

# Concentrations and human health risk assessment of organochlorine pesticides in edible fish species from a Rift Valley lake—Lake Ziway, Ethiopia



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## ABSTRACT

Fish consumption is known to have several health benefits for humans. However, the accumulation of organic pollutants, like organochlorine pesticides (OCPs) could pose health hazards. Thus, OCPs in edible fish species (*Oreochromis niloticus*, *Tilapia zillii*, *Carassius* spp., and *Clarias gariepinus*) from Lake Ziway, an Ethiopian Rift Valley Lake were investigated to assess the potential human health hazards of these contaminants. Dichlorodiphenyltrichloroethanes (DDTs), hexachlorocyclohexanes (HCHs), chlordanes, and heptachlors were observed with  $\Sigma$ OCPs concentration ranging from 1.41 to 63.8 ng g<sup>-1</sup> ww. DDTs were the predominant contaminants (0.9 to 61.9 ng g<sup>-1</sup> ww), followed by HCHs. The predominance of DDTs may be attributed to their current use in vector control and contamination from past usage. The estimated daily intakes (EDIs) of OCPs from all fish species were much lower than the acceptable daily intakes (ADIs), indicating that consumption of fish is at little risk to human health at present. However, the cancer risk estimates in the area of concern and the hazard ratios (HRs) of HCHs, DDTs, and heptachlors exceeded the threshold value of one, indicating daily exposure to these compounds is a potential concern. This may result in a lifetime cancer risk greater than of 1 in 10<sup>6</sup>.

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## 1. Introduction

Organochlorine pesticides (OCPs) have been widely used and become a worldwide concern due to their persistence, bioaccumulative potential, chronic toxicity, and potential negative impacts on humans and wildlife (UNEP (United Nations Environmental Protection), 2001). It is known that most of the total intake of pesticide residues by human beings is through the food chain (Martinez et al., 1997). Fish are known to biomagnify pesticides from the surrounding environment (Mackay and Fraser, 2000), and transfer the pesticides to humans when consumed. Epidemiological studies indicate that some of these compounds may be associated with cancers in humans (Snedeker, 2001; Beard, 2006; IARC (International Agency for Research on Cancer), 2008), and also influence the concentration of thyroid hormones (Meeker et al., 2007). Eskenazi et al. (2006) reported delays in neurodevelopment

during early childhood due to the impacts of prenatal exposure to dichlorodiphenyltrichloroethanes (DDTs).

Although the use of OCPs has been banned or restricted, developing countries like Ethiopia still use them for agricultural and health purposes, and as a consequence they can be found in aquatic (Deribe et al., 2011; Yohannes et al., 2013a, 2013b) and terrestrial ecosystems, for example in cow's milk (Gebremichael et al., 2013). Because it is landlocked, Ethiopia is highly dependent on lake aquatic environments for its economic development. The Ethiopian Rift Valley region, encompassing seven principal lakes, is a densely populated area confined with various agricultural activities where there is still an increasing trend of pesticide usage (Amera and Abate, 2008). Moreover, Ethiopia has implemented indoor residual spraying (IRS) with DDT for malaria control in the past few decades (WHO (World Health Organization), 2007). Approximately 400 metric tons of active-ingredient DDT per year is used for IRS in many parts of the country including the Rift Valley, a malaria epidemic prone region (Biscoe et al., 2005; Van den Berg, 2009). In addition, Ethiopia is one of the many African countries burdened with the problem of obsolete pesticides, which have been accumulated since the first imports in the

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1960s (Haylamicheal and Dalvie, 2009). These were mostly organochlorine compounds such as chlordane, DDT, dieldrin and lindane that are banned or restricted in most countries. In this view, there is great likelihood that the Ethiopian Rift Valley ecosystem is exposed to large amounts of pesticides.

Lake Ziway, one of the Ethiopian Rift Valley lakes, is located in an area with many agricultural activities but few soil conservation efforts in its catchment area. Intensive agriculture in the proximity of the lake and municipal waste discharges are sources of pollution into this fresh water ecosystem (Hengsdijk and Jansen, 2006). It is therefore necessary to evaluate the current status of the OCPs in different fish species from Lake Ziway. A recent study on the lake examined only the levels and biomagnification of DDTs (Deribe et al., 2013). No other studies have been carried out on the levels and risk assessment of other OCPs in the lake.

Therefore, objectives of this study are to assess the accumulation levels of OCPs in edible fish species collected from Lake Ziway and to evaluate the potential risks to human health posed through dietary consumption of these fish. This study gives a comprehensive overview of OCPs' status in the fish species of different trophic levels in Lake Ziway and provides a basis for decision-makers to take effective measures aimed at mitigating potential health and ecological risks.

## 2. Materials and methods

### 2.1. Study area

The study area, Lake Ziway (surface area: 434 km<sup>2</sup>) is a shallow freshwater lake located in the northern section of the Rift Valley (Fig. 1). It is fed by two inflowing rivers, the Meki River from the north-west and the Katar River from the east, and drains towards the Lake Abijata, through the Bulbula River. The lake has a large littoral zone containing emergent and submergent vegetation, which provides feeding, breeding and nursery habitats for fish (Admassu and Ahlgren, 2000; Erko et al., 2006). Lake Ziway contains different fish species including Nile tilapia (*Oreochromis niloticus*), Redbelly tilapia (*Tilapia zillii*), African big barb (*Barbus intermedius*), African sharptooth catfish (*Clarias gariepinus*), and *Carassius* spp. (*Carassius carassius* and *Carassius auratus*) (Lemma, 2005). Fisheries on Lake Ziway are an open and easily accessible source of income and have always been a source

of food and income for the people living on the shores of the lake. The landings of Lake Ziway used to be dominated by *O. niloticus*, but species of *C. gariepinus*, *T. zillii*, and *Carassius* spp. (*C. carassius* and *C. auratus*) are increasingly becoming a part of the catch. The potential yield of all the species of the lake is estimated to range between 2500 and 6680 t yr<sup>-1</sup> (Spliethoff et al., 2009).

### 2.2. Sampling

A total of 100 individual fish belonging to *O. niloticus*, *T. zillii*, *Carassius* spp., and *C. gariepinus* fish species of Lake Ziway were purchased from the local fishermen in January 2011. Samples were transported to Ziway fisheries research laboratory where the body size and body weight were recorded. General information about the fish is given in Table 1. Fishes were dissected to obtain dorsal muscles and stored at -20 °C. The frozen samples were then transported to Japan for analysis. Each individual sample was lyophilized, homogenized separately and used for chemical analysis.

### 2.3. OCPs analysis

Samples were processed and analyzed using a method described by Yohannes et al. (2013a) with slight modifications. Approximately 10 g of muscle tissue from each fish was taken and mixed with anhydrous sodium sulfate. After spiking with the surrogate standard of 2,4,5,6-tetrachloro-*m*-xylene (TCmX), each sample was extracted using Soxtherm apparatus (S306AK Automatic Extractor, Gerhardt, Germany) with *n*-hexane:acetone (3:1, v/v) for 4 h. An aliquot of the extract (20 percent) was used for lipid measurement using gravimetric method. The remaining extract was applied to a column filled with 6 g florisil (activated at 150 °C overnight) for clean-up and eluted with a mixture of *n*-hexane:dichloromethane (7:3, v/v). The eluate was concentrated to 2 mL on rotary evaporator, and further to near dryness under gentle nitrogen flow. Finally, the extract was redissolved in 100 µL *n*-decane, and the internal standard pentachloronitrobenzene was added before instrumental analysis.

OCPs including DDTs (*o,p'*-DDT, *p,p'*-DDT, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD and *p,p'*-DDD), hexachlorocyclohexanes (HCHs;  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -HCH), heptachlors (HPTs; heptachlor, *cis*- and *trans*-heptachlor epoxide), chlordanes (CHLs; *cis*- and *trans*-chlordane, *cis*- and *trans*-nonachlor and oxychlordane), drins (aldrin, dieldrin and endrine) and hexachlorobenzene (HCB) were analyzed by gas chromatography equipped with an electron capture detector (Shimadzu GC-2014, Kyoto, Japan). An ENV-8 MS capillary column (30 m  $\times$  0.25 mm i.d., 0.25 µm film thickness) with splitless injection was used to separate OCPs. One µL of each sample was injected. The column oven temperature was initially set at 100 °C for 1 min, increased to 180 °C at 20 °C min<sup>-1</sup> and then to 260 °C at 4 °C min<sup>-1</sup>, which was held for 5 min. The injector and detector temperatures were 250 °C and 310 °C, respectively.

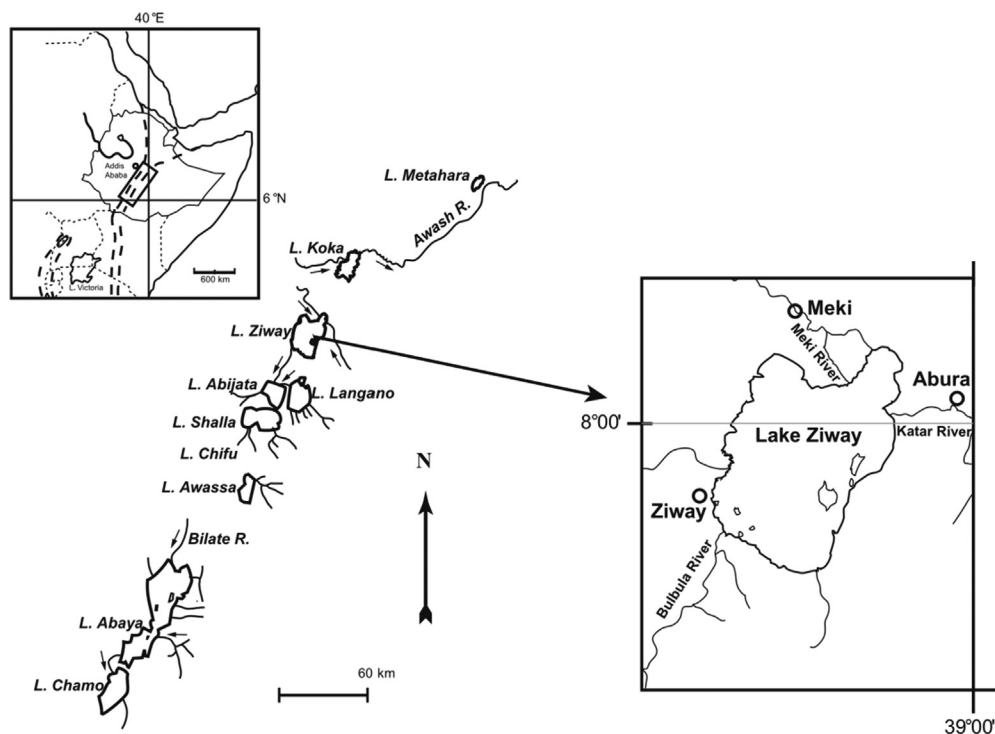


Fig. 1. The map of Lake Ziway (Deribe et al., 2013).

**Table 1**  
Biometry data of fish species in this study from Lake Ziway.

Fish species	N	Length (mm) Mean $\pm$ SD Min–max	Weight (g) Mean $\pm$ SD Min–max	Lipid content (percent) Mean $\pm$ SD Min–max	Main food <sup>b</sup>
<i>O. niloticus</i>	27	213 $\pm$ 28 167–270	315 $\pm$ 111 178–554	<sup>a</sup> 0.75 $\pm$ 0.68 0.10–3.60	Blue green algae, detritus, macrophytes
<i>T. zillii</i>	19	174 $\pm$ 21 120–205	199 $\pm$ 59 111–312	<sup>a</sup> 0.90 $\pm$ 0.48 0.18–2.13	Macrophytes
<i>Carassius</i> spp.	27	267 $\pm$ 39 160–332	585 $\pm$ 230 231–1199	<sup>a</sup> 0.87 $\pm$ 0.59 0.15–2.14	Macrophytes, detritus, green algae
<i>C. gariepinus</i>	27	353 $\pm$ 88 235–560	559 $\pm$ 454 154–1910	<sup>a</sup> 1.34 $\pm$ 2.52 0.23–5.3	Insect, fish eggs, fish, gastropods

N=number of samples.

Mean  $\pm$  standard deviation (SD).

<sup>a</sup> Means with different letter superscript are significantly different (Tukey test is applied;  $p < 0.05$ ).

<sup>b</sup> Ref. Deribe et al. (2013).

Helium at a flow rate of 1.0 mL min<sup>-1</sup> and nitrogen at 45 mL min<sup>-1</sup> were used as carrier gas and make-up gas, respectively.

#### 2.4. Quality control and quality assurance

OCPs were identified by comparing their retention time with the reference to the corresponding standards. Multi-level calibration curves were created for the quantification and linearity ( $R^2 \geq 0.995$ ) was achieved. Quality control was performed by analysis of procedural blanks and spiked blanks. Results showed that no target analytes were detected in blank samples and recoveries for spiked blanks ranged from 90 percent to 105 percent. The recovery rate of the surrogate, TCmX was 85  $\pm$  11 percent. To check for the validity of the method used for the extraction and analysis of the samples, the standard reference material SRM 1947 (Lake Michigan Fish Tissue) was analyzed during the analysis of samples, and the recoveries ranged from 85 percent to 105 percent with RSD < 10 percent. The values reported here were not corrected for recoveries. Detection limits based on 3:1 signal to noise ratio (S/N) were between 0.05 and 0.1 ng g<sup>-1</sup> for all OCPs. Concentrations were expressed on a wet weight (ww) basis.

#### 2.5. Risk assessment

Various international organizations have subsequently established a series of standards and instructions to estimate the risks to human health from environmental pollutants in fish (USEPA (United States Environmental Protection Agency), 2013). A straight forward risk assessment is performed through comparison with the levels set by laws and guidelines. However, this comparison was made without the consideration of factors like different eating habits and consumption rates. Thus, in this study, we investigated the risk assessment by two approaches. To comprehensively evaluate the health risk assessment, the 50th and 95th percentile measured concentrations were used.

##### 2.5.1. Estimated daily intake (EDI)

Estimated dietary intakes of OCPs were calculated as follows:

$$EDI = \frac{C \times DR}{BW} \quad (1)$$

where C is the measured concentration of OCPs (ng g<sup>-1</sup> ww), DR is average daily consumption rate of fish (g d<sup>-1</sup>) and BW is body weight (kg), which was set at 60 kg (WHO (World Health Organization), 2010). The average daily consumption rate was derived from FAO (Food and Agriculture Organization) (2011). Though Ethiopians are traditionally meat eaters, eating habits have been shifting in favor of fish in areas and communities where there is regular and sufficient supply. In those communities, annual fish consumption can exceed 10 kg person<sup>-1</sup> (FAO (Food and Agriculture Organization), 2011). Thus, the DR was estimated at 30 g d<sup>-1</sup> per person.

##### 2.5.2. Potential carcinogenic risks

To assess public health risks posed through fish consumption, the cancer risk estimates and hazard ratios (HRs) were assessed on the basis of the guidelines of the United States Environmental Protection Agency (USEPA). Cancer risks associated with OCPs were estimated by combining the exposure dose and slope factor (USEPA (United States Environmental Protection Agency), 2005). A public screening criteria for carcinogens is set at a carcinogenic risk level of 10<sup>-6</sup>. Carcinogenic risks below 10<sup>-6</sup> are considered acceptable, while carcinogenic risks above 10<sup>-4</sup> are considered unacceptable. An area of concern is present between 10<sup>-6</sup> and 10<sup>-4</sup> (USEPA (United States Environmental Protection Agency), 2005).

HR for cancer risks was assessed by comparing the EDI with the benchmark concentration (BMC) (Solomon et al., 2000; Jiang et al., 2005) using the following equation:

$$HR = \frac{EDI}{BMC} \quad (2)$$

The BMC for carcinogenic effects was derived from the cancer slope factor (CSF), which was obtained from the USEPA (United States Environmental Protection Agency) (2012)). The BMC for carcinogenic effects represents the exposure concentration at which lifetime cancer risk is one in a million for lifetime exposure. A hazard ratio that is greater than one indicates that there is potential risk to human health (Dougherty et al., 2000).

#### 2.6. Statistical analysis

Statistical analysis was performed using JMP 9 (SAS Institute, Cary, NC, USA). Descriptive statistics using one-way analysis of variance (ANOVA) were used to characterize the levels of OCPs in the studied fish species. Concentrations below the limit of detections were given a value of zero. Multiple comparisons among the fish species were tested using Tukey's HSD post hoc test. A significant level of  $p < 0.05$  was used.

### 3. Results and discussion

The length and weight of the studied fish species varied from 120 to 560 mm and from 111 to 1910 g, respectively (Table 1). A continuous increase in length and weight was observed for all individuals with a significant and positive correlation ( $R^2 = 0.70$ ,  $p < 0.001$ ). The mean lipid content was in the range 0.75  $\pm$  0.68 percent to 1.34  $\pm$  2.52, and there was no significant difference ( $p > 0.05$ ) among the studied fish species (Table 1). There was no significant correlation between the biometric data and lipid content ( $p > 0.05$ ).

#### 3.1. Levels of OCPs

OCPs were detected in muscle samples of all fish species, indicating their widespread contamination in Lake Ziway. DDTs, HCHs, HPTs, and CHLs were detected with varying concentrations (Table 2). The total concentrations of OCPs ranged from 1.41 to 63.8 ng g<sup>-1</sup> ww, with a mean concentration of 7.72  $\pm$  6.90 ng g<sup>-1</sup> ww. The highest concentrations of OCPs were found in *C. gariepinus* ( $p < 0.05$ ), which is a carnivorous fish and found at top trophic position. Among the OCPs analyzed, DDTs were the most commonly detected and were dominant in all samples. It accounted for 64.5  $\pm$  10 percent (SD) (ranging from 52 to 78 percent) of the total OCPs. In general, the contamination pattern of OCPs in fish samples detected in this study was in the order of DDTs > HCHs > CHLs  $\cong$  HPTs. This result indicates the high degree of exposure to DDTs in biota from the Ethiopian Rift Valley region,

**Table 2**  
Levels of OCPs (ng g<sup>-1</sup> ww) in muscle of four fish species from Lake Ziway.

	<i>O. niloticus</i>	<i>T. zillii</i>	<i>Carassius</i> spp.	<i>C. gariepinus</i>
α-HCH	0.22 ± 0.06	0.19 ± 0.03	0.25 ± 0.09	0.27 ± 0.12
β-HCH	ND	0.31 ± 0.09	0.03 ± 0.11	ND
γ-HCH	0.67 ± 0.33	0.68 ± 0.52	0.22 ± 0.18	0.47 ± 0.42
δ-HCH	ND	0.27 ± 0.04	0.11 ± 0.21	ND
ΣHCHs*	<sup>a</sup> 1.26 ± 1.04	<sup>a</sup> 1.45 ± 0.61	<sup>b</sup> 0.61 ± 0.31	<sup>b</sup> 0.72 ± 0.47
Heptachlor	0.29–5.10	0.91–3.54	0.16–1.85	0.27–2.01
cis-Heptachlor-epoxide	ND	ND	ND	ND
trans-Heptachlor-epoxide	0.57 ± 0.27	0.08 ± 0.10	0.24 ± 0.11	0.23 ± 0.11
ΣHPTs*	0.32 ± 0.09	0.20 ± 0.02	0.31 ± 0.23	0.42 ± 0.29
	<sup>a</sup> 0.90 ± 0.35	<sup>c</sup> 0.42 ± 0.11	<sup>b,c</sup> 0.59 ± 0.27	<sup>b</sup> 0.65 ± 0.28
oxy-chlordane	0.44–2.27	0.19–0.69	0.20–1.52	0.34–1.56
cis-Chlordane	0.04 ± 0.04	0.16 ± 0.07	0.11 ± 0.06	0.10 ± 0.07
trans-Chlordane	0.18 ± 0.04	0.26 ± 0.11	0.12 ± 0.07	0.16 ± 0.05
trans-Nonachlor	0.16 ± 0.05	0.20 ± 0.03	0.26 ± 0.21	0.29 ± 0.12
ΣCHLs*	0.03 ± 0.07	0.29 ± 0.10	0.37 ± 0.59	0.35 ± 0.23
	<sup>b</sup> 0.40 ± 0.10	<sup>a</sup> 0.91 ± 0.22	<sup>a</sup> 0.87 ± 0.82	<sup>a</sup> 0.90 ± 0.25
p,p'-DDE	0.17–0.61	0.65–1.32	0.19–4.00	0.58–1.50
o,p'-DDE	1.32 ± 0.81	1.89 ± 2.02	2.42 ± 1.60	6.92 ± 11.47
p,p'-DDD	0.10 ± 0.08	0.35 ± 0.12	0.26 ± 0.36	0.12 ± 0.10
o,p'-DDT	0.40 ± 0.21	0.85 ± 0.41	0.58 ± 0.35	0.79 ± 0.68
p,p'-DDT	0.43 ± 0.17	0.53 ± 0.21	0.68 ± 0.74	0.43 ± 0.11
o,p'-DDT	0.31 ± 0.18	0.77 ± 0.66	0.57 ± 0.73	0.62 ± 0.40
ΣDDTs*	<sup>b</sup> 2.33 ± 1.09	<sup>a,b</sup> 4.38 ± 2.67	<sup>a,b</sup> 4.55 ± 2.80	<sup>a</sup> 9.0 ± 11.7
	0.90–5.12	1.35–13.2	0.77–10.6	2.36–61.9
ΣOCPs*	<sup>b</sup> 4.89 ± 1.85	<sup>a,b</sup> 7.16 ± 2.63	<sup>a,b</sup> 6.62 ± 3.71	<sup>a</sup> 11.2 ± 11.7
	2.46–10.9	3.59–15.2	1.41–15.0	4.00–63.8

ND=below detection limit.

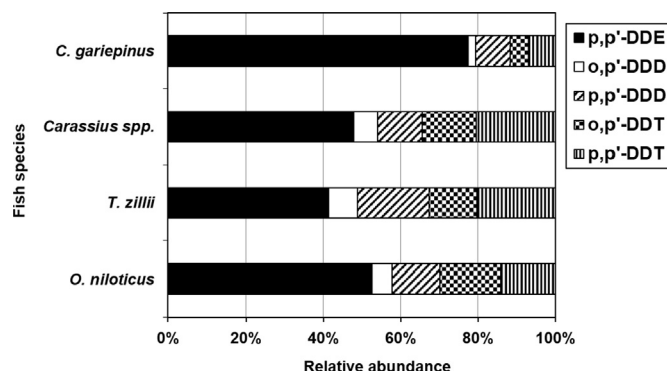
Mean ± standard deviation (SD).

\* Min-max. Values with different letters (a, b, c) within a row are significantly different at  $p < 0.05$  level (Tukey test is applied).

which is most likely due to recent use of DDT for malaria control through IRS (Biscoe et al., 2005; Van den Berg, 2009) as well as from past usage and spills from obsolete pesticides (Haylamicheal and Dalvie, 2009). It is also reported that DDT is still ongoing use by farmers in the region (Ameria and Abate, 2008). Log transformed OCPs show a positive correlation with total length for all fish species ( $R^2=0.18$ ;  $p < 0.001$ ), whereas no significant correlation was found between lipid content and concentration of OCPs ( $R^2=0.00$ ;  $p=0.140$ ).

### 3.1.1. DDTs

DDT and its metabolites were detected in all fish species (Table 2). Concentrations of DDTs in the muscle tissue are found at large variations ranging from 0.77 to 61.9 ng g<sup>-1</sup> ww (mean concentration of 5.27 ± 6.73 ng g<sup>-1</sup> ww). *C. gariepinus* with 9.0 ± 11.7 ng g<sup>-1</sup> ww and *O. niloticus* with 2.33 ± 1.09 ng g<sup>-1</sup> ww had the highest and lowest concentrations, respectively. This may be attributed to their different feeding habits because *C. gariepinus* is a carnivorous and *O. niloticus* is almost herbivorous fish species (Table 1). Overall, the concentrations of DDTs were higher than those of other OCPs. The possible reasons for the presence of high level of DDTs in the region may be its current use in vector control, illegal usage and contamination from obsolete pesticides (Haylamicheal and Dalvie, 2009; Van den Berg, 2009). Reports from other African lakes also indicate much higher levels of DDT in aquatic organisms compared to other OCPs. In Lake Koka, Ethiopia DDT ranged from 0.05 to 72.53 ng g<sup>-1</sup> ww and it was the predominant pesticide by a factor of 10 when compared to the other OCPs (Deribe et al., 2011) and in Lake Malawi DDT concentrations were up to 60 times higher than other OCPs (Kidd et al., 2001). Concentrations of DDTs found in this study (mean concentration of 2.33 to 9.0 ng g<sup>-1</sup> ww) are higher than those found in Lake Victoria, Uganda (mean 1.39 to 1.67 ng g<sup>-1</sup> ww) (Kasozzi et al., 2006). However, they are lower than those in fish from Southern Lake Victoria, Tanzania (mean 15 and 20 ng g<sup>-1</sup> ww) (Henry and



**Fig. 2.** Relative abundance of individual DDT components in four fish species from Lake Ziway.

Kishimba, 2006) and fish from Lake Burullus, Egypt (mean 2.76 to 45.13 ng g<sup>-1</sup> ww) (Said et al., 2008), and comparable to fish from Lake Awassa, Ethiopia with ΣDDTs mean concentration of 1.80 and 9.0 ng g<sup>-1</sup> ww for *O. niloticus* and *C. gariepinus*, respectively (Yohannes et al., 2013a). Direct comparisons should be made with caution since these studies were conducted on different species. With all the data pooled together, the concentration of DDTs (log transformed) was significantly correlated ( $R^2=0.18$ ;  $p < 0.001$ ) to total length of the fish, but not with percent lipid content ( $R^2=0.02$ ;  $p=0.139$ ).

The composition profiles of DDTs in the muscle tissue of the four fish species are shown in Fig. 2. Among the metabolites, p,p'-DDE was the predominant congener, accounting for 55 percent ± 15.72 (from 41 to 77 percent), followed by p,p'-DDT (15 percent ± 6.42), and p,p'-DDD (13 percent ± 4.80). The proportion of p,p'-DDE was higher in *C. gariepinus* than in the others, comprising 77 percent of the mean DDT concentrations, showing that *C. gariepinus* found at high trophic level is more likely feeding on prey (both fish and invertebrates) and accumulates DDE, a more



degraded form of DDT. In addition, this may be attributed to the more persistent nature of *p,p'*-DDE, and to its rate of biomagnification along the food chain in freshwater ecosystems (Rognerud et al., 2002). In contrast, the proportions of parent compounds (*o,p'*- and *p,p'*-DDT) in *O. niloticus* (29.8 percent), *T. zillii* (32.6 percent), and *Carassius* spp. (34.4 percent) were higher than in *C. gariepinus* (11.7 percent). This may be probably as a result of more efficient transfer of DDT to phytoplankton and macrophyte consuming herbivorous fish (Zhou et al., 2007). Technical DDT generally contains 75 percent *p,p'*-DDT, 15 percent *o,p'*-DDT, 5 percent *p,p'*-DDE, and < 5 percent others. DDT can be metabolized into DDE under aerobic conditions or into DDD in anaerobic environments (Hitch and Day, 1992). Thus, the ratio of (*p,p'*-DDE + *p,p'*-DDD)/ $\Sigma$ DDTs can indicate past or recent usage of technical DDT. A ratio greater than 0.5 generally indicates long term biotransformation of DDT, whereas a ratio of less than 0.5 may indicate recent input of DDT. In the present study, the ratio ranged from 0.55 to 0.87, suggesting that DDTs in fish from Lake Ziway were mainly due to historical use, and to its current use for vector control in the region since the Ethiopian government decided to continue using DDT because of the high incidence of malaria and the corresponding fatalities (Biscoe et al., 2005; WHO (World Health Organization), 2007).

### 3.1.2. HCHs

HCHs were the second most prevalent OCP contaminants in the studied fish species and accounted for 17 percent (from 10 percent to 25 percent) of the total OCPs measured. The levels of HCHs in *T. zillii* ( $1.45 \pm 0.61$  ng g<sup>-1</sup> ww) and *O. niloticus* ( $1.26 \pm 1.04$  ng g<sup>-1</sup> ww) were significantly higher ( $p < 0.05$ ) than that of *Carassius* spp. ( $0.61 \pm 0.31$  ng g<sup>-1</sup> ww), and *C. gariepinus* ( $0.72 \pm 0.47$  ng g<sup>-1</sup> ww) (Table 2). A negative relationship ( $R^2 = 0.07$ ; slope = -0.02;  $p < 0.01$ ) between log transformed  $\Sigma$ HCH and length of fish was found, whereas no significant relationship ( $p > 0.05$ ) was found between lipid content and concentration of HCHs. Of the HCHs measured,  $\alpha$  and  $\gamma$ -HCHs were frequently detected and the  $\gamma$ -isomer (lindane) was the predominant, accounting for 60 percent on an average of  $\Sigma$ HCHs in the muscle tissue. The higher  $\gamma$ -HCH concentrations in the samples indicate current usage of lindane around the lake. A recent study in the Ethiopian rift valley region also showed high concentrations of lindane in tissues taken from cattle with the highest level of  $0.14$  mg kg<sup>-1</sup> ww in liver samples obtained from Holeta, Ethiopia (Letta and Attah, 2013). In general, the concentrations of HCHs in this study are lower than those in fish from Lake Taabo, Cote d'Ivoire (Roche et al., 2007), and fish from Lake Burullus, Egypt (Said et al., 2008).

### 3.1.3. CHLs and HPTs

With regard to the residual levels of CHLs, *trans*-chlordane, *cis*-chlordane and *trans*-nonachlor were detected in most of the samples as they are the dominant constituents in technical chlordane (Xu et al., 2004) whereas oxy-chlordane was rarely

encountered. The presence of these compounds in the environment at relatively high concentrations as compared to oxy-chlordane likely indicates recent inputs of chlordane to the environment. The mean residual levels of CHLs in the muscle tissues in the present study ranged from  $0.40$  to  $0.91$  ng g<sup>-1</sup> ww (Table 2). The use of chlordane is permitted in Ethiopia as a general insecticide (Ritter et al., 1995). Chlordane is imported to Ethiopia under the regulation of Ministry of Agriculture for termiticide usage only (EICDCR (Export and Imports of Certain Dangerous Chemicals Regulations), 2004).

It was found that HPTs (*cis*-heptachlor epoxide and *trans*-heptachlor epoxide) were also present in most of the fish collected. The *cis* and *trans*-heptachlor epoxides predominated with a mean concentration of  $0.28 \pm 0.27$  ng g<sup>-1</sup> ww and  $0.31 \pm 0.21$  ng g<sup>-1</sup> ww, respectively (Table 2). The highest residual levels of HPTs ( $0.90 \pm 0.35$  ng g<sup>-1</sup> ww) were found in *O. niloticus*, the herbivorous fish species.

## 3.2. Human health risk assessment

Fish consumption has been proven to be one of the major routes of human exposure to organic contaminants. To better understand the concentration levels, the concentrations of OCPs in the present study were evaluated against international existing limits. The EDI was calculated and compared with the acceptable daily intake (ADI) recommended by the Food and Agriculture Organization and the World Health Organization (FAO/WHO) Joint Meeting on Pesticide Residue (WHO (World Health Organization), 2010). To comprehensively evaluate risk exposure, the 50th and 95th percentile EDIs of OCPs for each fish species were calculated. The EDIs of OCPs expressed as nanogram per kilogram body weight per day (ng kg<sup>-1</sup> bw d<sup>-1</sup>) through consumption of fish for the population are presented in Table 3. EDI of HCHs, HPTs, CHLs, and DDTs at both exposure levels were far below the ADI, indicating that consumption of fish at present would not pose a human health risk.

A carcinogenic risk assessment for OCPs was conducted using cancer risk estimates and HRs at the 50th and 95th percentile measured concentrations. As shown in Table 4, heptachlors showed much higher carcinogenic risk than other OCPs in all fish species. Regard to DDTs, the cancer risk for the 50th exposure level ranged from 3.7 in *O. niloticus* to  $8.4 \times 10^{-4}$  in *C. gariepinus* suggested that a person would have a chances of about 4 and 8 in 10,000 to develop cancer from DDTs, respectively. This carcinogenic risk increased from 7.6 to  $36 \times 10^{-4}$  on 95th exposure level, which was unacceptable for human health. In general, the overall cancer risk estimates for all OCPs ranged from  $0.7 \times 10^{-4}$  to  $36 \times 10^{-4}$  on both the 50th and 95th exposure levels, and when compared to a target risk of  $> 1 \times 10^{-4}$ , are considered unacceptable. Thus, the carcinogenic risk of HCHs, HPTs, CHLs and DDTs among humans at present should be of concern.

**Table 3**

Estimated daily intake values (ng kg<sup>-1</sup> bw d<sup>-1</sup>) of OCPs through the studied fish species by human.

	ADI	50th (95th) percentile measured concentrations (ng g <sup>-1</sup> ww)				50th (95th) estimated daily intakes			
		<i>O. niloticus</i>	<i>T. zillii</i>	<i>Carassius</i> spp.	<i>C. gariepinus</i>	<i>O. niloticus</i>	<i>T. zillii</i>	<i>Carassius</i> spp.	<i>C. gariepinus</i>
HCHs	5,000 <sup>a</sup>	1.08 (3.39)	1.32 (2.60)	0.52 (1.20)	0.54 (1.53)	0.54 (1.70)	0.66 (1.30)	0.26 (0.66)	0.27 (0.77)
HPTs	100	0.86 (1.34)	0.42 (0.56)	0.53 (0.93)	0.60 (1.20)	0.43 (0.67)	0.21 (0.28)	0.27 (0.49)	0.30 (0.60)
CHLs	500	0.39 (0.60)	0.86 (1.26)	0.65 (2.41)	0.85 (1.41)	0.19 (0.30)	0.43 (0.63)	0.33 (1.20)	0.42 (0.72)
DDTs	10,000	2.20 (4.49)	3.97 (8.23)	4.61 (9.21)	4.91 (21.21)	1.10 (2.24)	1.99 (4.12)	2.30 (4.61)	2.46 (10.61)

ADI = Acceptable daily intake (ng kg<sup>-1</sup> bw d<sup>-1</sup>).

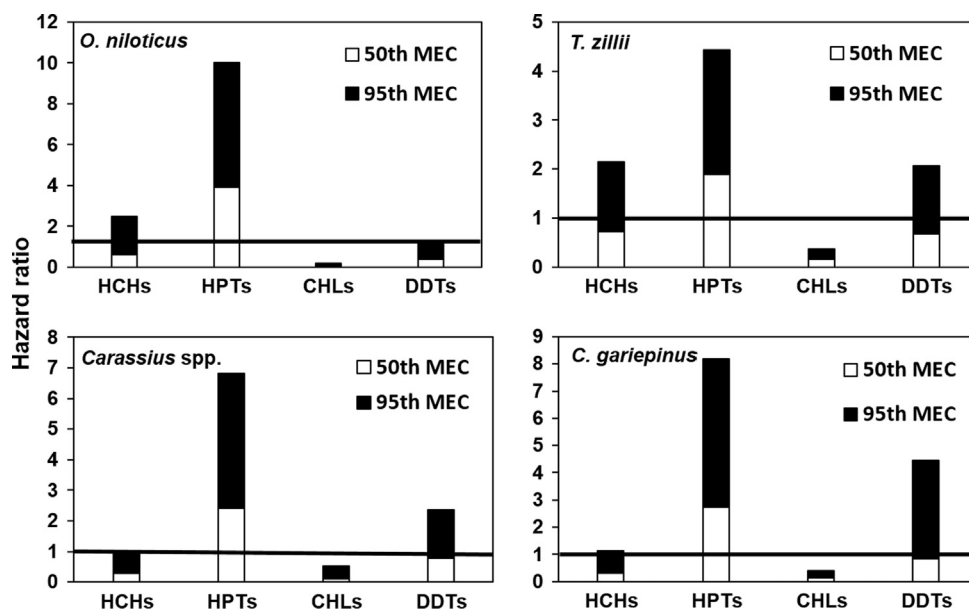
<sup>a</sup> for  $\gamma$ -HCH. (WHO (World Health Organization), 2010).

**Table 4**  
Cancer risk estimates for HCHs, HPTs, CHLs and DDTs.

OCPs	Cancer slope factor <sup>b</sup> [per (mg kg <sup>-1</sup> d <sup>-1</sup> )]	50th (95th) percentile cancer risks (× 10 <sup>-4</sup> )			
		<i>O. niloticus</i>	<i>T. zillii</i>	<i>Carassius</i> spp.	<i>C. gariepinus</i>
HCHs	1.1 <sup>a</sup>	5.9 (18.7)	7.2 (14.3)	2.8 (6.6)	2.9 (8.4)
HPTs	4.5	19 (30)	0.9 (13)	12 (22)	13 (27)
CHLs	0.35	0.7 (1.0)	1.5 (2.2)	1.1 (4.2)	1.5 (2.5)
DDTs	0.34	3.7 (7.6)	6.7 (14.0)	7.8 (15.7)	8.4 (36)

<sup>a</sup> For  $\gamma$ -HCH.

<sup>b</sup> Cancer slope factors were from the USEPA (United States Environmental Protection Agency), 2013.



**Fig. 3.** Carcinogenic hazard ratios for daily consumption of fish from Lake Ziway, Ethiopia. MEC, measured concentration. (The horizontal line represents the hazard ratio of > 1, and any ratio higher than that indicates a risk.).

HRs based on the 50th and 95th percentile exposure levels were assessed in each fish species and the results are shown in Fig. 3. HRs for cancer risk based on the 95th percentile concentrations of HCHs, HPTs, and DDTs were greater than one. The HRs for the OCPs followed almost the following sequence: HPTs > DDT ≥ HCHs > CHLs. For all fish species, the HRs for HPTs were greater than one, showing that consuming fish is harmful to humans. Based on landings, *O. niloticus* is the most caught fish in Lake Ziway. The carcinogenic risk due to HCHs for this fish species is also greater than one while for DDTs is less than one. However, for *T. zillii*, *Carassius* spp. and *C. gariepinus* the HRs for DDTs were greater than one. In general, cumulative daily exposure to OCPs because of fish consumption would yield a lifetime cancer risk of greater than one in a million. The results indicate that these compounds may be of particular concern because they are still in use.

#### 4. Conclusion

This is the first study reporting on the levels and risk assessment of some OCPs in the most commonly caught fish species from the Ethiopian Rift Valley lake—Lake Ziway. The rift valley region is a populated area that is influenced by heavy pollution stemming from urban, agricultural and industrial activities. Our results indicated the presence of HCHs, HPTs, CHLs and DDTs with varying concentrations among the fish species. The overall

conclusion of the evaluation is that DDTs were the main abundant pollutants, attributed to its current use in vector control and contamination from past usage. Dietary intakes estimated from the 50th and 95th percentile exposure level were far below ADIs. In contrast, the calculated cancer risk estimates and HRs of the studied fish species indicated that the consumption of most of the fish species could cause cancer as HR for cancer risk based on the 95th percentile concentrations of HCHs, HPTs and DDTs was greater than one. In this study, only fish and some OCPs were investigated to assess the risk. The consumption of water, vegetables, and animal meat, and the levels of other environmental pollutants were not considered. Therefore, the actual health risk for local people through dietary intake could be higher.

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