Biological and chemical monitoring of the ecological risks of pesticides in Lake Ziway, Ethiopia

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HIGHLIGHTS
- Organophosphates and pyrethroids pesticides were ubiquitously detected in Lake Ziway.
- Water concentrations of many pesticides pose high acute risks to aquatic organisms.
- Arthropods and fishes are expected to be highly affected by mixtures of pesticides.
- Agricultural and urban activities are the main water pollution drivers.
- EPT richness index is an effective tool to assess ecological status of surface water.

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ABSTRACT
Lake Ziway, a freshwater lake located in Ethiopia, is under the pressure of pesticide and nutrient pollution due to agricultural activity and urbanization. This study has analysed concentrations of insecticides, fungicides and nutrients in water and sediment samples of Lake Ziway taken in the wet and dry season at 13 sites expected to be under different environmental stress and assessed their expected ecological impacts. Malathion, dimethoate, metalaxyl, diazinon, chlorpyrifos, fenitrothion and endosulfan were detected in more than half of the water samples, while diazinon, α-cypermethrin and endosulfan were frequently detected (>25%) in sediment samples. Higher levels of physicochemical parameters were observed at sample locations proximate to agricultural and urban activities. Risk quotients (RQ) and multi-substance Potentially Affected Fraction (msPAFRA) were calculated to assess the ecological risk of individual and mixture of pesticides, respectively. The majority of the pesticides detected in the water of the lake showed a potential acute risk (RQ > 1), specifically the insecticides chlorpyrifos, λ-cyhalothrin and α-cypermethrin for which high potential acute risks were calculated using a 2nd tier risk assessment. Levels of pesticides in sediment showed low ecological risks. Arthropods and fishes are expected to be highly affected by mixtures of pesticides (msPAFRA = < 1–80%) detected at locations that are proximate to smallholders’ farms, and receive largescale farms’ wastewater and at sites where inflow rivers join the lake. Macroinvertebrates based redundancy analysis showed the effectiveness of EPT richness to assess ecological status of the lake. Training for smallholder farmers on pesticides safety and usage, and implementation of improved effluent management mechanisms by floriculture farms are urgently needed intervention measures to reduce the pollution.

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1. Introduction
The agricultural sector of Ethiopia has recorded a significant growth, where the total crop yield grew from 142 million tonnes in 2004/05 to 320 million tonnes in 2014/15 (Bachewe et al., 2018). The growth is mainly due to the expansion of agriculture to new...
lands and the intensification of the use of agrochemicals (Bachewe et al., 2018; Pretty, 2011). For instance, the agricultural use of pesticides and fertilizers in Ethiopia in 2017 were 4128 tonnes (active ingredient (a.i.)) and 320,035 tonnes, respectively (FAO, 2019). Compared to 2002, the country’s 2017 fertilizer consumption increased by 91%, while pesticide consumption was 20 times higher than the consumption in 1993 (FAO, 2019). As a result, nutrients and toxic (in)organic chemicals released from agricultural activities has continued to pose environmental concerns in the country (Laurance et al., 2014; Teklu et al., 2018). This pollution may compromise the ecological integrity of the water ecosystem as observed in many sub-Saharan African lakes and reservoirs (Fetahi, 2019; Njenje et al., 2010; Wenaty et al., 2019).

In the central rift valley (CRV) region of Ethiopia, particularly around Lake Ziway and its catchment, smallholders and commercial farmers have been practicing intensive agricultural activities (Merga et al., 2020; Teklu et al., 2018). Data obtained from irrigation offices of the three districts that border Lake Ziway showed that a total of 8537 ha of land was irrigated in the 2016/17 cropping season to produce vegetables by smallholder farmers (unpublished data). However, only 5000 ha of irrigated land was reported for a decade earlier (Jansen et al., 2007), showing the expansion of irrigated land by 71%. Moreover, about 950 ha of land proximate to Lake Ziway is in use by horticulture companies (Fig. 1). Residuals of pesticides from these farms may contaminate Lake Ziway via various routes such as drainage, runoff, and airborne deposition during spraying (Teklu et al., 2016, 2018).

Monitoring studies of toxic pollutants are important to assess their distribution and concentration levels in order to evaluate their risk to non-target organisms (Añasco et al., 2010; Ccanccapa et al., 2016). Monitoring studies of pesticides in Ethiopian surface waters are rare as only a few studies are available (Deribe et al., 2013; Teklu et al., 2016, 2018). The majority of previous studies in Lake Ziway focused on physicochemical variables (Merga et al., 2020). Recently, Teklu et al. (2018) studied the distribution and impacts of pesticides as well as nutrients and trace metals in the lake. But, the levels of pesticides have never been evaluated in sediments, nor in combination with biological sampling, despite their high importance for environmental risk assessment as biological communities disclose historical anthropogenic disturbances that further strengthen the risk assessment of the present pollution (Aazami et al., 2015; Abbasi and Abbasi, 2011; Ccanccapa et al., 2016; Kebede et al., 2020).

To address these issues, the objectives of the present study were to 1) assess the concentrations of insecticides and fungicides in water and sediment samples, and the levels of physicochemical parameters in water samples of Lake Ziway, 2) perform a risk assessment for the insecticide and fungicide concentrations measured in both matrices 3) correlate the abundance of biological organisms (macroinvertebrates and fish) to monitored pesticide concentrations and levels of physicochemical parameters and 4) evaluate the correlation between macroinvertebrate based biotic indices and the monitored pesticide concentrations and levels of physicochemical parameters. This with the aim to assess the risks posed by pesticides to aquatic, non-target (macroinvertebrates and fish) organisms in Lake Ziway and to select appropriate biological indices to assess future changes in biological water quality.

2. Materials and methods

2.1. Lake Ziway

Lake Ziway (Fig. 1), is situated between 7°51’ to 8°07’ N and 38°43’ to 38°56’ E with an altitude of 1636 m above sea level located about 160 km to the south of Addis Ababa, Ethiopia. The lake covers a surface area of 442 km² with a catchment area of 7380 km². It is a shallow freshwater lake with average and maximum depths ranging between 2.5 – 4 m and 7 – 9 m, respectively. The depth variations are partially explained by seasonal rain fall differences (Merga et al., 2020). The perennial Meki River and Katar River flow into the lake, and as an exorheic lake, Lake Ziway outflows into Lake
Abjata via Bulbula River (Ayenew, 2007; Teklu et al., 2018).

2.2. Water and sediment samples

Water and sediment samples were collected during the dry season (between 17–25 May 2017) and the wet season (between 13–21 November 2017) at 13 selected shoreline sites of Lake Ziway (Fig. 1) to assess the levels of physicochemical parameters and residuals of pesticides. Simultaneously, macroinvertebrates and fishes were sampled to assess the abundance and distribution of the species along the selected shoreline sites of the lake.

The sites were selected based on their proximity and vulnerability to shoreline human activities as depicted in Fig. 1. Floriculture1 and Floriculture2 sites receive wastewater from floriculture farms. Kidanemihiret and Korokonch sites receive urban waste from Abatu town. Locations at Edo–Kontola, Abosa, Tepho-Choroke, and Mekidela are proximate to very smallholder vegetable farms. Bochessa and Bulbula locations are also close to smallholder farms, but the farms along these sites were not as large as in the case of the other sites. Meki-River and Ketar-River locations receive inflow rivers from the upper catchment of the lake. At the Reference sampling site, the agricultural and urban activities are minimal (Fig. 1).

2.2.1. Water sample collection and analysis

For physicochemical analysis, water samples were collected into pre-cleaned 1L polyethylene bottles, and transported to the laboratory using an ice-box and stored at 4 °C until analysis. Parameters, including pH, temperature, conductivity, dissolved oxygen (DO) and total dissolved solids, were measured in-situ, while nitrate, phosphate, sulphate, ammonia, alkalinity, chemical oxygen demand, chlorophyll-a and turbidity were measured according to methods described by US-EPA (1983).

Nineteen (19) pesticides (15 insecticides and 4 fungicides; see Table SI 1 for names and physicochemical properties) were selected to be monitored, because these pesticides are widely used by farmers in the vicinity of Lake Ziway based on a survey we carried out in 2017 (unpublished data). For the analysis, water samples were collected into cleaned 1L amber glass bottles and transported to laboratory using a cooled ice-box. In the laboratory, 5 mL of 2 N H2SO4 and 10 mL methanol were added to the sample which was stored at 4 °C until analysis. Parameters, including pH, temperature, conductivity, dissolved oxygen (DO) and total dissolved solids, were measured in-situ, while nitrate, phosphate, sulphate, ammonia, alkalinity, chemical oxygen demand, chlorophyll-a and turbidity were measured according to methods described by US-EPA (1983).

For clean-up and quantification of the residual pesticides, similar procedures used for the water samples were fully employed. More detailed information is given in SI, section B.

2.2.2. Sediment sample collection and analysis

Sediment samples (0–5 cm) were collected using an Ekman grab sampler, wrapped into aluminium foil and kept in zipped polyethylene bags. The samples were transported to the laboratory using a cooled ice-box which was kept in a freezer at −20 °C. Total organic matter (TOM%), and fraction of organic carbon (fOC) were analysed using the dichromate method (Ryan et al., 2001). Pesticides extraction from sediment was performed using methanol-water (in 4:1 v/v ratio) solvent as described by Vega et al. (2005). For clean-up and quantification of the residual pesticides, similar procedures used for the water samples were fully employed. More detailed information is given in SI, section B.

2.2.3. Method validation, quality assurance and quality control for pesticides determination

To validate the analytical method, we performed various validation procedures including the plotting of calibration curves and recovery analysis (Vega et al., 2005). The obtained r^2 values for calibration graphs ranged from 0.9668 to 0.9995 (Table SI 2). The recoveries ranged from 79.8% to 94.1% for water and 75.3%–99.5% for sediment (Table SI 2). For detailed information, see SI, section C.

A signal-to-noise ratio (Sadatii et al., 2013) based calculation of the limit of detection (LOD) and limit of quantification (LOQ) were performed for each pesticide using water and sediment samples collected from an unpolluted temporary pond. For the results of the LOD and LOQ calculations, see Table SI 2.

2.3. Biological samples and biotic indices

Macroinvertebrates were monitored according to the protocol by the Ontario Benthos Biomonitoring Network (Jones et al., 2007) in the littoral part of Lake Ziway using a D-shaped net (500 μm mesh). Sorting was done in the laboratory. Taxonomic identification was performed to the family level using expert knowledge and guide books by Kriska (2014). Nylon made beach seine net (40 mm mesh) was used to sample littoral invertebrates following the suggestion by Portt et al. (2006) and EPP (2009). Length (cm) and weight (g) were measured, and taxonomic identification was performed. Afterwards, the fish were released back into the lake, for more information see SI, section D.

Macroinvertebrate based indices were computed to evaluate the applicability of the indices to discriminate the sampling sites according to their level of pesticide and nutrient impacts due to shoreline activities. Fifteen indices were calculated, including Biological Monitoring Working Party index (BMWPscore) and the BMWP based Average Score Per Taxa index (BMWP–ASPT) (Armitage et al., 1983), the Invertebrate Community Index (ICIscore) (Pinel-Alloul et al., 1996), the South African Scoring System index (SASSscore) and SASS–ASPT index (Dickens and Graham, 2002), diversity indices (Shannon Weiner and Simpson indices), species richness indices (Margalef’s and Menhinick’s indices), and an evenness index (Pielou evenness) (Magurran, 1988). In addition, abundance and compositional indices including total number of individual (#Totalabun), the total number of Ephemeroptera, Plecoptera and Trichoptera (#EPTabun), the total number of taxa (#Totaltaxa), number of EPT taxa (#EPTtaxa), and percentage of EPT taxa (%EPTtaxa) were included.

2.4. Data analysis

2.4.1. Risk assessment

Assessment of the ecological risks of the insecticides and fungicides was performed by computing acute tier-1 and tier-2 based risk quotients (RQ) as described by Van Wijngaarden et al. (2015) and Rico et al. (2019), respectively. As triplicate samples (n = 3) of water and sediment were collected from each sampling site, the geometric mean values were calculated and used as exposure concentrations. The minimum and maximum measured exposure concentrations of the pesticides at all sites in the lake were included in the RQ calculation, hereby providing a range of RQs possible with the highest RQ representing the worst-case risk scenario. As toxicity data is very scarce for sediments, the pore water concentration (Cpow) was assumed to be the bioavailable concentration and used for risk assessment of the sediment concentrations of the pesticides (Diepens et al., 2017). The pore water concentrations were calculated according to Eq. (1) (Cancapca et al., 2016). For pesticides detected with a maximum concentration of < LOQ, the pore water concentration was calculated using

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Concentration (PNEC) for insecticides (Van Wijngaarden et al., 2011) divided by an AF of 100 to calculate the acute tier-1 Predicted No Effect Concentration (PNEC) for insecticides (Van Wijngaarden et al., 2011) divided by an AF of 10 to calculate the chronic tier-1 PNEC values, respectively. Risk characterization categories were made as: RQ < 1 = no risk, 1–10 = low risk, 10–100 = high risk and >100 = very high risk.

Site-specific impacts of mixtures of pesticides to aquatic organisms via water and sediment exposure were also evaluated. Two freshwater community groups, arthropods and fishes, were considered for the impact assessment of the measured mixtures of the insecticides and fungicides, as they are expected to be more sensitive than primary producers and non-arthropod invertebrates (Maltby et al., 2005, 2009). As aforementioned for individual pesticide risk assessment, the geometric mean values of the three samples taken at each location were calculated and used as exposure concentrations. For the detected pesticides with a concentration of < LOQ, the exposure concentration was set at 0.5×LOQ.

The mixture risk assessment was performed by applying mixture toxicity mixed-models (Posthuma et al., 2002). First, the pesticides were classified according to their toxicological mode of action (TMoA) with the help of the database of the Insecticide Resistance Action Committee (https://www.irac-online.org/modes-of-action/) for insecticides and the Fungicide Resistance Action Committee (https://www.frac.info/publications/downloads/) for fungicides (Table SI 4). Secondly, for each pesticide, toxicity values with 1–4 days test duration using immobility, growth or mortality as effect endpoints for fish and arthropods were collected from the aforementioned toxicity database and were log transformed, while the median (m) and standard deviation (σ) were estimated for arthropods and fishes separately (Table SI 4). Hazard units (HU) for each pesticide were computed per site by dividing the exposure pesticide concentration by 10\(^{4}\), where m is the log-transformed median of acute toxicity values of the respective pesticide. Thirdly, the concentration addition model was implemented to calculated multi-substance potentially affected fraction based on concentration addition (msPAFA) for pesticides with a similar TMoA by employing the function NORM.DIST in Excel.

The obtained L(EC)\(_5\) values were divided by an assessment factor (AF) of 100 to calculate the acute tier-1 Predicted NO Effect Concentration (PNEC) for insecticides (Van Wijngaarden et al., 2015). For fungicides the L(EC)\(_5\) of D. magna and O. mykiss were divided by an AF of 100, and the EC\(_50\) value of algae (R. subcapitata or D. subspicatus) was divided by AF 10 (Rico et al., 2019). The lowest PNECs (Table SI 3) were selected for the RQs calculation. For the tier-2 acute risk assessment, additional toxicity values for arthropods for insecticides and all species (fishes, arthropods and algae) for fungicides were collected, with a 1–4 days test duration and evaluating immobility, growth or mortality as effect endpoints (Maltby et al., 2005, 2009) from the same data bases as stated above. To calculate the tier-2 PNEC, the species sensitivity distribution (SSD) approach was employed (Van Wijngaarden et al., 2015). An SSD was constructed using the ETX 2.1 software (Van Vlaardingen et al., 2003). The tier-2 PNEC (Table SI 3) was calculated by dividing the median HC\(_i\) (hazardous concentration protective for 95% of the population) by an AF of 6 (Van Wijngaarden et al., 2015).

Chronic tier-1 RQs were calculated using the selected chronic toxicity values for D. magna (21-d NOEC/EC\(_{10}\)) or Chironomus spp. (28-d NOEC/EC\(_{10}\)) or A. bahia (28-d NOEC/EC\(_{10}\)) for insecticides (Broek et al., 2016), and for D. magna (21-d NOEC/EC\(_{10}\)) or O. mykiss (28-d NOEC/EC\(_{10}\)) or algae (72-h/96-h EC\(_{50}\)) for fungicides (Rico et al., 2019). The toxicity values were divided by an AF of 10 to obtain chronic tier-1 PNECs and the lowest PNEC values (Table SI 3) were used for RQs calculations (Broek et al., 2016; Rico et al., 2019). The tier-1 and tier-2 RQs were calculated by dividing the measured environmental concentrations of the pesticides by their the tier-1 and tier-2 PNEC values, respectively. Risk characterization categories were made as: RQ < 1 = no risk, 1–10 = low risk, 10–100 = high risk and >100 = very high risk.

2.4.2. Redundancy analysis

To assess the significance of the variation in species composition and abundance (see Table SI 5) between the sites explained by the different physicochemical parameters and pesticides, redundancy analyses (RDA) were performed using Canoco 5 (Ter Braak and Smilauer, 2018). First, the physicochemical parameters (Table SI 6) and pesticide concentrations in the water and sediment (Table SI 7; Table SI 8) were transformed when no 0 values are present and Ln(\(ax+1\)) transformed when 0 values were present. In the formula, the value of a was calculated for each parameter separately with 0 yields 2 with x being the lowest number above 0 (Van den Brink et al., 2000). An RDA using physicochemical parameters as species and sampling date and site as explanatory variables was performed to get an overview of the differences in parameter values between sampling dates and sites. In order to
make all parameters equally important in the analysis their values were centred and standardized.

The significance of each environmental parameter with respect to the differences in species composition between the different samples was tested by an RDA introducing all environmental variables as explanatory variables and sampling date as covariable. Besides the simple effects also the conditional effects were tested. The resulting RDA biplot shows the correlations between the species and the environmental variables. After that an RDA was performed including the environmental variables which were significant in the simple and conditional effects as explanatory variables, and sampling date and sample site as passive explanatory variables. This yields a triplot showing the correlations between species, sites, sampling dates and the environmental variables, which are represented by a limited set as selected by the conditional effects. The same analysis was performed for the biotic indices (Table SI 9), which played the role of the species, but their values were centred and standardized within the analysis in order to make them equally important within the analysis (Ter Braak and Smilauer, 2018). Pearson correlations between species abundance and msPAFRA, and between biotic indices and msPAFRA were calculated to evaluate the contribution of the msPAFRA to the variation observed in species abundance and composition, and biotic indices between sampling sites.

3. Results and discussion

3.1. Physicochemical parameters

Turbiditity, temperature and alkalinity was higher in the samples taken in the dry season (May) compared to the wet season (November), which showed higher SO4\(^{2-}\) concentrations. The sites receiving waste water effluent from the floriculture farms showed higher chlorophyll-a, EC, TDS, COD and NO3 values were centred and standardized within the analysis in order to make them equally important within the analysis (Ter Braak and Smilauer, 2018). Pearson correlations between species abundance and msPAFRA, and between biotic indices and msPAFRA were calculated to evaluate the contribution of the msPAFRA to the variation observed in species abundance and composition, and biotic indices between sampling sites.

3.2. Residual of pesticides in water samples

A total of 19 pesticides were monitored and the majority (63%) of them were detected in water samples of the studied lake. During both sampling seasons (dry season and wet season), malathion, dimethoate, metalaxyl, fenitrothion, diazinon, chlorpyrifos and endosulfan were frequently detected in water samples (Table 1). The distribution of pesticides in aquatic ecosystems is affected by the physicochemical properties of the active ingredient (Weber, 1995). The ubiquitous presence of malathion, dimethoate and metalaxyl pesticide can be explained by their low logKow and high aqueous hydrolysis and photolysis half-life (DT50) values (Table 1). As reported by Teklu et al. (2016), the low detections of λ-cyhalothrin and α-cypermethrin are likely due to their high logKow and low aqueous photolysis DT50 values (Table 1). Higher mean and maximum concentrations were observed for the majority of pesticides in the wet season compared to the dry season (Table 1). Runoff from agricultural lands in the wet season is an important transportation route for pesticides to surface waters (Otieno et al., 2012; Papadakis et al., 2015) and likely explains the observed seasonal variation in this study.

Endosulfan, diazinon and deltamethrin were reported with

### Table 1

| Pesticides | a. Water sample | b. Sediment sample |
|------------|----------------|--------------------|
|            | Detection frequency #(% DF) | Concentration (μg/L; n = 3) | Detection frequency #(% DF) | Concentration (μg/Kg_dw; n = 3) |
|            | Dry season | Wet season | Mean | Min. | Max. | Mean | Min. | Max. | Mean | Min. | Max. |
| Propamocarb | 5(38.5%) | 3(23.1%) | 0.72 | <0.13 | 0.91 | 0.503 | 0.41 | 0.62 | nd | nd | — |
| Acephate | nd | nd | — | — | — | — | — | — | — | — | — |
| Ethoprophos | nd | nd | — | — | — | — | — | — | — | — | — |
| Dimethoate | 10(76.9%) | 11(84.6%) | 0.54 | <0.05 | 0.88 | 0.63 | <0.05 | 0.99 | nd | 2(15.4%) | — |
| Diazinon | 9(69.2%) | 9(69.2%) | 0.42 | <0.08 | 0.74 | 0.51 | <0.08 | 0.88 | 5(38.5%) | 6(46.1%) | 0.44 | <0.36 | 0.53 | — | 0.42 | <0.36 | 0.74 |
| Chlorothalonil | nd | nd | — | — | — | — | — | — | — | — | — |
| Carbaryl | 4(30.8%) | 4(30.8%) | 0.18 | 0.02 | 0.36 | 0.23 | <0.02 | 0.38 | nd | nd | — |
| Metalaxyl | 9(69.2%) | 10(76.9%) | 0.72 | <0.1 | 1.9 | 0.75 | 0.14 | 1.41 | nd | nd | — |
| Fenitrothion | 10(76.9%) | 8(61.5%) | 0.38 | <0.08 | 0.69 | 0.48 | 0.19 | 0.74 | nd | 3(23.1%) | 0.91 | 0.89 | 0.94 |
| Malathion | 12(92.3%) | 10(76.9%) | 0.38 | <0.07 | 0.85 | 0.42 | <0.07 | 0.55 | nd | nd | — |
| Chlorpyrifos | 10(76.9%) | 8(61.5%) | 0.55 | <0.15 | 0.87 | 0.58 | 0.31 | 0.88 | nd | 4(30.8%) | 0.79 | 0.71 | 0.88 |
| Profenofos | nd | nd | — | — | — | — | — | — | — | — | — |
| Iprovalicarb | 6(46.1%) | 5(38.5%) | 0.57 | <0.17 | 0.93 | 0.59 | 0.38 | 0.88 | nd | nd | — |
| Endosulfan | 9(69.2%) | 8(61.5%) | 0.76 | <0.42 | 1.01 | 1.11 | <0.42 | 1.85 | 3(23.1%) | 4(30.8%) | 2.1 | <0.61 | 2.22 | 2.69 | <0.63 | 2.95 |
| Dicofol | nd | nd | — | — | — | — | — | — | — | — | — |
| λ-cyhalothrin | 3(23.1%) | 3(23.1%) | — | <0.45 | <0.45 | — | <0.45 | <0.45 | nd | 3(23.1%) | 0.19 | 1.88 | 2.08 |
| Acrinathrin | nd | nd | — | — | — | — | — | — | — | — | — |
| α-cypermethrin | 3(23.1%) | 5(38.5%) | — | <0.61 | <0.61 | 0.75 | <0.61 | 0.81 | 2(15.4%) | 6(46.1%) | — | <0.71 | 0.71 | 1.75 | 1.58 | 1.97 |
| Deltamethrin | nd | nd | — | — | — | — | — | — | — | 2(15.4%) | — | <0.54 | <0.54 |

Note: nd — not detected.
mean concentrations of 0.1, 0.345 and 0.01 µg/L, respectively in Lake Ziway by Teklu et al. (2018). Similarly, Jansen and Harmsen (2011) reported malathylax, iprovalicarb, propamocarb, carbaryl, and fenitrothion, with mean values of 0.215, 0.14, 0.6, 0.05 and 0.16 µg/L, respectively in the lake. These values are lower than the values measured in this study, except for deltamethrin. This suggests increasing concentration levels of the pesticides in the water column of the lake over time, to which a year-to-year expansion of smallholder irrigation lands and large-scale farms may have a major contribution.

Compared to our results, Mekonen et al. (2016) measured higher mean values of malathion (7.7 µg/L) and diazinon (5.6 µg/L) in water samples collected from rivers surrounded by agricultural fields close to Jimma, Ethiopia, located 200 km to the east of Lake Ziway. These values indicate that rivers and streams surrounded by agricultural fields are likely to have higher pesticides concentrations, and may serve as transport routes of pesticides to the receiving downstream waters.

Internationally banned organochlorine pesticides including endosulfan and DDT have been widely studied in surface waters of other African countries (Taiwo, 2019), while a few reports on other pesticides’ classes. Abong’o et al. (2018), Wenaty et al. (2019) and Okoya et al. (2013) have reported mean concentrations of endosulfan for Nyaro River of Kenya (0.64 µg/L), Lake Victoria of Tanzania (0.134 µg/L) and Agro River of Nigeria (1.65 µg/L), respectively, which are quite similar to the concentrations measured in the current study (Table 1). According to the authors, endosulfan is widely used by subsistence farmers producing vegetables, fruits and sugarcane in the catchment of the studied waters. Similarly, the smallholder farmers in the catchment of Lake Ziway widely use the pesticide to protect onion, cabbage and tomato from bollworm (Mengistie et al., 2017; Teklu et al., 2016).

Other chemical classes of pesticides were also detected in African surface waters, which are under similar agricultural pressures as Lake Ziway. Malathion was detected in the Sebyea River of Rwanda (Houbraken et al., 2017), and in the Ankobra River Basin of Ghana (Affum et al., 2018) with mean values of 0.19 µg/L and 0.13 µg/L, respectively, which are lower than the concentrations found in the current study. Cypermethrin (0.186 (ND - 0.925) µg/L) and deltamethrin (0.020 (ND - 0.925) µg/L) were detected in the Ankobra River Basin, Ghana (Affum et al., 2018). In the current study we found much higher levels for cypermethrin in the wet season, while its dry season concentrations and the dry and wet season concentrations of deltamethrin are difficult to compare since the LOD of cypermethrin and deltamethrin in the current study were relatively high, i.e. 0.19 and 0.15 µg/L, respectively (Table SI 2). Chlorpyrifos was detected in Lake Naivasha, Kenya (Otierno et al., 2012) and in the Ankobra River Basin, Ghana (Affum et al., 2018) with mean values of 12 µg/L and 0.34 µg/L, respectively, the latter being comparable to levels found in the current study. Furthermore, metalaxyl was detected in Lake Kivu, Rwanda (Houbraken et al., 2017) and fenitrothion in Ankobra River, Ghana (Affum et al., 2018) with mean values of 2.44 µg/L and 0.035 µg/L, respectively, which are higher and lower than the concentrations reported in Table 1, respectively. Agricultural activity related differences in types and quantities of pesticides use likely to contribute to these variations, although the concentrations of many pesticides do correspond.

The composition and detection frequency of pesticides were spatially variable in Lake Ziway. The majority of the pesticides (>50%) were detected in waters sampled from locations proxime to smallholder farms receiving inflow from the rivers (Table SI 10). Those sites receiving wastewater from floriculture farms also detected a considerable number of pesticides (30–50%) (Table SI 10). Similar to earlier reports (Mengistie et al., 2017; Teklu et al., 2016), our survey in 2017 (unpublished data) showed that the pesticides included in our monitoring programme were intensively used in CRV region by subsistence vegetable farmers and large-scale flower farmers. Therefore, the observed ubiquitous of the pesticides at the aforementioned locations is likely to be related to these activities.

3.3. Residual of pesticides in sediment samples

Only 3 (16%) and 9 (47%) of the monitored pesticides (n = 19) were detected in sediment samples collected in dry season and in wet season, respectively (Table 1). In the dry season, diazinon was the most frequently detected pesticide (39% DF) and its concentrations ranged from <0.36–0.53 µg/kg-dw (Table 1). In the wet season diazinon, chlorpyrifos, endosulfan and α-cypermethrin were frequently detected (DF > 30%) and their concentrations ranged from <0.36–2.95 µg/kg-dw (Table 1). Their high hydrophobicity (logKow > 3; Table SI 1) can explain the accumulation of the pesticides in the sediment of the lake (Cancappa et al., 2016; Teklu et al., 2016). Similar to the observation for water samples, the wet season sediment samples were more contaminated compared to the dry season samples (Table 1), indicating seasonal variations. Similarly, Otierno et al. (2012) reported the wide distributed and high level of chlorpyrifos in wet season sediment samples compared to the lower levels found in the dry season in Lake Naivasha, Kenya.

This study is the first to report the concentrations of pesticides in the sediment of Ethiopian surface waters. Few studies reported pesticides in other African surface waters mainly for obsolete organochlorine pesticides as discussed earlier. Endosulfan concentrations ranged from 3.75 to 14.40 µg/kg-dw (Darko et al., 2008) and 0.03–9.67 µg/kg-dw (Wasswa et al., 2011) in sediments of Lake Bosomtwi (Ghana) and Lake Victoria (Uganda), respectively. These values are higher than the values measured in our study (maximum concentration = 2.95 µg/kg-dw; Table 1). Moreover, diazinon (0.56–1.08 µg/kg-dw) and dimethoate (0.02–0.29 µg/kg-dw) in Nyando-Sondu-Miriu River of Kenya (Musa et al., 2011a), malathion (<0.01 µg/kg-dw) in Yala-Nzoia River of Kenya (Musa et al., 2011b) and chlorpyrifos (4.7–30.1 µg/kg-dw) in Lake Naivasha of Kenya (Otierno et al., 2012) have been reported. In the current study, similar values were reported for diazinon and dimethoate, while higher and lower values were reported for malathion and chlorpyrifos, respectively (Table 1). According to the authors, the studied surface waters received pesticide residuals from smallholder vegetables, sugarcane and fruits farms in their catchment (Otierno et al., 2012; Wasswa et al., 2011), which are comparable sources of pesticides as in the current study on Lake Ziway. As mentioned earlier, regional source differences of pesticides likely contribute to the differences in chlorpyrifos concentrations.

Pesticides were detected in sediment samples collected from the majority (85%) of locations (Table SI 10), but their composition and DF varied between the sampling sites. The differences are likely due to differences in the types and application intensity of pesticides used in the areas closer to the sampling sites. The highest DF in the dry season was 16% and observed at the inflow where Meki River joins the lake. In the wet season large numbers of pesticides (DF > 20%) were detected in the sediments at locations near to smallholder farms, the point of effluvent from the floriculture and the point of inflow of the rivers (Table SI 10). This indicates that the sediment of the lake are probably contaminated with pesticides released from the surrounding agricultural and floricultural activities. The observed high concentrations and number of pesticides in the wet season sediment samples is likely a result of the high load of pesticides absorbed to sediments via runoff (Papadakis et al., 2015) from agricultural area in the catchment of the studied lake.
3.5. Tier-1 and tier-2 risk quotients based ecological risk presence in the water and sediment of Lake Ziway.

Table 2

| Pesticides   | Acute Tier-1 RQ range and % of RQ > 1 | Chronic Tier-1 RQ range and % of RQ > 1 | Acute Tier-2 RQ range and % of RQ > 1 |
|--------------|-------------------------------------|----------------------------------------|--------------------------------------|
|              | Dry season | Wet Season | % RQ > 1 | Dry season | Wet Season | % RQ > 1 | Dry season | Wet Season | % RQ > 1 |
| Propamocarb  | 0.01–6     | 0.01–6     | 0        | 0.01–6     | 0.01–6     | 0        | 0.01–6     | 0.01–6     | 0        |
| Dimethoate   | 1.93–68    | 2.77–77   | 100      | 0.26–9     | 0.3–11     | 67       | 0.09–3     | 0.09–3     | 67       |
| Diazinon     | 7–130      | 7–155     | 100      | 0.71–13    | 0.71–16    | 67       | 0.52–9     | 0.5–12     | 67       |
| Carbaryl     | 0.21–4    | 0.10–4    | 50       | <0.01–0.01 | <0.01–0.01 | 0        | <0.01–0.01 | <0.01–0.01 | 0        |
| Metalaxyl    | 1–18      | 5–19      | 100      | 5–79       | 22–85     | 100      | 0.6–11     | 3–12       | 94       |
| Fenithionth   | 9–212     | 9–137     | 100      | 6–142      | 6–92      | 100      | 0.4–9      | 0.4–6      | 52       |
| Chlorpyrifos | 187–2175  | 775–2200  | 100      | 7.5–87     | 31–88     | 100      | 9–102      | 36–101     | 100      |
| Iprovalcarb  | 17–80     | 17–146    | 100      | 0         | <0.01     | 0        | 9–43       | 9–78       | 100      |
| Endosulfan   | 1906–1906 | 1907–1907 | 100      | 1022–1022  | 1022–1022 | 100      | 959–959    | 959–959    | 100      |
| e-Cypermethrin| 2346–2346 | 2346–6230 | 100      | 101–101    | 101–270   | 100      | 227–228    | 227–604    | 100      |

3.4. Role of farmers’ pesticide use practices for pesticide pollution of Lake Ziway

Poor management of pesticides by African smallholder farmers is one of the major cause of pesticide pollution in surface waters (Loha et al., 2018; Onwona-Kwakye et al., 2019; Stadlinger et al., 2011). Studies (Mengistie et al., 2017; Teklu et al., 2016) have reported the mismanagement and malpractices of pesticide use by smallholder farmers in the Ethiopian CRV region. According to Teklu et al. (2016), the majority of farmers in CRV region lack adequate knowledge about routes through which pesticides enter into water bodies and its ecological impacts. Overuse (e.g., too high application rate) and misuse (e.g., spraying on crops for which a pesticide is not prescribed) are also major problems (Mengistie et al., 2017; Teklu et al., 2016). Mixing pesticides close to water-bodies, washing pesticides' containers into surface waters/canal, and disposing of pesticides’ containers and expired pesticides to the environment are also the commonly observed malpractices in the region (Mengistie et al., 2017; Teklu et al., 2016). Furthermore, Adami Tulu Pesticide Processing factory located in CRV, formulates a variety of pesticides including malathion, endosulfan, diazinon, fenithionth, deltamethrin and dimethoate (Brenner et al., 2014; PMI, 2009) so the pesticides are easily available in the pesticide shops for the farmers in the region. This may also contribute to their presence in the water and sediment of Lake Ziway.

3.5. Tier-1 and tier-2 risk quotients based ecological risk assessment

For the majority of the pesticide concentrations measured in water samples, a RQ higher than 1 was calculated, indicating a potential ecological risk (Table 2). Based on the acute tier-1 RQ, diazinon, malathion, chlorpyrifos, λ-cyhalothrin and ζ-cypermethrin pose a very high acute ecological risk (RQ > 100) in both seasons. Dimethoate and fenithionth pose a high acute risk (RQ = 10–100; Table 2). For endosulfan high (dry season) to very high (wet season) acute ecological risks were calculated. According to the acute tier-2 RQs, chlorpyrifos, λ-cyhalothrin and ζ-cypermethrin were expected to pose very high acute risks (Table 2). Diazinon measured in the wet season, and fenithionth and endosulfan measured in both seasons pose high acute ecological risks (acute tier-2 RQ > 10; Table 2). Furthermore, chronic tier-1 RQ indicated that water concentrations of malathion (dry season), λ-cyhalothrin and ζ-cypermethrin pose very high chronic risks (Table 2). The ecological risks calculated from the sediment concentrations in the lake were low compared to risks of pesticides from water exposure (Table 3). The tier-1 acute RQ indicates that in the wet season dimethoate, chlorpyrifos, λ-cyhalothrin, ζ-cypermethrin and deltamethrin pesticides pose high acute ecological risks (Table 3). According to its acute tier-2 RQ, λ-cyhalothrin (in the wet season) poses a high acute risk (Table 3). Moreover, chronic tier-1 RQ values showed that deltamethrin poses a very high chronic risk whereas fenithionth and λ-cyhalothrin pose a high chronic ecological risks in the wet season (Table 3).

Higher RQ values were calculated for pesticides measured in the wet season samples compared to the dry season for both water and sediment samples (Table 2; Table 3), indicating that wet season pesticides exposure may pose higher ecological risks than the dry season exposure. Moreover, for the majority of the pesticides (>55%) found in water and in sediment the %RQ > 1 were above 50% (Table 2; Table 3), indicating that the pesticides can pose an acute and chronic risks at the majority of the sampling locations where they were detected.

Generally, as expected, the acute tier-1 RQ values were higher than the acute tier-2 RQ values (Table 2; Table 3). Based on tier-1 RQ values, the majority of the pesticides pose a high to very high acute ecological risks in both seasons.
ecological risk to the lake ecosystem, but pose no risk to low risk according to tier-2 RQ values (Table 2; Table 3). This shows that the lower tier is more conservative than the second tier, which should be the case in a functioning tiered risk assessment (Brock et al., 2011). For the majority of the detected pesticides (71% in water, 44% in sediment), the acute tier-2 RQ values are > 1, thus expected to pose ecological risks by affecting the ecological integrity and health (Ccanccapa et al., 2016) of the studied lake. Teklu et al. (2018) reported only for two pesticides (endosulfan and deltamethrin) tier-2 RQ > 1 for Lake Ziway, but only 8 pesticides were detected in this study. This indicated that pesticide contamination of the lake may be increasing over time. Similar to our results, Onwona-Kwakye et al. (2020) reported that dimethoate, chlorpyrifos, \( \lambda \)-cyhalothrin and \( \alpha \)-cypermethrin pose risks to aquatic ecosystems in Ghana by estimating an acute tier-2 RQ values for these pesticides using the PRIMET model.

3.6. Site specific risk assessment for arthropods and fishes

Most risk assessment tools evaluate individual pesticides for regulatory purposes. But, in reality, aquatic ecosystems are often exposed to a mixture of pesticides (Silva et al., 2015). The calculated acute toxicity data based msPAF_{RA} to evaluate the site specific risk of the mixture of measured pesticides in Lake Ziway to arthropods and fish are summarized in Fig. 2 and Table SI 10.

Our results based on water concentrations at all sites, indicate that arthropods (median msPAF_{RA} = 37%) are more affected compared to the fish community (median msPAF_{RA} = 20%). At the majority of sample locations, the msPAF_{RA} values for arthropods from water exposure were >5% (i.e. higher than the acceptable threshold value in risk assessment) (Brock et al., 2011). In both sampling seasons, at sites of the lake close to smallholder farms, sites which receive floriculture farm’s wastewater and those receiving inflow from rivers, pesticide mixtures pose high to very high acute risks to arthropods (msPAF_{RA} > 25%) through water exposure (Fig. 2a). During both seasons, fishes were under high to very high acute risks (msPAF_{RA} > 25%) due to water exposure to pesticide mixtures at locations nearby smallholder farms and those receiving the inflow from rivers (Fig. 2c). The maximum msPAF_{RA} values found in this study for arthropods (80%) and fishes (60%) from water exposure are higher than the values reported by Ramo et al. (2018) for arthropods (25%) and fishes (0.2%) in Madre de Dios River, Costa Rica. Silva et al. (2015) reported for Sado, Tejo and Mondego river basins msPAF_{RA} values of 72% for Sado, 43% for Tejo and 35% for Mondego for arthropods and 25% for Tejo and 18% for Mondego for fishes. This shows that both communities were under higher risks due to exposure to pesticide mixtures in these river basins, like also is the case for Lake Ziway.

The risks of exposure to mixtures of pesticides through exposure by the sediment were low for arthropods and fishes. At most of the locations the sediment msPAF_{RA} values were <1%, indicating negligible risks (Fig. 2b and d; Table SI 10).

Furthermore, our results indicate that the risk of the pesticides mixtures was not determined by an individual pesticide. The mixture of fenitrothion, malathion, chlorpyrifos, endosulfan, \( \lambda \)-cyhalothrin and \( \alpha \)-cypermethrin contributed to 75–100% of the msPAF_{RA} for both community groups due to water exposures (Table SI 11). Similarly, 88–100% of arthropods msPAF_{RA} from sediment exposure was determined by a mixture of dimethoate, diazinon, fenitrothion, chlorpyrifos, \( \lambda \)-cyhalothrin, \( \alpha \)-cypermethrin and deltamethrin (Table SI 12a). Moreover, the mixture of ethoprophos, diazinon, endosulfan, \( \lambda \)-cyhalothrin and \( \alpha \)-cypermethrin contributed to 75–100% of the fish msPAF_{RA} due to sediment exposure (Table SI 12b). Similarly, Ramo et al. (2018) reported that the mixture of chlorpyrifos, diazinon, ethoprophos difenoconazole and carbaryl explained about 90% of the msPAF_{RA} for arthropods.
and fish in the River Madre de Dios, Costa Rica. However, a high contribution of a single pesticide to the msPAFRA for arthropods (chlorfenvinphos) and fish (endosulfan) was reported by Silva et al. (2015) for Mondego and Sado rivers, while high contribution of mixture of chlorfenvinphos and chlorpyrifos was reported for the Tejo river.

Our results indicate that evaluating mixtures of pesticides instead of individual pesticides in the ecological risk assessment using the msPAF model is important to avoid underestimation of overall risks as it also reported by Ramo et al. (2018). The approach can be applied for regulatory purposes as it may support a decision regarding further risk quantification, intervention actions, or approval of the ecological status of an ecosystem (Faggiano et al., 2010; Ramo et al., 2018). As this study only evaluated the risks of insecticides and fungicides, we recommend future studies focusing on the risks of herbicides, although their use is expected to be lower compared to insecticides and fungicides (Merga et al., 2020).

3.7. Effects on measured functional and structural parameters

The RDA analysis showed that 97% of the variation in species composition and abundance between the sampling locations (Table SI 13) was explained by the monitored environmental variables (Fig. 3; Fig. SI 2). Fourteen environmental variables (Table SI 13) that explain a significant part of the variation between the sites were identified using Monte Carlo permutation tests with simple term effects. But, the variables were reduced to four (metalaxyl, NO3, carbaryl and diazinon) based on the conditional term effects (Fig. 3). These four variables explained 55% of the variation, where 68% of the variation was displayed on the first two axes.

The abundance of the majority of the macroinvertebrates species was negatively correlated with higher values of the environmental variables (Fig. 3; Fig. SI 2). The EPT taxa (e.g., Polymitarcyidae, Caenidae, Baetidae, Limnephilidae and Taeniopterygidae) and Odonata (e.g. Coenagrionidae) showed a strong negative correlation to high levels of nutrients and pesticides (Fig. 3). This indicates that these taxa might be sensitive to water pollution. Similarly, many studies (Beyene et al., 2009; Costas et al., 2018; Getachew et al., 2012; Mereta et al., 2013) reported the sensitivity of EPT taxa and some Odonata species to water quality disturbances. Studies reported the tolerance of Chironomidae to water pollution (Beyene et al., 2009; Kebede et al., 2020). We also found that Chironomidae, Corixidae, Notonectidae taxa were positively correlated to sites with higher levels of nutrients and pesticides (Fig. 3).

The Pearson correlation test between species abundance and msPAFRA showed a significant negative correlation with species from Polymitarcyidae, Baetidae, Caenidae, Taeniopterygidae, Limnephilidae and Glossiphoniidae families ($r^2 = 0.389–0.583$), and a significant positive correlation with species from Chironomidae, Psychodidae, Hydrophilidae, Noteridae, Gerridae and Pisasuridae families ($r^2 = 0.399–0.641$). But, for the majority of the species, the correlations were not significant, indicating the insensitivity of these taxa for the studied stressors or a contribution of other stressors including higher levels of nutrients.

Concentration levels of pesticides and physicochemical variables explained a significant (99%) part of the variation observed in the values of biotic indices between sampling locations (Fig. 4; Fig. SI 3). Metalaxyl, NO3, SO4, endosulfan (sediment) and carbaryl were identified as significant using Monte Carlo permutation test with conditional term effects, and explained 62% of the variation (Table SI 14). Although significant in the conditional effects, TDS was not included as it did not explain a significant part when tested individually. The RDA result (Fig. 4) shows that biotic indices are negatively correlated to high levels of nutrients and pesticides. ICI_score, BMWPscore, #EPTtaxa, #EPTabund and %EPTtaxa indices were highly associated to the sites with low values of nutrients and pesticides (e.g., Bochessa and Reference) (Fig. 4). The indices were negatively correlated to the disturbed locations i.e. locations correlated with high values of variables (Fig. 3; Fig. 4).

Pearson correlation result showed a negative correlation between biotic indices and msPAFRA values. Significant correlations were observed for #EPTabund, #EPTtaxa, %EPTtaxa and ICI_score indices ($r^2 = 0.565–0.723$). However, the correlations were not significant for the majority (73%) of biotic indices, showing that the effect of pesticides does not fully explain the variations observed in community composition between locations of the lake.

Furthermore, our result showed the sensitivity and applicability of biotic indices to monitor the water quality status of the studied lake. Some indices (e.g. based on EPT data) effectively distinguished pesticide impacted sites from sites with minimal disturbance (Fig. 4). As many studies (Aazami et al., 2015; Beyene et al., 2009;
Mereta et al., 2013) recommended for surface waters affected by agricultural, industrial and urbanization activities, this study also showed the suitability of #EPTtaxa, #EPTabun and %EPTtaxa indices for water quality monitoring of Lake Ziway. The indices are easy and sensitive compared to conventional methods such as monitoring of physical and chemical variables (Abbasi and Abbasi, 2011). Similarly, Odume et al. (2012) have indicated that EPT richness index has the power to discriminate impacted from less impacted sites of Swartkops River, South Africa. Hamid and Rawi (2017) applied EPT richness tool on three Malaysian rivers (Tupah, Batu Hampar and Teroi), and reported the effectiveness of the tool, and recommended its application for surface water quality assessment. It should, however, be noted that these indices show the general water quality, not specifically water quality degradation due to pesticides (Schuwirth et al., 2015).

4. Conclusions

Pesticides released from small- and large-scale agricultural activities are posing ecological risks to biological communities in Lake Ziway. High contamination of pesticides was observed in water samples compared to sediment samples of the lake. Organophosphates and pyrethroids were the most ubiquitous pesticides in both matrices. Compared to the previous reported values (Jansen and Harmsen, 2011; Teklu et al., 2018) an increasing trend in water concentration levels of many pesticides was observed, indicating lack of effective management of pesticides waste from agricultural activities. Our study was more comprehensive compared to Jansen and Harmsen (2011) and Teklu et al. (2018) in the sense that also biological endpoints were assessed and that the risk assessment went beyond the RQ method to calculate PAF values which also enables the evaluation of mixtures. This study shows the added value of this approach as more weight of evidence is obtained to link stressors with calculated risks as well to evaluate the risks posed by mixtures of pesticides instead of individual ones.

The levels of the majority of the pesticides exceeded 1st and 2nd tier PNECs, thus can cause detrimental effects on structural and functional characteristics of the lake. Intervention measures including smallholder farmers' training on pesticides safe management and use, strict monitoring of floriculture effluent and encouraging large-scale farmers to implement integrated pest management programmes (Mengistie, 2016) are urgently needed to avert the pollution and related risks. Management of urban waste from the nearby towns required attention. Assessing of ecological status of the lake with a simple and cheap tool, e.g. EPT richness, is crucial for regulatory purposes.

Credit author statement

The research question and its scientific and social perspective were proposed during a discussion between all authors. The authors then discussed and fashioned out an approach to reveal the structure and described how the research question fits in the current pesticide use in the Central Rift Valley and the aim to assess the realistic risks these pesticides pose to the ecology of the lake. The first author used empirical data from the monitoring programme carried out by himself in the field. The risk assessments were performed by the first and last author. The first author wrote the first draft and revised it after the comments from the other co-authors.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2020.129214.

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