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# Biomagnification of DDT and its metabolites in four fish species of a tropical lake

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ABSTRACT

The concentrations and biomagnifications of dichlorodiphenyltrichloroethane (DDT) and its metabolites were examined in four fish species (*Clarias gariepinus, Oreochromis niloticus, Tilapia zillii,* and *Carassius auratus*) from Lake Ziway, Rift Valley, Ethiopia. Paired stomach content analysis, and stable isotope ratio of nitrogen ($\delta^{15}$N, ‰) and carbon ($\delta^{13}$C, ‰) were used to study the trophic position of the fish species in the lake. 4,4′-DDE, 4,4′-DDT and 4,4′-DDD were the main DDTs identified in the fish samples, with 4,4′-DDE as the most predominant metabolite, with mean concentration ranging from 1.4 to 17.8 ng $g^{-1}$ wet weight (ww). The concentrations of DDTs found in fish from Lake Ziway were, in general lower than those found in most studies carried out in other African Lakes. However, the presence of DDT in all tissue samples collected from all fish species in the lake indicates the magnitude of the incidence. Moreover, the observed mean 4,4′-DDE to 4,4′-DDT ratio below 1 in *C. auratus* from Lake Ziway may suggest a recent exposure of these species to DDT, indicating that a contamination source is still present. 4,4′-DDE was found to biomagnify in the fish species of the lake, and increases with trophic level, however, the biomagnification rate was generally lower than what has been reported from other areas. Significantly higher concentrations of 4,4′-DDE were found in the top consumer fish in Lake Ziway, *C. gariepinus* than in *O. niloticus* ($t=2.6$, $P<0.01$), *T. zillii* ($t=2.5$, $P<0.02$) and *C. auratus* ($t=2.2$, $P<0.03$).



## 1. Introduction

DDT is an organochlorine pesticide that has been used for vector and pest control since World War II (Foreman and Gates, 1997). This pesticide is grouped under the persistent organic pollutants (POPs) due to its toxic, lipophilic and persistent nature (Burreau et al., 2004; Holden, 1966; Jones and de Voogt, 1999). Coupled with its ability to bioaccumulate and magnify in the food chain (Alexander et al., 2007; Burreau et al., 2004; Mackay and Fraser, 2000; Rognerud et al., 2002), it has potential impact on top predator species, including humans. DDT and some of its metabolites are reported to affect the nervous and reproductive systems, and cause cancer (Beard, 2006; Kelce et al., 1995; McBlain, 1987). While the use of DDT has been limited internationally, some countries continued to use it in disease control programs as it was found a valuable short term line of attack for controlling malaria (Goldberg, 1991). In recognition of this pressing need, SC permits the production and use of DDT for disease vector control only by notifying the convention secretariats, provided that no safe, effective, and affordable alternatives are locally available (Stockholm Convention on Persistent Organic Pollutants, 2008).

Technical grade DDT is mainly a mixture of 4,4′-DDT (85 percent) and 2,4′-DDT (15 percent). Both DDE (1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene) and DDD (1,1-dichloro-2,2-bis (4-chlorophenyl)ethane) exist as impurities in commercial DDT formulations. In the environment, DDT breaks down to form DDE or DDD (Foght et al., 2001; Pirnie et al., 2006; Sayles et al., 1997). DDT may enter rivers and lakes mainly through industrial release point sources, as runoff from agricultural fields, as well as from atmospheric deposition due to volatilization (Binelli and Provini, 2003; Schwarzbauer et al., 2001). DDT, DDD and DDE are strongly retained by soils, sediments, and biota lipids due to their low aqueous solubility and high octanol–water partitioning

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coefficients. 4,4′-DDE can often account for 70 percent of the total DDT in fish (Schmitt et al., 1990). The higher accumulation of 4,4′-DDE than the other metabolites is attributed to mixed-function oxidases that may have induced the dechlorination of 4,4′-DDT to 4,4′-DDE. The ratio of 4,4′-DDE to 4,4′-DDT is a helpful tool in revealing the significance of the degradation of DDT and to evaluate the current use of DDT in the given region (Strandberg and Hites, 2001). However, this method is limited in regions where dicofol is used. This is because dicofol contains high levels of DDT as an impurity (Qiu and Zhu, 2010).

There are two main routes by which fish can bioaccumulate chemicals in their natural aquatic habitat: (i) from water via body surfaces (e.g. gills) and (ii) through the diet (Burreau et al., 2004; Campbell et al., 2000; Holden, 1966). Stomach content analyses and stable nitrogen isotope ratio ($\delta^{15}$N) provide complementary information which can be used in analysis of the trophic transfer and biomagnification rate of persistent contaminants, including DDTs (Rognerud et al., 2002; Sharma et al., 2009). It is well established that lipophilic compounds such as DDT preferentially accumulate in lipids of fishes and other animals (Mackay and Fraser, 2000), and the extent of accumulation is greater in fish that have high lipid content (Muir et al., 1990).

The Ethiopian Rift Valley Lakes (ERVLs) are the most northern part of the East African Rift Valley Lakes. In Central Ethiopia, the Great Rift Valley splits the Ethiopian highlands into northern and southern halves, and the ERVLs occupy the floor of the rift valley between the two highlands. Most lakes are highly productive and well known for their aquatic diversity and indigenous populations of edible fish species (Golubtsov et al., 2002). With changing environmental conditions under increasing anthropogenic influences, the nature of the Ethiopian Rift Valley Lakes is also changing.

Due to the intensive agricultural and deforestation activities in the catchments of the Ethiopian Rift Valley Lakes (Zinabu, 2002; Zinabu and Elias, 1989), there is a risk of chemical pollution from fertilizers and pesticides. Run off and erosion from the surrounding catchment could release pesticides (e.g. DDTs) sequestrated in the soil to the lake may enter the food chain, and reaching out to the fish. Hence, the abundance and quality of commercially important fish species, an important ecosystem service of the Rift Valley Lakes, may be at risk. Furthermore, consumption of contaminated fish is one of the main exposure routes to toxic organic chemicals like DDT for humans (e.g. Han et al., 2000; Svensson et al., 1995). However, the level and extent of DDTs contamination in fish species at various trophic levels, has not been studied. The objective of this study is therefore to determine the concentration levels of DDTs and their biomagnifications in relation to the trophic position of fish species from Lake Ziway, which is one of the important Ethiopian Rift Valley Lakes.

## 2. Material and methods

### 2.1. Description of the study area

The study area, Lake Ziway, is located in the Rift Valley in the southeastern part of Ethiopia, at 1636 m a.s.l. (coordinates 7° 52′N and 38°4 5′E) (Fig. 1). It is part of 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 (Vallet-Coulomb et al., 2001). There are two inflowing rivers, the Meki River from the north-west, and the Ketar River from the east. The lake drains towards the Lake Abiyata, through Bulbula River. The climate of the region is characterized by bimodal rainfall distribution with short-term, highly variable, relatively low rain fall from February to June, and higher rain fall from July to September (Zegeye et al., 2006). The mean annual air temperature is 25.5 °C, and the mean annual rainfall is about 702 mm (Zegeye et al., 2006). The pH of the lake ranges from 7 to 8, and the average conductivity is about 400 μS cm$^{-1}$, which is low compared to most Ethiopian Rift Valley Lakes (Erko et al., 2006; Zinabu et al., 2002).

The lake has an extended littoral zone, containing emergent and submerged macrophytes, which provide feeding, breeding, and nursery habitats for fish (Admassu and Ahlgren, 2000; Erko et al., 2006). 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 sharptooth catfish (*Clarias gariepinus*), common carp (*Cyprinus carpio*), Golden carp (*Carassius auratus*) and *Tilapia zillii* (Negassa and Getahun, 2003). The lake has long been used as a resource of water supply for small scale irrigation, domestic water use, and fisheries. The recent expansion of floriculture industries around the lake may discharge untreated effluents directly into the lake, and as a result, excessive fertilizer and pesticide residues from the greenhouses may deteriorate the water quality as well as the aquatic life.

### 2.2. Sampling

Fish sampling was carried out between February and April 2008, partly by purchasing fish from the local fishermen upon landing, and partly by gillnetting, using experimental gill nets with mesh sizes from 5 to 45 mm (bar mesh). The total length (cm), weight (g) and sex of each fish were recorded (Table 1). The contents of the esophagus and stomach/first part of intestine were removed and preserved in 96 percent ethanol. Muscle samples were taken from each specimen, following the procedures in the EMERGE protocol, as described by Rosseland et al. (2001), and frozen. The frozen samples were transported to Norway for analysis of DDTs, stable isotopes of carbon ($^{13}$C and $^{12}$C) and nitrogen ($^{15}$N and $^{14}$N). A total of 93 (40 females and 53 males) samples from four fish species (*C. auratus, C. gariepinus, O. niloticus,* and *T. zillii* ) were examined and analyzed with respect to DDTs, and stable isotopes ratios of nitrogen and carbon (Table 1).

### 2.3. Stomach content analyses

The stomach content analyses were done at Hawassa University, Department of Applied Biology, Awassa, Ethiopia. A total of 143 stomach contents were examined for food composition. The relative importance and contribution of each food item to the diet of each fish species was determined using the frequency of occurrence method and the percent composition by volume (percent) – volumetric analyses (Hyslop, 1980). The identification of the stomach contents was carried out using either a dissecting microscope for larger items, or by a compound light microscope for smaller items such as phytoplankton. The following food item categories were identified: phytoplankton (blue green algae, green algae and diatoms), macrophytes, detritus, zooplankton, aquatic insects, ostracods, gastropods and fish.

### 2.4. Stable isotope analyses

Stable isotope analyses were carried out at the Environmental Chemistry Section, Department of Plant and Environmental Sciences, Norwegian University of Life Sciences (UMB). The stable isotopes of nitrogen ($^{15}$N and $^{14}$N) and carbon ($^{13}$C and $^{12}$C) were analyzed in homogenized and freeze-dried muscle samples subjected to combustion in a Flash Elemental Analyzer (EA) as described in Desta et al. (2007) and Sharma et al. (2009). The isotopic ratios ($^{15}$N/$^{14}$N, $^{13}$C/$^{12}$C) were expressed in delta-values as follows:

$$\delta^{15}\text{N and } \delta^{13}\text{C } (‰) = [(R_{\text{Sample}}/R_{\text{Standard}})-1]*1000$$

where, $R = {}^{15}\text{N}/{}^{14}\text{N}$ for $\delta^{15}$N or $R = {}^{13}\text{C}/{}^{12}\text{C}$ for $\delta^{13}$C

### 2.5. Lipid content analyses

The relative lipid content (percent) in the fish muscle tissue was determined by a gravimetric method adopted from Lee et al. (1996). The method was tested using Standard Reference Material (SRM) 1946: Lake Superior fish tissue from USA National Institute Standard and Technology (NIST). The standard reference material was analyzed according to the proposed method and the result was within the certified range. About 5 g of fish tissue was defrosted, chopped into pieces, weighted and transferred into a 50 mL centrifuge tube. Each sample was completely homogenized using 25 mL of methyl tertbutyl ether (MTBE) and blended for 2 min with Polytron (Kinematica AG) at a moderate speed. To maintain a moderate and constant speed during blending is important because the high speed resulted in solvent vaporization and temperature rise. The extraction was repeated on the remaining, using 25 mL of MTBE to extract the fat completely. The extract was transferred to the same flask, and the volume was adjusted to 50 mL. Five milliliters of the extract (triplicate) was taken into a pre-weighted beaker. The sample was allowed to evaporate completely over night before the weight was determined, and finally the percentage of relative lipid content was calculated.

### 2.6. DDTs analyses

The DDTs (2,4′-DDE, 4,4′-DDE, 2,4′-DDD, 4,4′-DDD, 2,4′-DDT and 4,4′-DDT) were analyzed at the laboratory of Norwegian Institute for Agricultural and