Bulletin of Environmental Contamination and Toxicology (2022) 108:830–838
https://doi.org/10.1007/s00128-022-03497-4

Levels and Trophic Transfer of Selected Pesticides in the Lake Ziway Ecosystem

Mekuria Teshome Mergia[1] · Ermias Deribe Weldemariam[2] · Ole Martin Eklo[3] · Girma Tilahun Yimer[1]

Received: 10 April 2021 / Accepted: 24 February 2022 / Published online: 22 March 2022

Abstract

The levels of 30 selected pesticides and trophic biomagnification of DDT were investigated in biota samples of the Lake Ziway in the Rift valley region, Ethiopia. Carbon source and trophic position were calculated by using ^{13}C and ^{15}N stable isotopes, individually, and trophic magnification factors (TMFs) were inferred. Only DDT and its metabolites were quantified in all samples analyzed. The most prominent metabolite was p,p′-DDE with mean concentration ranging from the 0.82–33.69 ng g^{-1} lipid weight. Moreover, the ratio of DDT/DDD + DDE in all the biota samples was less than 1 signifying historical DDT application. Regression of log [ΣDDT] vs TL (trophic level) among all biota species showed a significant correlation, indicating that DDTs are biomagnifying along with the food web of Lake Ziway with an estimated TMF of 2.75. The concentrations of DDTs and other organochlorine pesticides found in biota from Lake Ziway were, in general, lower than studies found in previous studies carried out in the same lake.

Keywords Biomagnification · DDTs · Lake Ziway · Pesticides · Stable isotopes · Trophic level

The use of pesticides within the agricultural sector in Ethiopia has contributed to a significant advancement in agricultural technology and development. Pesticide use in Ethiopia has supported agribusiness improvement, economic growth, and poverty reduction (Mengstie et al. 2017). Comprehensively, the use of agrochemicals in crop production is shared with many farmers using pesticides for pest control to increase harvest and advance quality. The World Health Organization (WHO) reports that only 2% of pesticides utilized in the world are focused on developing countries (PAN 2012). For the last ten years, a quick increase in the amount and use of pesticides in the agriculture sector has been observed. In Ethiopia, for several years, organochlorine pesticides (OCPs), organophosphorus pesticides (OPPs), Pyrethroid, and Carboxamide have been utilized for controlling pests on agricultural fields as well as for controlling malaria at the household level (Negatu et al. 2016). Recent agricultural growth in Ethiopia has led to higher demand for pesticides. However, there is no accurate record of the particular volume of pesticides utilized in agriculture in Ethiopia (Mengistie et al. 2017).

The broad use of pesticides for agricultural and non-agricultural activities has resulted in the prevalence of their residues in numerous environmental compartments including water, air, and soil (Schäfer et al. 2011). Some organic pesticides are resistant to biological or chemical degradation. These persistent pesticides are moreover mobile in the environment and can bioaccumulate in plants and animal tissues, and thus, directly or indirectly affect the health of societies (Picó et al. 2007). Lake Ziway is presently unprotected from numerous anthropogenic pressures because of the intensification of agricultural activities around the lake (Desta et al. 2017; Teklu et al. 2018). Thus, the use of excessive pesticides around the lake is growing (Meshesha et al. 2012). Malefia (2012) and Jansen and Harmsen (2011) showed that the lake water and the surrounding surface waters are polluted by the discharge of pesticide residue from the agricultural fields into the lake waters. Moreover, the occurrence of residues of organochlorine pesticides was reported in the fish samples (Deribe et al. 2013; Yohannes et al. 2014) of Lake Ziway, Ethiopia. These findings have given an alarm

✉ Mekuria Teshome Mergia
mekuriamergia@gmail.com

[1] Department of Biology, Hawassa University, P.O.Box 05, Hawassa, Ethiopia

[2] Kotebe Metropolitan University (KMU), Addis Ababa, Ethiopia

[3] Norwegian University of Life Science (NMBU), Ås, Norway

for the possibility of the occurrence of other frequently used pesticides such as organophosphorus pesticides (OPPs).

Biomagnification of persistent contaminants can impact the health of the food web within the ecosystem because the feeding habit is a major exposure route for many organic pollutants (Post 2002). Several studies including a study by Mazzoni et al. (2020) investigated the trophic magnification factor (TMFs) of DDT and its metabolites in freshwater environments. Stable isotope nitrogen ratio is a common biomarker technique to investigate the biomagnification of organic pollutants, trophic level, and feeding preferences in aquatic food webs (Fisk et al. 2001). Likewise, stable isotope examination has appeared as a tool in identifying the origin of food in the ecosystem and is used commonly to investigate aquatic ecology (Mazzoni et al. 2020). Studies investigated levels of organochlorine pesticides in Lake Ziway have focused on fish species (Deribe et al. 2013; Yohannes et al. 2014). However, the biomagnification of organochlorine pesticide and the influence of trophic position on contaminant profiles within an aquatic food web has not been addressed in this region. The objectives of this study were to investigate the levels of selected pesticide residues in the biota and examine the biomagnification and trophic transfer of DDTs in Lake Ziway.

Materials and Methods

Lake Ziway is a shallow freshwater lake located in Rift Valley, in the southeast part of Ethiopia, at 1636 m a. s. l.(meters above sea level) (71° 52′ N, 38° 14.5′ E, Fig. 1) which belongs to the Ziway–Shala basin and has a catchment area of about 7000 km^2 and an average surface area of 490 km^2. The lake has an average volume of 1.8 km^3 and a maximum depth of 9 m (average depth, 2.5 m) (Vallet-Coulomb et al. 2001). There are two inflowing rivers, the Meki River to the north-west, and the Ketar River to the east. The lake flows into Lake Abiyata, via the Bulbula River. The lakeshore is secured with enormous scopes of sand and grass, infrequently trees, and permanent wetland habitats such as shallow pools overwhelmed by grasses, lilies, and more profound reed beds dominated by *Typha* grass. The fish species of the lake include indigenous species like Nile tilapia (*Oreochromis niloticus*) and African big barb (*Barbus intermedius*) and introduced species such as African sharp tooth catfish (*Clarias gariepinus*), common carp (*Cyprinus carpio*), Golden carp (*Carassius auratus*) and redbelly (*Tilapia zillii)* (Negassa and Getahun 2003).

Biological samples were collected from Lake Ziway in December 2018. Aquatic organisms including zooplankton were collected by pumping large volumes of water through plankton nets with 50 µm mesh sizes. Aquatic macrophytes (*Typha latifolia* and *Aurudo donax)* were collected by hand, thoroughly rinsed to remove organic matter and invertebrates, and placed into plastic bags and held on ice. Aquatic insects (Diptera larvae) were sampled with 500-µm D frame nets by flipping rocks and from aquatic macrophytes and submerged substrates using a sweep net or searching by hand. Fish sampling was carried out by purchasing fish from the local fishermen upon landing. A total of 50 (30 females and 20 males) samples from four fish species (*C. auratus, C. gariepinus, O. niloticus*, and *C. carpio*) were sampled.

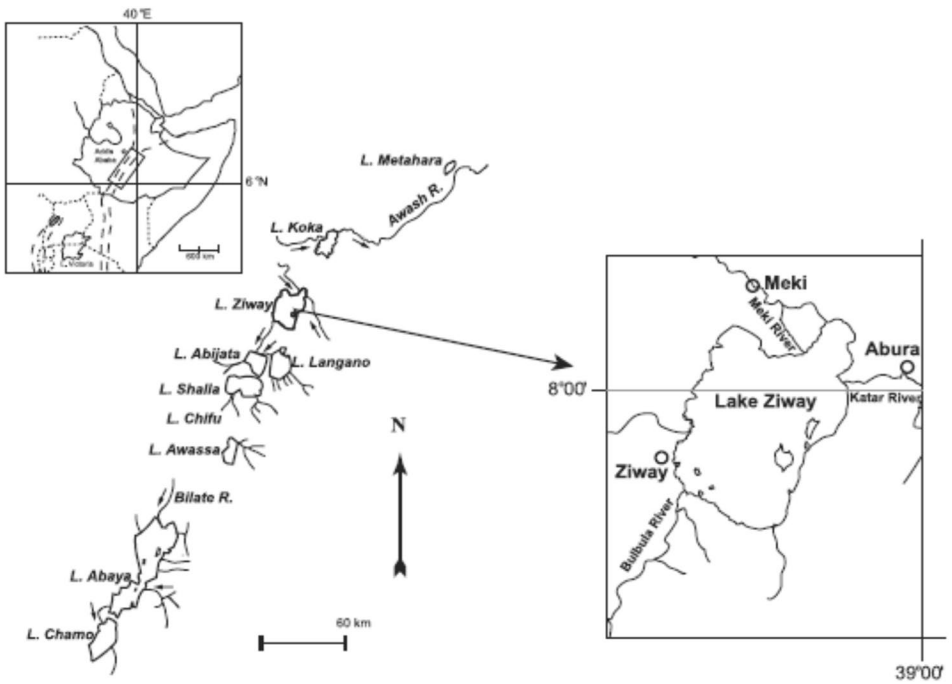

Fig. 1 Map of Lake Ziway (adapted from Deribe et al. 2013)

Muscle samples were taken from each fish species, according to the procedures in the EMERGE protocol, as depicted by Rosseland et al. (2001), and frozen. The frozen biological samples were transported to Norway and were analyzed for stable isotopes of nitrogen and carbon to determine trophic pathways, and the level of pesticides (selected OCPs, OPPs, carbamate, and pyrethroid derivatives).

A total of 30 selected pesticides, Organochlorine pesticides (aldrin, chlordane-cis, chlordane-trans, o,p'DDD, p,p'DDD, o,p'DDE, p,p'DDE, o,p'DDT, p,p'DDD, dieldrin, α-endosulfan, β-endosulfan, endosulfan-sulfate, HCB, α-HCH, β-HCH, γ-HCH, heptachlor, heptachlor epoxide cis, heptachlor epoxide trans, metalaxyl, methoxychlor, oxychlordane), Organophosphorus pesticides (chlorpyrifos, diazinon) and other pesticides (bupirimate, fenarimol, tetradifon), and Pyrethroid (deltamethrin), Carboxamide (boscalid) were analyzed in biota samples (macrophyte, zooplankton, Diptera larvae, and fish species) from Lake Ziway were analyzed at the laboratory of the Norwegian Institute of Bio-economy Research (NIBIO): Pesticides and natural products chemistry, Norway. Frozen biota tissue samples were slowly thawed in a refrigerator; were homogenized using a kitchen blender (Braun GmbH, Kronberg, Germany) into small pieces and mixed using Polytron (Kinematica AG) for 30 s with a speed of 2000–3000 rpm. Individual standards of pesticides were obtained from the laboratory of the Norwegian Institute of Bio-economy Research (NIBIO). Pesticides then were extracted from biota samples with acetonitrile following a modified quick, easy, cheap, effective, rugged, and safe (QuEChERS) procedure (Norli et al. 2011).

Pesticide analyses were determined by using gas chromatography coupled with mass spectrometry with a QP 2010 GC–MS system attached to a mass spectrometer detector (MSD5973). The GC system was equipped with a 2xHP -5MS capillary column, with an internal diameter of 0.25 mm and film thickness of 0.25 µm film thickness and 30 m length. The carrier gas was purified helium. The splitless mode was used to inject 1 µL of sample onto the GC column with injector and detector temperatures set at 250 and 280°C, respectively. The oven temperature was programmed from 120°C, increased to 290°C with a ramping rate of 14°C/min, and held for 2 min. The MS source was operated at 250°C and quad at 200°C. The results from the analysis of the standard were all within the certified range. Estimation of the limit of quantification (LOQ) and limit of detection (LOD) was made by spiking codfish or lettuce (for macrophytes) with pesticides, shown to have no traces of the compounds included in the analysis. A rough estimate of LOQ was performed on acetonitrile extracts of lettuce and cod spiked. Method blanks and spiked control were included with each batch of 15 samples to check background contamination and monitor any instrument carryover. Three quality control standard solutions (20 ng mL^{-1} pesticide standards mixture) were run to monitor sensitivity drift along with each 8–12 real samples. Recovery tests were carried out in triplicate to evaluate the precision of the method. In biota samples, recoveries varied from 90‰ to 120‰, and precision as percent relative standard deviation (‰RSD) was below 20‰ for all pesticides. Pesticide concentrations were normalized to the lipid content (lw) to infer trophic magnification factor.

Stable isotope analyses were carried out at the Environmental Chemistry Section, Department of Plant and Environmental Sciences, Norwegian University of Life Sciences (NMBU). The stable isotopes of nitrogen (^{15}N and ^{14}N) and carbon (^{13}C and ^{12}C) were examined in homogenized and freeze-dried samples subjected to combustion in a Flash Elemental Analyzer (EA) as described in Deribe et al. (2013). $^{15}N/^{14}N$, and $^{13}C/^{12}C$ were conveyed according to the following formula:

$$\delta R‰ = \left[\left(\frac{R\ \text{sample}}{R\ \text{standard}}\right) - 1\right] * 1000 \quad (1)$$

where, $R = {}^{15}N/{}^{14}N$ for $\delta^{15}N$ or $R = {}^{13}C/{}^{12}C$ for $\delta^{13}C$. Atmospheric nitrogen (N_2) was used as an R standard for nitrogen.

Based on the process of ^{15}N enrichment in consumers over their prey (Post 2002), the trophic position of the sampled organism was determined according to their relative abundance of $\delta^{15}N$ using the dipteran larvae as the baseline for TL $\delta^{15}N$ estimation (mean value of *dipteran larvae;* $\delta^{15}N_{baseline} = 8.7‰$) (Assumed to occupy a trophic level = 2) as the mean enrichment of $\delta^{15}N$ per trophic level is 3.4 (Post 2002), trophic level (TLs) for each species were estimated from raw $\delta^{15}N$ value using the following equation:

$$TL = \frac{\left(\delta^{15}\text{Nconsumer} - \delta^{15}\text{baseline}\right)}{3.4} + 2 \quad (2)$$

where TL is the trophic level, δ^{15}Nconsumer is the $\delta^{15}N$ signature in the specified organism, $\delta^{15}N_{Baseline}$ is the mean $\delta^{15}N$ value for the dipteral larvae as this genus is known to graze on primary producers (mainly macrophytes) and 3.4 is the trophic enrichment factor for $\delta^{15}N$ in an aquatic food web recommended to be used for constructing food webs when a priori knowledge of $\Delta^{15}N$ is unavailable (Hobson et al. 2002).

TMFs for DDTs were determined according to Fisk et al. (2001). Trophic magnification factors (TMFs) were calculated to determine ∑DDT and p,p′DDE magnification in the food web. TMF calculation was performed for the lake food web (which included macrophytes, invertebrates, and fish) to determine the total DDTs that trophically magnified from, macrophyte to fish. TMFs were derived from the plots of the natural log of ΣDDT or p,p′DDE concentrations (lipid-normalized concentration) to TL:

$$\text{Log10}[\Sigma\text{DDT}] = a + (b \times \text{TL}) \quad (3)$$

where a is the y-intercept (constant dependent on the background concentration) and b is the slope of regression $\log_{10}[\Sigma\text{DDT}_{\text{Lipid}}]$ function to TL calculated based on δ^{15}N (indicating the biomagnification power of the contaminant). The above equation was used to calculate TMF (Fisk et al. 2001): The trophic magnification factor (TMF), also called food web magnification factor (FWMF), is calculated from the slope using the following formula:

$$\text{TMF} = 10^{b} \quad (4)$$

A contaminant with TMF greater than 1 is considered to biomagnify in the food chain while TMF values comprised between 0 and 1 indicate that the contaminant is not biomagnified in the food web. A TMF value inferior to zero indicates that the contaminant is excreted by the organisms in the food chain (Fisk et al. 2001).

Results and Discussion

Among 30 pesticides analyzed in biological samples, only DDT and its metabolites (o,p′-DDD, o,p′DDE, p,p′DDD, and p,p′DDE) were quantified, all other pesticides analyzed were below the detectable limit in all biological samples (Table 1). The absence of organochlorine pesticides in the biota sample, such as dieldrin, endosulfan, HCB, HCH, chlordane was probably because, no current use of these pesticides by the farmers around the Lake Ziway, in their farming activities. Our recent survey also revealed that small-scale vegetable farmers around the littoral zone of Lake Ziway in Ethiopia, do not use the most hazardous pesticides of WHO class 1a and 1b and banned pesticides such as notorious DDT, dieldrin, HCB, HCH, chlordane, and Endosulfan (Mergia et al. 2021).

Compared to previous studies conducted in the Lake Ziway ecosystem, a decreasing trend of the concentration of banned organochlorine was observed over the last 10 years (Table 2). This could be related to the effectiveness of the National Implementation Plan (NIP) for the Stockholm Convention in Ethiopia. According to the Ministry of Agriculture (MoA) banned or restricted pesticides in Ethiopia will not be used for agricultural activities (MoA 2014). NIP also focuses to promote less toxic alternatives to synthetic pesticides and Integrated Pest Management (IPM), such as practicing the use of non-chemical means of pest control (FEPA 2006). However, in our recent survey conducted along the litoral of lake Ziway, none of the small-scale farmers used IMP (Mergia et al. 2021). Besides, in contrast to this study, Negatu et al. (2016) and Mengstie et al. (2017) reported illegal use of DDT by small-scale farmers around the reft valley Region in Ethiopia. Therefore the DDT residues in the present study in Lake Ziway biota could be from historical use and long environmental persistence. Moreover, the present study showed that the organochlorine levels in both fish and other biota were considerably lower than those recorded in other environmental and biological samples (Mzoughi et al. 2016; Unyimadu et al. 2018).

Table 1 Mean (SD) and range of DDTs concentration (ng g^{-1} lipid weight) in zooplankton, Dipteral larvae, and fish (Oreochromis niloticus, Carassias autratus), Cyprinus carpio & Clarais gariepinus muscle tissue)

Organochlorine	Zooplankton (n = 5)	Dipteral larvae (n = 5)	Fish species			
			O.niloticus (n = 14)	*C.carpio* (n = 10)	*C.auratus* (n = 13)	*C.gariepinus* (n = 13)
o,p′ DDD	nd	nd	nd	nd	nd	0.18 (0.66) nd–2.38
p,p′ DDD	0.47 (0.27) nd–0.80	nd	nd	nd	nd	5.43 (10.58) nd–28.57
o,p′ DDE	nd	nd	nd	nd	nd	0.084 (0.30) nd–1.09
p,p′ DDE	0.82 (0.89) 0.19–4.40	3.22 (2.06) 1.19–6.09	7.02 (14.69) nd–17.14	6.04 (4.65) nd–17.14	11.60 (5.99) 2.44–24.01	33.69 (48.27) 1.75–142.86
o,p′ DDT	0.32 (0.71) nd–1.60	nd	2.77 (5.80) nd–18.18	nd	nd	2.25 (4.61) nd–14.29
p,p′ DDT	0.18 (0.24) nd–0.48	nd	4.26 (8.05) nd–22.22	nd	5.81 (1.02) nd–28.01	8.04 (13.41) nd–38.10
Σ DDT	1.76 (1.19) nd–5.20	3.22 (2.06) nd–6.09	14.06 (18.21) nd–54.55	6.04 (4.65) nd–17.14	17.60 (13.59) nd–52.01	49.67 (68.96) nd–195.24

Sampled from Lake Ziway

nd means below detectable limit

Table 2 A comparison of DDTs and other organochlorine pesticides concentrations [Mean(SD) and ranges] by different authors of Lake Ziway fish species

Sampling period	Species	Concentrations (ng g^{-1} wet weight)							References
		p,p′DDT	p,p′DDE	p,p′DDD	ΣDDT	ΣHPTsn	ΣHCHsn	CHls	
2008	*C. gariepinus*	6.22 (2.82) 3.28–17.37	17.81 (22.61) 3.8–122.77	3.98 (5.73) 0.37–30.6	28.78 (30.92) 7.8–171.96	*	*	*	Deribe et al. (2013)
	C. aurtus	12.49 (13.96) 4.94–56.49	7.10 (4.57) 1.53–20.3	2.84 (3.38) 0.35–14.12	18.33 (15.49) 3.65–76.17	*	*	*	
	O. niloticus	5.3 (1.51) 2.86–8.95	5.67 (4.53) 1.00–19.31	4.87 (11.24) 0.77–56.87	18.93 (26.33) 4.78–139.01	*	*	*	
	T. zilli	nd	4.7 (8.57) 0.89–40.73	1.42 (2.84) 0.33–12.73	6.04 (11.28) 0.89–53.47	*	*	*	
2011	*C. gariepinus*	0.62 (0.40)	6.92 (0.10)	0.79 (0.68)	9.00 (11.70) 2.36–61.90	0.65 (0.28) 0.34–1.56	0.72 (0.48) 0.27–2.01	0.90 (0.25) 0.58–1.50	Yohannes et al. (2014)
	C. aurtus	0.57 (0.73)	2.48 (0.36)	0.58 (0.35)	4.55 (2.80) 0.77–10.6	0.59 (0.27) 0.20–1.52	0.61 (0.61) 0.16–1.85	0.87 (0.22) 0.19–4.00	
	O. niloticus	0.31 (0.18)	1.32 (0.08)	0.40 (0.21)	2.33 (1.09) 0.90–5.12	0.90 (0.35) 0.44–2.27	1.26 (1.04) 0.29–5.10	0.40 (0.10) 0.17–0.61	
	T.zilli	0.77 (0.66)	1.89 (0.12)	0.85 (0.41)	4.38 (2.67) 1.35–13.2	0.42 (0.11) 0.19–0.69	1.45 (0.61) 0.91–3.94	0.91 (0.22) 0.65–1.32	
2018/19	*C. gariepinus*	2.32 (5.51) nd–12.01	7.71 (6.12) 1.01–30.02	1.31 (1.51) nd–6.03	12 (7.80) 1.00–52	nd	nd	nd	Our study
	C. aurtus	1.92 (1.02) nd–7.02	4.02 (0.61) 1.01–9.02	nd	5.92 (6.32) 1.00–16	nd	nd	nd	
	C. carpio	nd	2.33 (0.53) nd–6.03	nd	2.31 (2.61) nd–6.00	nd	nd	nd	
	O. niloticus	0.93 (0.71) nd–5.01	1.01 (0.02) nd–6.03	nd	2.43 (7.25) nd–15.50	nd	nd	nd	

nd below detectable limit, * not analyzed

None of the analyzed organophosphorus pesticides (chlorpyrifos, diazinon), carboxamide (boscalid), pyrethroids (deltamethrin), and other pesticides (bupirimate, fenarimol, tetradifon) were detected in any of the samples analyzed despite all of them being registered in Ethiopia and some are used heavily by small scale vegetable farmers along the littoral zone of Lake Ziway, especially chlorpyrifos, dimethoate, and diazinon used in vegetable farms (applied on onion, cabbage, and tomato), and chlorpyrifos-methyl in wheat (Negatu et al. 2016; Mengstie et al. 2017). These pesticides are known as non-persistent compounds of relatively high water solubility (Aislabie et al. 1997), and therefore, the absence of their residues in biota was as expected. This may be because they rapidly degrade, depending on their formulation, the rate and method of application, and climatic factors. Further, high solubility and relatively short life in the environment are factors in the degradation (Aislabie et al. 1997).

In the present study, the mean concentrations of ∑DDT ranged from 0.31 to 12.01 ng g^{-1} wet weight (ww) (Table 2). This is generally lower than a previous study of fish sampled in 2008 in the same lake with mean concentrations ranging from 6.04 to 28.78 ng g^{-1} lw (Deribe et al. 2013). A similar previous study from fish sampled by Yohannes et al. (2014) revealed that the concentration of ΣDDT ranged from 2.33 to 9.00 ng g^{-1} ww and was lower than Deribe et al. (2013) investigation. This shows the decreasing trend of DDTs in the Lake Ziway biota (Table 2). The possible explanation for the decrease could be no current use of DDTs and other banned pesticides by local farmers for agriculture and no use of DDTs for the control of the mosquito malaria vector (Mergia et al. 2021).

The p,p'DDT, p,p'DDE, and p,p'DDD were the most commonly detected metabolites (Table 1). In the current study, the p,p′DDE was the most commonly detected metabolite, with a mean concentration ranging from 0.82 to 33.69 ng g^{-1} lipid weight (lw). This is in agreement with other studies conducted in Lake Ziway (Deribe et al. 2013; Yohannes et al. 2014). Likewise, many studies have found p,p′DDE the most abundant and persistent of the metabolites analyzed in

freshwater fish (Wepener et al. 2012; Mzoughi et al. 2016). Mzoughi et al. (2016) have shown that p,p'DDE is resistant against degradation so that it persists in the environment and living organisms. Degradation of p,p′DDT by the process of mixed-function oxidases to the metabolite p,p′DDE could be a good explanation for high levels and accumulation of p,p′DDE in biota (Schmitt et al. 1990). Also, the biological transformation of DDT to DDE may contribute to the higher levels of p,p′DDE in biota samples (Wepener et al. 2012). In the present study zooplankton and fish (*Clarias gariepinus*) samples where DDD and DDE were simultaneously detected, the DDD/DDE ratio in the biota sampled was much less than 1 in all cases. These results are indications that the degradation pathways in the Lake Ziway biota were aerobic (Aislabie 1997).

The increasing concentrations of DDTs were observed in the Lake Ziway food web from macrophytes to dipteran larvae and then to the various fish species analyzed in this study. This result was similar to those reported in other studies from the same lake and Lake Hawassa Ethiopia (Deribe et al. 2013; Yohannes et al. 2014). The $\delta^{15}N$ values of the biota in the present study varied from 2‰ to 16‰ (Table 3). A clear pattern of $\delta^{15}N$ enrichment with trophic level was observed from dipteran larva to planktivorous Tilapia (*O.niloticus*) to carnivorous (Fig. 2). The mean values of the $\delta^{15}N$ were in the order of 14.7‰ > (13.8‰), > (13.4‰) > (10.4‰) > (8.7‰) (2‰) > (2‰) for *C. gariepinus*, *C.carpio C.aurtus O. niloticus,* dipteran larva, *T.latifolia,* and *A. donax* respectively. In this study, Significant positive increases of concentrations in ∑DDTs and p,p DDE with an increase of $\delta^{15}N$ values through the Lake Ziway food web were detected ($F = 8.32$. $df = 1$, $p = 0.005$, $N = 62$ and $F = 8.44$, $df = 1$, $p = 0.005$, $N = 62$) respectively. This result is in agreement with the study conducted in the Mekong Delta, South Vietnam (Ikemoto et al. 2008). Similarly, Kidd et al. (1995) and Hoekstra

Table 3 Mean (SD), minimum and maximum values of stable isotope ratios of nitrogen ($\delta^{15}N$, ‰), and carbon ($\delta^{13}C$, ‰), samples size (N) of the examined biota from Lake Ziway, Ethiopia, sampled in 2018

Species	N	$\delta^{15}N$ (‰)	$\Delta^{13}C$ (‰)	Trophic (TL)*
C. gariepinus	13	[c]14.72 (0.95) 13.01, 16.01	[b]– 21.7 (0.44) – 22.01, – 21.30	3.6
C. carpio	10	[c]13.80 (0.79) 13.00,15.02	[b]– 22.90 (0.88) – 25.01, – 23.20	3.3
C. auratus	13	[c]13.38 (0.77) 12.01, 15.03	[b]– 22.31 (0.63) – 23.02, – 21.00	3.2
O. niloticus	14	[b]10.43 (1.9) 8.10, 13.01	[b]– 22.6 (1.87) – 17.01, – 19.00	2.4
Diptera larvae	5	[b]8.74 (0.0.66) 8.67, 8.81	[a]– 26.51 (0.71) – 27.10,– 26.00	2.0
T. latifolia	5	[a]2 (1.8) 0, 4.10	[a]– 26.60 (0.89) – 28.00, – 26.01	0.2
A. donax	5	[a]2 (1.4) 0, 4.10	[a]– 26.8 (0.84) – 28-, – 26	0.2

a, b c means with different letter superscripts are significantly different within the column (Tukey test is applied; $p < 0.05$)

*Trophic level calculated according to Eq. 2

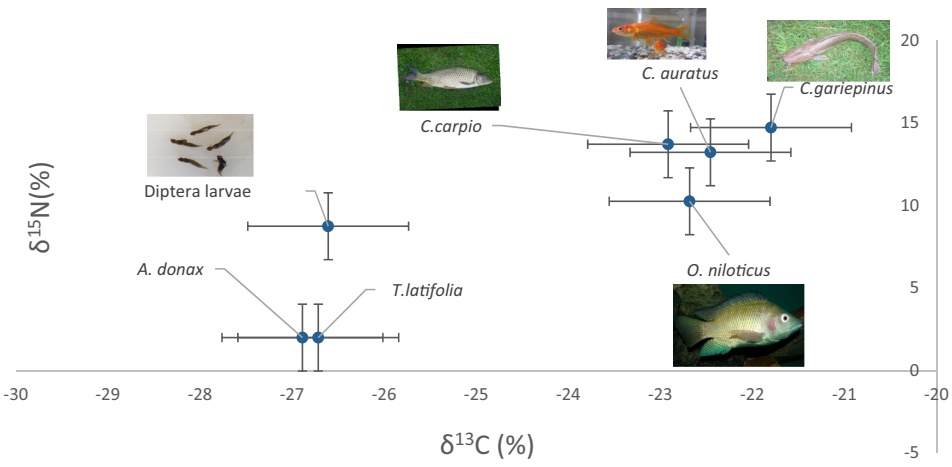

Fig. 2 Relative trophic position of biota (C. gariepinus, C.autratus, O. niloticus, C. carpio, dipteran larva, and Zooplanktons), sampled in December 2018 from Lake Ziway, values are based on the mean of the stable isotope ratios of nitrogen ($\delta^{15}N$, %) and carbon ($\delta^{13}C$, %)

et al. (2003) reported a significant correlation between ΣDDT concentrations (on wet weight base) and $\delta^{15}N$ in the aquatic food web. These authors argued that this correlation supported their results that $\delta^{15}N$ could be used as a measure of trophic position.

The results of the linear regression between $\log_{10}$ [ΣDDT] and trophic position-based $\delta^{15}N$ ($\log_{10}$ [ΣDDT] = 0.44($TL_{\delta 15N}$) − 0.41) show that there is an indication of biomagnification of DDTs in the food web. The biomagnification power (0.44) of ΣDDT observed in Lake Ziway food web was higher in magnitude than measured in freshwater fishes (i.e., 0.2–0.3) from various lakes by Kidd et al. (1995) and Hobson et al. (2002), who also investigated trophic position using $\delta^{15}N$ values in fish muscle tissue. Conversely, Lake Ziway exhibited lower biomagnification of DDTs compared to studies conducted in other areas, such as Lake Malawi, East Africa (Kidd et al. 2001), subarctic lakes in Yukon Territory (Kidd et al. 1998), marine food web from south-eastern Norway (Russ et al. 1999), the Southern Beaufort- Chukchi Seas, in the Arctic (Hoekstra et al. 2003), as well as Mekong Delta, South Vietnam (Ikemoto et al. 2008).

Average trophic levels (TLs) calculated based on $\delta^{15}N$ for each organism were 0.2, 0.26, 2.0, 2.4, 3.2, 3.3, and 3.6 for *T. latifolia*, *A.donax,* Dipteran larva, *O. niloticus C.autratus C. carpio,* and *C. gariepinus* respectively (Table 3). Figure 3 illustrates the biomagnification of ΣDDTs with the trophic level in biota from Lake Ziway. The trophic magnification factor (TMF) calculated for ∑DDT and p,p′-DDE were 2.75 and 2.47 respectively. A significant relationship was found between log-transformed concentrations of ΣDDT (log10 [ΣDDT]) *versus* TL calculated based on $\delta^{15}N$ signatures of organisms in Lake Ziway ($r^2 = 0.93$, F = 37.8 df = 1, $p < 0.001$, N = 62)(Fig. 3). Similarly, a significant positive correlation was observed between p,p′-DDE and TL ($r^2 = 0.92$, F = 28.2 df = 1, $p < 0.001$, N = 62). In the present study, the TMF value for ∑DDT and p,p′-DDE exceeded 1, indicating that the level of DDT bioamplify along with the food webs (Fisk et al. 2001). The TMFs in the present study are higher than studies reported by Kidd et al. (2001) in the Malawi lake food web with TMF of 1.16 and 1.25 for ∑DDT and DDE respectively.

Similarly, in a study conducted in the Congo Basin River, the TMF of DDTs was 1.7 (Verhaert et al. 2013). However, the TMF values of ΣDDT in this study were similar to those reported by Sun et al. (2017) in South China mangroves with TMF of 2.61 for DDTs. Likewise, a study in Arctic food webs by Jarman et al. (1996) reported a TMF of 2.20 for DDTs. The value of biomagnification factors could be influenced by the length of the food chain in the aquatic environment. The possible explanation for the variability of trophic magnification factors reported in the different ecosystems could be related to the scale of trophic levels than in other ecosystems. Although there are many possible reasons for the variability of biomagnification rate, the main reason is probably due to the complex food web, the species diversity and species abundance in tropical lakes result in different food resources with variable DDT burdens. Besides the specific growth rate of individual species within the food web, a high growth rate causes of dilution of POPs residues that can manifest itself as a lower TMF. Moreover, the greater DDTs level in fish compared to zooplankton and the dipteran larva is also an indication of the feeding ecology and following dietary exposure as well as pollutants bioaccumulation and possible biotransformation (Fisk et al. 2001).

Our findings demonstrated that except for DDT and its metabolite the other pesticides analyzed are below the detectable limit in the Lake Ziway ecosystem. The high concentrations of p,p'DDE, and low p,p'DDT levels in biota suggest the use of DDTs from historical application in the region. Unlike previous studies banned pesticides such as dieldrin, endosulfan, HCB, HCH, chlordane were below the detectable limit in all biota samples from Lake Ziway. Likewise, the concentrations of organochlorine pesticides found in biota from Lake Ziway were, in general, lower than studies found in previous studies carried out in the same lake. Even though pesticides such as OPPs, Pyrethroid, deltamethrin, boscalid, and other pesticides such as bupirimate, fenarimol, and tetradifon being registered in Ethiopia and

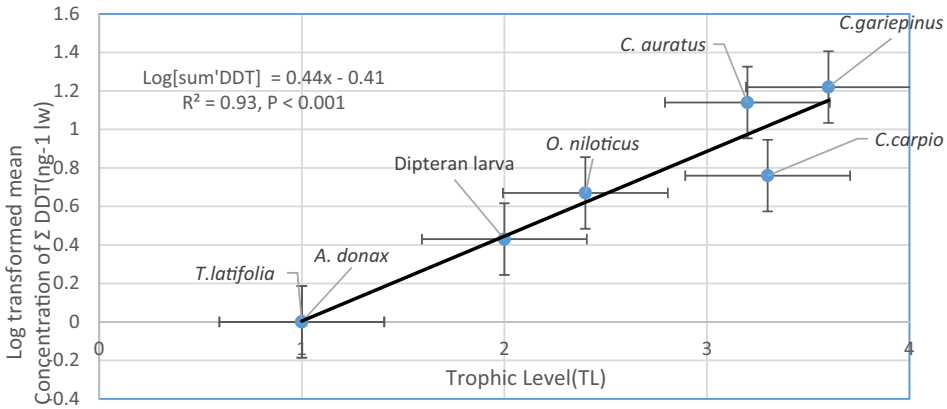

Fig. 3 The relationship between log10-transformed, concentration for DDTs (ng g^{-1} lw), and isotopically determined trophic level (TL) from Eq. (2). Mean values for each species macrophyte, dipteran larva, and four fish species

used heavily by small scale vegetable farmers along the littoral zone of Lake Ziway, none of them have been detected in any of the samples analyzed. The TMF data derived in Lake Ziway showed that biomagnification occurs for DDTs, with TMFs equal to 2.75 and the study demonstrates biomagnification of persistent contaminants (e.g. DDTs) in tropical lakes.

Acknowledgements This research was funded by the Institutional Collaboration program between Hawassa University and the Norwegian University of Life science (NMBU-HU ICOP –IV). We thank Marianne Stenrød, the head of the Pesticide and natural product chemistry section, Roman Florinski, and Agnethe Christiansen for their help during lab work at Bioforsk in Norway. The authors are extremely grateful to Hans Christian Teien and Marit Nanrup for their help in the analysis of isotopes at the Environmental Chemistry Section, Norwegian University of Life Sciences. We thank the Ziway Fishery research center staff for their help during sample collection.

References

Aislabie JM, Richards NK, Boul HL (1997) Microbial degradation of DDT and its residues—a review. N Z J Agric Res 40(2):269–282. https://doi.org/10.1080/00288233.1997.9513247

Deribe E, Rosseland BO, Borgstrøm R, Salbu B, Gebremariam Z, Dadebo E, Eklo OM (2013) Biomagnification of DDT and its metabolites in four fish species of a tropical lake. Ecotoxicol Environ Saf 95:10–18. https://doi.org/10.1016/j.ecoenv.2013.03.020

Desta H, Lemma B, Gebremariam E (2017) Identifying sustainability challenges on land and water uses the case of Lake Ziway watershed, Ethiopia. Appl Geogr 88:130–143. https://doi.org/10.1016/j.apgeog.2017.09.005

Dromard CR, Bouchon-Navaro Y, Cordonnier S, Guéné M, Harmelin-Vivien M, Bouchon C (2018) Different transfer pathways of an organochlorine pesticide across marine tropical food webs assessed with stable isotope analysis. PLoS ONE 13(2):e0191335. https://doi.org/10.1371/journal.pone.0191335

Federal Democratic Republic of Ethiopia (FEPA) 2006: National Implementation Plan for the Stockholm Convention July 2006. file:///C:/Users/PC/Downloads/UNEP-POPS-NIP-Ethiopia-1.English.pdf. Accessed 20 March 2020

Fisk AT, Hobson KA, Norstrom RJ (2001) Influence of chemical and biological factors on trophic transfer of persistent organic pollutants in the Northwater Polynya marine food web. Environ Sci Technol 35:732–738. https://doi.org/10.1021/es001459w

Hobson KA, Fisk A, Karnovsky N, Holst M, Gagnon JM, Fortier MA (2002) Stable isotope ($\delta^{13}C$ and $\delta^{15}N$) model for the north water food web: implications for evaluating trophodynamics and the flow of energy and contaminants. Deep-Sea Res II 49(22–23):5131–5150. https://doi.org/10.1016/S0967-0645(02)00182-0

Hoekstra PF, O'hara TM, Fisk AT, Borgå K, Solomon KR, Muir DCG (2003) Trophic transfer of persistent organochlorine contaminants (OCs) within an Arctic marine food web from the southern Beaufort-Chukchi Seas. Environ Pollut 124(3):509–522. https://doi.org/10.1016/S0269-7491(02)00482-7

Ikemoto T, Tu NPC, Watanabe MX, Okuda N, Omori K, Tanabe S, Takeuchi I (2008) Analysis of biomagnification of persistent organic pollutants in the aquatic food web of the Mekong Delta, South Vietnam using stable carbon and nitrogen isotopes. Chemosphere 72(1):104–114. https://doi.org/10.1016/j.chemosphere.2008.01.011

Jansen HC, Harmsen J (2011) Pesticide monitoring in the Central Rift Valley 2009–2010. Report 2083. Alterra, Wageningen, http://library.wur.nl/WebQuery/clc/1966024. Accessed 15 Dec 2020

Jarman WM, Hobson KA, Sydeman WJ, Bacon CE, McLaren EB (1996) Influence of trophic position and feeding location on contaminant levels in the Gulf of the Farallones food web revealed by stable isotope analysis. Environ Sci Technol 30(2):654–660. https://doi.org/10.1021/es950392n

Kidd KA, Schindler DW, Hesslein RH, Muir DCG (1995) Correlation between stable nitrogen isotope ratios and concentrations of organochlorines in biota from a freshwater food web. Sci Total Environ 160:381–390. https://doi.org/10.1016/0048-9697(95)04371-7

Kidd KA, Hesslein RH, Ross BJ, Koczanski K, Stephens BJ, Muir DCG (1998) Bioaccumulation of organochlorines through a remote freshwater food web in the Canadian Arctic. Environ Pollut 102:91–103. https://doi.org/10.1016/S0269-7491(98)00068-2

Kidd KA, Bootsma HA, Hesslein RH, Muir DC, Hecky RE (2001) Biomagnification of DDT through the benthic and pelagic food webs of Lake Malawi, East Africa: the importance of trophic level and carbon source. Environ Sci Technol 35(1):14–20. https://doi.org/10.1021/es001119a

Malefia T (2012) Environmental impacts of floriculture industries on Lake Ziway: pollution profiles of Lake Ziway along with floriculture industries. LAP LAMBERT Academic Publishing, Germany

Mazzoni M, Ferrario C, Bettinetti R, Piscia R, Cicala D, Volta P, Polesello S (2020) Trophic magnification of legacy (PCB, DDT, and Hg) and emerging pollutants (PFAS) in the fish community of a small protected Southern Alpine Lake (Lake Mergozzo, Northern Italy). Water 12(6):1591. https://doi.org/10.3390/w12061591

Mengistie BT, Mol AP, Oosterveer P (2017) Pesticide use practices among smallholder vegetable farmers in Ethiopian Central Rift Valley. Environ Dev Sustain 19:301–324. https://doi.org/10.1007/s10668-015-9728-9

Mergia MT, Weldemariam ED, Eklo OM, Yimer GT (2021) Small-scale farmer pesticide knowledge and practice and impacts on the environment and human health in Ethiopia. J Health Pollut 11(30):210607. https://doi.org/10.5696/2156-9614-11.30.210607

Meshesha DT, Tsunekawa A, Tsubo M (2012) Continuing land degradation: cause-effect in Ethiopia's Central Rift Valley. Land Degrad Dev 23(2):130–143. https://doi.org/10.1002/ldr.1061

Mzoughi N, Ennouri R, Chouba L (2016) Organochlorine pesticides in Cyprinus carpio from Sidi Salem Dam, north-western Tunisia. Afr J Aquat Sci 41(4):463–471. https://doi.org/10.2989/16085914.2016.1224762

Negassa A, Getahun A (2003) Breeding Season, length-weight relationship and condition factor of introduced fish, Tilapia zillii Gervais 1948 (Pisces: Cichlidae) in Lake Zwai, Ethiopia. SINET 26(2):115–122

Negatu B, Kromhout H, Mekonnen Y, Vermeulen R (2016) Use of chemical pesticides in Ethiopia: a cross-sectional comparative study on knowledge, attitude, and practice of farmers and farmworkers in three farming systems. Ann Occup Hyg 60(5):551–566. https://doi.org/10.1093/annhyg/mew004

Norli HR, Christiansen A, Deribe E (2011) Application of QuEChERS method for extraction of selected persistent organic pollutants in fish tissue and analysis by gas chromatography-mass spectrometry. J Chromatogr A 1218(41):7234–7241. https://doi.org/10.1016/j.chroma.2011.08.050

PAN G (2012) Pesticides and health hazards facts and figures. Bochum: Pestizide und Gesundheitsgefahren: Daten und Fakten. https://www.pan-germany.org. Accessed 12 May 2020

Picó Y, Fernández M, Ruiz MJ, Font G (2007) Current trends in solid-phase-based extraction techniques for the determination of pesticides in food and the environment. J Biochem Biophys Methods 70(2):117–131. https://doi.org/10.1016/j.jbbm.2006.10.010

Post DM (2002) Using stable isotopes to estimate trophic position. Models, methods, and assumptions. Ecology 83:703–718. https://doi.org/10.1890/00129658

Russ A, Ugland KI, Espeland O, Skaare JU (1999) Organochlorine contaminants in a local marine food chain from Jarford, Northern Norway. Mar Environ Res 48:131–214. https://doi.org/10.1016/S0141-1136(99)00037-9

Schäfer RB, van den Brink PJ, Liess M (2011) Impacts of pesticides on freshwater ecosystems. Ecol Impacts Toxic Chem 2011:111–137

Schmitt CJ, Zajicek JL, Peterman PH (1990) National contaminant biomonitoring program: residues of organochlorine chemicals in US freshwater fish, 1976–1984. Arch Environ Contam Toxicol 19(5):748–781. https://doi.org/10.1007/BF01183992

Sun R, Luo X, Tang B, Chen L, Liu Y, Mai B (2017) Bioaccumulation of short-chain chlorinated paraffin in a typical freshwater food web contaminated by e-waste in south China: bioaccumulation factors, tissue distribution, and trophic transfer. Environ Pollut 222:165–174. https://doi.org/10.1016/j.envpol.2016.12.060

Teklu BM, Hailu A, Wiegant DA, Scholten BS, Van den Brink PJ (2018) Impacts of nutrients and pesticides from small-and large-scale agriculture on the water quality of Lake Ziway, Ethiopia. Environ Sci Pollut Res 25(14):13207–13216. https://doi.org/10.1007/s11356-016-6714-1

Unyimadu JP, Osibanjo O, Babayemi JO (2018) Polychlorinated biphenyls in Brackish Water Fish in the River Niger, Nigeria. J Health Pollut 17:31–42. https://doi.org/10.5696/2156-9614-8.17.31

Vallet-Coulomb C, Legesse D, Gasse F, Travi Y, Chernet T (2001) Lake evaporation estimates in tropical Africa (Lake Ziway, Ethiopia). J Hydrol 245(1–4):1–18. https://doi.org/10.1016/S0022-1694(01)00341-9

Verhaert V, Covaci A, Bouillon S, Abrantes K, Musibono D, Bervoets L, Blust R (2013) Baseline levels and trophic transfer of persistent organic pollutants in sediments and biota from the Congo River Basin (DR Congo). Environ Int 59:290–302. https://doi.org/10.1016/j.envint.2013.05.015

Wepener V, Smit N, Covaci A, Dyke S, Bervoets L (2012) Seasonal bioaccumulation of organohalogens in tigerfish, *Hydrocynus vittatus* Castelnau, from Lake Pongolapoort, South Africa. Bull Environ Contam Toxicol 88(2):277–282. https://doi.org/10.1007/s00128-011-0439-0

Yohannes YB, Ikenaka Y, Saengtienchai A, Watanabe KP, Nakayama SM, Ishizuka M (2014) Concentrations and human health risk assessment of organochlorine pesticides in edible fish species from a Rift Valley lake—Lake Ziway, Ethiopia. Ecotoxicol Environ Saf 106:95–101. https://doi.org/10.1016/j.ecoenv.2014.04.014