Detections of Organochlorine Pesticides in Water, Sediment, and Fish Samples in Lake Tana and Lake Hayqe, Ethiopia

Dessie Tibebe (dessie.1977@gmail.com)
University of Gondar
Tarekegn Fentie
University of Gondar
M. L. Akele
University of Gondar
Marye Mulugeta
University of Gondar
Addis Kokeb
University of Gondar
Dereje Yenealem
University of Gondar
Asresie Kahaliw
University of Gondar
Zerubabel Moges
University of Gondar
Yezbie Kassa
University of Gondar
Tsegaye Adane
University of Gondar

Research Article

Keywords: pesticides, OCPs, water, fish, sediment, QuEChERS

Posted Date: May 9th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1626954/v1

Abstract

The extensive use of pesticides considered as a global threat to the ecological integrity of aquatic ecosystems. Most developing countries including Ethiopia are burdened with these toxic and persistent pesticides due to their wider used for agricultural pest and malaria control. The present study was aimed to investigate the concentration of Organochlorine pesticides water, sediment and fish samples in Lakes Tana and Hayqe. Eight samples of each water and sediment and five fish samples were collected. A laboratory based cross sectional study was conducted from Dec 2020 to March 2021 in Lakes Tana and Hayqe. A more sensitive method for the determination of 18 Organochlorine pesticides in water, sediments, and fish samples were adopted using QuEChERS and the analyses were done using GC-MS. Water samples were processed using a liquid–liquid extraction technique and gas chromatograph equipped with mass spectroscopy (GC-MS). Dispersive-solid-phase extraction (d-SPE) was used for fish and sediment samples followed by cleanup and gas chromatograph Mass Spectroscopy. In the method validation, Percent of recovery ranged from 88.4-107.6%. From the result lindane (1.11 μg/L) was recorded the lowest concentration of OCPs in water samples and total endosulfan was the highest (14.97μg/L). In sediment samples, deltamethrin (11.21 μg/kg) was the lowest and endrin (70.42 μg/kg) was the highest OCPs. From fish samples, lindane (12.63 μg/kg) was the lowest and total endosulfan (68.78 μg/kg) was the highest concentration. The ANOVA test and t-test also depicted that the levels of most pesticides were significantly varied with different sampling sites and between Lakes.

Introduction

Organochlorine pesticides (OCPs) are the most commonly used pesticides around the world and have a wide range of applications as agricultural and disease controlling chemicals [1]. OCPs routinely used throughout the world, due to increase crop yield and to kill insect pests [2]. Most OCPs extensively used in developed and developing countries [3]. Excessive use of pesticides may lead to the destruction of aquatic biodiversity [4]. The environmental pollution with pesticides is one of the most serious problems facing the world due to their potential toxicity, high persistence, slow degradation and bioaccumulation [5]. The unauthorized dumping of pesticide products and their containers are the main causes of the aquatic environment pollution [6]. Due to their hydrophobic characteristics, pesticides are going from surface water column to sediment and settle at the bottom [7]. Therefore, soil is the main route for pesticides to contaminate surface water as such away, runoff, direct application, spray drift, aerial spraying or erosion [8]. Most pesticides are considered as a global threat for the ecological integrity of aquatic ecosystems because of OCPs are persistent organic pollutant (POPs) and can be accumulate by food chain in the aquatic environment [9, 10].

The residues of OCPs have still been detected in sediments, water, aquatic species, livestock and poultry products in the world [11]. The agricultural production and pesticide uses increased due to world population alarmingly increase [12]. According to the United States Environmental Protection Agency (USEPA) report, 2012, world pesticide usage were > 2.7 million tons of active ingredients, mostly in agriculture to prevent crop losses [13]. The pesticides used in Africa from 1990 to 2016 were estimated 69,355.36 tons active ingredient, accounting for 2.1% world total pesticide usage [14]. in this cause Africa is burdened with an estimated amount of 50,000 tonnes of obsolete pesticides [15].According to FAO 2019 report, the agricultural use of pesticides in Ethiopia in 2017 were 4,128 tonnes active ingredient, and this pesticide consumption was 20 times higher than the consumption in 1993 [16]. According to the obsolete pesticide inventory report of FAO 2011, Ethiopia burdened with obsolete pesticide (over 1500 tone) mostly OCPs such as chlordane, DDT, dieldrin and lindane [15]. Most dangerous pesticides residue are found in these dumpsites and it will leak into the surrounding environment [17]. In Ethiopian there is agricultural practice and horticulture companies around the river and Lakes where farmers and companies utilize pesticide intensively. Small-scale farmers in the region extensively used to protect pests without applying any precaution and poor knowledge about the eco-toxicological properties of pesticides and inappropriate handling of agrochemicals [18], and empty pesticide containers thrown at farms or reused at home for other purposes [19]. This improper application of pesticides supported the studies conducted in Lake Awassa (2013), in Lake Ziway (2014), and Lake Koka OCP residues were detected [14, 15, 20]. OCPs use in Ethiopia for agricultural and health purposes, and as a consequence they can be found in aquatic, and terrestrial ecosystems even cow's milk [14, 16, 20].

Lake Tana has significant socio-economic importance for Sudan and Egypt downstream. More than 80% of the Nile water comes from Ethiopian highlands [21]. The Lake Tana and the adjacent wetlands provide directly and indirectly a livelihood for more than 500,000 people. In Lake Tana fisheries there are ten districts that have a potential for fishing and more than 5400 fishers have been engaged in fishing in a seasonal and full time basis at this time [22]. However the widespread expansion of water hyacinth suppresses the algae growth and development which is the main source of food for fishes by preventing enough sunlight and oxygen penetration. It also reduced the potential of fish production of Lake Tana from 13,000 tons to 1,000 tons per year currently [23]. There is still an increasing trend in pesticide use for improving agricultural production around Lake Tana, where it is a densely populated area with various agricultural activities; with three cropping times per year. Consequently, high concentrations of pesticides can be found in the environment and fish foods in Lake Tana [19].

Lake Hayq is a highland Lake in Ethiopia and it was stocked with Tilapia fish [24]. However increases in the biomass of plankton, the major symptom of eutrophication may result reduced water clarity and oxygen levels, test and odour problems, and losses of fisheries. This is because accelerated eutrophication of the Lake. Increased impute of nutrients is the major cause of eutrophication [24]. Due to reduced levels of precipitation and watershed destruction, the volume of the Lake is decreasing. Small and large scale agricultural investors are engaged in irrigation based investments that consume large quantity of water. In addition to these they are using more intensive agricultural inputs specially pesticides, which may pollute the water body having long term effect on the aquatic biota. In addition to the above factors, pollution from infrastructures like road construction and urbanization are contributing factors in the case of Lake Hayq [25].

Materials And Methods

3.1 Description of the study area

Lake Tana is located in Amhara National Region State which is 491 km away from the capital city Addis Ababa. It is the largest freshwater body in Ethiopia, located at an altitude of 1786 meter above sea level. The Lake has an average depth of 9m and maximum depth of 14m with surface area of 3,150 km^2 [26] (Fig. 1). Although about 40 feeder rivers enter the lake, the major four inflow rivers are Gilgel Abay, Rib, Gumara and Megech which contribute 93% of the total inflow, and the only outflow is the Blue Nile (Abay) River [27]. The water level depends on the outflows of Blue Nile River, Tana-Belles hydropower dam, and irrigation scheme decreased the volume of the Lake, and inflows of rivers and main-rainy season increase the volumes of the Lake [28]. The mean annual rainfall of the area is 1355.74mm and the volumes of the Lake fluctuate up to 1m within rainfall season [29]. The catchment area receives most of the agricultural and urban runoff and domestic waste effluents drained from the city of Bahir Dar. The Lake is also recognized as a biosphere reserve by UNESCO[28], [30] (Fig. 1).

The area around the Lake has been cultivated for centuries. Recent studies have shown that the increasing trend in cultivated land use on the Lake watershed which has great effects on current point and non-point sources of sediment and nutrient input [30], [31]. Due to agricultural activities, there was high external loading of sediment and nutrients from the catchment in to the lake [27]. The Lake is important for fisheries, local transport, hydroelectric power generation, ecological restoration, and dry season irrigation supply and tourism attractions. Also the basin’s biodiversity is striking with the presence of many endemic plant species, endemic birds, endemic fishes and large areas of wetlands [28], [30], [32]. Tilapia fish was the most available and used for food by the local communities [25], and it was sampled in Take Tana.

Lake Hayq is located in Northern Ethiopia, it serving as the major freshwater reservoir and it is utilized for the surrounding human consumption and aquatic lives. This lake is a typical example of highland Lakes of Ethiopia at an altitude of 2,030 m. The Lake lies between latitude of 11^0 15‘N and a longitude of 39^0 57’E [33], [34]. The Lake has a closed drainage system and the total watershed area is about 77 km^2 of which 22.8 km^2 is occupied by Lake Hayqe. The average depth of Lake Hayq is 37 m, and the maximum depth is 81 m [35] (Fig. 1). The only stream that entering the Lake is the Anchercah River, which flows into its southeast corner, but now permanently dry due to upper irrigation scheme and it is known, there is no drainage out of it. The area is characterized by a sub-humid tropical climate with an average annual rainfall of 1211.4 mm and a mean annual temperature of around 25.9 ^oC [34]. The fish diversity known in Lake Hayq consists of only 4 species, Tilapia, Catfish, Dubie, and Garra. However, only three species are used for food by the local communities (Tilapia, Catfish and Carp) [25].

3.4. Sample collection and preparation

Different representative sampling sites were selected based on access, safety, potential sources of pollutions, waste disposal sites, tributaries and geographical proximity. Those sampling sites were taken from the two selected Lakes found in ANRS. These sampling sites were seven for water and sediment and three for Fish in Lake Tana, whereas, one for water and sediment samples and two for fish sample in Lake Hayqe. Sampling was carried out within the period of January 2021 to May 2021.

3.4.1. Water sampling

From each eight sampling sites one liters of water samples were collected and stored in a 1L pre-cleaned amber glass bottle and transported to laboratory using ice-box, and preserved in a 4^{o}c refrigerator for further pesticide analysis. The stored samples were transported to Addis Ababa, Ethiopia for the qualitative identification and quantitative determination of pesticides by GC- MS.

3.4.2. Sediment sampling

Eight representative sediment samples were collected from different sampling sites of a 500g weight sediment samples were collected from the study areas using an Ekman grab sampler, and transferred into polythene bags and transported to laboratory. The sediment samples that packed in plastic bags were dried in the air for 5 day in cleaned laboratory room. The air dried sediment samples were grinded with ceramic coated mortar and pestle, and passed through 2 mm sieve with in ethanol washed aluminum foil and then the analyses were done using GC- MS.

3.4.3. Fish sampling

Tilapia fish (*Oreochromisniloticus)* in Lake Tana, and Dubie (*Cyprinuscarpio*) and Tilapia fish in Lake Hayqe were selected because of they are most abundant species in the Lakes. Four Tilapia and one Dubie fish samples were collected randomly with the help of local fishermen using plastic nets. The samples were immediately dissected in the field using plastic knife and only the muscle parts of the fish was transferred to plastic bags and kept in an ice box at 4^{o}C and then transported to the laboratory. The fish samples were dried in air for 6 days in cleaned laboratory room and collected with plastic bag. The air dried fish samples were grinded by electronic grinder and then, the analyses were done using GC- MS.

3.5. Extraction and clean-up procedures for pesticide analysis

QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method with liquid-liquid extraction (LLE) for water samples and Dispersive-solid-phase extraction (d-SPE) extraction for sediment and fish samples were employed [36].

3.5.1 Extraction and clean-up of pesticides from water sample

A liquid-liquid extraction procedure was adopted for the extraction of pesticides in water samples as described by Association of Official Analytical Collaboration (AOAC) 2007 and Olisah et al., (2021*)*with slight modification [37]. 300 mL of water samples were measured into each eight a separating funnel and 40 g of NaCl was added to each and it was shacked vigorously until the salt dissolved. At this point, the sample was spiked with 50 µL of 500 µg mL^{-1} mixed surrogate standards. The clear mixture was extracted used 300 mL of ethyl acetate with periodic shacked and vented. The separating funnel was allowed to stand undisturbed for 15 min to allow the formation of two distinct phases. The organic phase was collected into a pre-cleaned round bottom flask, and the same extraction process was performed on the sample two times used 60 mL of fresh ethyl acetate. All three portions were combined and evaporated to dryness with a rotary evaporator at 40∘C. The content was re-solubilized with 1 mL of toluene, kept in a 2 mL sealed amber coloured vial, and refrigerated before GC-MS analysis.

3.5.2. Extraction and clean-up of pesticides from sediment samples

A Dispersive-solid-phase extraction (d-SPE) and clean up procedure was adopted for the extraction of pesticides in sediment samples as described by Association of Official Analytical Collaboration (AOAC) 2007 and Olisah et al., (2021) with slight modification [37]. An aliquot (10 g) of sub-sample was weighed, quantitatively transferred into a 50 mL centrifuge tube, and spiked with 50 µL of 500 µg mL^{-1} mixed surrogate standard. Then 10 mL of acetonitrile was added, sealed, and shaken thoroughly with a VWR incubating mechanical shaker for 10 min. About 7.5 g of anhydrous $MgSO_4$ and 1 g of NaCl were added afterwards, shaken vigorously for 5 min, and it was centrifuged at 5000 rpm for 5 min at 10°C. Approximately 1mL of extract was transferred into an Eppendorf tube containing 150 mg anhydrous $MgSO_4$, 50 mg of primary secondary amines (PSA), and 50 mg of graphitized carbon black (GBC).The mixture was shacked vigorously for 3 min and centrifuged at 10,000rpm for 5 min. The supernatant was carefully transferred into a 2 mL amber coloured vial for GC-MS analysis.

3.5.3. Extraction and clean-up of pesticides from Fish sample

The fish samples extraction and clean-up were done based on the QuEChERS and Dispersive-solid-phase (d-SPE) extraction method and for pesticides adopted by AOAC 2007 and Rahman et al., (2021) [38]. In a 50 mL centrifuge tube, an aliquot of 10 g homogenized sample and 10 mL of acetonitrile was mixed. The mixture was vortexed for one minute followed by added 4 g of magnesium sulphate ($MgSO_4$) and 1 g of sodium chloride (NaCl). The sample was centrifuged at 5000 rpm for 5 min and the supernatant was removed for clean-up. During clean-up, 2 mL supernatant was transferred into another tube that contained 50 mg of primary and secondary amine (PSA), 50 mg of graphite carbon black (GCB) and 150 mg of magnesium sulphate. After proper agitation and centrifugation at 10,000 rpm for 5 min, the aliquots of the extracted was evaporated through nitrogen system and reconstituted with 1 mL toluene for GC-MS analysis.

3.7. Method performance and validation

3.7.1. Precision

The precision of the method was evaluated by means of the repeatability and intermediate precision of the results obtained from the Lakes. The relative standard deviation (RSD) of the three replicate results was used to express precision. The sample's relative standard deviation (RSD) was calculated as follows:

$$\%RSD = \frac{standarddeviation(SD)}{Meanvalue} x100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Relative standard deviation is the parameter of choice for expressing precision in analytical sciences. The precision determined at each concentration level should not excessed 15% of the relative standard deviation (RSD) [39], [40]. Linearity was assessed by constructing individual analytical curves for each analyte. The determination coefficient (r^2) and linearity range were calculated for each analyte determined by GC-MS [36], [41].

3.7.2. Recovery

Recovery is the measured amount of pesticide in the spiked Quality Control (QC) sample expressed as percentage of the amount spiked; ideally 100 percent. In order to improve the reliability of the method for the determinations of the samples for pesticides of interest, spiking method was adopted. In spiking a known amount of analyte was added (spiked) in to the test matrix and how much we have recovered the amount that we added were determined. It was determined by replicate analysis of samples.

$$\%\mathrm{Recovery} = \frac{\mathrm{conc.\,inspikedsample} - \mathrm{conc.\,inunspikedsample}}{\mathrm{Amountaddconc.}} \mathrm{x100} \ldots\ldots\ldots\ldots\ldots (11)$$

Recovery results in this work are summarized in Table 1. All the values of this study was within the acceptable ranges of percentage recoveries from 80–120% [42].

Table 1
Recovery of pesticides for water, sediment and fish samples

Pesticides	Fish samples (µg/kg)				Sediment samples (µg/kg)				Water sample (µg/L)			
	Spiked conc.	Un spiked conc.	add conc.	%R	Spiked conc.	Un spiked conc.	add conc.	%R	Spiked conc.	Un spiked conc.	add conc.	%R
Lindane	75.01	8.5	72	92.4	75.01	11.33	72	88.4	71.01	1.3	70	99.6
α-Endosulfan	76.4	11.5	72	90.1	73.4	13.5	65	92.2	75.4	10.5	72	90.1
β-Endosulfan	128.42	25.5	116	88.7	102.42	17.36	96	88.6	113.42	4.31	110	99.2
4.4-DDE	69.56	9.5	66	91.0	63.56	12.67	56	90.9	67.56	1.35	66	100.3
4,4-DDD	71.3	10	65	94.3	75.3	15.36	65	92.2	71.3	1.34	65	107.6
4,4-DDT	64.31	9.5	60	91.4	64.31	13.07	55	93.2	57.31	1.46	55	101.5
Dieldrin	58.96	11	50	95.9	98.96	70.42	32	89.2	46.56	1.28	45	100.6
Endrin	45.79	7.5	38	100.8	49.79	14.97	38	91.6	39.79	1.39	38	101.1
Deltamethrin	28.5	7.5	20	105.0	29.67	11.21	20	92.3	20.12	0	20	100.6

Table 1

All analytical procedures were subjected to a rigorous quality control process and analyses were performed in triplicate. A spiked sample and a procedural blank were analyzed with each batch of water, sediment, and fish samples. Mean values of pesticides were detected in blanks was subtracted from the analyte concentration in sample extracted. All reagents used in this study were chromatography graded. All glassware were soaked by diluted chromic acid for 24 hr, and then washed by tap water with soap, in the last rinsed by distilled water and subsequently rinsed with acetone before use. During sample injection, the GC syringe was programmed to wash two times before and after sample injection with ethyl acetate and toluene to avoid cross contamination.

3.7.3. Statistical Analysis

Descriptive statistics and one way ANOVA were computed using STATA version 14 software. Mean and range were used to describe the levels of OCPs in water, sediment, and fish in Lake Tana and Lake Hayqe. The significance level was set at $p < 0.05$.

Results And Discussion

4.1.2. Accuracy and Precision

All the percent of recovery values were within the acceptable range of 80%-120% for pesticide analysis (Table 1). The % RSD values were ranged from 0.03–8.66% for water, sediment and fish samples, which was under the required control limits ≤ 15%. These confirm that the method was good precision and accuracy. The correlation coefficients of all the calibration curves were ≥ 0.9986 or ranged (0.9986–0.9998) (Annex Table 2) and this showed that there was linear relationship between concentration and intensity. The instrumental detection limits (IDL) were 1.0 µg/L, 10 µg/kg and 10 µg/kg for water, sediment and fish samples, respectively. LOQ of GC-MS was < 10µ/kg.

Table 2
Organochlorine pesticides (OCPs) Results in Water sample (µg/L)

	Lake Tana								**Lake Hayqe**	**WHO 2017**	**EPA**
OCP's	**B/dar**	**Gumara**	**Ribe**	**Megech**	**Gorgora**	**Sekelet**	**Deke**	**Mean**			
α-BHC	ND	ND	ND	ND	ND	ND	ND	-	ND	-	-
β-BHC	ND	ND	ND	ND	ND	ND	ND	-	ND	-	-
δ-BHC	ND	ND	ND	ND	ND	ND	ND	-	ND	-	-
Lindane	1.11	1.13	1.15	1.12	1.11	1.08	1.06	1.11	1.11	2	0.2
α-Endosulfan	10.11	10.25	12.61	11.55	10.01	10.00	10.10	10.66	8.21	20	-
β-Endosulfan	5.11	4.12	6.7	5.8	3.13	3.14	2.15	4.31	3.12	20	-
ΣEndosulfan	**15.22**	**14.37**	**19.31**	**17.35**	**13.14**	**13.14**	**12.25**	**14.97**	**11.33**	**20**	**-**
4,4-DDT	1.12	1.56	1.66	1.48	1.40	1.11	1.08	1.35	1.45	1	-
4.4-DDE	1.14	1.48	1.65	1.55	1.15	1.20	1.21	1.34	1.35	1	-
4,4-DDD	1.16	1.68	1.70	1.69	1.45	1.12	1.45	1.46	1.53	1	-
ΣDDTs	**3.42**	**4.72**	**5.01**	**4.72**	**4.00**	**3.43**	**3.74**	**4.15**	**4.33**	**1**	**-**
β-Heptachlorepoxide	ND	ND	ND	ND	ND	ND	ND	-	ND	-	-
Endrin	1.16	1.35	1.82	1.29	1.18	1.11	1.12	1.28	1.09	0.6	2
Endrin aldehyde	ND	ND	ND	ND	ND	ND	ND	-	ND	-	-
Endrin ketone	ND	ND	ND	ND	ND	ND	ND	-	ND	-	-
Aldrin	ND	ND	ND	ND	ND	ND	ND	-		-	-
Dieldrin	1.12	1.53	2.45	1.16	1.25	1.11	1.12	1.39	1.61	0.03	-
Deltamethrin	ND	ND	ND	ND	ND	ND	ND	-	ND	-	-
Dichlorobenzonitrile	ND	ND	ND	ND	ND	ND	ND	-	ND	-	-
Hexachlorobenzene	ND	ND	ND	ND	ND	ND	ND	-	ND	-	-

P-value was ≤ 0.001or ($P < 0.05$) most detected OCPs among all sampling sites, and between Lake Tana and Lake Hayqe except lindane ($P = 0.96205$), DDE (0.01963), and DDD (0.01342).

4.2. Concentrations of Organochlorine pesticides (OCPs) in water samples

From the result, the concentrations of OCPs ranged from ND to 12.61µgL^{-1}. The highest concentration of OCPs was detected α-Endosulfan (12.61µg L^{-1}) at Rib river sampling site in Lake Tana (Table 2). There was significant difference in the concentration of all detected pesticides for water samples among all sampling sites ($P < 0.05$) and between Lake Tana and Lake Hayqe except Lindane ($p > 0.05$) not significant.

The DDT and its metabolites of 4, 4 -isomers (4, 4-DDE, and 4, 4-DDD) were the predominant groups next to endosulfan, and they were detected in most sampling sites. The concentrations of 4, 4-DDT in Lake Tana ranged from 1.08 to 1.66 µg/L. The lowest and highest concentrations were recorded at sampling sites Deke (1.08 µg/L) and Ribe (1.66 µg/L), respectively. The concentrations of 4, 4-DDE in Lake Tana ranged from 1.14 to 1.65 µg/L (Table 2). The lowest and highest concentrations were recorded at sampling sites Bahir Dar and Ribe, respectively. The concentrations of 4, 4-DDD in Lake Tana ranged from 1.12 to 1.70 µg/L. The lowest and highest concentrations were recorded at sampling sites Sekelet and Ribe, respectively. The mean concentration of DDT, DDE, and DDD were 1.35µg/L, 1.34µg/L, and 1.46µg/L for water samples in Lake Tana, and1.45 µg/L, 1.35µg/L, and 1.53µg/L for water samples in Lake Hayqe, respectively (Table 2). While the mean concentrations of DDTs found in water samples that collected from Lake Hayqe were higher than that obtained in Lake Tana. Therefore, there were statistically significant difference in the concentration of DDTs and their metabolites between Lake Tana and Lake Hayqe ($P < 0.05$). This might be due to the anthropogenic impact around the Lake Hayqe.

The concentrations of □DDTs ranged from 3.42–5.01µg L^{-1} in Lake Tana and 4.33 µg L^{-1}in Lake Hayqe. The higher total DDTs concentration (5.01µg L^{-1}) and the Lower (3.42µg L^{-1}) was found in Ribe and Bahir Dar sampling site of Lake Tana, respectively. The composition distinction of DDT and its metabolites are useful for identifying the source of DDTs. When (DDE + DDD)/□DDTs is more than 0.5 was suggests historical accumulation of DDTs, which may have gone through a long-term weathering [17]. The concentrations of total DDTs next to endosulfan were higher than other OCPs. The possible reasons for the presence of high level of DDTs in the Amhara Regional State Lakes may be its current use in vector control, illegal usage and contamination from obsolete pesticides [20]. And also it might be due to attributed to the run-off and deposition of DDT, which is used for agricultural and public health purposes (malaria control) in Ethiopia. DDT was used illegally for public health purposes until recently. The presence of DDTs in most of the water samples collected from Lake Tana and Lake Hayqe could be attributed to increased surface runoff carrying pesticide residues from various sources. Ethiopia is one of the many African countries burdened with the problem of obsolete pesticides and DDTs is still used for agricultural and public health programs [17]. In this present study the total levels of DDTs were found in water samples collected from Lake Tana and Lake Hayqe was higher than the study conducted in Akaki River catchment, central Ethiopia (nd-0.092µg/L) [17], in Tekeze Dam, Ethiopia (0.071ppb) [43], in Lake Bosomtwi, Ghana (0.073µg/L) [44], in Nile river, Sudan (nd-0.8) [45], in Densu river basin, Ghana (0.01–0.04 µg/L) [7], in Lake Victoria Basin, Kenya (0.29–0.36 µg/L) [46].

The α and β-Endosulfan were detected pesticides in most water samples that collected from Lake Tana and Lake Hayqe. The concentrations of α-Endosulfan in Lake Tana ranged from 10.00 to 12.61µg L^{-1}. The lowest and highest concentrations were recorded at sampling sites Sekelet and Ribe, respectively. The mean concentrations of α-Endosulfan were 8.21µg/L in Lake Hayqe. The concentrations of β-Endosulfan in Lake Tana ranged from 2.15 to 6.7 µg L^{-1}. The lowest and highest concentrations were recorded at sampling sites Deke and Ribe, respectively. The mean concentrations of β-Endosulfan were 3.12 µg/L in Lake Hayqe (Table 2).

The concentrations of ΣEndosulfan were ranged from 12.25µg L^{-1} to 19.31µg L^{-1} in Lake Tana and 11.33µg L^{-1} in Lake Hayqe water samples. The lowest and highest total endosulfan concentrations were recorded at sampling sites of Deke and Rib of Lake Tana, respectively (Table 2). This might be due to the land which is found in around Ribe river were suitable for farming and the farmers located to Rib river extensively used endosulfan pesticide to protect pests. The total concentration of endosulfan that found in water samples collected from Lake Tana was higher than the concentration that found in water samples collected from Lake Hayqe. Therefore, there was statistically significant difference in the concentration α and β- isomers of endosulfan between Lake Tana and Lake Hayqe for water samples ($P < 0.05$). This finding was also supported by the study conducted in Northwest Ethiopia, According to the authors report, endosulfan is widely used by subsistence farmers producing vegetables, onions, fruits and sugarcane around the Lake Tana. Most farmers around the Lake Tana area used synthetic pesticides to control pests on vegetables, onion, tomato and field crops under irrigation and rain-fed conditions and this pesticide residues inter to the Lake Tana by run-off, and leaching [19]. The total endosulfan concentrations of the present study that found in water samples collected from Lake Tana and Lake Hayqe was much higher than all of the other investigated OCPs (Table 2). This might be due to endosulfan was used recently for agricultural purpose in Northwest Ethiopia. The concentration of total endosulfan was much higher than the study conducted in Lake Ziway, Ethiopia (0.76–1.11µg/L) [16], in Tekeze Dam, Ethiopia (0.046 ppb) [43], in Owan River, Edo State, Nigeria (0.3µg/L) [10],in Lake Bosomtwi, Ghana (0.064µg/L) [44], in Head Ballokion the River Ravi, Pakistan (nd-0.42µg/L) [47], in Lake Victoria Basin, Kenya (0.06–0.33µg/L) [46].

Lindane was detected pesticide in most water samples that collected from both Lake Tana and Lake Hayqe. The concentrations of lindane in Lake Tana was ranged from 1.06 to1.15µg L^{-1}.The lowest and highest concentrations were recorded at sampling sites Deke and Rib, respectively. The mean concentrations of lindane was 1.11µg/L in Lake Hayqe (Table 2). In the present study the mean concentration of lindane have the same magnitude in both study areas of water samples were collected from Lake Tana and Lake Hayqe. Therefore, there were no statistically significant difference ($p = 0.96205$) of lindane residue between Lake Tana and Lake Hayqe. This might be due to the application of lindane for agricultural and health purpose could be the same trends. The mean concentrations of lindane was much higher than the study conducted in Akaki River catchment, central Ethiopia (nd-0.015µg/L) [17], in Tekeze Dam, Ethiopia (0.058µg/L) [43], in Owan River, Edo State, Nigeria (0.22µg/L) [10], in Lake Bosomtwi, Ghana (0.071µg/L) [44], in Lake Victoria Basin, Kenya (0.03 µg/L) [46].

Endrin was detected pesticide in most water samples that were collected from ANRS Lakes of Lake Tana and Lake Hayqe. The concentrations of endrin were ranged from 1.11 to1.82 μg L^{-1} for water samples that taken from in Lake Tana. The lowest and highest concentrations were recorded at sampling sites Sekelet and Rib, respectively. The mean concentrations of endrin was 1.09 μg/L in Lake Hayqe (Table 2). The maximum concentration (1.82 μg L^{-1}) of endrin was found in Rib sampling sites of Lake Tana and the minimum concentration (1.09 μg L^{-1}) was recorded in Lake Hayqe. The mean level of endrin was 1.28 μg L^{-1} and 1.09 μg L^{-1} for water sample that collected from Lake Tana and Lake Hayqe, respectively. Based on the present study the overall level of endrin found in water samples collected from Lake Tana was higher than that found for water samples collected from Lake Hayqe. This might be due to the different application of endrin for agricultural and health purposes and the anthropogenic effects within the studied lakes. In this current study the level of endrin that found in water samples collected from Lake Tana and Lake Hayqe was higher than the study conducted in Owan River, Edo State, Nigeria (0.06 μg/L) [10], in Densu river basin, Ghana (0.01–0.015 μg/L) [7], and in Lake Victoria Basin, Kenya (0.04–0.09 μg/L) [46].

Dieldrin was the metabolite of aldrin, was detected pesticide in most water samples collected from Lake Tana and Lake Hayqe. However aldrin was not detected in the water samples that were taken from Lake Tana and Lake Hayqe. The concentrations of dieldrin were ranged from 1.11 to2.45 μg L^{-1}in Lake Tana. The mean concentrations of dieldrin were 1.61 μg/L in Lake Hayqe (Table 2). The highest concentration (2.45 μg L^{-1}) and the lowest concentration (1.11 μg L^{-1}) of dieldrin was recorded in water samples that collected from Ribe and Sekelet sampling sites in Lake Tana. This might be due to more or less the agricultural wastages simply interred to Ribe River and the farming trend around Ribe river were intensive than around Sekelet sampling sites in Lake Tana. The mean concentration of dieldrin was 1.39 μg L^{-1} and 1.61 μg L^{-1} for water samples were collected from Lake Tana and Lake Hayqe, respectively. This finding indicates the level of dieldrin that found in water samples taken from Lake Hayqe was higher than that found in water samples collected from Lake Tana. The concentration difference in two Lakes might be due to the anthropogenic activities that could be intensively usages of dieldrin with smallholder farmers around Lake Hayqe. In the present study the levels of dieldrin was higher than the study conducted in Akaki River catchment, central Ethiopia (nd-0.005 μg/L) [17], in Owan River, Edo State, Nigeria (0.14 μg/L) [10], in Densu river basin, Ghana (nd-0.015μg/L) [7], and in Lake Victoria Basin, Kenya (0.14–0.31 μg/L) [46].The possible reason for this discrepancy might be due to smallholders and commercial farmers have been practicing intensive agricultural activities and urbanization around Lake Tana and Lake Hayqe.

Table 2

4.4. Concentrations of Organochlorine Pesticides (OCPs) in sediment

From the result the detection of most OCPs in sediment samples was not surprising because OCPs have been identified to be among the major pollutants introduced into the aquatic environment in Ethiopia and are discharged into the aquatic environment from both industrial and agricultural activities [30]. The concentrations of analyzed OCPs were ranged from ND to 125.65 μg kg^{-1}. The highest (125.65 μg kg^{-1}) concentrations of OCPs was endrin, detected at Bahir Dar sampling site, Lake Tana (Table 3). There was significant difference in the concentration of all detected pesticides for sediment samples among all sampling sites ($P < 0.05$) and Between Lake Tana and Lake Hayqe except Chloropyrifos ($p > 0.05$) not significant.

Table 3
Organochlorine pesticides in Sediment sample (μg/kg)

	Lake Tana								Lake	WHO	EPA
OCP's	B/dar	Gumara	Ribe	Megech	Gorgora	Sekelet	Deke	Mean	Hayek	2017	
α –BHC	ND	ND	ND	ND	ND	ND	ND	-	ND	-	-
β-BHC	ND	ND	ND	ND	ND	ND	ND	-	ND	-	-
δ-BHC	ND	ND	ND	ND	ND	ND	ND	-	ND	-	-
Lindane	10.12	11.85	12.66	11.64	11.78	11.09	10.18	11.33	10.96	2	0.2
α-Endosulfan	14.77	15.64	16.52	12.36	11.48	11.22	11.44	13.35	11.26	20	-
β-Endosulfan	18.55	19.61	21.15	21.06	16.74	11.87	12.55	17.36	14.52	20	-
ΣEndosulfan	**33.32**	**35.25**	**37.67**	**33.42**	**28.22**	**23.09**	**23.99**	**30.71**	**25.78**	**20**	**-**
4.4-DDT	13.5	14.3	13.8	12.4	12.2	11.4	11.12	12.67	11.9	1	-
4,4-DDE	14.2	18.4	17.6	18.7	15.6	11.93	11.11	15.36	20.0	1	-
4,4-DDD	13.01	13.67	13.85	14.18	12.65	12.86	11.25	13.07	13.27	1	-
ΣDDTs	**40.71**	**46.37**	**45.25**	**45.28**	**40.45**	**36.19**	**33.48**	**41.11**	**45.17**	**1**	**-**
DDT/Σ(DDE + DDD)	**0.496**	**0.446**	**0.439**	**0.377**	**0.432**	**0.460**	**0.497**	**0.450**	**0.358**	**-**	**-**
β-Heptachlorepoxide	ND	ND	ND	ND	ND	ND	ND	-	ND	-	-
Endrin	125.65	56.8	68.9	86.3	60.5	54.6	40.2	70.42	21.41	0.6	2
Endrin aldehyde	ND	ND	ND	ND	ND	ND	ND	-	ND	-	-
Endrin ketone	ND	ND	ND	ND	ND	ND	ND	-	ND	-	-
Aldrin	ND	ND	ND	ND	ND	ND	ND	-	ND	-	-
Dieldrin	16.61	15.64	14.54	16.83	16.09	13.17	11.91	14.97	18.07	0.03	-
Deltamethrin	10.57	13.45	11.55	11.28	11.05	10.46	10.11	11.21	11.54	-	-
Dichlorobenzonitrile	ND	ND	ND	ND	ND	ND	ND	-	ND	-	-
Hexachlorobenzene	ND	ND	ND	ND	ND	ND	ND	-	ND	-	-
P-value was ≤ 0.001or ($P < 0.05$) for all detected OCPs among all sampling sites, and between Lake Tana and Lake Hayqe											

Endrin was found in most sediment samples collected from Lake Tana and Lake Hayqe. The concentrations of endrin in Lake Tana ranged from 40.2 to 125.65 μg/kg. The lowest and highest concentrations were recorded at sampling sites Deke and Bahir dar, respectively. The mean concentration of endrin in Lake Tana was 70.42 μg/kg. The mean concentrations of endrin was 21.41μg/kg in Lake Hayqe (Table 3). Endrin was the predominant OCPs investigated in sediment samples that collected from Lake Tana and Lake Hayqe. The level of endrin found in sediment samples collected from Lake Tana was much higher than that found in sediment samples taken from Lake Hayqe. In this finding the level of endrin was much higher than the study conducted in the Mae Klong river, Central Thailand (0.00001–0.00005 μg/kg) [48], and in Lake Victoria Basin, Kenya (7.96–10.99 μg/kg) [46].

DDT and its metabolites were detected in most sediment samples were collected from Lake Tana and Lake Hayqe. The concentrations of 4, 4-DDTs were ranged from 11.11 to 18.7 μg/kg, and11.9 to 20.0 μg/kg in Lakes Tana and Hayqe, respectively. The4, 4-isomers of DDT and its metabolites (4, 4-DDE, and 4, 4-DDD) were the predominant groups next to endrin. 4, 4-DDT was detected in most sediment samples in Lake Tana and Lake Hayqe. The concentrations of 4, 4-DDTin Lake Tana were ranged from 11.12 to 14.3μg/kg. The lowest and highest concentrations were recorded at sampling sites Deke and Gumara, respectively (Table 3).The mean concentrations of 4, 4-DDT in Lake Tana was 11.9 μg kg^{-1}, and 4, 4-DDT was 11.9 μg kg^{-1} in Lake Hayqe

(Table 4). DDE was detected in most sediment samples collected from Lake Tana and Lake Hayqe. The concentrations of 4, 4-DDE in Lake Tana were ranged from 11.11 to 18.7 μg/kg. The lowest and highest concentrations were recorded at sampling sites of Deke and Megech, respectively. The mean concentrations of 4, 4-DDE in Lake Tana was 15.36 μg kg^{-1}.The mean concentrations of 4, 4-DDEin Lake Hayqe was 20.0 μg kg^{-1}. 4, 4-DDD was detected in most sediment samples in Lake Tana and Lake Hayqe. The concentrations of 4, 4-DDD in Lake Tana were ranged from 11.25 to 14.18 μg/kg. The lowest and highest concentrations were recorded at sampling sites of Deke and Megech, respectively. The lowest and highest concentrations were recorded at sampling sites of Deke and Megech, respectively. The mean concentrations of 4, 4-DDD were 13.07 μg kg^{-1}, and 13.27 μg kg^{-1} in Lake Tana and Lake Hayqe, respectively (Table 3).

Table 4
Organochlorine pesticides (OCPs) in Fish Samples (μg/kg)

	Conc. in Fish L.			**Mean**	**Fish in Lake Hayqe**		**Mean**	**WHO**	**EPA**
	Tilapia	Tilapia	Tilapia	Lake	Tilapia	Dubie	Lake		
OCP's	Fogera	B/dar	Gorgora	Tana	Hayqe	Hayqe	Hayqe	2017	
α-BHC	ND	ND	ND	-	ND	ND	-	-	-
β-BHC	ND	ND	ND	-	ND	ND	-	-	-
δ-BHC	ND	ND	ND	-	ND	ND	-	-	-
Lindane	16.15	11.20	10.54	12.63	18.26	10.67	14.47	2	0.2
α-Endosulfan	20.5	19.6	28.9	23.00	13.2	12.85	13.03	20	-
β-Endosulfan	45.6	40.6	51.15	45.78	14.59	12.5	13.55	20	-
ΣEndosulfan	**66.1**	**60.2**	**80.05**	**68.78**	**27.79**	**25.35**	**26.57**	**20**	**-**
4.4-DDT	17.5	18.5	19.8	18.60	21.12	19.11	20.12	1	-
4,4-DDE	18.7	14.2	19.2	17.37	18.8	13.6	16.2	1	-
4,4-DDD	18.1	19.2	19.1	18.8	21.25	19.23	20.24	1	-
ΣDDTs	**54.3**	**51.9**	**58.1**	**54.77**	**61.17**	**51.94**	**56.56**	**1**	**-**
DDT/Σ(DDE + DDD)	**0.476**	**0.554**	**0.517**	**0.516**	**0.527**	**0.582**	**0.555**	**-**	**-**
β-Heptachlorepoxide	ND	ND	ND	-	ND	ND	-	-	-
Endrin	22.12	21.8	21.38	21.77	20.1	21.9	21.0	0.6	2
Endrin aldehyde	ND	ND	ND	-	ND	ND	-	-	-
Endrin ketone	ND	ND	ND	-	ND	ND	-	-	-
Aldrin	ND	ND	ND	-	ND	ND	-	-	-
Dieldrin	11.15	11.60	15.31	12.69	14.20	11.73	12.97	0.03	-
Deltamethrin	ND	ND	ND	-	ND	ND	-	-	-
Dichlorobenzonitrile	ND	ND	ND	-	ND	ND	-	-	-
Hexachlorobenzene	ND	ND	ND	-	ND	ND	-	-	-
P-value was ≤ 0.001or (P < 0.05) for most detected OCPs among all sampling sites, and between Lake Tana and Lake Hayqe except α-Endosulfan (P = 0.0259), Endrin (0.0032), and Dieldrin (0.0248).									
List of figures									

The ΣDDTs concentrations were ranged from 33.48 to 46.37 μg kg^{-1}in Lake Tana (Table 4). The mean concentrations of total DDTs in Lake Tana was 41.11μg kg^{-1}.The mean concentrations of total DDTs in Lake Hayqe was 45.17μg kg^{-1}. The highest (46.37 μg

kg^{-1}) and lowest (33.48 μg kg^{-1}) total concentrations of DDTs were found in sediment samples were sampled from Gumara and Deke sampling sites of Lake Tana, respectively (Table 3). The levels of 4, 4-DDTs varied depending on sampling sites indicating variable sources in different locations. The mean concentration of 4, 4-DDE found in the sediment samples that collected from Lake Tana and Lake Hayqe was higher than both 4, 4-DDT and 4, 4-DDD. This might be due to the metabolic resistant and stability of 4, 4-DDE that could leads to be accumulated in sediment matrix. The possible reasons for the presence of high level of 4, 4-DDTs and its metabolites may be attributed to the run-off and atmospheric deposition of DDT which is used for agricultural and malaria control activities in Ethiopia [49]. The ratio of 4,4-DDT with the sum of their metabolites (4, 4-DDE and 4, 4-DDD) was less than one indicates DDTs were not recently discharged to the aquatic environment; it may be accumulated for several years with sediment matrix [50] (Table 3). The concentrations of DDTs next to endrine were higher than those of other OCPs. The possible reasons for the presence of high level of DDTs in the Amhara Regional State Lakes may be its current use in vector control, illegal usage and contamination from obsolete pesticides [20]. In the present study, the level of total DDTs found in sediment samples collected from ANRS Lakes were much lower than the study conducted in Akaki River catchment, central Ethiopia (1.91- 1076.73 μg/kg) [17]. This could be due to the common application of pesticides for urban agricultural practices near to Akaki River. While the finding was higher than the study conducted in Tekeze Dam, Ethiopia (14.82ppb) [43], in the Mae Klong river, Central Thailand (0.00006–0.0027μg/kg) [48], in Lake Bosomtwi, Ghana (12.752 ng/g) [44], and in Lake Victoria Basin, Kenya (24.42–36.38 μg/kg) [46].

Endosulfan pesticide is a broad spectrum contact insecticide and acaricide used by many farmers. In this investigation α and β isomers of Endosulfan were detected OCP for composited sediment samples were collected from Lake Tana and Lake Hayqe. The concentrations of α-Endosulfan in Lake Tana were ranged from 11.32 to 16.52 μg/kg. The lowest and highest concentrations were recorded at sampling sites Sekelet and Rib, respectively. The mean concentration of α-Endosulfan in Lake Tana was 13.35 μg/kg. Whereas the mean concentrations of α-Endosulfan was 11.26 μg/kg in Lake Hayqe (Table 4). The concentrations of β-Endosulfan in Lake Tana were ranged from 12.55to 21.15 μg/kg. The lowest and highest concentrations were recorded at sampling sites Deke and Rib, respectively, while the mean concentrations of β-endosulfan in Lake Tana were 17.31μg/kg. The mean concentrations of β-Endosulfan were 14.52μg/kg in Lake Hayqe (Table 3). Therefore both the highest and lowest concentration of α and β-Endosulfan were found at Rib and Sekelet sampling sites of Lake Tana, respectively. The result showed that the level of β-Endosulfan was much higher than the level of α-Endosulfan, those found in sediment samples collected from ANRS Lakes of Lake Tana and Lake Hayqe (Table 3). This might be due toβ isomers of Endosulfan could be persistent and slower degradation in matrix of sediment relative to isomer of α-Endosulfan [51].

The ΣEndosulfan concentrations in Lake Tana were ringed from 23.19 to 37.67 μg/kg. The lowest and highest concentrations were recorded at sampling sites Sekelet and Ribe, respectively. The mean concentration of total Endosulfanin Lake Tana was 30.71 μg/kg, whereas the mean concentrations of total endosulfan were 25.78 μg/kg in Lake Hayqe (Table 3). The levels of total endosulfan found in sediment samples collected from Lake Tana was higher than that found Lake Hayqe. This might be due to the farmers they farmed around Lake Tana and Ribe River has been used endosulfan pesticide extensively to control pests on vegetables and field crops under irrigation and rain-fed conditions. The excessive application of endosulfan 35% EC by farmers they located around Lake Tana used for pest control in agricultural purpose was supported by the study conducted in Northwest Ethiopia, Lake Tana [19]. The findings of Birhan Agmas et al., (2020), tells the attitudes and practices of farmers were developed they found in Northwest Ethiopia with regarding to endosulfan pesticide usages for agricultural purpose. In the present study the level of total endosulfan that detected for sediment samples collected from Lake Tana and Lake Hayqe was much higher than the study conducted in Lake Ziway, Ethiopia (2.1–2.69μg/kg) [16], in Tekeze Dam, Ethiopia (10.622 ppb) [43], in the Mae Klong river, Central Thailand (0.00004-0.00016 μg/kg) [48], in Lake Tashk, Iran (15.263 ppb) [52], in Lake Bosomtwi, Ghana (9.685 ng/g) [44], in Head Balloki on the River Ravi, Pakistan (3.74–23.06 μg/kg) [47], and in Lake Victoria Basin, Kenya (5.96–13.47μg/kg) [46]. While this finding was much lower than the study conducted in Akaki River catchment, central Ethiopia (nd-127.78 μg/kg) [17].

Lindane was detected in most sediment samples collected from Lake Tana and Lake Hayqe. The concentration of lindane in Lake Tana was ranged from 10.12 to 12.66 μg/kg. The lowest and highest concentrations were recorded at sampling sites Bahir dar and Rib, respectively. The mean concentration of lindane in Lake Tana was 11.33 μg/kg. Whereas the mean concentrations of lindane was 10.96 μg/kg in Lake Hayqe (Table 3). The levels of lindane found in sediment samples collected from Lake Tana was higher than that found in sediment samples collected from Lake Hayqe. The present study was higher than the study conducted in Tekeze Dam, Ethiopia (6.920 ppb) [43],in the Mae Klong river, Central Thailand (0.00002-0.00018 μg/kg) [48],in Lake Tashk, Iran (8.475 ppb) [52], in Lake Bosomtwi, Ghana (6.755 ng/g) [44], in Lake Victoria Basin, Kenya (3.37–23.12 μg/kg) [46]. The finding was much lower than the study conducted in Akaki River catchment, central Ethiopia (nd-1161.20 μg/kg) [17], this might be due to large numbers of untreated or partially treated industrial wastes, domestic and agricultural wastes were released into nearby water bodies of Addis Ababa, and this polluted water interred to Akaki river.

Dieldrin was detected in most sediment samples collected from Lake Tana and Lake Hayqe. The concentrations of dieldrin in Lake Tana were ranged from 11.91 to 16.83 μg/kg. The lowest and highest concentrations were recorded at sampling sites Deke and Megech, respectively. The mean concentration of dieldrin in Lake Tana was 14.97 μg/kg, whereas the mean concentration of dieldrin was 18.07 μg/kg in Lake Hayqe (Table 3). The levels of dieldrin found in sediment samples collected from Lake Tana was lower than that found in sediment samples sampled from Lake Hayqe. The present finding was much higher than the study conducted in the Mae Klong river, Central Thailand (0.00001–0.00007 μg/kg) [48], and in Lake Bosomtwi, Ghana (0.072ng/g) [44]. While it was lower than the study conducted in Lake Victoria Basin, Kenya (11.94–69.55 μg/kg, this might be due to the extensive uses of pesticide for agricultural and health purposes around lake basin and establishments of different chemical industries in the country [46]. And also it was lower than the study conducted in Akaki River catchment, central Ethiopia (nd-78.56 μg/kg) [17], this might be due to around the Akaki river different industries were established, and the agricultural and domestic wastes may be simplify released to the environment.

Deltamethrin was found in most composited sediment samples collected from Lake Tana and Lake Hayqe. The concentrations of deltamethrin in Lake Tana were ranged from 10.11 to 13.45 μg/kg. The lowest and highest concentrations were recorded at sampling sites Deke and Gumara, respectively. The mean concentration of deltamethrin in Lake Tana was 11.21 μg/kg. Whereas the mean concentrations of deltamethrin was 11.54 μg/kg in Lake Hayqe (Table 4).The level of deltamethrin found in sediment samples collected from Lake Tana was lower than that found in sediment samples taken from Lake Hayqe. The finding was much higher than the study conducted in Lake Ziway, Ethiopia (0.54 μg/kg) [16], and in Head Balloki on the River Ravi, Pakistan (nd-0.37 μg/kg) [47]. This might be due to illegal applications of pesticides practiced by farmers for agricultural and household purposes in Amhara National Regional States (ANRS) than other parts of Ethiopia and world.

Table 3

4.6. Concentrations of Organochlorine Pesticides (OCPs) in fish

The concentrations of investigated OCPs ranged from ND to 51.5 μg kg^{-1}. The highest concentration of OCPs was β-Endosulfan (51.5μg kg^{-1}), detected in Tilapia Fish collected from Gorgora sites of Lake Tana (Table 4). There was significant difference in the concentration of all detected pesticides for Fish samples among all sampling sites ($P < 0.05$) and Between Lake Tana and Lake Hayqe.

The isomers of DDTs investigated in the fish tissue samples were 4, 4-DDT, 4, 4 -DDE, and 4, 4 -DDD. The DDT and its metabolites of 4, 4 -isomers (4, 4-DDE, and 4, 4-DDD) were the predominant groups next to endosulfan, and they were detected in most fish samples. The level of 4, 4-DDT in Lake Tana was ranged from 17.5 to 19.8 μg/kg. The lowest and highest concentrations were recorded at sampling sites of Fogera and Gorgora, respectively. The mean concentration of 4, 4-DDT in Lake Tana was 18.60 μg kg^{-1}. The level of 4, 4-DDT in Lake Hayqe was 21.12 μg/kg and 19.11 μg/kg for Tilapia and Dubie fish, respectively. The lowest and highest concentrations in Lake Hayqe were recorded in Dubie and Tilapia fish samples, respectively. The mean concentrations of 4, 4-DDT was 20.12 μg kg^{-1} in Lake Hayqe (Table 4). The level of 4, 4-DDE in Lake Tana was ranged from 14.2 to 19.2 μg/kg. The lowest and highest concentrations were recorded at sampling sites of Bahir dar and Gorgora, respectively. The mean concentrations of 4, 4-DDE in Lake Tana was 17.37 μg kg^{-1}.The level of 4, 4-DDE in Lake Hayqe were 18.8 μg/kg and 13.6 μg/kg for Tilapia and Dubie fish, respectively. The lowest and highest concentrations in Lake Hayqe were recorded at Dubie and Tilapia fish samples, respectively. The mean concentration of 4, 4-DDE was 16.2 μg kg^{-1} in Lake Hayqe (Table 4). The level of 4, 4-DDD in Lake Tana was ranged from 18.1 to 19.2 μg/kg. The lowest and highest concentrations were recorded at sampling sites of Fogera and Bahir dar, respectively. The mean concentration of 4, 4-DDD in Lake Tana was 18.8 μg kg^{-1}.The concentrations of 4, 4-DDDin Lake Hayqe were 21.25 μg/kg and 19.23 μg/kg for Tilapia and Dubie fish, respectively. The lowest and highest concentrations in Lake Hayqe were recorded in Dubie and Tilapia fish samples, respectively. The mean concentration of 4, 4-DDD was 20.24 μg kg^{-1} in Lake Hayqe (Table 4).

The ΣDDTs concentration in Lake Tana fish samples were ranged from 51.9 to 58.1μg kg^{-1}. The lowest and highest concentrations of total 4, 4-DDTs were recorded at sampling sites of Bahir dar and Gorgora, respectively. The mean concentration of total DDTs in Lake Tana was 54.77μg kg^{-1}. The concentrations of total 4, 4-DDTs in Lake Hayqe were 61.17 μg/kg and 51.94 μg/kg for Tilapia and Dubie fish, respectively. The lowest and highest concentrations of total DDTs were found in Dubie and Tilapia fish samples, respectively. The mean concentration of total 4, 4-DDTs was 56.56μg kg^{-1} (Table 4). The levels of 4, 4-DDD found in the fish samples of Lake Tana and Lake Hayqe was higher than both 4, 4-DDT and 4, 4-DDE. This might be due to the metabolic resistant and stability of 4, 4-DDD that could leads to be accumulated in fish tissue. The possible reasons for the presence of high levels of DDTs and its metabolites may be attributed to the run-off and atmospheric deposition of DDTs which is used for agricultural and malaria control activities in Ethiopia [49]. The total concentrations of 4, 4 -DDE and 4, 4-DDD was higher than that of the parent 4, 4-DDT. Whereas the ratio of DDT/(DDE + DDD) was less than one (< 1) in most fish samples (Table 6). The low concentration of 4, 4-DDT compare to total concentration of its metabolites is an indication that there might not be fresh input of the parent DDT in the study area[50]. This also suggests that the DDT concentrations in the fish samples collected from Lake Tana and Lake Hayqe might be due to historical use of DDT for various activities. The possible reasons for the presence of high level of DDTs in the Fish samples of ANRS Lakes might be due to the intensive utilization of DDT for vector control, agricultural activities, and illegal usage contaminations of Lakes from obsolete pesticides [20].

The lower concentration (51.9 μg/kg) and higher concentration (61.17 μg/kg) of total 4, 4-DDTs were recorded in Lake Tana and Lake Hayqe fish samples, respectively (Table 4). The concentrations of total DDTs obtained in this current study were higher than the study conducted in Lake Awassa, Ethiopia (1.80-21.34 ng/g) [49], Tekeze Dam, Ethiopia (8.89 ng/g) [43], in Rift Valley Lake-Lake Ziway, Ethiopia (2.33-9.0 ng/g) [20], in Lake Koka, Ethiopia (4.53–15.15 ng/g) [15], in Africa fish of Volta basin, Kpando Torkor, Ghana (0.15–10.06 ng/g) [50], in Lake Nyasa, Tanzania (10.6–18.9 ng/g) [53], and in Calicut region, Kerala, India (12.31ng/g) [54], this might be due to DDT was still used for malaria control in some parts of Ethiopia [51]. While there was much lower than the study conducted in iSimangaliso Wetland Park, South Africa (645–2399 ng/g)[51],in Lake Burullus, Egypt (100.6-284.3 ng/g) [1], and in Lake Tanganyika, Tanzania (207–319 ng/g) [53]. This could be due to the long history of DDTs in agriculture and disease-vector control programs in South Africa and other world countries.

The isomers of α-and β-endosulfan were detected in most fish samples of Lake Tana and Lake Hayqe. The detected α and β-endosulfan concentrations in Lake Tana were ranged from 19.6 to 51.15 μg/kg. Whereas in Lake Hayqe Dubie and Tilapia fish samples were ranged from 12.5 to 14.59 μg/kg. The concentrations of α-Endosulfan in Lake Tana fish samples were ranged from 19.6 to 28.9 μg/kg. The lowest and highest concentrations were recorded at sampling sites of Bahir dar and Gorgora, respectively. The mean concentration in Lake Tana fish samples was 23.0 μg/kg. The concentrations of α-Endosulfan in Lake Hayqe fish samples were12.85μg/kgand13.2 μg/kg for Tilapia and Dubie fish, respectively. The lowest and highest concentrations were recorded Dubie and Tilapia fish samples, respectively. The mean concentration was 13.03 μg/kg in Lake Hayqe (Table 6). The concentration of β-Endosulfan in Lake Tana fish samples was ranged from 40.6 to 51.15 μg/kg. The lowest and highest concentrations were recorded at sampling sites of Bahir dar and Gorgora, respectively. The mean concentration in Lake Tana fish samples was 45.78 μg/kg, whereas the concentrations in Lake Hayqe fish samples were14.59 μg/kg and 12.5 μg/kg for Tilapia and Dubie fish, respectively. The mean concentration was 13.55 μg/kg in Lake Hayqe (Table 4).

The present study showed that the β-endosulfan was found in higher concentration than there corresponding isomer of α-endosulfan in all fish samples. The concentration difference between the two isomers could be accounted for the persistence and slower degradation of β-endosulfan relative to the isomer of α-endosulfan [51]. In this current research finding β -isomer endosulfan was the dominant group in the fish tissues, it was consistence with the finding that was reported in middle Volta basin, Kpando Torkor, Ghana which is β-isomer endosulfan was the dominant pesticide in the fish samples. This is due to in Ghana endosulfan had extensively used for agricultural activities and in cotton industry [50], and this is the same as in Ethiopia.

The ΣEndosulfan concentrations in Lake Tana fish samples were ranged from 60.2 to 80.05 μg/kg. The lowest and highest concentrations of total endosulfan in Lake Tana were recorded at Bahir dar and Gorgora sampling sites, respectively. The mean concentration in Lake Tana fish samples was 68.78 μg/kg. The concentrations of total endosulfan in Lake Hayqe were 25.35 μg/kg and 27.79 μg/kg for Dubie and Tilapia fish, respectively. The lowest and highest concentrations of were determined in Dubie and Tilapia fish samples, respectively. The mean concentration in Lake Hayqe fish samples was 26.57 μg/kg (Table 4). The concentration of endosulfan that found in Tilapia fish collected from Lake Tana was much higher than the concentration found in fish samples collected from Lake Hayqe. This might be due to the intensive use of endosulfan pesticide for pest control and agricultural practice by farmers around Lake Tana. This finding was also supported by the study conducted in Northwest Ethiopia, which reported that most of the farmers around lake Tana used endosulfan for agricultural activity extensively [19]. Endosulfan is normally not used in fish farming as some fish species are very sensitive to the effect of endosulfan and therefore no international standard has so far been set for endosulfan residues in fish [53]. The recent studies showed that the total concentration of endosulfan was found as the most abundant of all pesticides.

The total concentrations of endosulfan that detected in fish samples was much higher than all other tested pesticides (Table 4). This might be due to endosulfan was used recently for agricultural practice in Ethiopia. Endosulfan could be easily absorbed by the stomach, lungs and through the skin of fish, meaning that all routes of exposure can pose a potential hazard for fish as well as other micro flora and fauna, and it's also hazardous and can stay several years in the environment [55]. In the current study the levels of total endosulfan was higher than the study conducted in lake Koka, Ethiopia (1.2–4.3 ng/g) [15], in Tekeze dam, Ethiopia (0.82ng/g) [43], in River Ravi, India–Pakistan(6.88–19.15 ng/g) [47], in Africa fish tissue of middle Volta basin, Kpando Torkor, Ghana (0.56–1.43 ng/g) [50], and in Lake Bosomtwi, Ghana (0.84–2.32 ng/g) [44]. However, endosulfan had been extensively used for agricultural activities and cotton industry in Ghana [50]. while it was much lower than the study conducted in iSimangaliso Wetland Park, South Africa (456.9–1495 ng/ g) [51], and in Owan River, Edo State, Nigeria (250–510 ng/g) [10]. the possible reason might be due to the surrounding of studied areas were much farmed and farmers used pesticide excessively for Cocoa, plantain and pepper production [10]. And also this variations could be linked to the difference in the trend of agricultural practices in these study areas.

Endrine was detected in most fish samples were collected from the Lake Tana and Lake Hayqe. The concentrations of Endrine in Lake Tana fish samples were ranged from 21.38–22.12µg/kg. The lowest and highest concentrations were recorded at sampling sites of Gorgora and Fogera, respectively. The mean concentration in Lake Tana fish samples was 21.77 µg/kg. The concentrations of endrin in Lake Hayqe fish samples were 20.1 µg/kg and 21.9 µg/kg for Tilapia and Dubie fish, respectively. The lowest and highest concentrations were recorded Dubie and Tilapia fish samples, respectively. The mean concentration was 21.0 µg/kg in Lake Hayqe (Table 4). The present study showed that the level of endrin in Lake Tana was higher than Lake Hayqe, this might be due to the extensive agricultural trends of farmers located around Lake Tana by irrigation and rain field farming. The current study showed that the level of endrin was higher than the study conducted in Calicut region, Kerala, India (0.01–1.35 ng/g) [54], in Owan River, Edo State, Nigeria (0.07–0.45 ng/g) [10], in African Lake Taabo, Cote d'Ivoire (15.89 µg/kg), and Densu, River, Ghana (5.45 µg/kg) [56]. while in this study the concentration of endrin in Lake Tana and Lake Hayqe was much lower than the study conducted in iSimangaliso Wetland Park, South Africa (195.6-4331.1 ng/g), and in Lake Burullus, Egypt (55.5–78.0 ng/g), this might be due to the lake drains catchment areas of iSimangaliso Wetland Park, in South Africa all have been affected by anthropogenic activities, including agricultural and health purpose for malaria control [51], and Lake Burullus was major disposal areas for agricultural drainage water in Egypt [1].

Lindane was detected in most fish samples were collected from the Lake Tana and Lake Hayqe. The concentrations of lindane in Lake Tana fish samples were ranged from 10.54-16.115 µg/kg. The lowest and highest concentrations were recorded at sampling sites of Gorgora and Fogera, respectively. The mean concentration in Lake Tana fish samples was 12.63 µg/kg. The concentrations of lindane in Lake Hayqe fish samples were 10.67 µg/kg and 18.26 µg/kg for Dubie and Tilapia fish, respectively. The lowest and highest concentrations were recorded Dubie and Tilapia fish samples, respectively. The mean concentration was 14.47 µg/kg in Lake Hayqe (Table 4). The current study showed that the mean concentration of Lindane in Lake Hayqe was higher than Lake Tana (Table 4),this might be due to Lake Hayqe was have been more stagnant water to hold lindane pesticide for long ranges of time and it might be accumulated fish muscle without any disturbance. In the present study the concentration of lindane in Lake Tana and Lake Hayqe was much higher than the study conducted in Tekeze Dam, Ethiopia (0.138 ng/g) [43], in Rift Valley lake- Lake Ziway, Ethiopia (0.22–0.68 ng/g) [20], and in Lake Bosomtwi, Ghana (0.70–1.36 ng/g) [44], While the present study was much lower than the study conducted in iSimangaliso Wetland Park, South Africa (71.9–412.0 ng/g) [51], this might be due to the lake drains catchment areas of South Africa lakes that have all been affected by anthropogenic activities, including agriculture. The drainage system of South Africa lakes was connected to the ocean via a long sinuous channel [51].

Dieldrin has been identified in fish samples, and it was detected in most fish samples that were collected from the Lake Tana and Lake Hayqe. The concentrations of dieldrin in Lake Tana fish samples were ranged from 11.15–15.31 µg/kg. The lowest and highest concentrations were recorded at sampling sites of Bahir dar and Gorgora, respectively. The mean concentration in Lake Tana fish samples was 12.69 μg/kg. The concentrations of dieldrin in Lake Hayqe fish samples were 11.73 μg/kg and 14.20 μg/kg for Dubie and Tilapia fish, respectively. The lowest and highest concentrations were recorded Dubie and Tilapia fish samples, respectively. The mean concentration was 12.97 μg/kg in Lake Hayqe. The mean concentration of aldrin metabolite dieldrin that detected in fish samples collected from Lake Hayqe was higher than in Lake Tana (Table 4).

Aldrin was not detected in all fish samples that were collected in Lake Tana and Lake Hayqe. However, dieldrin which is the metabolites of aldrin that was detected in all fish samples. This suggests that the dieldrin residues found are not the product of aldrin decomposition, but rather of dieldrin application and bioaccumulation as an insecticide that of studied lakes and fish tissues. Aldrin pesticide used as an anti-termite agent against crops especially eucalyptus in Ethiopia. In the environment, aldrin gets converted to dieldrin, which is more stable. In the present study, the ratio observed was may not much higher, suggesting high persistency of chemical in the environment [57]. In the current study the concentration of dieldrin in Lake Tana and Lake Hayqe was much higher than the study conducted in Calicut region, Kerala, India (0.09–0.31 ng/g) [54], and in Lake Bosomtwi, Ghana (0.30–0.56 ng/g) [44]. While in this study the concentration of dieldrin was much lower than the study conducted in iSimangaliso Wetland Park, South Africa (117.3–404.0 ng/g) [51], this might be due to large quantities of OCPs have also been widely used in the region and/or iSimangaliso Wetland Park of South Africa for agricultural purposes and rapidly growing local communities who live in close proximity to the wetland park. The use of dieldrin as an insecticide has been banned in South Africa since 1983, however, dieldrin presence within fish tissues, therefore, likely reflects the degradation of aldrin. and also it was much lower than the study conducted in Lake Burullus, Egypt (ND-56.5 ng/g) [1], this might be due to in Egypt Lake Burullus is one of the major disposal areas for agricultural drainage water. It was much lower than the study conducted in Owan River, Edo State, Nigeria (80–530 ng/g) [10]. This might be due to the surrounding area of the river in Nigeria is typically comprised of commercial cocoa farmers, which constantly make used of agrochemicals to boost their production.

The most ubiquitous OCPs detected in the fish samples were α-and β-Endosulfan, Endrin, DDTs and its metabolites of (4, 4 - DDD, and 4, 4 - DDE). In general, the contamination pattern of OCPs for fish samples based on the mean values were total endosulfan > total DDTs > β-Endosulfan > α-Endosulfan > Endrin > 4, 4-DDD > 4, 4-DDT > 4, 4- DDE > Dieldrin > Lindane for fish samples collected from Lake Tana. The highest mean concentrations of OCPs recorded in Lake Hayqe was Endrin (21.00 μg/kg) and the lowest was dieldrin (12.97 μg/kg). The contamination orders of detected OCPs based on the mean values were total DDT > total endosulfan > Endrin > 4, 4-DDD > 4, 4-DDT > 4, 4- DDE > Lindane > β-Endosulfan > α-Endosulfan > Dieldrin for fish samples collected from Lake Hayqe (Table 4). This result indicated the high degree of exposure to endosulfan and DDTs in Lake Tana. Whereas Endrin, total endosulfan and total DDTs in Lake Hayqe for aquatic biota (Fish)of the Amhara National Regional State Lakes (ANRSL), Ethiopian.

Table 4

Generally; the levels of Lindane and total Endosulfan found in water samples collected from Lake Tana and Lake Hayqe were below the permisiable limits of WHO guideline, while the rest were above the permisiable limits of WHO and USEPA guideline. The levels of Lindane, total Endosulfan, total DDTs, Endrin, and Dieldrin found in sediment and fish samples collected from Lake Tana and Lake Hayqe were above the permisiable limits of WHO and USEPA guideline. This might be due to the non-degradable natures of OCPs within the sediment and fish matrix. Most pesticides used in Ethiopia are generic because they are cheaper and more familiar as they have been used for a long time. Although official registration is required, importers do not bother to register pesticides whose patents have expired; they only submit dossiers to ministry of agriculture (MoA) for patented pesticides. Ethiopia has by no means an effective pesticide governance system. The country has not been able to commit the relevant state authorities and private sectors in setting up a well-functioning, legitimate, transparent and accountable system for pesticide distribution and use [58].The levels of most of the pesticide residues in sediment and fish were higher than those found in water. This may be due to Organochlorine pesticides are low soluble in water. Organochlorine pesticide residues in the Lake are likely to originate from nonpoint sources via runoff, atmospheric deposition, and leaching due to agricultural applications and vector control practices [3], [59]. In the Lake sediments act as a sink for the persistent contaminants, whose resuspension during the lake’s mixing may increase pesticide bioavailability and accumulation in the fish. Pesticide pollution to the lake is therefore, likely to pose a danger to both aquatic organisms and humans [60].

Conclusion And Recommendation

This is the first study reporting on the levels OCPs in the water, sediment and fish samples from the Lake Tana and Lake Hayqe, Ethiopia. In this study the totals of 18 OCPs were investigated. Most of the organochlorine pesticides were highly detected in Fish and sediment than water. The concentrations of detected individual OCPs in water samples were ranged from 1.06–12.61 μg/L in Lake Tana; while 1.09–8.21 μg/L in Lake Hayqe. The concentration of detected OCPs residues in sediment samples were also ranged from 10.11-125.65 μg/kg in Lake Tana; and 10.96–21.41 μg/kg in Lake Hayqe. The concentrations of detected OCPs residues in fish samples were also ranged from 10.54–51.5 μg/kg in Lake Tana; and 10.67–21.25 μg/kg in Lake Hayqe. Therefore, pesticides may be accumulated in Fish and sediment when they are discharged in to water bodies which might be because of their low solubility in water. Most of the pesticides were exceeded WHO and USEPA residue limits except endosulfan. All the detected pesticides in the water samples exceeded the MPL of the Ethiopian standard or the EU standard that is 0.1 μg/L. The ANOVA analysis also found that the concentrations of most pesticides were significantly varied with different sampling sites and between Lakes.

The study recommends reducing the use of pesticides to the recommended doses, but preferably to lower dosages by promoting integrated pest management (IPM) practices in Amhara, Ethiopia. We also suggest future studies (e.g. modelling study) to determine the route of pesticide exposure to the aquatic systems, so that pesticide contamination may be reduced through the proper implementation of mitigation measures. And also it should be investigated seasonal variations of pesticide distribution for water, sediment and fish matrix.

Declarations

Ethics approval and consent to participate:-“Not Applicable (NA)”

Consent for publication: - “Not Applicable (NA)”

Availability of data and materials:-The datasets used and/or analyzed and included in the article

Competing interests:- The authors declare that they have no competing interests.

Funding: - Funding is not applicable for this study.

Authors’ contributions:-TF, AK,ML, DY, DT and MM collected the samples and conducted the analysis. MM and AK, ZM, designed the research and finalized the manuscript. TA, DT& YK edited the manuscript. All authors read and approved the final manuscript.

Acknowledgment: - The authors gratefully acknowledge Gondar University support the work.

References

1. A. F. El Nahas, M. A. S. Abdel-Razek, N. M. Helmy, S. Mahmoud, and H. A. Ghazy, ‘Impaired antioxidant gene expression by pesticide residues and its relation with other cellular biomarkers in Nile Tilapia (Oreochromis niloticus) from Lake Burullus’, Ecotoxicol. Environ. Saf., vol. 137, no. 8, pp. 202–209, 2017, doi: 10.1016/j.ecoenv.2016.12.006.
2. A. Agrawal, R. S. Pandey, and B. Sharma, ‘Water Pollution with Special Reference to Pesticide Contamination in India’, J. Water Resour. Prot., vol. 02, no. 05, pp. 432–448, 2010, doi: 10.4236/jwarp.2010.25050.
3. X. Li, Q. Zhang, J. Dai, Y. Gan, J. Zhou, X. Yang, H. Cao, G. Jiang, M. Xu,‘Pesticide contamination profiles of water, sediment and aquatic organisms in the effluent of Gaobeidian wastewater treatment plant’, *Chemosphere*, vol. 72, no. 8, pp. 1145–1151, 2008, doi: 10.1016/j.chemosphere.2008.03.049.
4. R. Kaur, G. K. Mavi, S. Raghav, and I. Khan, ‘Pesticides Classification and its Impact on Environment’, Int. J. Curr. Microbiol. Appl. Sci., vol. 8, no. 03, pp. 1889–1897, 2019, doi: 10.20546/ijcmas.2019.803.224.
5. G. Ma and K. Ms, ‘The Effect of Pesticides Pollution on Our Life and Environment’, J. Pollut. Eff. Contro, vol. 4, no. 2, pp. 4–5, 2016, doi: 10.4172/2375-4397.1000159.
6. O. Akoto, A. A. Azuure, and K. D. Adotey, ‘Pesticide residues in water, sediment and fish from Tono Reservoir and their health risk implications’, *Springerplus*, vol. 5, no. 1, pp. 1–11, 2016, doi: 10.1186/s40064-016-3544-z.

7. H. Kuranchie-Mensah, S. M. Atiemo, L. M. Palm, S. Blankson-Arthur, A. O. Tutu, and P. Fosu, 'Determination of organochlorine pesticide residue in sediment and water from the Densu river basin, Ghana', *Chemosphere*, vol. 86, no. 3, pp. 286–292, 2012, doi: 10.1016/j.chemosphere.2011.10.031.
8. R. D. Acayaba, A. F. de Albuquerque, R. L. Ribessi, G. de A. Umbuzeiro, and C. C. Montagner, 'Occurrence of pesticides in waters from the largest sugar cane plantation region in the world', Environ. Sci. Pollut. Res., vol. 28, no. 8, pp. 9824–9835, 2021, doi: 10.1007/s11356-020-11428-1.
9. E. E. Eissa, K. Radwan, E. Radwan, N. A. Hakeem, K. A. Aziz, and H. O. Hashem, 'Impact of Chlorpyrifos on Mosquito Larvae as Bioindicator in El-Beheira Governorate, Egypt. Ebrahim', Int. J. Limnol., vol. 1, no. 1, pp. 16–19, 2018.
10. O. Ogbeide, I. Tongo, and L. Ezemonye, 'Risk assessment of agricultural pesticides in water, sediment, and fish from Owan River, Edo State, Nigeria', Environ. Monit. Assess., vol. 187, no. 10, pp. 1–16, 2015, doi: 10.1007/s10661-015-4840-8.
11. G. R. Chang, 'Persistent organochlorine pesticides in aquatic environments and fishes in Taiwan and their risk assessment', *Environ. Sci. Pollut. Res.*, vol. 25, no. 8, pp. 7699–7708, 2018, doi: 10.1007/s11356-017-1110-z.
12. A. Deknock, N. De Troyer, M. Houbraken, L. Dominguez-Granda, I. Nolivos, W. Van Echelpoel, M. Anne Eurie Forio, P. Spanoghe, P. Goethals 'Distribution of agricultural pesticides in the freshwater environment of the Guayas river basin (Ecuador)', Sci. Total Environ., vol. 646, pp. 996–1008, 2019, doi: 10.1016/j.scitotenv.2018.07.185.
13. H. Xie, X. Wang, J. Chen, X. Li, G. Jia, Y. Zou, Y. Zhang, Y. Cui,'Occurrence, distribution and ecological risks of antibiotics and pesticides in coastal waters around Liaodong Peninsula, China', Sci. Total Environ., vol. 656, pp. 946–951, 2019, doi: 10.1016/j.scitotenv.2018.11.449.
14. C. Olisah, O. O. Okoh, and A. I. Okoh, 'Occurrence of organochlorine pesticide residues in biological and environmental matrices in Africa: A two-decade review', *Heliyon*, vol. 6, no. 3, pp. 1–19, 2020, doi: 10.1016/j.heliyon.2020.e03518.
15. E. Deribe, B. O. Rosseland, R. Borgstrøm, B. Salbu, Z. Gebremariam, E. Dadebo, H. R. Norli, O. M. Eklo 'Bioaccumulation of persistent organic pollutants (POPs) in fish species from Lake Koka, Ethiopia: The influence of lipid content and trophic position', Sci. Total Environ., vol. 411, pp. 136–145, 2011, doi: 10.1016/j.scitotenv.2011.09.008.
16. L. B. Merga, A. A. Mengistie, M. T. Alemu, and P. J. Van den Brink, 'Biological and chemical monitoring of the ecological risks of pesticides in Lake Ziway, Ethiopia', *Chemosphere*, vol. 266, no. x, pp. 1–12, 2021, doi: 10.1016/j.chemosphere.2020.129214.
17. A. B. Kassegne, J. O. Okonkwo, T. Berhanu, A. P. Daso, O. I. Olukunle, and S. L. Asfaw, 'Ecological risk assessment of organochlorine pesticides and polychlorinated biphenyls in water and surface sediment samples from Akaki River catchment, central Ethiopia', *Emerg. Contam.*, vol. 6, no. x, pp. 396–404, 2020, doi: 10.1016/j.emcon.2020.11.004.
18. B. M. Teklu, P. I. Adriaanse, M. M. Ter Horst, J. W. Deneer, and P. J. Van den Brink, 'Surface water risk assessment of pesticides in Ethiopia', Sci. Total Environ., vol. 508, pp. 566–574, 2015, doi: 10.1016/j.scitotenv.2014.11.049.
19. B. Agmas and M. Adugna, 'Attitudes and practices of farmers with regard to pesticide use in NorthWest Ethiopia', Cogent Environ. Sci., vol. 6, no. 1, pp. 1–16, 2020, doi: 10.1080/23311843.2020.1791462.
20. Y. B. Yohannes, Y. Ikenaka, A. Saengtienchai, K. P. Watanabe, S. M. Nakayama, and M. Ishizuka, 'Concentrations and human health risk assessment of organochlorine pesticides in edible fish species from a Rift Valley lake-Lake Ziway, Ethiopia', Ecotoxicol. Environ. Saf., vol. 106, pp. 95–101, 2014, doi: 10.1016/j.ecoenv.2014.04.014.
21. M. G. Dersseh, T. S. Steenhuis, A. A. Kibret, B. M. Eneyew, M. G. Kebedew, F. A. Zimale, A. W. Worqlul, M. A. Moges, W. B. Abebe, D. A. Mhiret, A. M. Melesse, and S. A. Tilahun 'Water Quality Characteristics of a Water Hyacinth Infested Tropical Highland Lake: Lake Tana, Ethiopia', *Front. Water*, vol. 4, no. March, pp. 1–17, 2022, doi: 10.3389/frwa.2022.774710.
22. E. Asmare, 'Current Trend of Water Hyacinth Expansion and Its Consequence on the Fisheries around North Eastern Part of Lake Tana, Ethiopia', J. Biodivers. Endanger. Species, vol. 05, no. 02, pp. 1–5, 2017, doi: 10.4172/2332-2543.1000189.
23. N. Dechassa and B. Abate, 'Current Status of Water Hyacinth (Eichhornia crassipes) in Ethiopia: Achievements, Challenges and Prospects: A Review', J. Environ. Earth Sci., vol. 10, no. 12, pp. 1–13, 2020, doi: 10.7176/jees/10-12-03.
24. T. Fetahi, S. Mengistou, and M. Schagerl, 'Zooplankton community structure and ecology of the tropical-highland Lake Hayq, Ethiopia', *Limnologica*, vol. 41, no. 4, pp. 389–397, 2011, doi: 10.1016/j.limno.2011.06.002.
25. Z. Seid, 'Fish Diversity, Abundance, Socioeconomic Importance and the Status of the Fisheries of Lake Hayq, South Wollo, Ethiopia.', Addis Ababa University, Etiopia, 2016.

26. D. Tibebe, Y. Kassa, A. Melaku, and S. Lakew, 'Investigation of spatio-temporal variations of selected water quality parameters and trophic status of Lake Tana for sustainable management, Ethiopia', Microchem. J., vol. 148, pp. 1–32, 2019, doi: 10.1016/j.microc.2019.04.085.
27. A. Wondie and S. Mengistou, 'Seasonal variability of secondary production of cladocerans and rotifers, and their trophic role in Lake Tana, Ethiopia, a large, turbid, tropical highland lake', African J. Aquat. Sci., vol. 39, no. 4, pp. 403–416, 2014, doi: 10.2989/16085914.2014.978835.
28. H. Muche, T. Mucheye, and D. Tadesse, 'Water quality and transpiration responses of Eichornia crassipes', Sustain. Water Resour. Manag., vol. 42, no. 6, pp. 1–7, 2020, doi: 10.1007/s40899-020-00392-w.
29. E. Dejen, J. Vijverberg, L. A. Nagelkerke, and F. A. Sibbing, 'Temporal and spatial distribution of microcrustacean zooplankton in relation to turbidity and other environmental factors in a large tropical lake (L. Tana, Ethiopia)', Hydrobiologia, vol. 513, pp. 39–49, 2004.
30. D. Tibebe, Y. Kassa, A. Melaku, and S. Lakew, 'Investigation of spatio-temporal variations of selected water quality parameters and trophic status of Lake Tana for sustainable management, Ethiopia', Microchem. J., vol. 148, pp. 1–32, 2019, doi: 10.1016/j.microc.2019.04.085.
31. *Int. J. Technol. Enhanc. Emerg. Eng. Res.*, vol. 3, no. 11, pp. 1–16, 2015.
32. J. Vijverberg, F. A. Sibbing, and E. Dejen, 'Lake Tana: Source of the Blue Nile', pp. 163–192, 2009, doi: 10.1007/978-1-4020-9726-3_9.
33. R. M. Baxter and D. L. Golobitsh, 'A Note on the limnology of Lake Hayq, Ethiopia', J. Limnol. Oceanogr., vol. 15, pp. 144–149, 1970.
34. D. Tibebe, D. Lemma, and G. Teshome, 'Determination of Heavy Metals in Tilapia (Oreochromis Niloticus) and Water Samples from Lake Hayq, South Wollo, Ethiopia', Int. J. Chem. Mater. Res., vol. 7, no. 1, pp. 10–19, 2019, doi: 10.18488/journal.64.2019.71.10.19.
35. M. Demlie, T. Ayenew, and S. Wohnlich, 'Comprehensive hydrological and hydrogeological study of topographically closed lakes in highland Ethiopia: The case of Hayq and Ardibo', J. Hydrol., vol. 339, no. 4, pp. 145–158, 2007, doi: 10.1016/j.jhydrol.2007.03.012.
36. E. Lima, J. Domingos, T. Costa, P. Henrique, G. Dias, U. R. Oliveira, J. R. Souza, 'Distribution of organochlorine, organophosphates, carbamate, thiocarbamate, pyrethroids, and strobilurins in surface sediments of the Rio de Ondas watershed by GC-MS', J. Environ. Sci. Heal. Part B, vol. 56, no. 4, pp. 357–369, 2021, doi: 10.1080/03601234.2021.1885263.
37. C. Olisah, G. Rubidge, L. R. Human, and J. B. Adams, 'A translocation analysis of organophosphate pesticides between surface water, sediments and tissues of common reed Phragmites australis', *Chemosphere*, vol. 284, pp. 1–12, 2021, doi: 10.1016/j.chemosphere.2021.131380.
38. M. Rahman, S. Hoque, S. Bhowmik, S. Ferdousi, M. P. Kabiraz, and M. L. van Brakel, 'Monitoring of pesticide residues from fi sh feed, fish and vegetables in Bangladesh by GC-MS using the QuEChERS method', *Heliyon*, vol. 7, pp. 1–8, 2021, doi: 10.1016/j.heliyon.2021.e06390.
39. By Michelle L. Hladik and Megan M. McWayne, 'Methods of Analysis- Determination of Pesticides in Sediment Using Gas Chromatography/Mass Spectrometry', U.S. *Geol. Surv. Tech. Methods 5–C3*, vol. 18, pp. 1–28, 2012, [Online]. Available: http://pubs.usgs.gov/tm/tm5c3/.
40. D. A. Skoog, D. M.West, F. J. Holler, and S. R. Crouch, *Fundamentals of Analytical Chemistry*, Ninth Edit. BROOKS/COLE CENEGANG Learning, 2013.
41. J. Gan, H. Liu, Y. Chen, J. Peng, T. Liu, J. Chen, L. He,'One step extraction followed by HPLC-ESI-MS/MS for multi-residue analysis of diacylhydrazine insecticides in water, sediment, and aquatic products', Ecotoxicol. Environ. Saf., vol. 210, pp. 1–9, 2021, doi: 10.1016/j.ecoenv.2020.111853.
42. J. D. Martin, W. W. Stone, D. S. Wydoski, and M. W. Sandstrom, 'Adjustment of pesticide concentrations for temporal changes in analytical recovery, 1992–2006', US Virginia, 2009. [Online]. Available: http://pubs.er.usgs.gov/usgspubs/sir/sir20095189.
43. T. G. Ambaye, 'Residues Analysis of Organochlorine Pesticides in Fish, Sediment and Water Samples from Tekeze Dam, Ethiopia', J. Environ. Anal. Toxicol., vol. 6, no. 1, pp. 1–5, 2016, doi: 10.4172/2161-0525.1000342.

44. G. Darko, O. Akoto, and C. Oppong, 'Persistent organochlorine pesticide residues in fish, sediments and water from Lake Bosomtwi, Ghana', *Chemosphere*, vol. 72, no. 3, pp. 21–24, 2008, doi: 10.1016/j.chemosphere.2008.02.052.
45. G. A. latif A. Nesser, A. O. Abdelbagi, A. E. Ishag, A. M. Hammad, and M. Tagelseed, 'Seasonal levels of pesticide residues in the main and the Blue Nile waters in Sudan', Arab. J. Geosci., vol. 13, no. 994, pp. 1–13, 2020.
46. S. Musa, J. W. Gichuki, P. O. Raburu, and C. M. Aura, 'Risk assessment for organochlorines and organophosphates pesticide residues in water and Sediments from lower Nyando/Sondu-Miriu river within Lake Victoria Basin, Kenya', Lakes Reserv. Res. Manag., vol. 16, no. 4, pp. 273–280, 2011, doi: 10.1111/j.1440-1770.2011.00486.x.
47. S. Mahboob, F. Niazi, K. AlGhanim, S. Sultana, F. Al-Misned, and Z. Ahmed, 'Health risks associated with pesticide residues in water, sediments and the muscle tissues of Catla catla at Head Balloki on the River Ravi', Environ. Monit. Assess., vol. 187, no. 3, pp. 1–10, 2015, doi: 10.1007/s10661-015-4285-0.
48. T. Poolpak, P. Pokethitiyook, M. Kruatrachue, U. Arjarasirikoon, and N. Thanwaniwat, 'Residue analysis of organochlorine pesticides in the Mae Klong river of Central Thailand', J. Hazard. Mater., vol. 156, no. 3, pp. 230–239, 2008, doi: 10.1016/j.jhazmat.2007.12.078.
49. Y. B. Yohannes, Y. Ikenaka, S. M. Nakayama, A. Saengtienchai, K. Watanabe, and M. Ishizuka, 'Organochlorine pesticides and heavy metals in fish from Lake Awassa, Ethiopia: Insights from stable isotope analysis', *Chemosphere*, vol. 91, no. 6, pp. 857–863, 2013, doi: 10.1016/j.chemosphere.2013.01.047.
50. G. Gbeddy, P. Yeboah, D. Carboo, L. Doamekpor, S. Afful, V. Nartey, S. Frimpong, I. Doyi, T. Glover, and C. Egbi 'Organochlorine pesticide residues in African catfish muscle, Nile tilapia Muscle and gills from the middle Volta basin, Kpando Torkor, Ghana and their potential health risks to humans', Elixir Int. J., vol. 49, pp. 9724–9730, 2012.
51. A. Buah-Kwofie, M. S. Humphries, and L. Pillay, 'Bioaccumulation and risk assessment of organochlorine pesticides in fish from a global biodiversity hotspot: iSimangaliso Wetland Park, South Africa', Sci. Total Environ., vol. 621, pp. 273–281, 2018, doi: 10.1016/j.scitotenv.2017.11.212.
52. K. Farshid, 'Assessment of Organochlorine Pesticide Residues in Water, Sediments and Fish from Lake Tashk, Iran', *Achiev. Life Sci.*, vol. 9, no. x, pp. 107–111, 2015, doi: 10.1016/j.als.2015.12.003.
53. A. Polder, M. B. Müller, J. L. Lyche, R. H. Mdegela, H. E. Nonga, F. P. Mabiki, T. J. Mbise, J. U. Skaare, M. Sandvik, E. Skjerve, E. Lie, 'Levels and patterns of persistent organic pollutants (POPs) in tilapia (Oreochromis sp.) from four different lakes in Tanzania: Geographical differences and implications for human health', Sci. Total Environ., vol. 489, no. 1, pp. 252–260, 2014, doi: 10.1016/j.scitotenv.2014.04.085.
54. T. V. Sankar, A. A. Zynudheen, R. Anandan, and P. G. Viswanathan Nair, 'Distribution of organochlorine pesticides and heavy metal residues in fish and shellfish from Calicut region, Kerala, India', *Chemosphere*, vol. 65, no. 4, pp. 583–590, 2006, doi: 10.1016/j.chemosphere.2006.02.038.
55. G. L. Tadesse and T. Kasa, 'High Human Exposure and Measurable Environmental Impact of Pesticides Application on Agriculture: A Review Article', Adv. Life Sci. Technol., vol. 55, pp. 13–22, 2017.
56. A. M. Taiwo, 'A review of environmental and health effects of organochlorine pesticide residues in Africa', *Chemosphere*, vol. 220, pp. 1126–1140, 2019, doi: 10.1016/j.chemosphere.2019.01.001.
57. P. Pandey, P. S. Khillare, and K. Kumar, 'Assessment of Organochlorine Pesticide Residues in the Surface Sediments of River Yamuna in Delhi, India', J. Environ. Prot. (Irvine,. Calif)., vol. 2, pp. 511–524, 2011, doi: 10.4236/jep.2011.25059.
58. B. T. Mengistie, A. P. Mol, and P. Oosterveer, 'Private Environmental Governance in the Ethiopian Pesticide Supply Chain: Importation, Distribution and Use', NJAS - Wageningen J. Life Sci., vol. 76, pp. 65–73, 2015, doi: 10.1016/j.njas.2015.11.005.
59. J. A. Aguilar, V. Andreu, J. Campo, Y. Picó, and A. Masiá, 'Pesticide occurrence in the waters of Júcar River, Spain from different farming landscapes', Sci. Total Environ., vol. 608, pp. 752–760, 2017, doi: 10.1016/j.scitotenv.2017.06.176.
60. H. Yu, F. Li, W. Yu, Y. Li, G. Yang, S. Zhou, T. Zhang, Y. Gao, H. Wan, 'Assessment of organochlorine pesticide contamination in relation to soil properties in the Pearl River Delta, China', Sci. Total Environ., vol. 447, pp. 160–168, 2013, doi: 10.1016/j.scitotenv.2012.12.070.

Figures

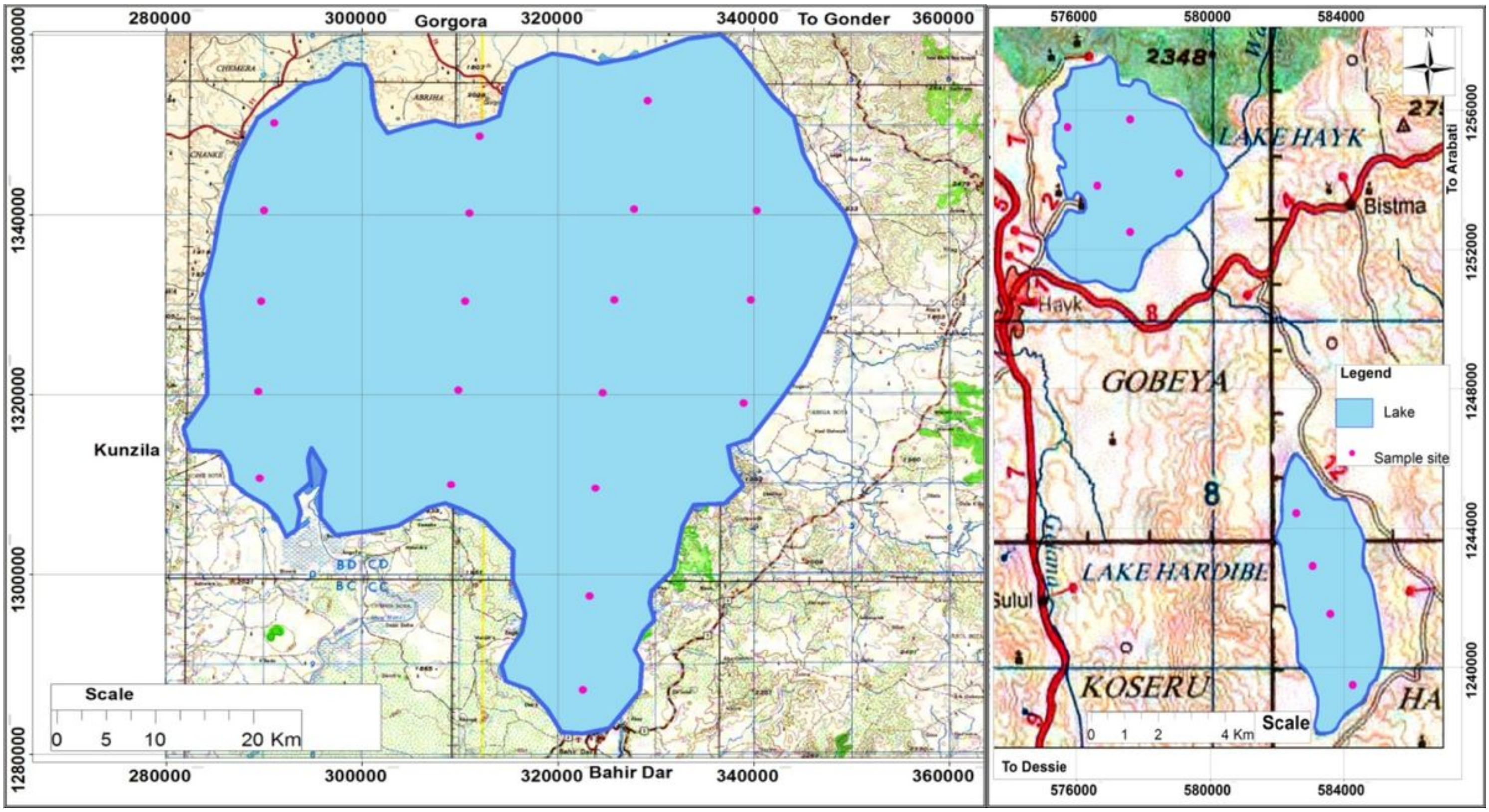

Figure 1

Sampling sites of Lake Tana (Left side) and Lake Hayq (right side)