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1 Concentrations and human health risk assessment of organochlorine pesticides in edible fish
2 species from a Rift Valley Lake – Lake Ziway, Ethiopia

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19 **Abstract**

20 Fish consumption is known to have several health benefits for humans. However, the
21 accumulation of organic pollutants, like organochlorine pesticides (OCPs) could pose health
22 hazards. Thus, OCPs in edible fish species (*Oreochromis niloticus*, *Tilapia zillii*, *Carassius*
23 spp., and *Clarias gariepinus*) from Lake Ziway, an Ethiopian Rift Valley Lake were
24 investigated to assess the potential human health hazards of these contaminants.
25 Dichlorodiphenyltrichloroethanes (DDTs), hexachlorocyclohexanes (HCHs), chlordanes,
26 and heptachlors were observed with Σ OCPs concentration ranging from 1.41 to 63.8 ng g⁻¹
27 ww. DDTs were the predominant contaminants (0.9 to 61.9 ng g⁻¹ ww), followed by HCHs.
28 The predominance of DDTs may be attributed to their current use in vector control and
29 contamination from past usage. The estimated daily intakes (EDIs) of OCPs from all fish
30 species were much lower than the acceptable daily intakes (ADIs), indicating that
31 consumption of fish is at little risk to human health at present. However, the cancer risk
32 estimates in the area of concern and the hazard ratios (HRs) of HCHs, DDTs, and
33 heptachlors exceeded the threshold value of one, indicating daily exposure to these
34 compounds is a potential concern. This may result in a lifetime cancer risk greater than of 1
35 in 10⁶.

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41 Key words: Organochlorine pesticides, Fish, Lake Ziway, Risk assessment

42 **1. Introduction**

43 Organochlorine pesticides (OCPs) have been widely used and become a worldwide concern
44 due to their persistence, bioaccumulative potential, chronic toxicity, and potential negative
45 impacts on humans and wildlife (UNEP, 2001). It is known that most of the total intake of
46 pesticide residues by human beings is through the food chain (Martinez et al., 1997). Fish
47 are known to biomagnify pesticides from the surrounding environment (Mackay and Fraser,
48 2000), and transfer the pesticides to humans when consumed. Epidemiological studies
49 indicate that some of these compounds may be associated with cancers in humans (Snedeker,
50 2001; Beard, 2006; IARC, 2008), and also influence the concentration of thyroid hormones
51 (Meeker et al., 2007). Eskenazi et al. (2006) reported delays in neurodevelopment during
52 early childhood due to the impacts of prenatal exposure to dichlorodiphenyltrichloroethanes
53 (DDTs).

54 Although the use of OCPs has been banned or restricted, developing countries like Ethiopia
55 still use them for agricultural and health purposes, and as a consequence they can be found
56 in aquatic (Deribe et al., 2011; Yohannes et al., 2013a,b) and terrestrial ecosystems, for
57 example in cow's milk (Gebremichael et al., 2013). Because it is landlocked, Ethiopia is
58 highly dependent on lake aquatic environments for its economic development. The
59 Ethiopian Rift Valley region, encompassing seven principal lakes, is a densely populated
60 area confined with various agricultural activities where there is still an increasing trend of
61 pesticide usage (Amera and Abate, 2008). Moreover, Ethiopia has implemented indoor
62 residual spraying (IRS) with DDT for malaria control in the past few decades (WHO, 2007).
63 Approximately 400 metric tons of active-ingredient DDT per year is used for IRS in many
64 parts of the country including the Rift Valley, a malaria epidemic prone region (Biscoe et al.,

65 2005; Van den Berg, 2009). In addition, Ethiopia is one of the many African countries
66 burdened with the problem of obsolete pesticides, which have been accumulated since the
67 first imports in the 1960s (Haylamicheal and Dalvie, 2009). These were mostly
68 organochlorine compounds such as chlordane, DDT, dieldrin and lindane that are banned or
69 restricted in most countries. In this view, there is great likelihood that the Ethiopian Rift
70 Valley ecosystem is exposed to large amounts of pesticides.

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

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

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87 2. Materials and methods

88 2.1. Study area

89 The study area, Lake Ziway (surface area: 434 km²) is a shallow freshwater lake located in
90 the northern section of the Rift Valley (Fig. 1). It is fed by two inflowing rivers, the Meki
91 River from the north-west and the Katar River from the east, and drains towards the Lake
92 Abijata, through the Bulbula River. The lake has a large littoral zone containing emergent
93 and submergent vegetation, which provides feeding, breeding and nursery habitats for fish
94 (Admassu and Ahlgren, 2000; Erko et al., 2006). Lake Ziway contains different fish species
95 including Nile tilapia (*Oreochromis niloticus*), Redbelly tilapia (*Tilapia zillii*), African big
96 barb (*Barbus intermedius*), African sharptooth catfish (*Clarias gariepinus*), and Carp spp.
97 (*Carassius carassius* and *Carassius auratus*) (Lemma, 2005). Fisheries on Lake Ziway are
98 an open and easily accessible source of income and have always been a source of food and
99 income for the people living on the shores of the lake. The landings of Lake Ziway used to
100 be dominated by *O. niloticus*, but species of *C. gariepinus*, *T. zillii*, and *Carassius* spp. (*C.*
101 *carassius* and *C. auratus*) are increasingly becoming a part of the catch. The potential yield
102 of all the species of the lake is estimated to range between 2,500 and 6,680 tons/yr
103 (Spliethoff et al., 2009).

104 2.2. Sampling

105 A total of 100 individual fish belonging to *O. niloticus*, *T. zillii*, *Carassius* spp., and *C.*
106 *gariepinus* fish species of Lake Ziway were purchased from the local fishermen in January
107 2011. Samples were transported to Ziway fisheries research laboratory where the body size
108 and body weight were recorded. General information about the fish is given in Table 1.

109 Fishes were dissected to obtain dorsal muscles and stored at $-20\text{ }^{\circ}\text{C}$. The frozen samples
110 were then transported to Japan for analysis. Each individual sample was lyophilized,
111 homogenized separately and used for chemical analysis.

112 2.3. OCPs analysis

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

124 OCPs including DDTs (*o,p'*-DDT, *p,p'*-DDT, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD and
125 *p,p'*-DDD), hexachlorocyclohexanes (HCHs; α -, β -, γ - and δ -HCH), heptachlors (HPTs;
126 heptachlor, *cis*- and *trans*-heptachlor epoxide), chlordanes (CHLs; *cis*- and
127 *trans*-chlordane, *cis*- and *trans*-nonachlor and oxychlordane), drins (aldrin, dieldrin and
128 endrine) and hexachlorobenzene (HCB) were analyzed by gas chromatography equipped
129 with an electron capture detector (Shimadzu GC-2014, Kyoto, Japan). An ENV-8MS
130 capillary column (30 m \times 0.25 mm i.d., 0.25 μm film thickness) with splitless injection was

131 used to separate OCPs. One μL of each sample was injected. The column oven temperature
132 was initially set at $100\text{ }^\circ\text{C}$ for 1 min, increased to $180\text{ }^\circ\text{C}$ at $20\text{ }^\circ\text{C min}^{-1}$ and then to $260\text{ }^\circ\text{C}$
133 at $4\text{ }^\circ\text{C min}^{-1}$, which was held for 5 min. The injector and detector temperatures were $250\text{ }^\circ\text{C}$
134 and $310\text{ }^\circ\text{C}$, respectively. Helium at a flow rate of 1.0 mL min^{-1} and nitrogen at 45 mL min^{-1}
135 were used as carrier gas and make-up gas, respectively.

136 *2.4. Quality control and quality assurance*

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

148 *2.5. Risk assessment*

149 Various international organizations have subsequently established a series of standards and
150 instructions to estimate the risks to human health from environmental pollutants in fish
151 (USEPA, 2013). A straight forward risk assessment is performed through comparison with
152 the levels set by laws and guidelines. However, this comparison was made without the

153 consideration of factors like different eating habits and consumption rates. Thus, in this
154 study, we investigated the risk assessment by two approaches. To comprehensively evaluate
155 the health risk assessment, the 50th and 95th percentile measured concentrations were used.

156 *2.5.1. Estimated daily intake (EDI)*

157 Estimated dietary intakes of OCPs were calculated as follows:

$$158 \quad EDI = \frac{C \times DR}{BW} \quad (1)$$

159 where C is the measured concentration of OCPs (ng/g ww), DR is average daily
160 consumption rate of fish (g/day) and BW is body weight (kg), which was set at 60 kg (WHO,
161 2010). The average daily consumption rate was derived from FAO (2011). Though
162 Ethiopians are traditionally meat eaters, eating habits have been shifting in favor of fish in
163 areas and communities where there is regular and sufficient supply. In those communities,
164 annual fish consumption can exceed 10 kg/person (FAO, 2011). Thus, the DR was estimated
165 at 30 g/day per person.

166 *2.5.2. Potential carcinogenic risks*

167 To assess public health risks posed through fish consumption, the cancer risk estimates and
168 hazard ratios (HRs) were assessed on the basis of the guidelines of the United States
169 Environmental Protection Agency (USEPA). Cancer risks associated with OCPs were
170 estimated by combining the exposure dose and slope factor (USEPA, 2005). A public
171 screening criteria for carcinogens is set at a carcinogenic risk level of 10^{-6} . Carcinogenic
172 risks below 10^{-6} are considered acceptable, while carcinogenic risks above 10^{-4} are
173 considered unacceptable. An area of concern is present between 10^{-6} and 10^{-4} (USEPA,
174 2005).

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

$$177 \quad HR = \frac{EDI}{BMC} \quad (2)$$

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

183 2.6. *Statistical analysis*

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

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195 3. Results and discussion

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

202 3.1. Levels of OCPs

203 OCPs were detected in muscle samples of all fish species, indicating their widespread
204 contamination in Lake Ziway. DDTs, HCHs, HPTs, and CHLs were detected with varying
205 concentrations (Table 2). The total concentrations of OCPs ranged from 1.41 to 63.8 ng g^{-1}
206 ww, with a mean concentration of $7.72 \pm 6.90 \text{ ng g}^{-1}$ ww. The highest concentrations of
207 OCPs were found in *C. gariepinus* ($p < 0.05$), which is a carnivorous fish and found at top
208 trophic position. Among the OCPs analyzed, DDTs were the most commonly detected and
209 were dominant in all samples. It accounted for $64.5 \pm 10\%$ (SD) (ranging from 52 to 78%)
210 of the total OCPs. In general, the contamination pattern of OCPs in fish samples detected in
211 this study was in the order of DDTs > HCHs > CHLs \cong HPTs. This result indicates the high
212 degree of exposure to DDTs in biota from the Ethiopian Rift Valley region, which is most
213 likely due to recent use of DDT for malaria control through IRS (Biscoe et al., 2005; Van
214 den Berg, 2009) as well as from past usage and spills from obsolete pesticides
215 (Haylamicheal and Dalvie, 2009). It is also reported that DDT is still ongoing use by farmers
216 in the region (Amera and Abate, 2008). Log transformed OCPs show a positive correlation

217 with total length for all fish species ($R^2 = 0.18$; $p < 0.001$), whereas no significant correlation
218 was found between lipid content and concentration of OCPs ($R^2 = 0.00$; $p = 0.140$).

219 3.1.1. DDTs

220 DDT and its metabolites were detected in all fish species (Table 2). Concentrations of DDTs
221 in the muscle tissue are found at large variations ranging from 0.77–61.9 ng g⁻¹ ww (mean
222 concentration of 5.27 ± 6.73 ng g⁻¹ ww). *C. gariepinus* with 9.0 ± 11.7 ng g⁻¹ ww and *O.*
223 *niloticus* with 2.33 ± 1.09 ng g⁻¹ ww had the highest and lowest concentrations, respectively.
224 This may be attributed to their different feeding habits because *C. gariepinus* is a
225 carnivorous and *O. niloticus* is almost herbivorous fish species (Table 1). Overall, the
226 concentrations of DDTs were higher than those of other OCPs. The possible reasons for the
227 presence of high level of DDTs in the region may be its current use in vector control, illegal
228 usage and contamination from obsolete pesticides (Haylamicheal and Dalvie, 2009; Van den
229 Berg, 2009). Reports from other African lakes also indicate much higher levels of DDT in
230 aquatic organisms compared to other OCPs. In Lake Koka, Ethiopia DDT ranged from
231 0.05–72.53 ng g⁻¹ ww and it was the predominant pesticide by a factor of 10 when compared
232 to the other OCPs (Deribe et al., 2011) and in Lake Malawi DDT concentrations were up to
233 60 times higher than other OCPs (Kidd et al., 2001). Concentrations of DDTs found in this
234 study (mean concentration of 2.33 to 9.0 ng g⁻¹ ww) are higher than those found in Lake
235 Victoria, Uganda (mean 1.39 to 1.67 ng g⁻¹ ww) (Kasozi et al., 2006). However, they are
236 lower than those in fish from Southern Lake Victoria, Tanzania (mean 15 and 20 ng g⁻¹ ww)
237 (Henry and Kishimba, 2006) and fish from Lake Burullus, Egypt (mean 2.76 to 45.13 ng g⁻¹
238 ww) (Said et al., 2008), and comparable to fish from Lake Awassa, Ethiopia with Σ DDTs

239 mean concentration of 1.80 and 9.0 ng g⁻¹ ww for *O. niloticus* and *C. gariepinus*,
240 respectively (Yohannes et al., 2013a). Direct comparisons should be made with caution
241 since these studies were conducted on different species. With all the data pooled together,
242 the concentration of DDTs (log transformed) was significantly correlated ($R^2 = 0.18$; $p <$
243 0.001) to total length of the fish, but not with % lipid content ($R^2 = 0.02$; $p = 0.139$).

244 The composition profiles of DDTs in the muscle tissue of the four fish species are shown in
245 Fig. 2. Among the metabolites, *p,p'*-DDE was the predominant congener, accounting for
246 $55\% \pm 15.72$ (from 41 to 77%), followed by *p,p'*-DDT ($15\% \pm 6.42$), and *p,p'*-DDD (13%
247 ± 4.80). The proportion of *p,p'*-DDE was higher in *C. gariepinus* than in the others,
248 comprising 77% of the mean DDT concentrations, showing that *C. gariepinus* found at high
249 trophic level is more likely feeding on prey (both fish and invertebrates) and accumulates
250 DDE, a more degraded form of DDT. In addition, this may be attributed to the more
251 persistent nature of *p,p'*-DDE, and to its rate of biomagnification along the food chain in
252 freshwater ecosystems (Rognerud et al., 2002). In contrast, the proportions of parent
253 compounds (*o,p'*- and *p,p'*-DDT) in *O. niloticus* (29.8%), *T. zillii* (32.6%), and *Carassius*
254 spp. (34.4%) were higher than in *C. gariepinus* (11.7%). This may be probably as a result of
255 more efficient transfer of DDT to phytoplankton and macrophyte consuming herbivorous
256 fish (Zhou et al., 2007). Technical DDT generally contains 75% *p,p'*-DDT, 15% *o,p'*-DDT,
257 5% *p,p'*-DDE, and <5% others. DDT can be metabolized into DDE under aerobic
258 conditions or into DDD in anaerobic environments (Hitch and Day, 1992). Thus, the ratio of
259 $(p,p'-DDE + p,p'-DDD)/\sum DDTs$ can indicate past or recent usage of technical DDT. A ratio
260 greater than 0.5 generally indicates long term biotransformation of DDT, whereas a ratio of
261 less than 0.5 may indicate recent input of DDT. In the present study, the ratio ranged from

262 0.55 to 0.87, suggesting that DDTs in fish from Lake Ziway were mainly due to historical
263 use, and to its current use for vector control in the region since the Ethiopian government
264 decided to continue using DDT because of the high incidence of malaria and the
265 corresponding fatalities (Biscoe et al., 2005; WHO, 2007).

266 3.1.2. HCHs

267 HCHs were the second most prevalent OCP contaminants in the studied fish species and
268 accounted for 17% (from 10% to 25%) of the total OCPs measured. The levels of HCHs in *T.*
269 *zillii* ($1.45 \pm 0.61 \text{ ng g}^{-1} \text{ ww}$) and *O. niloticus* ($1.26 \pm 1.04 \text{ ng g}^{-1} \text{ ww}$) were significantly
270 higher ($p < 0.05$) than that of *Carassius* spp. ($0.61 \pm 0.31 \text{ ng g}^{-1} \text{ ww}$), and *C. gariepinus*
271 ($0.72 \pm 0.47 \text{ ng g}^{-1} \text{ ww}$) (Table 2). A negative relationship ($R^2 = 0.07$; slope = -0.02 ; $p <$
272 0.01) between log transformed ΣHCH and length of fish was found, whereas no significant
273 relationship ($p > 0.05$) was found between lipid content and concentration of HCHs. Of the
274 HCHs measured, α and γ -HCHs were frequently detected and the γ -isomer (lindane) was
275 the predominant, accounting for 60% on an average of ΣHCHs in the muscle tissue. The
276 higher γ -HCH concentrations in the samples indicate current usage of lindane around the
277 lake. A recent study in the Ethiopian rift valley region also showed high concentrations of
278 lindane in tissues taken from cattle with the highest level of $0.14 \text{ mg kg}^{-1} \text{ ww}$ in liver
279 samples obtained from Holeta, Ethiopia (Letta and Attah, 2012). In general, the
280 concentrations of HCHs in this study are lower than those in fish from Lake Taabo, Cote
281 d'Ivoire (Roche et al., 2007), and fish from Lake Burullus, Egypt (Said et al., 2008).

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284 3.1.3. CHLs and HPTs

285 With regard to the residual levels of CHLs, *trans*-chlordane, *cis*-chlordane and
286 *trans*-nonachlor were detected in most of the samples as they are the dominant constituents
287 in technical chlordane (Xu et al., 2004) whereas oxy-chlordane was rarely encountered. The
288 presence of these compounds in the environment at relatively high concentrations as
289 compared to oxy-chlordane likely indicates recent inputs of chlordane to the environment.
290 The mean residual levels of CHLs in the muscle tissues in the present study ranged from
291 0.40-0.91 ng g⁻¹ ww (Table 2). The use of chlordane is permitted in Ethiopia as a general
292 insecticide (Ritter et al., 1995). Chlordane is imported to Ethiopia under the regulation of
293 Ministry of Agriculture for termiticide usage only (EICDCR, 2004).

294 It was found that HPTs (*cis*-heptachlor epoxide and *trans*-heptachlor epoxide) were also
295 present in most of the fish collected. The *cis* and *trans*-heptachlor epoxides predominated
296 with a mean concentration of 0.28 ± 0.27 ng g⁻¹ ww and 0.31 ± 0.21 ng g⁻¹ ww, respectively
297 (Table 2). The highest residual levels of HPTs (0.90 ± 0.35 ng g⁻¹ ww) were found in *O.*
298 *niloticus*, the herbivorous fish species.

299 3.2. Human health risk assessment

300 Fish consumption has been proven to be one of the major routes of human exposure to
301 organic contaminants. To better understand the concentration levels, the concentrations of
302 OCPs in the present study were evaluated against international existing limits. The EDI was
303 calculated and compared with the acceptable daily intake (ADI) recommended by the Food
304 and Agriculture Organization and the World Health Organization (FAO/WHO) Joint
305 Meeting on Pesticide Residue (WHO, 2010). To comprehensively evaluate risk exposure,

306 the 50th and 95th percentile EDIs of OCPs for each fish species were calculated. The EDIs of
307 OCPs expressed as nanogram per kilogram body weight per day (ng/kg bw/d) through
308 consumption of fish for the population are presented in Table 3. EDI of HCHs, HPTs, CHLs,
309 and DDTs at both exposure levels were far below the ADI, indicating that consumption of
310 fish at present would not pose a human health risk.

311 A carcinogenic risk assessment for OCPs was conducted using cancer risk estimates and
312 HRs at the 50th and 95th percentile measured concentrations. As shown in Table 4,
313 heptachlors showed much higher carcinogenic risk than other OCPs in all fish species.
314 Regard to DDTs, the cancer risk for the 50th exposure level ranged from 3.7 in *O. niloticus*
315 to 8.4×10^{-4} in *C. gariepinus* suggested that a person would have a chances of about 4 and 8
316 in 10000 to develop cancer from DDTs, respectively. This carcinogenic risk increased from
317 7.6 to 36×10^{-4} on 95th exposure level, which was unacceptable for human health. In general,
318 the overall cancer risk estimates for all OCPs ranged from 0.7×10^{-4} to 36×10^{-4} on both the
319 50th and 95th exposure levels, and when compared to a target risk of $>1 \times 10^{-4}$, are
320 considered unacceptable. Thus, the carcinogenic risk of HCHs, HPTs, CHLs and DDTs
321 among humans at present should be of concern.

322 HRs based on the 50th and 95th percentile exposure levels were assessed in each fish species
323 and the results are shown in Fig. 3. HRs for cancer risk based on the 95th percentile
324 concentrations of HCHs, HPTs, and DDTs were greater than one. The HRs for the OCPs
325 followed almost the following sequence: HPTs > DDT \geq HCHs > CHLs. For all fish species,
326 the HRs for HPTs were greater than one, showing that consuming fish is harmful to humans.
327 Based on landings, *O. niloticus* is the most caught fish in Lake Ziway. The carcinogenic risk
328 due to HCHs for this fish species in also greater than one while for DDTs is less than one.

329 However, for *T. zillii*, *Carassius* spp. and *C. gariepinus* the HRs for DDTs were greater than
330 one. In general, cumulative daily exposure to OCPs because of fish consumption would
331 yield a lifetime cancer risk of greater than one in a million. The results indicate that these
332 compounds may be of particular concern because they are still in use.

333

334 **4. Conclusion**

335 This is the first study reporting on the levels and risk assessment of some OCPs in the most
336 commonly caught fish species from the Ethiopian Rift Valley lake – Lake Ziway. The rift
337 valley region is a populated area that is influenced by heavy pollution stemming from urban,
338 agricultural and industrial activities. Our results indicated the presence of HCHs, HPTs,
339 CHLs and DDTs with varying concentrations among the fish species. The overall conclusion
340 of the evaluation is that DDTs were the main abundant pollutants, attributed to its current
341 use in vector control and contamination from past usage. Dietary intakes estimated from the
342 50th and 95th percentile exposure level were far below ADIs. In contrast, the calculated
343 cancer risk estimates and HRs of the studied fish species indicated that the consumption of
344 most of the fish species could cause cancer as HR for cancer risk based on the 95th percentile
345 concentrations of HCHs, HPTs and DDTs was greater than one. In this study, only fish and
346 some OCPs were investigated to assess the risk. The consumption of water, vegetables, and
347 animal meat, and the levels of other environmental pollutants were not considered.
348 Therefore, the actual health risk for local people through dietary intake could be higher.

349

350

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365 **Conflict of interest**

366 The authors declare no conflicts of interest.

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

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

492 *N* = number of samples.

493 Mean ± standard deviation (SD).

494 ^a Means with different letter superscript are significantly different (Tukey test is applied; *p* < 0.05).

496 * Reference: Deribe et al., 2013.

497 **Table 2**
 498 Levels of OCPs (ng g⁻¹ 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
∑HCHs	^a 1.26 ± 1.04	^a 1.45 ± 0.61	^b 0.61 ± 0.31	^b 0.72 ± 0.47
*	0.29–5.10	0.91–3.54	0.16–1.85	0.27–2.01
Heptachlor	ND	ND	ND	ND
<i>cis</i> -heptachlor-epoxide	0.57 ± 0.27	0.08 ± 0.10	0.24 ± 0.11	0.23 ± 0.11
<i>trans</i> -heptachlor-epoxide	0.32 ± 0.09	0.20 ± 0.02	0.31 ± 0.23	0.42 ± 0.29
∑HPTs	^a 0.90 ± 0.35	^c 0.42 ± 0.11	^{b,c} 0.59 ± 0.27	^b 0.65 ± 0.28
*	0.44–2.27	0.19–0.69	0.20–1.52	0.34–1.56
oxy-chlordane	0.04 ± 0.04	0.16 ± 0.07	0.11 ± 0.06	0.10 ± 0.07
<i>cis</i> -chlordane	0.18 ± 0.04	0.26 ± 0.11	0.12 ± 0.07	0.16 ± 0.05
<i>trans</i> -chlordane	0.16 ± 0.05	0.20 ± 0.03	0.26 ± 0.21	0.29 ± 0.12
<i>trans</i> -nonachlor	0.03 ± 0.07	0.29 ± 0.10	0.37 ± 0.59	0.35 ± 0.23
∑CHLs	^b 0.40 ± 0.10	^a 0.91 ± 0.22	^a 0.87 ± 0.82	^a 0.90 ± 0.25
*	0.17–0.61	0.65–1.32	0.19–4.00	0.58–1.50
<i>p,p'</i> -DDE	1.32 ± 0.81	1.89 ± 2.02	2.42 ± 1.60	6.92 ± 11.47
<i>o,p'</i> -DDE	0.10 ± 0.08	0.35 ± 0.12	0.26 ± 0.36	0.12 ± 0.10
<i>p,p'</i> -DDD	0.40 ± 0.21	0.85 ± 0.41	0.58 ± 0.35	0.79 ± 0.68
<i>o,p'</i> -DDT	0.43 ± 0.17	0.53 ± 0.21	0.68 ± 0.74	0.43 ± 0.11
<i>p,p'</i> -DDT	0.31 ± 0.18	0.77 ± 0.66	0.57 ± 0.73	0.62 ± 0.40
∑DDTs	^b 2.33 ± 1.09	^{a,b} 4.38 ± 2.67	^{a,b} 4.55 ± 2.80	^a 9.0 ± 11.7
*	0.90–5.12	1.35–13.2	0.77–10.6	2.36–61.9
∑OCPs	^b 4.89 ± 1.85	^{a,b} 7.16 ± 2.63	^{a,b} 6.62 ± 3.71	^a 11.2 ± 11.7
*	2.46–10.9	3.59–15.2	1.41–15.0	4.00–63.8

499 ND = below detection limit.

500 Mean ± standard deviation (SD).

501 * Min–max.

502 Values with different letters (a, b, c) within a row are significantly different at $p < 0.05$ level
 503 (Tukey test is applied).

504 **Table 3**

505 Estimated daily intake values (ng/kg bw/d) of OCPs through the studied fish species by human.

ADI	50 th (95 th) percentile measured concentrations (ng/g ww)				50 th (95 th) 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 5000 ^a	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 10000	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)

506 ADI = Acceptable daily intake (ng/kg bw/d).

507 ^a for γ -HCH. (WHO, 2010).

508

509 **Table 4**

510 Cancer risk estimates for HCHs, HPTs, CHLs and DDTs.

OCPs	Cancer slope factor * [per (mg/kg day)]	50 th (95 th) percentile cancer risks (x 10 ⁻⁴)				511 512 513 514 515 516 517 518 519	^a for γ - HC H. *Ca ncer slop e fact
		<i>O. niloticus</i>	<i>T. zillii</i>	<i>Carassius</i> spp.	<i>C. gariepinus</i>		
HCHs	1.1 ^a	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)		

520 sources were from the United States Environmental Protection Agency (USEPA, 2012).

521

522 Figure captions

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

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

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

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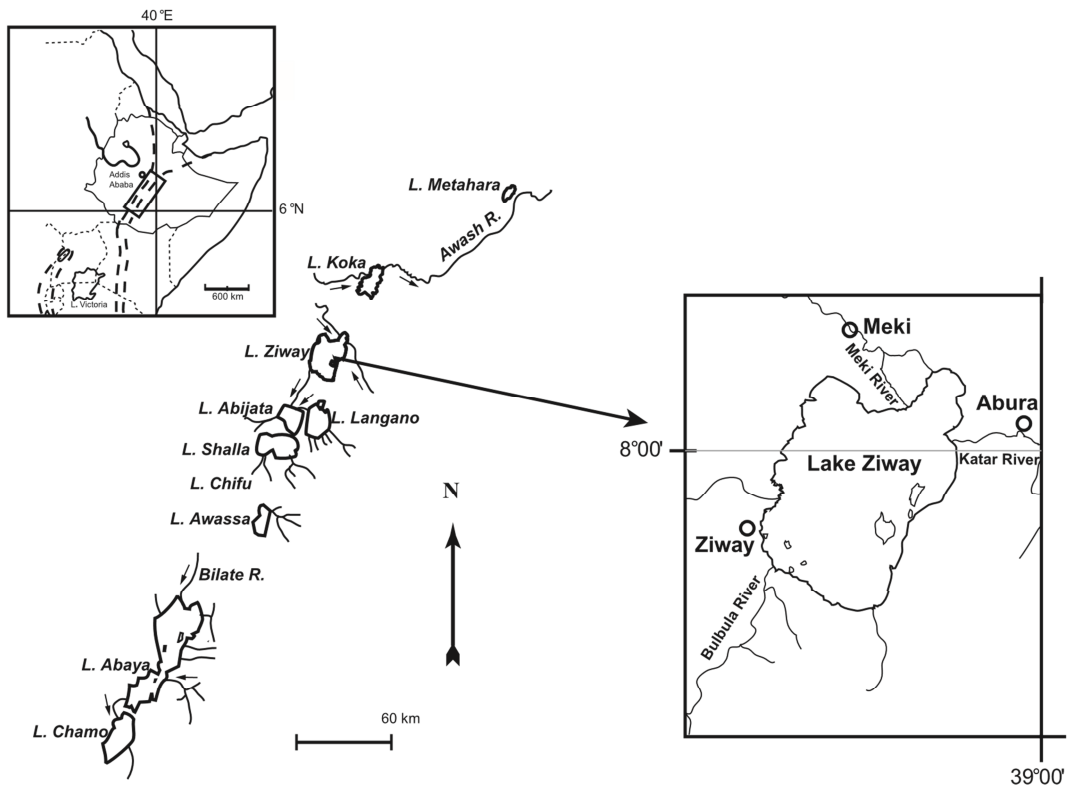


Fig. 1.

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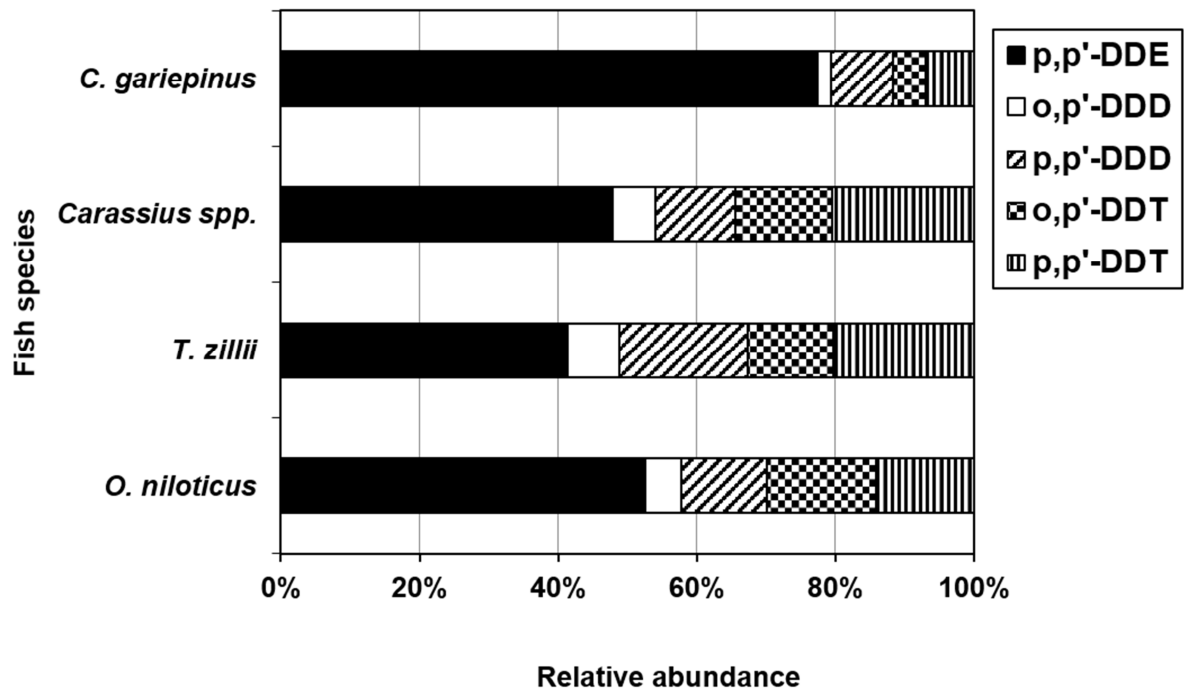


Fig. 2.

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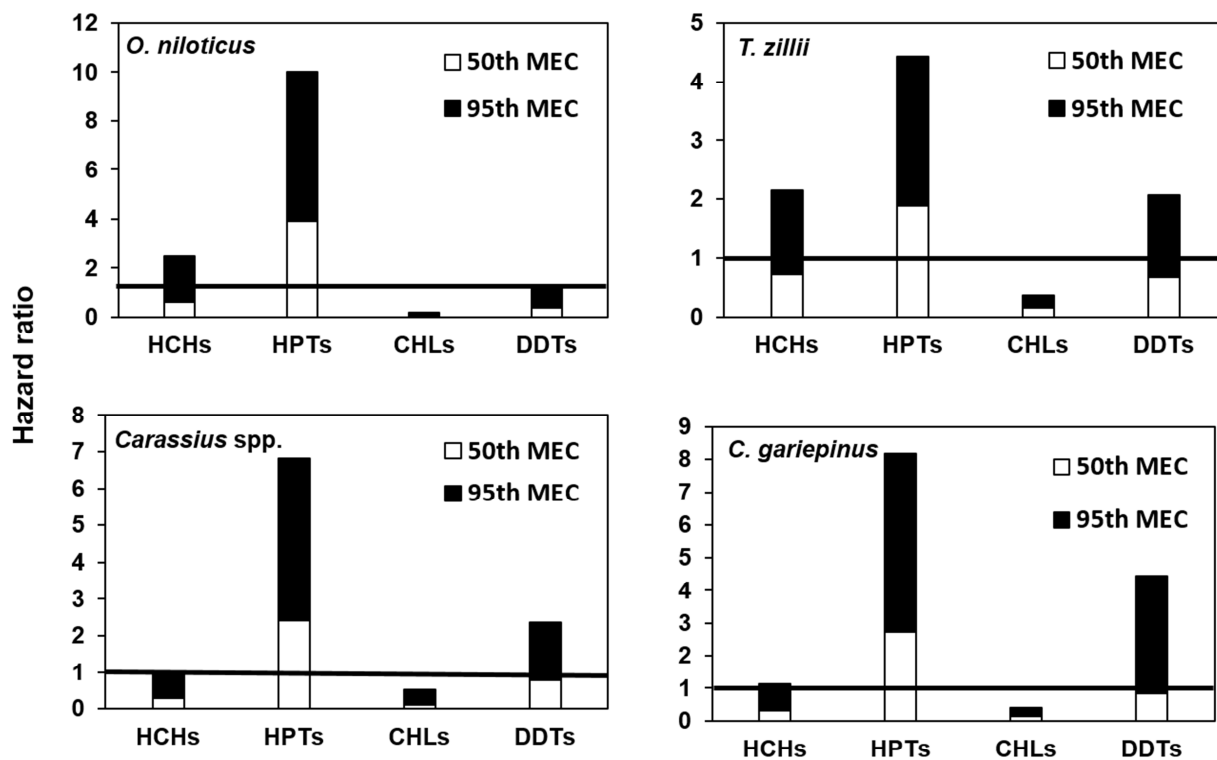
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Fig. 3.

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