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Environmental and Human Health Risks of Pesticide Presence in the Lake Tana Basin (Ethiopia)

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Abstract: Pesticides are widely used for safeguarding agricultural yields and controlling malaria vectors, yet are simultaneously unintentionally introduced in aquatic environments. To assess the severity of this pressure in the Lake Tana Basin (Ethiopia), we evaluated the occurrence of 17 pesticide residues in the lake, tributary rivers, and associated wetlands during the wet and dry season, followed by a questionnaire. These questionnaires indicated that 35 different compounds were available in the districts surrounding the lake, including pesticides that are banned in Europe, i.e., endosulfan, dicofol, and malathion. Nevertheless, only 7 pesticide residues were detected in the assessed aquatic habitats. Of these, DDE and bifenthrin occurred most often (97.7% and 62.3%, respectively), while alachlor displayed the highest mean concentration (594 ± 468 ng/L). No significant differences were observed in residue concentrations between seasons nor between habitats. Based on an ecotoxicological risk assessment, the observed concentrations of DDE and cypermethrin pose a high risk to aquatic life, while alachlor and DDT-op residues were below the threshold values. Furthermore, a human risk assessment indicated a low risk for the population that directly consumes water from the Tana basin, while acknowledging the potential of indirect exposure through the consumption of fish and locally grown crops.

Keywords: Africa; water safety; environmental pollution; pesticides; freshwater

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1. Introduction

Pesticides have been used for decades to increase or protect agricultural yields and control vector-borne diseases [1]. Success stories on the use of dichlorodiphenyl-trichloroethane (DDT) to control malaria or glyphosate to eliminate noxious weeds are well-documented [2,3], and created a basis for the industrial development of a suite of pesticides, often tweaked to affect specific organisms [4]. Accordingly, classification systems were developed to catalog pesticides according to (i) the target biotic groups (e.g., insecticides, herbicides, and fungicides), (ii) the active compound (e.g., organophosphates, neonicotinoids, and pyrethroids) [5], and (iii) the intrinsic toxicity and exposure hazard [6] (WHO 2020).

The application of pesticides has also resulted in strong environmental concerns, as active compounds and associated residues can easily be introduced into natural ecosystems such as rivers and lakes due to rainfall-associated run-off [6,7]. Within these aquatic environments, pesticides have the potential to affect non-target species and, therefore, alter the prevailing community structure and ecosystem functioning [8,9]. For this reason, DDT and its derivatives such as dichlorodiphenyldichloroethylene (DDE), dichlorodiphenyltrichloroethane-op (DDT-op), and dichlorodiphenyltrichloroethane-p,p′ (DDT- p,p′) are still a major environmental problem worldwide due to their persistence and potential to bioaccumulate [10,11]. The resulting reduction in biotic diversity complicates stable, resilient, and robust ecosystem functioning, and the associated provisioning of ecosystem services [12].

To protect aquatic ecosystems, regulations have been put in place for the sustainable use of pesticides both within Europe and the United States of America [13,14]. For example, one of the main actions includes the European Regulation 1107/2009 concerning the placing of plant protection products on the market, which aims to safeguard the environment and both animal and human health [13]. Unfortunately, proper legislation and follow-up are often lacking in developing countries, leading to misuse and overexploitation of pesticides including the ongoing use of banned compounds [15,16]. Several areas are characterized by a high risk of pesticide pollution, of which 34% is situated in high-biodiversity regions and 19% is located in low and lower middle-income countries [9].

Ethiopia is characterized by a high biodiversity and is among the top 30 countries with respect to biodiversity [9]. Yet, Ethiopia has been increasingly importing pesticides to improve agricultural yields and fight vector-borne diseases [17]. Of all pesticides imported between 2000 and 2012 (around 32,000 metric tons), the majority were herbicides and insecticides for the cultivation of commercial flowers and vegetables [18,19]. More importantly, pesticide use throughout Ethiopia has increased due to the intensification of cultivation and the efforts to control malaria through the use of malathion, bifenthrin, and DDT [20]. The latter has been sprayed both outdoors and indoors throughout Ethiopia until it became discontinued in 2009, due to increased resistance of the Anopheles mosquitoes (malaria vectors) [20]. Still, malaria remains a major public health issue and economic burden in Ethiopia, with a prevalence level of 13.61% among adults [21] and more than 60% of the Ethiopian population being at risk of the disease [22].

Despite the increased application of pesticides and the relatively high dependency of rural households on nearby freshwater systems for hygienic and dietary purposes, the presence and concentrations of various pesticide residues in Ethiopian freshwater ecosystems have rarely been studied. Exceptions are Mekonen et al. (2016) [23], who reported the presence of malathion in drinking water supplies in Jimma and Addis Abeba, and Teklit (2016) [24] who observed that DDE was the predominant residue within the Tekeze reservoir in northern Ethiopia. However, no information is available on the concentration of pesticide residues in the Lake Tana Basin, which is the largest Ethiopian lake and constitutes about 50% of all the surface freshwater in the country. Based on the reported import and environmental presence of pesticides in Ethiopia, we hypothesize that pesticide residues are present in the Lake Tana Basin and that these residues underlie both an environmental and human health risk. Therefore, the aims of this study were to assess (1) the presence and concentration of pesticide residues in surface water in the littoral zones, the tributaries, and the associated wetlands of Lake Tana; (2) the current availability and use of pesticides in the Lake Tana Basin; (3) the environmental risk of the detected pesticide residues; (4) the health risk of the present pesticide residues for the local population that consumes the water of the Lake Tana Basin.

2. Materials and Methods

2.1. Study Area

The Lake Tana Basin is located in the northwest part of the Amhara region, Ethiopia (Figure 1) and has an area of 15,000 km^2. The climate of the region is dominated by a tropical highland monsoon with an average annual rainfall of 1360 mm, most of which (70–90%) occurs between June and September [25]. The major types of land cover include farmland, water bodies, wetlands, forests, shrubs, grass lands, and settlements [26]. More than three million people inhabit the basin, of which 85% are farmers who cultivate crops such as teff, sorghum, chickpea, maize, and lentils [27]. Particularly at Dembia and Fogera flood plains and near the main rivers (Gumara, Rib), onion is an important crop and more than 80% of the onion growers use pesticides [28]. During the last 25 years, agricultural land use increased from 21.99% to 33.79% at the expense of forests, grasslands, and wetlands [29,30].

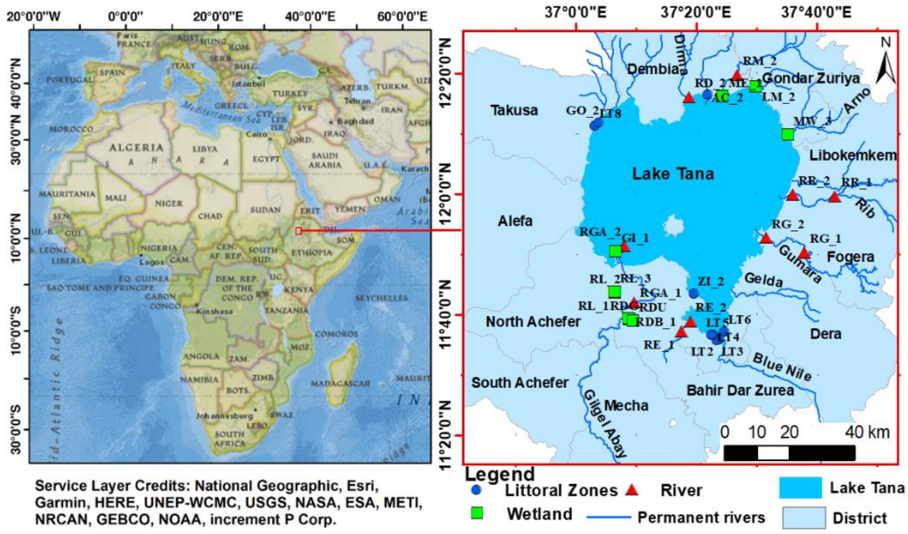

Figure 1. Maps of the Lake Tana Basin. (**Left**) The African map showing the location of Lake Tana Basin within Ethiopia. (**Right**) The sampling sites for pesticide analyses (Littoral Zones, River, and Wetland) and the districts surrounding the Lake Tana Basin.

Lake Tana is a tropical lake situated at an altitude of 1788 m above sea level and provides valuable ecosystem services (e.g., fisheries and water for crop cultivation). It is a shallow lake with a mean depth of 9.7 m (maximum depth of 14.8 m), a surface area of 3046 km^2, and an average volume of 29.6 km^3 [31]. The main tributary rivers (Gilgel Abay, Rib, Gumara, and Megech) account for more than 93% of the inflow to the lake [32,33], with an estimated discharge between 1162 mm and 2829 mm per unit area per year (based on data from 1960 to 1992 and from 1995 to 2005, respectively). In addition, the lake receives an estimated 1315 mm to 1451 mm per unit area per year through precipitation, while the outflow is estimated to be around 1600 mm per unit area per year (through the Blue Nile) supplemented with an estimated evaporation of 1560 mm per unit area per year in recent years [34]. Closing this water balance accurately is challenging due to (1) the variability of the system, (2) the limited data availability and collection, and (3) the extraction of water for domestic and production purposes [32]. Lake Tana, its rivers, and the associated wetlands have both a direct and indirect effect on the provisioning of food and drinking water for the people living on or near the lake shores.

2.2. Data Collection

2.2.1. Sampling Procedure and Analytical Methods

Water samples were collected during the dry (n = 27, April 2018) and wet (n = 16, September 2019) season from the same locations, resulting in a total of 43 samples. Sampling sites were selected by considering (1) accessibility, (2) potential sources of pollution, and (3) an optimal representation of the entire lake region. Main rivers were included due to their transporting role (input and output of pesticide residues), while wetlands were included for their accumulating and degrading role of contaminants (see Supplementary Information, Table S1). We took 12 samples from the littoral zones of Lake Tana, 20 samples from six tributary rivers, and 11 samples from wetlands (Figure 1).

At each sampling location, 1 L of surface water (sampled directly below the water surface) was collected in an amber-colored glass bottle, stored in a cooling box during transportation, and filtered in the laboratory through glass microfiber filters (47 mm diameter;

2.7 μm mesh size; GE Healthcare Life Sciences, Whatman, Grade GF/D, 1823-007, UK). Subsequently, the filtrate was pumped through an activated Sep-Pak® C18 cartridge to adsorb the prevailing pesticide residues on the internal silica phase through Solid-Phase Extraction (SPE) as described by Deknock et al. (2019) [35]. The Sep-Pak® C18 cartridges were wrapped with aluminum foil, labeled, and stored at −20 °C prior to transport to and analysis in Belgium.

Pesticide residues were desorbed via liquid–liquid extraction from loaded cartridges with 10 mL of acetonitrile (99.9%, UPLC grade, VWR, Leuven, Belgium). Subsequently, 4 mL aliquots of these pesticide-loaded solutions were evaporated using a rotavapor-R-100 at 153 Pa of vacuum pressure and at a temperature of 40 °C. After drying, residues were dissolved anew with 4 mL of hexane (99%, UPLC grade, VWR, Leuven, Belgium) and stored at −21 °C prior to Gas Chromatography Electron Capture Detector (GC-ECD) analysis. To perform the analyses, the following settings were used: helium was the mobile phase carrier with a volume of 1 μL and a flow rate of 1.1 mL/min, while the temperature of the injector and detector were 200 °C and 250 °C, respectively (see Supplementary Information, Table S2).

For each pesticide, a standard curve was developed based on a series of 5 standard concentrations (0.004, 0.01, 0.02, 0.04, and 0.1 mg/L; diluted from pure standards obtained from Sigma-Aldrich, Bornem, Belgium), relating the sample's concentration to the obtained signal (peak area). In addition, the calibration curves were used to infer compound-specific limits of detection (LODs) and limits of quantification (LOQs). The LOD and LOQ were determined as the instrumental limits for each pesticide separately by considering the obtained calibration curves according to Equations (1) and (2), respectively [36]. As such, the instrumental LODs and LOQs were between 0.001 and 0.008 mg/L and between 0.002 and 0.027 mg/L, respectively (see Supplementary Information, Table S3).

$$\mathrm{LOD} = \frac{3 \cdot \mathrm{RMSE}}{\mathrm{m}}, \tag{1}$$

$$\mathrm{LOQ} = \frac{5 \cdot \mathrm{RMSE}}{\mathrm{m}}, \tag{2}$$

where RMSE is the root-mean-squared error of the calibration curve (area as a function of concentration) and m is the slope of the calibration curve.

Subsequently, recovery values were determined by spiking one liter of deionized water with 100 μL of a concentrated pesticide standard mixture (100 ppm) to obtain a final concentration of 10 μg/L. The spiked samples were pumped through an activated Sep-Pak® C18 cartridge and followed the same procedure as mentioned above. The recovery (R%) was derived by dividing the observed concentration by the theoretically expected concentration (1 ppm, under 100% recovery efficiency).

Based on the abovementioned calibration curves and recoveries, the GC results were translated into environmental concentrations. More specifically, concentrations that exceeded the LOQ were divided by (1) the applied up-concentration factor (100) and (2) the pesticide-specific recovery efficiency. Pesticide signals that were not strong enough (i.e., exceeding the LOD, but not the LOQ) were not translated into environmental concentrations, but were included as part of the qualitative analysis. Hence, environmental detection and quantification limits were estimated to range from 0.01 to 0.2 μg/L and from 0.04 to 0.5 μg/L, respectively.

2.2.2. Pesticide Availability and Usage

A questionnaire-based assessment of ongoing pesticide availability for use was conducted in March 2019. Information was obtained on the type of pesticide compounds currently available in eleven districts surrounding Lake Tana (Figure 1). Based on face-to-face conversations with local sellers and officers, data on the type of pesticides and categories of pesticides were collected from 23 sources (the Regional Bureau of Agriculture, 11 pesticides retailers, and 11 plant protection section of districts). The questionnaire used for this assessment is included in the Supplementary Information (Figure S1).

2.3. Risk Characterization for Aquatic Biota

The potential ecotoxicological risk related to pesticide residues in water was predicted by calculating a risk quotient (RQ), which is defined as the ratio between the measured environmental concentration (MEC) and the predicted no-effect concentration (PNEC). Here, the MEC represents the quantified pesticide concentrations starting from the GC analyses, while the PNEC values were obtained by dividing the no-observed effect concentration (NOEC) of the most sensitive biotic level (algae, aquatic invertebrates, and fish) by the appropriate assessment factor (AF) [37–39]. Dividing by the AF allows one to account for uncertainties that might occur due to (i) inter- and intra-species variations and (ii) laboratory to environment extrapolation. In case no NOEC values were available, acute L(E)C50 values were used [5]. Table 1 provides an overview of the detected and quantifiable pesticides within the basin for which NOEC or L(E)C50 values are available. The applied assessment factor followed the approach of Papadakis et al. (2015) [39] and differed depending on the available information, ranging from 1000 (only short-term assays with associated L(E)C50 values) down to 10 (long-term assays with associated NOEC values for each biotic level). RQ values above 1 reflect a potential harmful risk, while RQ values below 1 reflect an acceptable risk.

Table 1. Critical pesticide residue concentrations for three trophic levels of aquatic organisms. NOEC (µg/L) for alachlor and cypermethrin, and L(E)C_{50} (µg/L) for DDE and DDT-op [5].

Pesticide	Algae	Aquatic Invertebrates	Fish	Lowest	Type	AF
Alachlor	20	220	190	20	NOEC	10
Cypermethrin	1300	0.04	0.03	0.03	NOEC	10
DDE	-	1	32	1	LC_{50}	1000
DDT-op	-	-	2500	2500	LC_{50}	1000

2.4. Human Health Risk Assessment

As indicated earlier, local populations are both directly and indirectly dependent on the surface water of Lake Tana. To understand the risk of the intake of the pesticide residues present in Lake Tana through water consumption, a human risk assessment was performed for different age groups (adult, children, and infants).

2.4.1. Exposure Assessment

The deterministic chronic exposure of the Ethiopian population to the water from Lake Tana was determined by calculating the estimated daily intake (EDI). The EDI was calculated by multiplying the maximum pesticide residue concentrations (µg/L) with the water intake rate (L/kg/day). The average intakes of drinking water for an adult (60 kg), child (10 kg), and infant (5 kg) were 2 L, 1 L, and 0.75 L per day, respectively [40,41]. The concentrations of DDT and its derivatives were summed (ΣDDT) per habitat (River, Wetland, and Lake) for the assessment, thereby assuming the equitoxicity of DDT-op, DDT-pp, and DDE [42].

2.4.2. Risk Characterization

For each pesticide, the chronic hazard quotient (HQ) (%) represents the exposure (EDI) relative to the acceptable daily intake (ADI) for alachlor and cypermethrin or the tolerable daily intake (TDI) for ΣDDT (µg/kg/day) [43]. The threshold values of alachlor and cypermethrin were obtained from the pesticide properties database [5], while values for ΣDDT were obtained from research by Pazou et al. (2013) [44]. The hazard index (HI) is the sum of all HQ's for all pesticides found in the water per habitat. If the HI is higher than 100, the mixture exceeds the maximum acceptable level; hence, a consumer health risk might occur. An initial screening was performed by considering the highest concentration per pesticide and per habitat. As such, a hypothetical worst-case scenario was created by pooling all sampling sites per habitat. In case the screening indicated a potential consumer health risk (i.e., HI > 100%), a more detailed sample-specific risk assessment would be performed.

2.5. Statistical Analysis

All statistical analyses were performed in RStudio [45,46]. For detected pesticides, it was hypothesized that season and habitat have an influence on the pesticide residue concentrations. To test these hypotheses, normality of the data was tested with the Shapiro–Wilk test and followed by Welch *t*-tests (season) or ANOVA (habitat) when the assumption of normality could not be rejected (all $p > 0.05$). In case normality could not be assumed (some $p < 0.05$), a nonparametric Kruskal–Wallis test was performed.

3. Results

3.1. Pesticide Use and Presence in Surface Water

3.1.1. Presence in Surface Water

In total, only seven pesticide compound residues were detected within surface water samples. Of these, DDE (the principal breakdown product of DDT) was the most frequently detected ($n_{>LOD} = 42$; $n_{>LOQ} = 35$), followed by bifenthrin ($n_{>LOD} = 27$; $n_{>LOQ} = 0$). Alachlor, DDT-op, DDT-pp, cypermethrin, and chlorothalonil were also detected, yet at a lower frequency ($n_{>LOD} < 5$) (Table 2). Pesticide concentrations that exceeded the LOQ were extrapolated to environmental concentrations and ranged from 0.08 ± 0.01 µg/L (DDE in wetland sites during the wet season) up to 0.59 ± 0.47 µg/L (alachlor in wetland sites during the dry season), see Table 2.

Table 2. Pesticide residues in surface water of the Lake Tana Basin (river, lake, and wetland), during the dry and wet season. For each pesticide, the number of sites with pesticide concentrations above the limit of detection ($n_{>LOD}$) and limit of quantification ($n_{>LOQ}$) is reported. In addition, pesticide occurrence is summarized with the mean and the associated standard deviation (SD) (ng/L). No standard deviation was derived when only a single sample was available.

						Dry (n = 27)						
Pesticides	**Rivers (n = 10)**			**Lake (n = 8)**			**Wetlands (n = 9)**			**All (n = 27)**		
	$n_{>LOD}$	$n_{>LOQ}$	**Mean ± SD (ng/L)**	$n_{>LOD}$	$n_{>LOQ}$	**Mean ± SD (ng/L)**	$n_{>LOD}$	$n_{>LOQ}$	**Mean ± SD (ng/L)**	$n_{>LOD}$	$n_{>LOQ}$	**Mean ± SD (ng/L)**
Alachlor	-	-	-	-	-	-	3	3	594 ± 468	4	3	594 ± 468
Bifenthrin	6	-	-	4	-	-	4	-	-	14	-	-
Chlorothalonil	-	-	-	1	-	-	-	-	-	1	-	-
Cypermethrin	-	-	-	1	1	545	-	-	-	1	1	545
DDE	10	8	94 ± 19	8	5	89 ± 14	8	6	94 ± 12	26	19	96 ± 15
DDT-op	1	1	316	-	-	-	1	1	168	2	2	242 ± 105
DDT-pp	-	-	-	-	-	-	1	-	-	1	-	-
						Wet (n = 16)						
Pesticides	**Rivers (n = 10)**			**Lake (n = 4)**			**Wetlands (n = 2)**			**All (n = 16)**		
	$n_{>LOD}$	$n_{>LOQ}$	**Mean ± SD (ng/L)**	$n_{>LOD}$	$n_{>LOQ}$	**Mean ± SD (ng/L)**	$n_{>LOD}$	$n_{>LOQ}$	**Mean ± SD (ng/L)**	$n_{>LOD}$	$n_{>LOQ}$	**Mean ± SD (ng/L)**
Alachlor	1	-	-	-	-	-	-	-	-	1	-	-
Bifenthrin	7	-	-	4	-	-	2	-	-	13	-	-
Chlorothalonil	1	-	-	-	-	-	-	-	-	1	-	-
Cypermethrin	-	-	-	1	1	135	-	-	-	1	1	135
DDE	10	10	105 ± 10	4	4	94 ± 13	2	2	80 ± 13	16	16	99 ± 14
DDT-op	-	-	-	-	-	-	-	-	-	-	-	-
DDT-pp	-	-	-	-	-	-	1	-	-	1	-	-

Table 2. *Cont.*

	All (n = 43)											
Pesticides	**Rivers (n = 20)**			**Lake (n = 12)**			**Wetlands (n = 11)**			**All (n = 43)**		
	$n_{>LOD}$	$n_{>LOQ}$	**Mean ± SD (ng/L)**	$n_{>LOD}$	$n_{>LOQ}$	**Mean ± SD (ng/L)**	$n_{>LOD}$	$n_{>LOQ}$	**Mean ± SD (ng/L)**	$n_{>LOD}$	$n_{>LOQ}$	**Mean ± SD (ng/L)**
Alachlor	1	-	-	-	-	-	3	3	594 ± 468	4	3	594 ± 468
Bifenthrin	13	-	-	8	-	-	6	-	-	27	-	-
Chlorothalonil	1	-	-	1	-	-	-	-	-	2	-	-
Cypermethrin	-	-	-	2	2	340 ± 290	-	-	-	2	2	340 ± 290
DDE	20	2	100 ± 15	12	9	91 ± 13	10	8	90 ± 13	42	35	96 ± 15
DDT-op	1	1	316	1	1	168	-	-	-	2	2	242 ± 105
DDT-pp	-	-	-	-	-	-	1	-	-	1	-	-

Overall, the highest concentrations of pesticides were measured from samples collected during the dry season. For example, cypermethrin (545 ng/L) was detected from LT3 (lake site in the southern part of the lake, near Bahir Dar); alachlor (1133 ng/L) from ME (Megech wetland, northern shore of Lake Tana); DDT-op (316 ng/L) from RR1 (Rib River, flowing into the lake from the east); DDE (118 ng/L) from RE_1 (Enfranze river, flowing into the lake from the south). More detailed information is available in Supplementary Information, Table S4.

Of the seven detected pesticide compound residues, only DDE was frequently quantifiable in the considered habitats and seasons to allow a statistical comparison. Still, the mean concentrations (± SD) of DDE during the wet and dry season were 99 ± 14 ng/L and 93 ± 16 ng/L, respectively, and reflected a nonsignificant difference (two-sample t-test: $t = -1.3141$; $p = 0.198$). At the habitat level, the mean concentration of DDE was highest at river sites (100 ± 15 ng/L) compared to the lake (91 ± 13 ng/L) and wetland sites (90 ± 13 ng/L), but this difference was also not statistically significant (one-way ANOVA: $F = 1.787$; $p = 0.184$).

3.1.2. Pesticide Availability and Usage

Based on the interviews, a total of 35 different pesticides were identified to be used within the Lake Tana Basin, with only three pesticides being included in the field sample analysis (Table 3). Remarkably, the list also includes compounds that are banned in Europe, USA, and China: diazinon, malathion, and endosulfan (see also Supplementary Information, Table S5) [47,48]. Among the available pesticides, 30 compounds (83%) can be classified as insecticides. Pesticides containing organophosphate, carbamate, and pyrethroid accounted for 51.4% of all reported pesticides. At the individual level, diazinon, chloropyrifos-ethyl, and dimethoate were reportedly available in every surveyed district, while both bifenthrin and malathion were reported in 91% (10/11) of the surveyed districts. In addition to these five compounds, an additional five compounds were reportedly available in at least nine of the surveilled districts (Table 4). Overall, more pesticides were used in districts surrounding the north-east parts of the basin (Takusa, Dembia, Dera, Libokemkem, and Gondar Zuria) than the southwestern part (Supplementary Information, Table S5).

Table 3. Subset of pesticides that are currently used in the Lake Tana Basin. Black dots indicate pesticide compounds available in the districts (columns) and investigated in the water samples. A complete overview of all reported pesticides can be found in Supplementary Information, Table S5. * = Banned or not approved in the European Union, USA, and China [47,48].

	Fogera	**Bahir Dar Zuria**	**North Achefer**	**South Achefer**	**Mecha**	**Alefa**	**Takusa**	**Dembia**	**Dera**	**Libokemkem**	**Gonder Zuria**
Bifenthrin *		•	•	•	•	•	•	•	•	•	•
Endosulfan *						•				•	
Chlorothalonil *				•		•	•	•	•	•	•

Table 4. List of pesticides that are used in at least 9 of the 11 districts in the Lake Tana basin.

Pesticides Reported through the Questionnaire	**Number of Districts**
Diazinon	11
Chloropyrifos	11
Mancozeb	11
Malathion	10
Lambda-cyhalothrin	10
Dimethoate	10
Deltamethrin	10
Bifenthrin	10
2,4-D	10
Profenofos	9

3.2. Environmental Risk for Aquatic Biota

The results of the ecological risk assessment of the maximum and minimum concentrations of the detected pesticides are presented in Table 5. Both the minimum and maximum concentrations of cypermethrin and DDE showed very high ecotoxicity risks (RQ > 1) toward the aquatic environment within each of the three habitats (lake, river, and wetland). By contrast, the concentrations of alachlor and DDT-op indicated no toxicity risk (RQ < 1).

Table 5. Ecotoxicological risk assessment based on risk quotient (RQ) using the minimum and maximum concentrations of the detected pesticides from lake, river, and wetland water. PNEC = predicted no-effect concentrations; RQ = risk quotient, with RQ values > 1 depicted in bold and underlined (unacceptable risk).

Pesticide	**Habitat**	**Concentration (ng/L)**	**PNEC (ng/L)**	**RQ**
Alachlor	Wetland	292–1133	2000	0.15–0.57
Cypermethrin	Lake	135–545	3	**<u>45–182</u>**
DDE	River	60.1–118.4	1	**<u>60–118</u>**
	Wetland	71.0–110.4	1	**<u>71–110</u>**
	Lake	71.9–109.9	1	**<u>72–110</u>**
DDT-op	River	316	2500	0.13
	Wetland	168	2500	0.07

3.3. Human Health Risk Assessment

The results from the human risk assessment indicated a low risk for consumers of the water of the Lake Tana Basin at the time and locations of the sampling campaign (Table 6). Infants appeared to have a higher risk for potential toxic chronic effects compared to children and adults. The hazard indices (HIs) in Table 6 indicate that the direct usage of water from the wetlands poses a higher risk compared to water from the rivers and lake. Based on the results of this initial screening, no additional site-specific hazard indices were calculated.

Table 6. Human risk assessment based on the hazard quotient (HQ) using the maximum concentrations of the detected pesticides from lake, river, and wetland water. ΣDDT represents the site-specific sum of DDT and DDE, assuming equitoxicity. EDI: Estimated daily intake; ADI: Acceptable daily intake, TDI: Tolerable daily intake.

Pesticide	**Habitat**	**Concentration (ng/L)**		**EDI (ng/kg/day)**		**ADI or TDI (ng/kg/day)**		**HQ (%)**	
			Infant	Child	Adult		Infant	Child	Adult
Alachlor	Wetland	1133.0	170.0	113.3	37.8	10,000	1.70	1.13	0.38
Cypermethrin	Lake	545.0	81.8	54.5	18.2	50,000	0.16	0.11	0.04
ΣDDT	River	420.8	63.1	42.1	14.0	10,000	0.63	0.42	0.14
	Wetland	278.1	41.7	27.8	9.3	10,000	0.42	0.28	0.09
	Lake	109.9	16.5	11.0	3.7	10,000	0.16	0.11	0.04
						HI (River)	0.63	0.42	0.14
						HI (Wetland)	2.12	1.41	0.47
						HI (Lake)	0.33	0.22	0.07

4. Discussion

The results of this study provide a baseline on the pesticide presence in the Lake Tana Basin and expand the regional knowledge on surface water pollution in Ethiopia. As such, it has the potential to support the development of local environmental protection programs. In total, 35 different pesticide compounds were reportedly available and used in the Lake Tana Basin, including several compounds that are banned in the EU, USA, or China [47,48] (Table 3 and Supplementary Information Table S4). This amount is not surprising, as a similar survey reported the use of 41 pesticides within the central Rift Valley (Ethiopia) [49] of which 24.4% were available for use in the Lake Tana Basin. This finding also corroborates earlier observations of Mengistie (2016) [50] on (1) the inefficient implementation of the national pesticide regulation, and (2) the uncontrolled imports of pesticides in Ethiopia, thereby highlighting that the application of pesticides needs to be evaluated and regulated from regional up to (inter)national levels.

4.1. Presence of Compound Residues

DDE was detected in almost every sample and represented the most widely detected compound in the basin. This corroborates other studies that were performed around the Tekeze Dam and Lake Ziway in Ethiopia, which also reported the relatively high presence of DDE [24,51,52]. These observations reflect the widespread use of DDT for controlling the spread of malaria in Ethiopia [17,20] and its tendency to persist in the environment, either as DDT or the breakdown product DDE [10]. Although bifenthrin was detected in 63% of the water samples, it always remained below the derived limit of quantification. As with DDE, the presence of bifenthrin is not surprising, as it is widely used for the control of malaria transmission in Ethiopia [20].

The concentrations of DDE were not significantly different between river, lake, and wetland sites nor between the wet and dry season. Overall, mean DDE concentrations were slightly higher during the wet season compared with the dry season, which contrasts the observation of the highest individual residue level being observed during the dry season. This nonsignificant result might be related to the opposing effects of (1) an increased input of pesticide residues into waterbodies following high rainfall events as reported by Delgado-Moreno et al. (2011) [53] and (2) the dilution effect of increased river flow (and, hence, a higher volume of water) during the wet season. In contrast to DDE, cypermethrin was only observed in two locations (i.e., at ZI_2 during the wet season and at LT3 during the dry season), both of which are situated in the southern part of the lake, near Bahir Dar city. This local presence can be associated with the active cultivation of vegetables in the surrounding lands and the high persistency of cypermethrin in the environment [54].

4.2. Environmental and Human Health Risk

Based on the environmental risk quotient (RQ) analysis, the observed concentrations of DDE are expected to generate a high risk for aquatic biota. This alarming observation is exacerbated by the fact that the majority of sampling sites (i.e., 35 out of 42) contain quantifiable DDE levels and, by extension, display a high environmental health risk. In addition, several other pesticide compounds can be present in those sites and increase the overall risk for aquatic biota [55]. For instance, cypermethrin levels exceeded the safety threshold levels in two sampling sites, thereby depicting a high pesticide-specific risk. By contrast, the concentrations of alachlor were sufficiently low to not expect a pesticide-specific environmental risk (RQ < 1). In addition to these pesticide-specific results, it should be noted that (1) more pesticides can be present at risk-inducing levels than screened during our study and (2) pesticide mixtures can result in additive, synergistic, or antagonistic effects [55]. The environmental health risk that is actually experienced by aquatic biota can, therefore, only be determined through controlled exposure experiments of the surface water in the Lake Tana Basin, distributed over different habitats and seasons. Nevertheless, these pesticide-specific findings suggest that aquatic biota in the Lake Tana Basin are already at risk due to the presence of pesticide residues and that protective regulations are indispensable.

Regarding the human risk assessment, the pesticide residues detected in the water at the different habitats displayed a low theoretical risk for the population drinking water directly from Lake Tana at present (see Table 6). Yet, considering that Lake Tana and its rivers support more than 6000 fishers [56] and water is used for both hygienic and domestic purposes, the reported pesticides might potentially be more harmful for local communities than calculated in the present study. Indirect exposure, bioaccumulation of pesticide residues in fish and locally grown crops, and biomagnification in the food chain can contribute greatly to the experienced health risk associated with the surface water quality within the Lake Tana Basin. For instance, studies performed in Lake Ziway (Ethiopia) observed biomagnification of DDE in four fish species [57], while the resulting levels of organochlorine pesticides (including DDT, hexachlorohexanes, and heptachlors) suggested a little risk to human health at present [52]. This highlights that complementary studies on (1) the concentrations of these compounds in the water column, sediment, suspended solids, and biota and (2) their associated human intake within the Lake Tana Basin are extremely valuable and crucial in safeguarding the health of local communities. Moreover, such studies provide valuable information to regulate the use of pesticides for disease control in the health and agriculture sectors.

A limitation of this study is the mismatch between the performed chemical analyses and the obtained data through the questionnaire, resulting in (1) the relatively low detection rate of reported pesticides and (2) the underestimation of the associated environmental and human health risk. Based on literature and prior knowledge of the region, the focus of this study was oriented toward persistent pesticides and their analysis via gas chromatography. Yet, our results of the questionnaire indicate that several recent and more water-soluble pesticides are currently available and being used, requiring a different analytical approach (e.g., through liquid chromatography). A new field study could resolve these issues by extending the list of reference pesticides and applying this different approach. For example, the results from the questionnaires indicated that 10 pesticides are available for use in the Lake Tana basin in at least 9 of the 11 districts (Table 4). From these 10 pesticides, only bifenthrin and chlorothalonil were analyzed and detected in the water samples. It is suggested for further research to assess the presence and concentration levels of the nine other pesticides.

5. Conclusions

The present study showed that banned pesticides are still being used and the overall use of pesticides poses a potential environmental health risk. Although no significant differences are observed between habitats or seasons, our observations indicate that continuous and long-term assessment and management of pesticide residues in the Lake Tana Basin are paramount to secure human health, food safety, and the concomitant socioeconomic aspects of fisheries. Moreover, further research is recommended to (1) investigate pesticide residues based on the compounds currently in use, (2) assess the presence and intake of pesticide residues in locally grown food products, and (3) evaluate and regulate the use of pesticides from regional to national levels.

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