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Levels of organochlorine pesticides in five species of fish from Lake Ziway, Ethiopia

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ABSTRACT

The Ethiopian Rift Valley (ERV) lakes region is an agricultural area in Ethiopia with intense year-round irrigated framing where widespread legal and illegal pesticide use was documented. The aim of the study is to assess tissue concentration of organochlorine pesticides (OCPs) in fillets of fives species of fish from Lake Ziway, an ERV lake. The influence of trophic position and fish size on accumulation of OCPs was investigated. Sample preparation for the analysis of OCPs was done following the QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method and OCPs were analyzed using gas chromatography and compound specification was made using mass spectrometry. Dichloro-diphenyl-trichloroethanes (DDTs) were dominant among investigated OCPs. 4,4'-dichloro-diphenyl-dichloro-ethylene (p,p'-DDE) was the predominant DDT metabolite constituting about 99.2% of total DDTs. Historic DDT input was suggested as the source of current DDT contamination dominated by p,p'-DDE. Geometric mean value of p,p'-DDE varied from 1.07 to 3.64 ng g^{-1}ww. Species variation in accumulation of p,p'-DDE was found that could result from differences in trophic level, lipid content, age, specific habitat, and feeding habit. Carassius carassius occupying a higher trophic position and with relative high lipid content had the highest p,p'-DDE levels. Positive associations between log-transformed p,p'-DDE, and total length were found for C. carassius and Cyprinus carpio. p,p'-DDE was biomagnified through the local food web. Generally, the levels of DDT in the present study are lower than levels reported from lake Ziway in earlier studies. The present findings may contribute contemporary OCP contamination data in investigated fish species.

Introduction

Organochlorine pesticides (OCPs) are among the persistent organic pollutants that are banned by the Stockholm convention (Stockholm Convention on persistent organic pollutants (POPs), 2019). Dichloro-diphenyl-trichloroethane (DDT), Dieldrin, Aldrin, Chlordane, Mirex, toxaphene constitutes some of the legacy OCPs contaminants, all of which are discontinued

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Table 1
Mean and ranges of total length and weight of fish species sampled from Lake Ziway.

Fish spp.	N	Total Length (cm) M±SD	Range	Weight (g) M±SD	Range
C. gariepinus	10	31.9 ± 3.2	28.0–37.5	240.4 ± 64.1	183.0- 383.0
O. niloticus	10	20.0 ± 1.2	19.0–23.0	156.5 ± 20.2	132.0–207.0
C. Carassius	10	29.3 ± 2.5	25.5–34.0	362.4 ± 98.3	242.0–581.0
C. carpio	10	21.0 ± 1.2	19.0–22.0	157.1 ± 30.1	115.0–195.0
T. zillii	10	16.8 ± 1.2	15.0–18.5	126.5 ± 30.4	92.0–193.0

as agricultural pest control agent due to their adverse effects on environment and biota [29]. However, due to their environmental persistence and biomagnification property, they are still being detected in different environmental and biological compartments [3]. In developing countries like Ethiopia, despite the general decrease in the use of DDT since 2009 [34], there is a fresh release of OCPs, particularly DDT into the environment through the continued use for malaria vector control [34], contamination from improper storage of obsolete pesticide stocks [18] and illegal diversion and use for agricultural purposes [25].

The Ethiopian Rift Valley (ERV) having mid-altitude climatic conditions is a malaria-prone region where an indoor residual spray of DDT for malaria vector control is common [4]. Moreover, the region is the main site for year-round irrigated vegetable farming through abstraction of water from Lake Ziway [1]. There are also large-scale flower farms adjoining the lake releasing effluents directly into the lake [24]. OCPs illegally applied in the agricultural activities surrounding the lake could contaminate the lake through runoff water [5]. Earlier studies carried out a decade ago have suggested the presence of OCPs in fish [10,39] and fish-eating birds [38]. The presence of several pollution threats implies the need for biomonitoring of OCPs in the area.

OCPs are lipophilic; they accumulate in the fatty tissue of organisms and biomagnify through food webs [3]. Fish are important indicators for biomonitoring of OCPs in aquatic habitats due to their high OCP accumulation capacity [40]. They constitute the key route for organochlorine exposure to humans [15] and wildlife such as fish-eating birds [38]. Exposure assessment and human health risk assessment studies have been made on fish from the present study site [10,39]. However, due to changes in species composition, some of the fish that were prevalent and dominant are currently rarely seen (such as *Carassius auratus*) and fish that were rarely catch currently constitute among the most dominant ones (such as *Cyprinus carpio and Carassius Carassius*) partly due to decrease in water level and increase in turbidity [1]. Consequently, contemporary exposure assessment of OCPs and investigation of factors influencing OCP accumulation is necessary. Therefore, the aim of the present study is to assess the presence, distribution, and factors affecting the accumulation of OCPs in five species of fish from Lake Ziway. We test the following hypotheses. (1) Fish at higher trophic positions would accumulate higher levels of OCPs in their tissues than fish occupying lower trophic positions. (2) Concentrations of OCPs in fish muscle tissue in the present study would be lower than values reported from earlier studies from the current site as a result of DDT ban for agricultural purposes.

Materials and methods

Study area

Lake Ziway is situated in the central rift valley region of Ethiopia between 8.0073° N latitude, and 38.8415° E, longitude and at an elevation of about 1650 m above sea level (asl). The lake has an average water surface area of 440 km^2 and average depth of 2.5 m [13]. Katar and Meki rivers constitute major inflow of water to the lake while river Bulbula is an outflow from the lake. Ziway, which is a densely populated town, is situated adjacent to the lake (Fig. 1).

In the vicinity of the lake, there are various agricultural activities that are being carried out throughout the year, including vegetable and flower farming [1]. About 7 km away from Lake Ziway there is the Adami-Tulu pesticide factory, which until 2009, was known to formulate DDT for the country's consumption [34].

Sample collection

Fish samples were collected in April and May, 2019. Fresh catches of fish were purchased from the fishing boats of the local fishermen. A total of 50 individual fishes, belonging to five species were sampled. The species sampled include crucian carp (*C. carassius)*, Nile tilapia (*Oreochromis niloticus)*, African sharp-tooth fish (*Clarias gariepinus)*, common carp (*C. carpio)*, and redbelly tilapia (*Tilapia zillii).* After fish samples were collected, length and weight measurements were recorded (Table 1). Fishes were dissected and fillet excised from each side. Each of the excised fish muscle samples was wrapped with aluminum foil, stored in labeled zipper plastic bags, and kept frozen at -18 °C until chemical analysis.

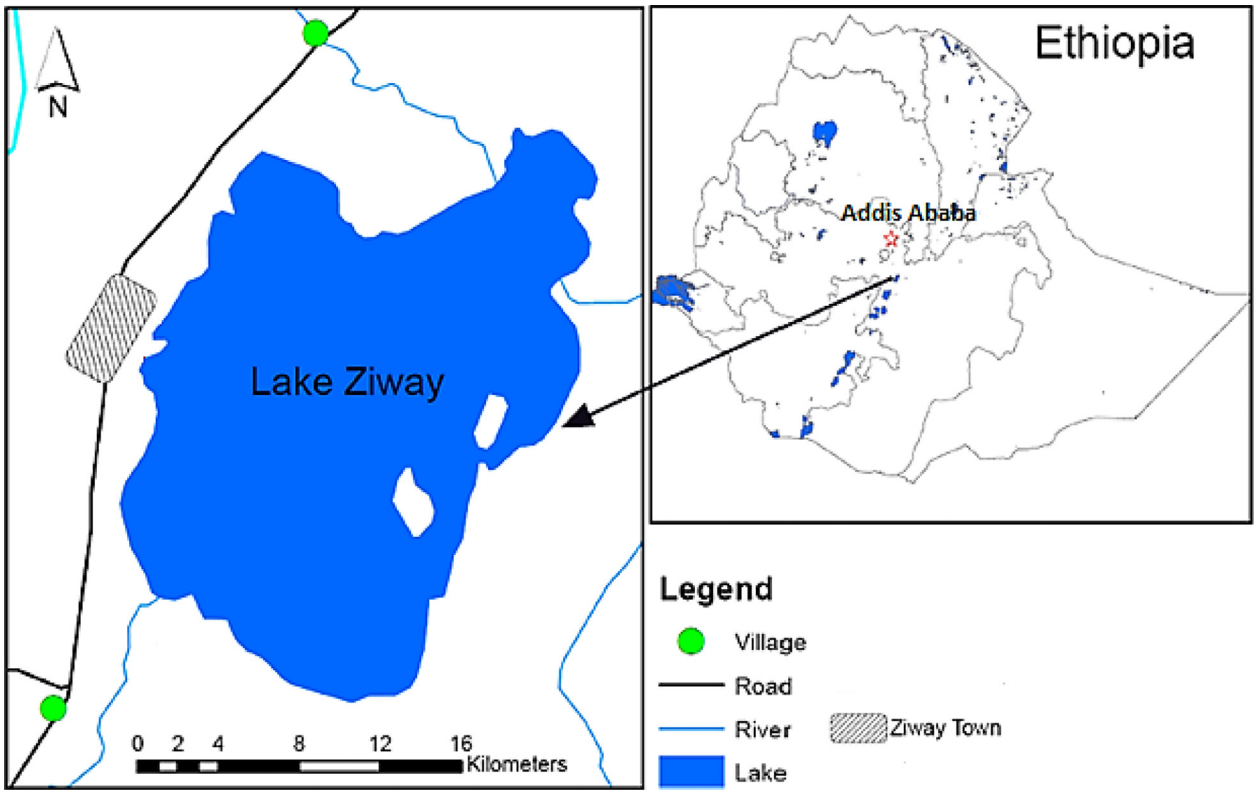


Fig. 1. The Map of Lake Ziway (Modified from [30]).

Lipid content determination

Lipid determination was performed using SOXTEC Auto Lipid extractor (2050 SOXTEC™, FOSS® Analytical, Hilleroed, Denmark). Lipid was determined using pooled homogenized muscle samples. Five grams of homogenized sample was mixed with sodium sulfate powder (EMSURE, Germany) using a mortar. The resulting mixture was transferred to cellulose extraction thimbles (Whatman™, China). Then, the thimbles were loaded into a lipid extraction unit. Extraction solution consist of a mixture of ethyl acetate: cyclohaxane (1:1) was added into extraction glass cups in a closed system. The extraction thimbles are lowered into extraction glass cups and boiled at 100 °C. The whole extraction process consists of boiling, rinsing, solvent recovery and pre-drying. Upon completion of extraction, remaining solvents evaporated by heating to dryness under a blowing nitrogen gas stream. Finally, the glass cups with residual lipid were weighed. Lipid content in the sample was determined by subtracting the weight of empty glass cups from the final weight (weight of the glass tube with residual fat). Percent lipid was calculated by the following formula. Percent lipid = (Weight of fat/Weight of sample)x100.

Stable isotope analysis

Stable isotope analysis of nitrogen (^{15}N and ^{14}N) and carbon (^{13}C and ^{12}C) was carried out in the Isotope Laboratory, Norwegian University of Life Sciences (NMBU), Norway. One gram of muscle tissue was taken in labeled plastic tubes from each sample and homogenized with 10 mL of water using Ultra-Turrax tissue disintegrator (ULTRA-TURRAX®, IKA-WERK GmbH & Co. KG). One mg of the homogenized sample was transferred into labeled plastic tubes. Each plastic tube containing a homogenized sample was covered with perforated parafilm and freeze-dried. Freeze-dried samples of 1 µg were packed in pre-weighed aluminum foil and were subjected to combustion in a Flash Elemental Analyzer. Stable isotopes of Nitrogen (^{15}N and ^{14}N), and Carbon (^{13}C and ^{12}C) were determined by a Continuous Flow-Infrared Mass Spectrometer. The isotopic ratios ($^{15}N/^{14}N$ and $^{13}C/^{12}C$) were expressed in delta-values as follows: $\delta^{15}N$ and $\delta^{13}C(‰) = [(R_{Sample}/R_{Standard} - 1]*1000$, Where $R = {}^{15}N / {}^{14}N$ for $\delta^{15}N$ or $R = {}^{13}C / {}^{12}C$ for $\delta^{13}C$ [11].

Sample preparation

Sample preparation and chemical analysis were carried out at Norwegian Institute of Bioeconomy Research (NIBIO), Department of Pesticides and Natural Products Chemistry. Sample preparation for the analysis of organochlorines (OCs) was

performed following the Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) method [2]. Each bird muscle sample was thawed and 5 g of the sample was measured into 50 mL extraction tube. 10 mL of Milli-Q water (obtained from a Milli-Q Gradient water system; Millipore, Bedford, USA) and 10 mL of acetonitrile were added to the sample. 0.1 µg (10 µL) internal standard mixture (containing 10 µg/mL of triphenylphosphate, 2-bromobiphenyl and decachlorbiphenyl in acetonitrile) was added to each sample. The resulting mixture was homogenized to a finely divided suspension of solvent and tissue using polytron homogenizer (P.T.3100, Kenematica, Switzerland). Citrate buffering salt (Sigma-Aldrich, Product No. 55227-U) was added into the sample, shaken for 10 min using an end-over-end instrument and subsequently centrifuged for 5 min at 3000 rpm (revolution per minute). Citrate buffering salt ensures phase separation between the tissue, water, and acetonitrile.

Then, the samples were treated with a two-stage dispersive clean-up to remove interferences. The first stage dispersive clean-up was done using Primary Secondary Amine (PSA) clean-up tube. Six mL of the supernatant was transferred to PSA clean-up tube (Sigma-Aldrich product, Product No. 55228-U). The tube was shaken for 10 min by the use of an "end-over-end" instrument, and centrifuged for 5 min at 3000 rpm. PSA removes acidic substances such as fatty acids, and $MgSO_4$ removes traces of water in the acetonitrile. The second stage clean-up was carried out using Enhanced Matrix Removal-lipid tube (EMR-Lipid tube). First, the EMR-Lipid tube was prepared by adding 5 mL of Milli-Q water. Then, it was shaken until no particles are visible, the dispersion is smooth and milky white. 5 mL of the extract resulting from PSA clean-up treatment was added to the prepared EMR-Lipid tube (Agilent Technologies). The sample was shaken for 10 min by the use of "end-over-end" instrument and subsequently centrifuged for 5 min at 3000 rpm. 5 mL of the resulting supernatant was transferred into $MgSO_4$ containing EMR-Lipid polishing tube (Agilent Technologies) to get phase separation. Finally, the aliquot of the supernatant (15 µl) was transferred into a gas chromatography (GC) injecting vial from which it was injected to gas chromatography-mass spectrometry (GC-MS) for OCPs analysis

Chemical analysis

OCPs (DDT, Oxychlordane, cis-chlordane, trans-Chlordane, Endosulpha-alpha, Endosulphan-beta, Endosulphan-sulphate, Aldrin and Dieldrin) were analyzed by gas chromatography (Agilent 6890 N) with solvent vent injection mode. The gas chromatography was equipped with Gerstel (Mühlheim Ruhr, Germany) programmable temperature vaporizing injector (PTV) with a sintered liner. Helium was used as carrier gas. The PTV program was as follows: The initial solvent vent temperature was kept at 50 °C in 1.89 min with a solvent vent flow at 200 mL/min. Injection was made at 720 °C in 1.80 min. After 1.80 min the split valve was closed and the injector temperature was raised by 720 °C/min to 280 °C and kept for 1.2 min. Pressurized air was used as a coolant for the PTV injector. The mass spectrometer was operated in selected ion monitoring mode with target and qualifier ions. Transfer line temperature was set at 280 °C, ion source temperature at 230 °C, and quadrupole temperature at 50 °C.

Single quadrupole mass spectrometer (Agilent 5973 N) with electron impact ionization (EI), 70 eV operating in selected ion monitoring (SIM) was used for compound specifications. Agilent HP-5MS UI column with 30 m x 0.25 mm i.d, 0.25 μm film thickness operated at 10 pound-force per square inch (psi) constant pressure mode was used for separation. A 2.5 m methyl deactivated pre-column (Agilent J&W GC Products) with same internal diameter was connected to the analytical column. The column temperature was initially set at 70 °C. This temperature was maintained for 3 min, and increased to 150 °C at a rate of 25 °C/min, then increased to 200 °C at a rate of 3 °C/min and then to 280 °C at a rate of 20 °C/min and maintained for 6 min, then increased to 325 °C at a rate of 50 °C/min and held for 1 min.

Quality assurance

Quality control was performed by analysis of procedural reagent blanks and spiked blanks. Reagent blank, consisting of 10 mL Milli-Q water and 10 mL of acetonitrile, run through the procedure. Results showed that no target analysts were detected in the blank samples. A five-level (0.0, 0.5, 1.0, 1.5, and 2.0) calibration curve was made by spiking a mixture of POP standards to a blank matrix of 5 g cod muscle for determining detector response for linearity and quantification. The coefficient of determination (r^2) for the calibration curve *was* $\geq$ 0.99. Spiking experiment on three replicates ($N = 3$) of 5 g of cod muscle spiked at 10 ng g^{-1} of a mixture of POP standards showed recovery ranged from 80 to 100% for all OCPs, except *o,p'*-DDT which has 64% recovery. The limit of detection (LOD) was 0.3 ng g^{-1} ww. Concentrations were expressed on a wet weight (ww) and lipid weight (lw) basis.

Statistical analysis

DDT residue concentration data were log-transformed to approximate to normal distribution. Geometric mean was used to summarize data. One-way analysis of variance (ANOVA) with Tukey honestly significant difference (HSD) post hoc test was used to determine mean variation in tissue concentration among species. Pearson correlation function was conducted to compute the association between DDT tissue concentrations with total length. Regression analysis between the log-transformed concentrations of *p,p'*-DDE and stable nitrogen isotope ratio (δ^{15}N) values was used to determine biomagnification of *p,p'*-DDE in the local food web. Statistical analyses were performed at the significant level of 0.05. SPSS statistical software (SPSS 20) was used in data analysis.

Table 2
Lipid content (%) and geometric mean (GM) of p,p'-DDE (ng g^{-1} ww [ng g^{-1} lw] with minimum and maximum values.

DDT	Species	%Lipid	GM±SD	Min.	Max.
p,p'-DDE	*C. gariepinus*	0.57	3.51 ± 3.61 [585.0]	0.84 [140]	11.67 [1,945.0]
	O. niloticus	0.53	2.83 ± 7.72 [566.0]	0.90 [180]	22.70 [4,540.0]
	C. Carassius	1.16	3.64 ± 1.37 [227.5][a]	1.46 [91.3]	5.58 [348.8]
	C. carpio	0.41	3.56 ± 1.76 [890.0][b]	1.76 [440]	8.07 [2,017.5]
	T. zillii	0.28	1.07 ± 0.90 [356.7][c]	0.69 [230]	3.64 [1,213.3]

GM values with different superscript alphabet letters (a,b,c) are statistically different

Results and discussions

Morphological measurements and lipid contents

The mean length and weight of fish were varied from 16.8 to 31.9 cm, and 126.5 to 362.4 g, respectively. Individual length measurments were varied from 15.0 to 37.5 cm. The minimum and maximum weights were 92 g and 581 g, respectively (Table 1). There was a positive and statistically significant association between weight and total length ($r = 0.80$; $p < 0.05$). The lipid content of fish ranges from 0.28 to 1.16% with the maximum percent lipid recorded for *C. Carassius* and minimum for *T. zillii.* There was a positive association between mean total length and percent lipid content, however, the association was not statistically significant ($r = 0.70$; $r > 0.05$).

Levels of OCPs

The levels of OCPs in muscle tissue of fish species is shown in Table 2. Among the target OCPs analyzed, only DDT was detected and it was detected in all tissue samples. All the rest OCPs were below detection limits. The predominance of DDT over the rest OCPs could be primarily due to the prevalent use of DDTs in malaria vector control programs [11] and illegal use of DDT for agricultural purposes [25] that could be washed by runoff water into the lake [5]. Findings from other studies have also suggested illegal use of DDT and application of DDT for malaria vector control as the main cause of contamination of water bodies [16]. The dominance of DDTs could also result from the relatively longer environmental half-life of DDTs than the rest of investigated OCPs leading to its environmental resistance, exposure, and bioaccumulation [17,29]. Similar findings were documented in earlier studies [21,37].

Among DDT metabolites, *p,p'*-DDE was detected in all samples and quantified in 82% of samples. It was the predominant metabolite constituting 99.2% of all the quantified DDTs in all species. 4,4'- dichloro-diphenyl-dichloro-ethane (*p,p'*-DDD) was detected only in one individual of *O. niloticus*. All the rest of DDT metabolites were below the detection limit. The present finding of the predominance of *p,p'*-DDE among DDT metabolites is consistent with a previous study [21]. The predominance of *p,p'*-DDE could be a result of its greater resistance to biological transformation and its biomagnification through the food web than the rest metabolites. The wide difference in half-life between *p,p'*-DDE (7 years) and *p,p'*-DDT (8 months) in fish tissue clearly indicates *p,p'*-DDE's stability and resistance to biological transformation [15]. Relative to *p,p'*-DDD, *p,p'*-DDE has a higher $\log K_{ow}$ value that is responsible for its greater capacity for biomagnification [10]. The predominance of *p,p'*-DDE could also result from fish exposure to *p,p'*-DDE, which is the main environmental degradation product of DDT [32] assuming the current contamination is a result of historic input. This, however, is substantiated by the value of the ratio of *p,p'*-DDE/*p,p'*-DDT. The ratio of *p,p'*-DDE/*p,p'*-DDT is used to indicate the time of DDT input [20]. While the value of the ratio of *p,p'*-DDE/*p,p'*-DDT higher than 0.6 indicates historic use, values less than 0.6 indicate fresh DDT input [36]. In the present study, the ratio of *p,p'*-DDE/*p,p'*-DDT was higher than 0.6 suggesting historic use of DDT [27], and the current exposure could be mainly due to *p,p'*-DDE which results from degraded past DDT input [34] has also noted the decline in the use of DDT in Ethiopia that may suggest the reason for the absence of fresh release of DDT.

The geometric mean of *p,p'*-DDE varied from 1.07 to 3.64 ng g^{-1} ww. The minimum and the maximum *p,p'*-DDE values recorded in individual fish were 0.84 and 22.70 ng g^{-1} ww, respectively. The highest geometric mean concentration of *p,p'*-DDE was recorded for *C. carassius* (3.64 ng g^{-1} ww), followed by *C. carpio* (3.56 ng g^{-1} ww) and *C. gariepinus* (3.51 ng g^{-1} ww) (Table 2). There was statistically significant variation among geometric mean *p,p'*-DDE concentrations ($F(4,45)=4.19$; $p < 0.05$). Species variation in *p,p'*-DDE accumulation may be a result of differences in the value of Nitrogen isotope ratio ($\delta^{15}N$) or trophic position [9], lipid content [15], feeding habits [33], age [11] and specific habitat [33].

The highest *p,p'*-DDE in *C. carassius* could be explained by its highest lipid content and top trophic position [3]. *p,p'*-DDE, as a result of its lipophilic character, accumulates in fat tissues and is biomagnified through the food web reaching higher concentrations in top trophic level consumers [3]. *C. carassius* is among the fish with the highest $\delta^{15}N$ values indicating its top trophic level position that could explain the accumulation of higher *p,p'*-DDE levels. The species' *(C. carassius)* feeding habit could also predispose the species to accumulation of high levels of *p,p'*-DDE due to preference of diets of animal origin such as insects and fish by adults [19,23]. It is a well-established fact that fish diets of animal origin generally accumulate relatively higher levels OCPs than aquatic plants due to their relatively high trophic position [14]. Declines in diets of phy-

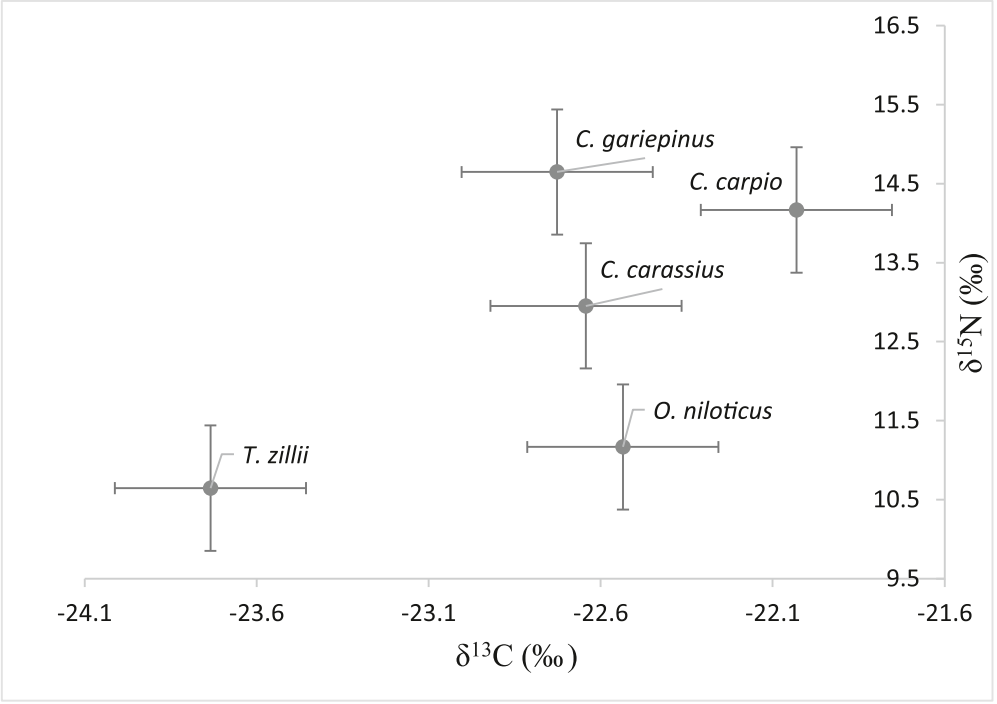


Fig. 2. Trophic position of five fish species from Lake Ziway.

toplankton and an increase in diets of insects with increasing length of *C. carassius* have also been documented [19]. The second highest *p,p'*-DDE level was recorded in *C. carpio* that could be attributed to its top position in the local food web and its specific habitat. *C. carpio* is a bottom-dwelling species and feeds at the bottom of the lake [33] where it could be exposed to DDT associated with sediments [27]. In aquatic habitats, DDT strongly associates with organic matter and sediments due to its lipophilic property [3,21].

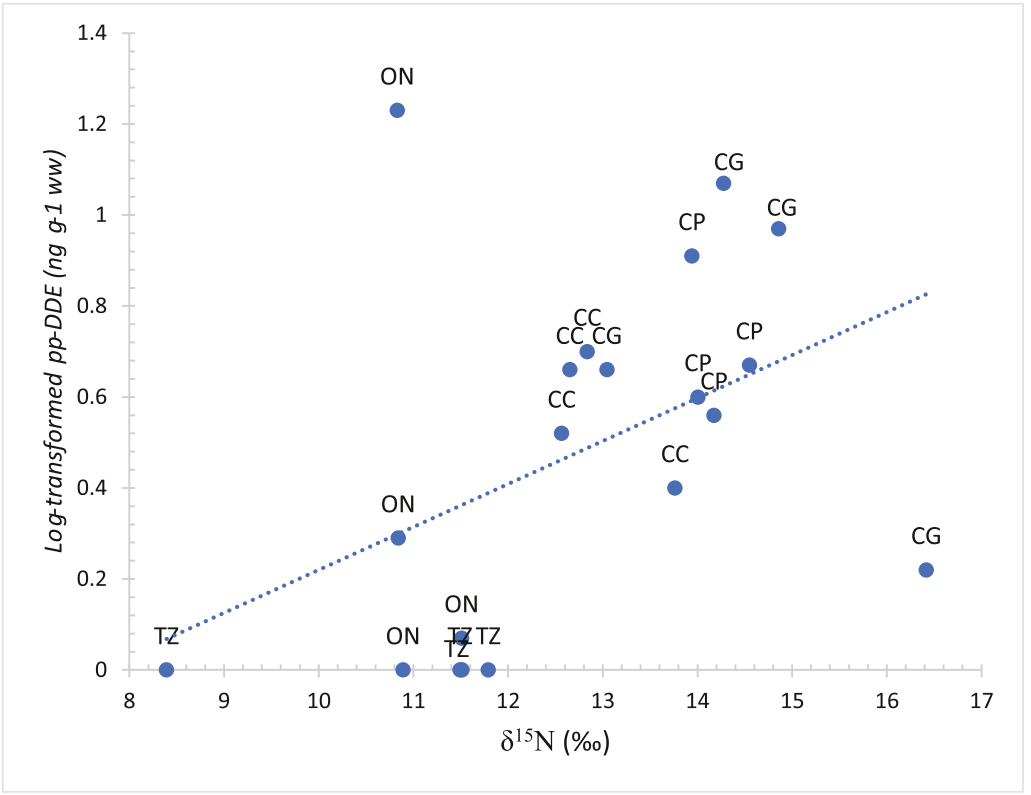
T. zillii species had the lowest δ^{15}N values and lowest percent lipid content that could explain the accumulation of significantly lower *p,p'*-DDE levels. Moreover, the low *p,p'*-DDE levels in *T. zillii* could be attributed to its herbivorous diet. *T. Zilli* mainly consumes on macrophytes, phytoplankton, and detritus [8] which are found at the base of the local food web [14]. The present finding is consistent with findings from a previous study [10].

The low trophic position [9] and preference of diet of plant origin by adults (total length > 15) of *O. niloticus* species [31] could explain the low level accumulation of *p,p'*-DDE. In the present study all individuals of *O. niloticus*' were greater than 15 cm total length (Fig. 4) indicating utilization of plant-based diets [31]. Earlier study indicates that *O. niloticus* from Lake Ziway predominantly feeds on algae and detritus; and occupies the lowest trophic position [10].

Generally, the levels of DDT found in the present study are lower than levels found in fish from several areas. The levels of ΣDDT (0.69–24.1 ng g^{-1} ww [230.0–4547.2 ng g^{-1} lw]) in the present study were higher than the levels found (0.44–1.74 ng g^{-1} ww) in fish from Chinese coastal fisheries, China [26]. They were also higher than levels found (0.15–2.2 ng g^{-1} ww) in fish from aquacultural ponds in France [33] and from Lake Victoria in Kenya (< 1 ng g^{-1} ww) [35]. However, the present levels were lower than values reported from Lake Malawi (0.59–58 ng g^{-1} ww) an East African Lake [22]. It is also lower than values reported in fish from Ethiopian lakes, namely, Lake Ziway (0.89 to 171.96 ng g^{-1} ww) [10], Lake Koka (0.05–72.53 ng g^{-1} ww) [9] and Lake Hawassa (1.65–409.6 ng g^{-1} ww) [11]. The present level is also lower than values (95.95–106,752.15 ng g^{-1} lw) in tigerfish *(Hydrocynus vittatus)* from certain rivers from South Africa [16] and in various fish (2.33–9.0 ng g^{-1} ww) from Lake Ziway [39].

Stable isotopes (δ^{13}C and δ^{15}N) and biomagnification of p,p'*-DDE*

The mean levels of the stable nitrogen isotope ratio (δ^{15}N) in this study varied from 10.6 to 14.6 ‰ (Fig. 2). Considering mean trophic enrichment factor of 3‰ [12], the difference of 4 between the highest and lowest mean δ^{15}N values may suggest the fish species may occupy two trophic positions (Fig. 2). *C. gariepinus, C. carpio* and *C. carassius* showed relatively higher mean δ^{15}N values in decreasing order than the rest of the fish species suggesting these species may occupy the same top trophic position. On the other hand, *T. zillii* and *O. niloticus*, both with relatively lower δ^{15}N values, may occupy lower trophic levels. This finding was consistent with findings from the previous study [10]. The feeding habits of the fish species are also in agreement with their trophic position. While *C. gariepinus, C. carpio* and *C. carassius* having omnivorous feeding



ON = *O. niloticus,* CG = *C. gariepinus*, CC = *C. Carassius*, CP = *C. carpio*, TZ = *T. zillii*

Fig. 3. Regression between log-transformed p,p'-DDE and δ^{15}N values ON = *O. niloticus,* CG = *C. gariepinus,* CC = *C. Carassius*, CP = *C. carpio*, TZ = *T. zillii.*

habits [6,7,19] occupy the top trophic level, *T. zillii* and *O. niloticus* having herbivorous feeding habits, they occupy the lower trophic position [8,9].

The carbon isotope ratio (δ^{13}C) values varied from -25.98 to -21.04‰. This may indicate the fish species mainly utilize carbon sources from the littoral zone except for *T. zillii* which utilize carbon sources mainly from the pelagic zone. The lowest and the highest mean δ^{13}C values that were recorded for *C. carpio* (-22.03‰) and *T. zillii* (-23.73‰) suggest that the two species utilize more of littoral and pelagic carbon source, respectively. The utilization of a wide range of carbon sources in fish in the present study was in agreement with findings from a previous study [10].

The regression between log-transformed *p,p'*-DDE and δ^{15}N values was performed to determine the biomagnification of *p,p'*-DDE in the local food web. The result shows a significant positive association ($F(1,18)=4.42$; $P < 0.05$) (Fig. 3) indicating biomagnification of *p,p'*-DDE. The value of the slope of the regression line (slope = 0.09, $R^2 = 0.2$) shows the rate of biomagnification of *p,p'*-DDE along the food web. The present rate of magnification is comparable with the rate of biomagnification from earlier studies (slope = 0.08, $R^2 = 0.099$) from Lake Ziway [10]. Biomagnification of DDTs has been also documented in fish from Lake Koka, an Ethiopian rift valley lake [9].

Association between p,p'*-DDE and total length*

The accumulation of OCPs in organisms depends on age or size [28]. In order to determine the influence of size on the accumulation of *p,p'*-DDE, we computed the association between log-transformed *p,p'*-DDE and total length. Regression results indicated a positive association in *C. carassius* ($r = 0.28$) and *C. carpio* ($r = 0.29$). In *C. gariepinus* there was no association (r = -0.00) and; and in *O. niloticus* (r = -0.32) and *T. zillii* (r = -0.45) the association was negative. All associations were not statistically significant (Fig. 4).

The absence of clear association in *C. gariepinus* and negative association in *O. niloticus* could probably result from the rightly skewed total length distribution (Shapiro-wilk test: $p < 0.5$; Skewness = 1.112 and 1.718, respectively). Skewed total length distribution in turn results from a higher proportion of similar-sized and smaller-length fish. Assuming size and age are positively related, similar-sized fish would have a similar exposure time periods and accumulate relatively equivalent levels of *p,p'*-DDE. This would cause a lack of clear relationship and unpredictable association than otherwise expected. On the other hand, the positive association in *C. carassius* and *C. carpio* could be a result of normal and near-normal distribu-

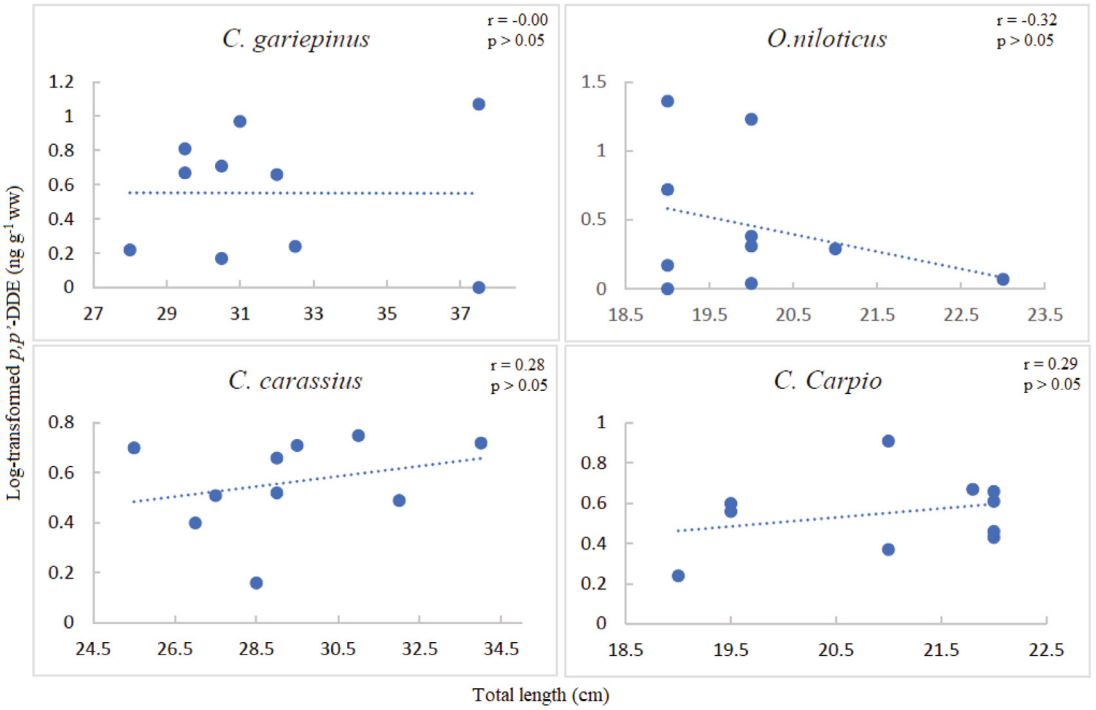


Fig. 4. The association between log-transformed p,p'-DDE (ng g^{-1} ww) and total length (cm).

tion of total length values in *C. carassius* (Shapiro-wilk test: $p > 0.05$; skewness = 0.491) and *C. carpio* (Shapiro-wilk test: $p < 0.05$; skewness = -0.744) that could enhance the variation in *p,p'*-DDE levels with differences in total length. The progressive shift in diets of animal origin with an increase in size in *C. carassius* [19] could also contribute to the found positive association. The diets of animal origin could contain higher levels of DDTs than diets of plant origin due to biomagnification [14].

The lack of significant association in *C. carpio* could be a result of less variability in total length (range = 19.0–22.0 cm) [10]. Less variability in total length, in turn, could result from a random sampling of individuals of fish with a narrow range of total length distribution. In addition to that, the lack of significant association could result from animal-based diets of smaller-sized fish and plant-based diets of larger individuals [7] that could level off *p,p'*-DDE concentrations between the smaller-sized and larger-sized individuals. In *C. carassius* a relatively wide range of total length distribution (range = 25.5–34.0 cm) was found. The species have also shown progressive shifts in diets of animal origin with an increase in size [19], which both facilitate an increase in *p,p'*-DDE level with increase in total length. Despite this, there was no significant association that could probably be the effect of a small sample size. Similarly, the negative association *in T. zillii* may result from a low percent of detection of *p,p'*-DDE (30%) and small sample size (Figure not shown due to low percent detection of *p,p'*-DDE).

Conclusion

Fish occupying higher trophic positions accumulated higher OCP levels than those fish occupying lower tropic positions. Generally, the levels of DDT in the present study are lower than levels reported from lake Ziway in earlier studies. The findings of the present study show that DDT is the most dominant contaminant in fish from Lake Ziway. *p,p'*-DDE is the predominant DDT metabolite that may result from the historic use. Feeding habits, lipid content, and size are suggested to influence the accumulation of *p,p'*-DDE. The findings of the present study may contribute data that could serve in an analysis of temporal changes in organochlorine pesticides in the study site.

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.

CRediT authorship contribution statement

Shiferaw Ayele: Writing – review & editing. **Yosef Mamo:** Supervision, Writing – review & editing. **Ermias Deribe:** Supervision, Writing – review & editing. **Ole Martin Eklo:** Supervision, Writing – review & editing.

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