According to the report by the Ethiopian Ministry of Health, DDT has been illegally diverted to agricultural pest control in some areas [40]. Ethiopia had a formulation facility for DDT, which was discontinued in 2009. Although its use in agriculture was officially banned in 2010, the use of DDT for vector control and sanitary purposes is still available [41]. There might also be recent inputs of DDT into the environment from obsolete pesticide sites.

When compared with other studies, the levels of DDTs in surface sediments in the present study were higher than those from Singapore coastal areas (2.2–11.9 μg/k; [42]); Danshui River estuary, Taiwan (nd–9.85 μg/kg; [43]); Lake Victoria, Uganda (0.41–8.07 μg/kg; [44]), but comparable to those in Lake Awassa (3.64–40.2 μg/kg; [45]); Casco Bay, Maine, USA (nd–455.5 μg/kg; [46]) and Lake Maryut, Egypt (0.07–105.6 μg/kg; [47]).

As for the other pesticide contaminants, α,β-endosulfan (127.78 μg/kg) and dieldrin (78.56 μg/kg) were determined only at S7 while heptachlor epoxide (B) was detected at S7 and S9 (average concentration, 6.96 μg/kg). The sampling station S7 is the confluence point of the two Akaki Rivers. Available information indicates that highly dangerous pesticides such as dieldrin and heptachlor are the main components of the obsolete stocks dumped at more than 1000 sites in Ethiopia, particularly in Addis Ababa [48]. Besides, non-point sources from agricultural fields and urban areas could be the other sources of these pesticides [15].

3.2.2. Concentrations and seasonal variations of PCBs in sediment

Tables 5 and 6 show the concentrations of PCBs in the analyzed surface sediments from the 12 sampling stations from Akaki River and Aba Samuel Reservoir in the dry and rainy seasons expressed in terms of dry weight. The analyzed sediment samples show the presence of PCB-52, PCB-101, and PCB-118 in the dry and all indicator PCBs (PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153, and PCB- 180) in the rainy seasons.

Many countries in the developing regions have several PCB sources such as uncontrolled (open) burning of municipal waste, PCB-containing waste imported from developed countries and the use of PCBs in condensers and transformers. So far, the environmental monitoring of PCBs in Ethiopia is not well developed; only limited data are available. PCBs concentrations were expressed as the sum of 7 individual congeners (PICES, PCB IUPAC # 28, 52, 101, 118, 153, 138 and 180) recommended by the International Council for the Exploration of the Sea (ICES) in order to harmonize data [49]. The total concentrations of PCBs (sum of 7 congeners) in sediments ranged from 3.15 to 63.78 μg/kg with a mean value of 8.56 in the dry season and 0.06–8.33 μg/kg with a mean value of 1.06 during the rainy season indicating that PCBs are widespread contaminants in the study area (Tables 5 and 6). During the dry season, PCB-52 and PCB-101 were measured at elevated concentrations in the majority of the sampling sites whereas PCB-118 was detected only at S12.

In the rainy season, PCBs were detected in 10 out of the 12 sampling stations, but at relatively low concentrations compared to the dry season. Great Akaki River before Akaki town, Aba Samuel Reservoir at the confluence point of LAR and GAR, Aba Samuel Reservoir at the midpoint and Aba Samuel Reservoir at the outlet (S2, S7, S8, and S10, respectively) were the predominant sites.

Table 5
Concentrations of indicator PCBs (μg/kg, dry weight) in sediment samples collected from Akaki River catchment and Aba Samuel reservoir in dry season.

No.	Sample Name	PCB-28	PCB-52	PCB-101	PCB-118	PCB-138	PCB-153	PCB-180	Total PCBs
S1	GAR at Entoto Kidanemihiret Monastery	nd	nd	nd	nd	nd	nd	nd	nd
S2	GAR at Tirunesh Beijing Hospital	nd	5.48	3.20	nd	nd	nd	nd	8.68
S3	GAR before mixing the Reservoir	nd	5.50	2.01	nd	nd	nd	nd	7.51
S4	LAR above Gefersa Reservoir	nd	nd	nd	nd	nd	nd	nd	nd
S5	LAR at Lafto Bridge	nd	10.57	2.33	nd	nd	nd	nd	12.90
S6	LAR at Jugan kebele	nd	33.37	4.23	nd	nd	nd	nd	37.60
S7	Aba Samuel Reservoir below the confluence point of GAR and LAR	nd	11.32	1.89	nd	nd	nd	nd	13.21
S8	Aba Samuel Reservoir at the midpoint	nd	7.11	0.29	nd	nd	nd	nd	7.40
S9	Aba Samuel Reservoir above the Dam	nd	nd	3.37	nd	nd	nd	nd	3.37
S10	Outlet of the Reservoir	nd	59.37	4.41	nd	nd	nd	nd	63.78
S11	About 1000 m downstream to the Reservoir	nd	nd	3.15	nd	nd	nd	nd	3.15
S12	LAR at German square, Gofa	nd	8.88	0.98	2.38	nd	nd	nd	12.24

NB. nd = not detected.

Table 6
Concentrations of indicator PCBs (mean ±% difference, μg/kg dw) in sediment samples collected from Akaki River catchment and Aba Samuel reservoir in rainy season.

No.	Sample Name	PCB-28	PCB-52	PCB-101	PCB-118	PCB-138	PCB-153	PCB-180	Total PCBs
S1	GAR at Entoto Kidanemihiret	nd	nd	nd	nd	nd	nd	nd	nd
S2	GAR at Tirunesh Beijing Hospital	nd	nd	0.45 ± 0.20	nd	0.61 ± 0.36	0.77 ± 0.13	1.30 ± 0.09	3.13
S3	GAR before mixing the Reservoir	nd	nd	0.36 ± 0.05	nd	nd	nd	0.49 ± 0.28	0.85
S4	LAR above Gefersa Reservoir	nd	nd	nd	nd	nd	nd	nd	nd
S5	LAR at Lafto Bridge	nd	nd	0.06 ± 0.01	nd	nd	nd	nd	o.o6
S6	LAR at Jugan kebele	nd	nd	nd	nd	nd	nd	nd	nd
S7	Below the confluence point of GAR and LAR	nd	2.50 ± 0.04	0.67 ± 0.03	1.15± 0.06	0.53 ± 0.05	0.48± 0.17	0.32 ± 0.21	5.65
S8	Reservoir at the midpoint	nd	2.68 ± 0.01	nd	nd	0.36 ± 0.40	0.34 ± 0.16	0.07 ± 0.41	3.45
S9	Reservoir above the Dam	nd	3.04 ± 0.01	nd	nd	nd	0.17 ± 0.34	nd	3.21
S10	Outlet of the Reservoir	1.27 ± 0.01	2.45 ± 0.02	0.52 ± 0.01	1.05 ± 0.02	0.79 ± 0.02	1.06 ± 0.08	1.19 ± 0.01	8.33
S11	About 1000 m downstream to the Reservoir	nd	3.28 ± 0.03	nd	nd	0.67 ± 0.38	nd	1.12 ± 0.01	5.07
S12	LAR at German square	nd	3.33 ± 0.15	nd	nd	nd	nd	0.64 ± 0.06	3.97

NB. nd = not detected, **sd** = standard deviation.

Among the congeners, PCB-180, PCB-52, PCB-101, PCB-138, and PCB-153 were the most abundant in this season. When considered among the whole sampling sites, Aba Samuel Reservoir at the outlet (S10) contained all indicator PCBs with a total concentration of 8.33 μg/kg d.w.

The PCB congener and homolog profiles in environmental matrices can often provide valuable information on sources, environmental transport, and the fate of PCBs [50]. Generally, a trend in seasonal difference was observed in the congener distribution in the river and reservoir sampling points. The distribution of PCB congeners in the sediment from Akaki River catchment and Aba Samuel Reservoir showed a predominance of lower chlorinated PCB congeners in the dry but both lower and highly chlorinated PCB congeners in the rainy season. Low chlorinated PCBs such as tri-CB is typically used in additives of paints and electrical appliances [51]. Hence direct disposal of waste from these industries could transport tri-CBs into the aquatic environment. However, higher chlorinated PCB congeners accumulation suggests a point source contamination. Electrical equipments like transformers and capacitors containing PCB contaminated oil are the main sources of PCB pollution in the environment. The abundance of these congeners is likely to be explained by their high presence in the commercial PCB mixtures, such as Aroclor 1260, and by their molecular structure and high lipophilicity, which facilitate stability and persistence; all these characteristics make easier their adsorption to sediments and accumulation in aquatic ecosystem [52]. In general, a dominance of higher chlorinated congeners in sediment samples from the Akaki River catchment and Aba Samuel Reservoir is observed, which is in good agreement with the previous study in some urban soils of Addis Ababa [21].

According to the inventory by UNEP-NIP (2006), there are many decommissioned transformers and capacitors in Ethiopia, particularly in Addis Ababa. Large quantities of transformers and capacitors are found at Gofa, Mexico square, and Kotebe maintenance centers. Due to poor management and handling of transformers and capacitors, and long years of open storage, the land in the vicinity of the main stores and the nearby streams are believed to be contaminated by PCBs that have spilled over or discarded dielectric fluids. The area is easily accessible to dogs, cattle and even human beings. As a result of the absence of awareness on the impacts of PCBs on human health, EEPCO technicians do not take any precautions during repair work. There is, therefore, a high possibility of dermal contact with PCBs and of inhaling PCB vapors. PCB containing dielectric fluids are stored in concrete pits located at the two repair and maintenance workshops of the corporation.

3.2.3. *Evaluation of the ecological risk of OCPs and PCBs in sediment*

The Canadian interim sediment quality guidelines (SQGs) for the protection of aquatic wildlife and probable effect levels (PELs) for adverse biological effects [26] can be used to estimate the likely biological effects of contaminants in Akaki river system sediment. The SQG is the concentration below which biological effects are not expected, while the PEL is a level above which adverse effects are likely to occur. In assessing the potential effects of contaminants determined in sediments, some OCPs and indicator PCBs levels in sediment were compared with SQG values in Table 7.

The concentration of lindane in the dry season and p'-DDT, p, p'-DDE, p, p'-DDD, heptachlore epoxide and dieldrin in the rainy seasons in the sediment samples from Akaki river and Aba Samuel reservoir were above the Canadian interim sediment quality guidelines at most of the sites and even higher than PEL at fewer stations. This suggests there is a greater possibility of higher

Table 7
Concentrations of PCB and OCP in surface sediments from Akaki River and Aba Samuel Reservoir (μg/kg, dw) and sediment quality guidelines.

Compound	SQGs values, μg/kg (dry mass)		This study percent incidence of effects					
			Dry season			Rainy season		
	ISQG	PEL	< ISQG	ISQG-PEL	> PEL	<ISQG	ISQG- PEL	>PEL
Σ_7PCBs	34.1	277	80	20	–	100	–	–
p, p'-DDT	1.19	4.77	100	–	–	8.3	36.4	58.3
p, p'-DDE	1.42	6.75	100	–	–	16.7	33.3	50
p, p'-DDD	3.54	8.51	100	–	–	41.7	25	33.3
lindane	0.94	1.38	–	9.1	90.9	–	–	–
Heptachlore epoxide	0.6	2.74	100	–	–	–	50	50
Dieldrin	2.85	6.67	100	–	–	–	–	100

biolofical effects associated with DDT residues, Lindane, heptachlore epoxide and dieldrin if organisms are exposed to these sediments. Total PCB concentrations at all sites in the rainy and dry seasons were below the SQG except two sites in the dry season (S6 and S10). During the dry season, the concentrations of p, p'-DDT, p, p'-DDE, p, p'-DDD, heptachlore epoxied and dieldrin, at all sites were significantly lower than the ISQG values, indicating that adverse effects would occur rarely.

4. Conclusions

The present study reported the levels of OCPs and PCBs in dry and rainy season in Akaki river catchment and Aba Samuel reservoir, Central Ethiopia. 8OCPs and 7PCBs were investigated in water and sediment samples from 12 sampling sites. The water samples contained detectable concentrations of DDT and its metabolites (DDE and DDD), lindane and dieldrin and three indicator PCBs (PCB-28, PCB-101 and PCB-118). Whereas, the sediment samples indicated the existence of lindane in the dry and p'-DDT, p,p'-DDE, p,p'-DDD, α,β-endosulfan, heptachlor epoxide (B) and dieldrin in the rainy seasons. Among the indicator PCBs, the analyzed sediment samples show the presence of PCB-52, PCB-101 and PCB-118 in the dry and all indicator PCBs (PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153, and PCB-180) in the rainy season.

Both OCPs and PCBs concentrations showed obvious seasonal variations. The congener distributions of contaminants in water samples indicated historical contamination of the river system with DDT and its metabolites. However, sediment sample results indicated that lindane and DDTs originated from the current release of these contaminants in the studied regions. The distribution of PCB congeners in the sediment from Akaki River catchment and Aba Samuel Reservoir showed a predominance of highly chlorinated PCB congeners. A lower level of higher chlorinated PCB congeners accumulation suggests a point source contamination. Contamination levels of OCPs and PCBs can be categorized as low to moderate in relation to similar areas worldwide. Based on quality guidelines, lindane in the dry and p'-DDT, p, p'-DDE, p, p'-DDD, heptachlore epoxide and dieldrin in the rainy seasons in the sediment samples from Akaki river and Aba Samuel reservoir were above the limit at most of the sites. This suggests there is greater possibility of higher ecological hazards in these residues. Therefore, special attention should be paid to this river system. However, the levels of total PCB concentrations and other OCPs at all sites were below the limit and thus their potential ecotoxicological risks were rather low.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.emcon.2020.11.004.

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