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Pesticide Residues in Cabbage and Nile Tilapia and Implications on Human Health and Ecosystems: A Case of Fogera District in Ethiopia

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Abstract

Pesticides have posed health risks to consumers and the ecosystems in different parts of the world, including Ethiopia, and researchers recommend continual assessments of pesticide residues in food items and ecosystems to know the level of risks. This study aimed to quantify the pesticide residues in samples of cabbage and fish and their risks to humans and the ecosystems. The cabbage samples were collected from April to May 2023 from 3 market centers, and the fish samples were collected in June 2023 from two fish ponds of Fogera District of Ethiopia using appropriate sampling procedures, extracted using the modified QuEChERS methods, and analyzed using a triple quadrupole GC/MS technique to quantify the pesticide residues and level the risks to humans and the ecosystems. The findings of the present study confirmed that all the samples of cabbage and fish were contaminated with pesticide residues. More than 44% and 37% of pesticide residues detected in both cabbage and fish samples were organochlorine and organophosphate pesticides, respectively. Furthermore, 92.86% of the pesticide residues and 96.43% of the maximum pesticide residues in cabbage exceeded the MRL and the TQ set by the Codex Alimentarius Commission. The sum total hazard indices of the pesticide residues in the cabbage (22.320) and fish (43.071) were much higher than the threshold value. Though Fogera District is a potential area for fish production in ponds, agricultural pesticides are a threat to the sector. Establishing an efficient system of monitoring for the pesticide supply chain and application procedures, choosing the appropriate pesticide types, timing in spraying, and establishing pesticide-free buffer zones are crucial steps in mitigating the negative effects of pesticides in the area.

Pesticides are mixtures applied to control harmful pests that affect the quantity and quality of foodstuff, and they consist of insecticides, herbicides, and fungicides (Hassaan and Nemr 2020; Khan et al. 2020). The releases of persistent pesticides into water bodies through runoff and agricultural spray drift (Landos et al. 2021; Singh et al. 2018) contaminate aquatic ecosystems and contribute to the loss of fisheries and aquatic biodiversity (Lakhani 2015; Landos et al. 2021). Pesticides have affected the non-target plants and animals and caused a chain of extinction of species (Darçın and Darçın, 2017; Kassa 2017).

The inherent property of pesticides to cause adverse effects to human health, the environment, or property is a hazard (FDRE 2018), and a function of the severity of an adverse effect, the exposure time, and its likelihood is the risk (FAO and WHO 2016; WHO and FAO 2014). A study conducted in Central Vietnam indicated that 81% of sampled vegetables were contaminated with pesticide residues (Chau Nguyen et al. 2022). In Vietnam, farmers producing vegetables were highly exposed to pesticide residues during application. Nearly half of them were suffering from chronic diseases and physiological disorders (Van et al. 2020).

Pesticide use is a very common practice in the Amhara Region, Ethiopia, to control pests, diseases, and weeds (Tassew et al. 2018). However, the government of Ethiopia focused only on short-term economic feasibility without

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considering its impacts (Gubena 2016). The land use/ land cover change in the study area is very intense and ever increasing (Asres et al. 2019). As a result, most wetlands and natural forests of the Lake Tana watershed have been changed to cultivated land, and this cultivated land has increased progressively from 37.42% to 50.12% in the last 28 years (ANRS 2015a). An increase in the size of cultivated land and frequency of cultivation increases pesticide usage (Amera and Abate 2008; Maurya et al. 2019). The uncontrolled use of banned and expired pesticides in the Lake Tana watershed increased the types and amount of pesticides used per cropping season (ANRS 2015b; Negatu et al. 2016). Farmers in the study area use obsolete and persistent pesticides to control crop pests and improve the attractiveness of vegetables (Abaineh et al. 2023). Different studies also showed that farmers sprayed vegetables with toxic pesticides, harvested, and supplied them to users within short time intervals (Abaineh et al. 2024a; Van et al. 2020).

Pesticide residues in vegetables are major sources of health risks to consumers (Akan et al. 2013; Khan et al. 2020). Even lower amounts of pesticide residues might have adverse negative effects on human health (Shuja et al. 2022). The synergetic effects of pesticide residues rise the health risks of pesticides to consumers more than the effects of the sum total effects of the individual pesticide residues (Chaikasem and Roi-et 2020; Dakuyo et al. 2020; Shalaby et al. 2021). Pesticide residues are major causes of chronic diseases such as cancer, respiratory diseases, cardiovascular system, and metabolic system failures in consumers (Andersson et al. 2014; Pironti et al. 2021; UNEP/ AMAP, 2011). A study in Ethiopia confirmed that the sampled food items contained one or more types of pesticide residues, and one-third of the analyzed samples had pesticide residues more than the maximum residual limit (MRL) set by Codex Alimentarius Commission (Mekonen et al. 2014). Though vegetables are the major type of food consumed next to grains, they become the major health concern for consumers as pesticide residues are deposited on/ in them (Lawal et al. 2018).

Exposures of aquatic life to pesticides at concentrations above toxic thresholds can cause reproductive failure, loss of tolerance to extreme temperatures, inability to avoid predators, and loss of normal growth and development (Helfrich et al. 2009; Landos et al. 2021; Maurya et al. 2019; UNEP/ AMAP, 2011). Previous studies have been proved that there were no sex ratio differences in fish species in different lakes of Ethiopia (Teferi and Admassu 2002). However, currently, the feminization effects of pesticide residues on male fish are proved (Helfrich et al. 2009; Landos et al. 2021; Pironti et al. 2021). Moreover, a study conducted in Lake Tana indicated that there was some sex ratio difference in fish with a higher number of females (Anteneh et al. 2007).

Lake Tana and its adjacent wetlands have been exposed to pesticide residues year-round. Pesticide residues were detected in sampled fish species harvested from the river mouths of the Rib River and Gumara River (Sishu et al. 2022). Pesticide residue testing in food items and environmental components is becoming crucial to know the level of risks of ecosystems and consumers (Benbrook and Baker 2014; Shalaby et al. 2021; Wolde and Abirdew 2019).

Farmers of the District produced rice, vetch/chickpea, and vegetables per year starting in July of each year. The cabbage samples were purposely collected from April to May 2023. These months were the peak season of vegetable production, including cabbage. Cabbage, tomato, and onion were also the most commonly used food items in the District. Farmers sprayed pesticides repeatedly on vegetables in general, and 6.53 ± 2.62 times on cabbage in particular per a cropping season, and supplied it to consumers on average after 6.23 ± 1.65 days of spray (Abaineh et al.. 2024a). Most consumers in the study area were primarily concerned about the pesticide residues in cabbage than other vegetables because they believed that cabbage had more surface contamination due to the frequent pesticide spraying and its enfolding nature. So, prioritizing the analysis of pesticide residues in cabbage is so important.

Assessments of pesticide residues in fish samples are also so important to understand the level of pesticide residues in freshwater ecosystems as they are bioindicators (Ntow 2005; Rajendran et al. 2005). The concentration of pesticide residues in fish is indicators of the pesticide residues in water and forage of fish (Akan et al. 2014). However, no previous studies have been conducted on the levels of pesticide residues in cabbage cultivated on farms and in fish cultivated in fish ponds in the present study area and its implications for aquatic ecosystems and consumers. Thus, the main objective of this study was to analyze and quantify the pesticide residues in cabbage and fish samples collected from suppliers and fish ponds, using gas chromatography mass spectrometry (GC–MS) techniques to determine the risks to humans and the ecosystems.

Materials and Methods

Description of the Study Area

Fogera District is one of the ten Districts bordering Lake Tana, and it is bordered on the South by Dera District, on the West by Lake Tana, on the North by Libo-Kemekem District, on the northeast by Ebenat District, and on the East by Farta District (Gebey et al. 2012; Mohammed et al. 2019). The District is located in South Gondar Administrative Zone, northwestern Ethiopia (Fig. 1). Woreta, the capital of the District, is located 625 km northwest of Addis Ababa and 55 km from the

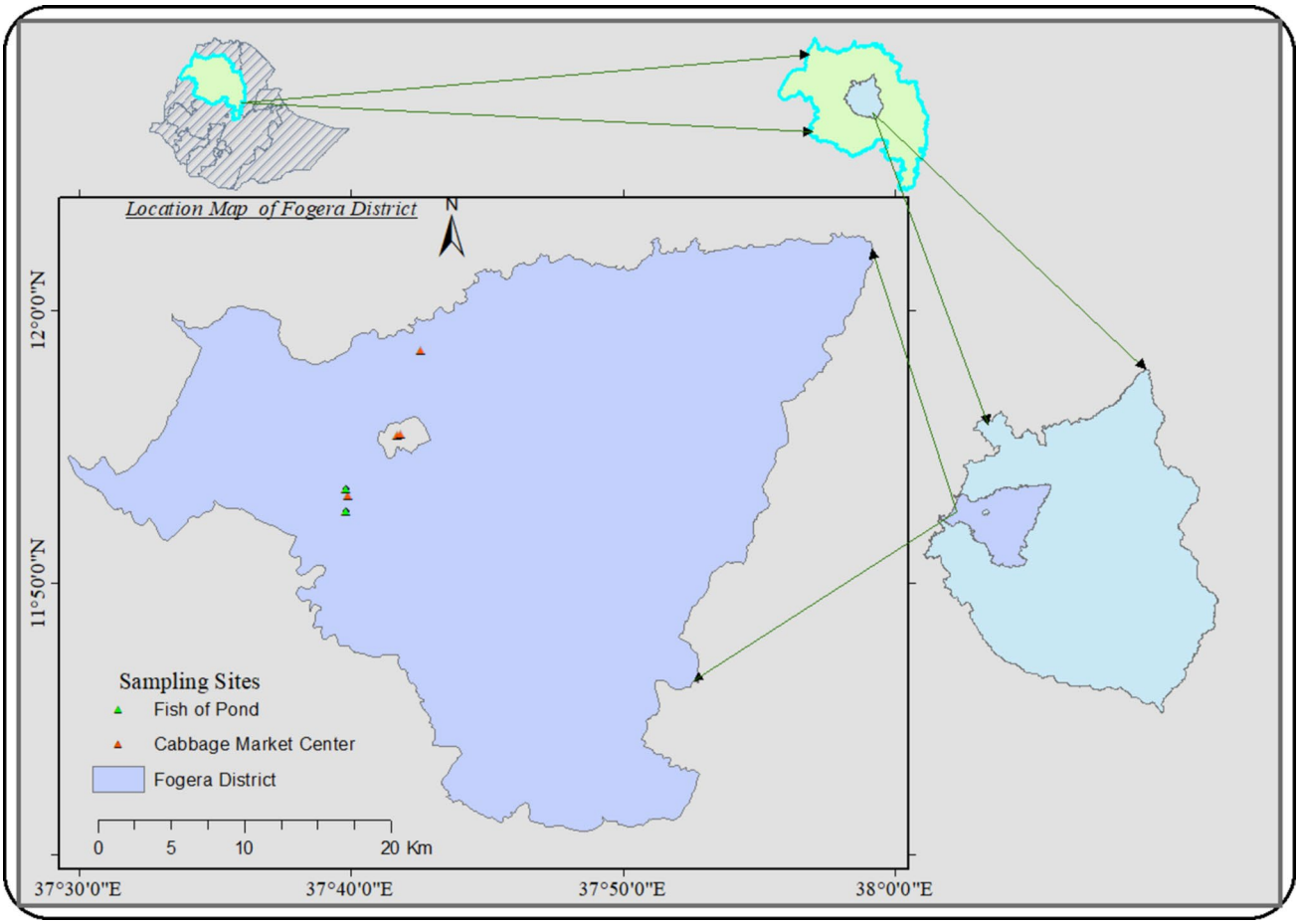

Fig. 1 Location map of sampling sites in Fogera District

Regional capital, Bahir Dar, and it is geographically located from 11°46' to 11°59'N latitude and 37°33' to 37°52'E longitude (Lema et al. 2017), and its altitude ranges from 1774 to 2415 m a.s.l. (Mohammed et al. 2019). The study area has an annual total rainfall ranging from 1103 to 1336 mm (Gebey et al. 2012). Among the 23,999.8 ha of wetlands in the Lake Tana watershed, 39.14% was in Fogera District (Hunegnaw et al. 2013). The floodplain of Fogera District is saturated for more than four months per year starting from July of each year. Fogera District is one of the cabbage-producing districts in the Amhara Region (Alula and Tesfaye 2021). From the 57,223 ha of farmlands cultivated in the District during the rainy season, 73.12% was used for cereal crop production, of which 53.35% was used for rice production (Fogera District Environment and Forest Protection Authority, 2022).

Methods of Data Collection

The samples of cabbage and fish were collected from three market centers and two fish ponds using a cross-sectional study design.

Cabbage Sample Collection

The cabbage samples were collected from local places named Nechafer, Woreta town, and Kokit Market Centers of the District. After collection, samples were temporarily stored in a cooler, transported to the laboratory, and put it in a -200c freezer for ten days in analytical chemistry laboratory of BDU until analysis. The cabbage samples were collected from suppliers using availability sampling techniques. A total of 22 cabbage samples weighing more than 2 kg each were collected for analyses as adapted from FSSAI, (2015, 2016) and Loha et al. (2020). The details of the cabbage sampling sites are shown in Table 1. The cabbages harvested within 24 h were purposely sampled, assuming that the time interval would have an effect on the concentration of the pesticide residues.

Fish Samples Collection

The fish samples were collected from two fish ponds located in Kuhar Michael sub-district of Fogera District in June

Table 1 Cabbage sampling site and date information

Source sub-district	Location of market centers (DMS)			Sample code	Harvest date
	X	Y	Elevation(meter)		
Shina	131° 43.7333′ 44"	35° 46.5333′ 32"	1821	SC_23_14aveg	04/04/2023
Shina				SC_23_24aveg	04/04/2023
Kuhar Michael				SC_23_34aveg	04/04/2023
Abuha Kokit	132° 41.3000′ 18"	36° 32.8167′ 49"	1794	SC_26_14aveg	04/04/2023
Abuha Kokit	132° 42.2000′ 72"	36° 35.4333′ 26"	1792	SC_26_24aveg	04/04/2023
Shina	131° 84.9667′ 58"	36° 19.1333′ 8"	1821	SC_27_14aveg	04/04/2023
Shina				SC_27_24aveg	04/04/2023
Kuhar Michael				SC_27_34aveg	04/04/2023
Shina				SC_27_44aveg	04/04/2023
Shina				SC_27_54aveg	04/04/2023
Shina				SC_27_64aveg	04/04/2023
Shina	131° 85.0500′ 3"	36° 21.9333′ 56"	1830	SC_188_14aveg	25/04/2023
Shina				SC_188_24aveg	25/04/2023
Shina				SC_188_34aveg	25/04/2023
Shina				Sc_188_44aveg	25/04/2023
Abuha Kokit				SC-188_54aveg	25/04/2023
Abuha Kokit				SC_188_64aveg	25/04/2023
Shina				SC_188_74aveg	25/04/2023
Shina				SC_188_84aveg	25/04/2023
Shina				SC_188_94aveg	25/04/2023
Shina				SC_188_104aveg	25/04/2023
Kuhar Michael				SC_B27_14aveg	25/04/2023

2023. The two ponds were selected purposely to compare the types and amounts of pesticide residues in the fish of the flood plain pond and outside the flood plain pond. One of the fish ponds is in the floodplain area and has been flooded yearly during the rainy season since July; the other is located outside of the floodplain. Six fish samples were collected from each fish pond for a total of 12 Nile tilapia (*Oreochromis niloticus*) using a net with a length of 50 m, a height of 2 m, and mesh size of 8 cm. The fish were then placed in a cooler during transportation and stored in a -20^{0}c freezer for 21 days in the analytical chemistry laboratory of BDU until analysis. The weight of the fish samples was measured in laboratory using an electronic analytical balance. The reason for the selection of the Nile tilapia species was its availability in several fish ponds in the district and the preference of the local community to consume Nile tilapia over other species of fish (Agmas and Adugna 2022). Fish sampling sites are summarized and presented in Table 2.

Materials and Chemicals

To analyze the pesticide residues, various chemicals and reagents were used. The solvents and acids used included: acetonitrile and methanol (99.8%) purchased from Alpha Chemika (Mumbai, India), and glacial acetic acid (99.8%) and acetone (chromatography and spectroscopy grade, 99.8%) purchased from Biochem Chemopharma (Cosne sur Loire, France). For extractions, QuEChERS extraction salts (6 g MgSo4 + 1.5 g NaOAc), QuEChERS clean-up reagents (900 mg MgSO4 + 300 mg PSA + 150 mg CGB), and extraction cartridges were purchased from Biocomma Limited (Shenzhen, China). A mixed pesticide reference standard was purchased from Sigma-Aldrich (GmbH, Switzerland). The analytical equipment utilized included a Model 7890B gas chromatograph coupled with a Triple Quadrupole 7000C series mass selective detector (MSD) supplied by Agilent Technologies (Wilmington, DE, USA). The mixed pesticide standard was bought and kept under low temperature, moisture, and light-free conditions to minimize the rate of degradation of each analytes. The pesticides in the mixed standard are summarized in Table (Table 3).

To undertake a multi-residue analysis, a pesticide stock solution (1 mg/mL) was prepared by dissolving 50 mg mixed pesticide standard in 50-mL volumetric flask using acetonitrile.

Table 2 Sampling sites of ponds in which Nile tilapia species collected

Sample	Weight (gram)	Pond types	Specific location of Sample Collection sites (DMS)		
			X	Y	Elevation (meter)
FS-1-2A	87	Fish pond 1	35° 44.5667′ 34"	131° 48.5000′ 30"	1750
FS-1-2D	83				
FS-1-2B	86				
FS-1-2E	87				
FS-1-2C	83				
FS-1-2F	84				
FS-2-1D	109	Fish pond 2	35° 44.7000′ 42"	131° 33.3833′ 23"	1835
FS-2-1A	102				
FS-2-1E	108				
FS-2-1B	108				
FS-2-1F	103				
FS-2-1C	105				

Table 3 Lists of pesticides in the mixed pesticide standard

Class of pesticides	Lists of pesticides in the mixed reference standard
organochlorine	BHC-alpha (benzene hexachloride), BHC-beta, BHC-delta, BHC-gamma (Lindane, HCH), DDE-o,p', DDD-o,p', DDE-p,p', DDT-o,p', DDT-p,p', Endosulfan I, Endosulfan II, Endosulfan sulfate, Endrin, Endrin aldehyde, Endrin ketone, Aldrin, Chlordane-cis (alpha), Chlordane-trans (gamma), Dieldrin, Heptachlor, Heptachlor exo-epoxide, Hexachlorobenzene, Methoxychlor, o,p'-, Indoxacarb
Organophosphate	Bromophos-ethyl, Chlorpyrifos-methyl, Diazinon, Disulfoton, Fenitrothion, Fenthion, Malathion, Parathion, Parathion-methyl, Profenofos, Dimethoate, Ethicon, Disulfoton, Phorate, Famphur, Sulfotep, Phosphorothioate, O,O,O-triethyl-, Thionazin
Pyrethroids	Cyfluthrin II, Cypermethrin I, Deltamethrin
Carbamate	Bendiocarb, Propoxur
Others	Piperonyl-butoxide, Dichlorobenzonitrile, 2,6-, Diphenylamine, Propargite

Sample Preparation and Analyte Extraction

The extraction of pesticide residues was executed using QuEChERS methods. The samples of cabbage were prepared following the buffered procedures as adapted from Adeniyi et al. (2016) and Koesukwiwat et al. (2010). The edible portions of the cabbages were separated, chopped, and homogenized without washing. Fifteen grams of homogenized cabbage samples in triplicates was added to 50-mL centrifuge tubes, and then, 15 ml of 1% acetic acid in acetonitrile was added and vortexed for 1 min. The steps used in the extraction of analytes are summarized in Table (Table 4).

The extraction of the analytes was carried out using the modified AOAC 2007.01 method (Rejczak and Tuzimski 2015) and the 2nd method used by Song et al. (2019).

Similar to cabbage, the dorsal muscles of the fish were separated and homogenized using a mini-homogenizer. Five grams of the homogenized samples was added into 50-ml centrifuge tubes; 10 mL acetonitrile was added and vortexed for 1 min. Then, the extractions of the analytes were carried out following a slightly modified AOAC 2007.01 QUECHERS method as used by Kankanamge et al. (2018) and Akor and Faruruwa (2021). The analyte extraction process was carried out in the analytical chemistry laboratory of BDU following the steps summarized in Table (Table 5).

Operating Conditions of the GC–MS/MS

The analysis of pesticide residues was performed using GC–MS/MS. The chromatographic separations were conducted with a DB-5 capillary column, having a length of 50 m, an internal diameter of 0.32 mm, and a film thickness of 0.17 µm (Fisher scientific). Samples were injected in a splitless mode, and helium was used as the carrier gas at a rate of 1 mL/min. The injector temperature was set at 250 °C, the transfer line temperature at 285 °C, the ion source temperature at 280 °C, and the quadrupole temperature at 150 °C. The oven temperature program started at

Table 4 Steps showing pesticide residue extraction from cabbage, clean-up, and GC–MS techniques. *Source*: Lawal et al. 2018 and Rejczak and Tuzimski 2015

Step-1
Homogenization of each of the cabbage samples
Adding 15 g homogenized sample into 50-mL centrifuge tube
Addition of 15 ml of 1% acetic acid in ACN to the homogenized sample
Shaking the mixture intensively for 1 min
Step-2
Adding 6 g anhydrous MgSO4 and 1.5 g sodium acetate to the mixture
Shaking the mixture intensively for 1 min
Vortexing the mixture for 5 min at 3200 rpm to separate supernatants
Step-3
Transferring 6 ml supernatant to a clean-up tube containing 900 mg MgSO4, 300 mg PSA and 150 mg GCB
Vortexing the mixture for 1 min
Centrifugation of the mixture at 3500 rpm for 1 min
Step-4
A cleaned extract was transferred to a vial passing through a syringe filter, plugged it and tightly bound the vials with Teflon
Kept it in deep freeze until the GC/MS analyses
A cleaned extract was transferred to a vial passing through a syringe filter, plugged it and tightly bound the vials with Teflon
Step-5
Analysis of the analytes using the GC–MS techniques

Table 5 Steps showing pesticide residue extraction from fish, clean-up, and GC-MS techniques *Source*: Rejczak and Tuzimski 2015; Adeniyi et al. 2016; Akor and Faruruwa, 2021

Step-1
Homogenization of the fish samples
Adding 5 g homogenized sample into 50-mL centrifuge tube
Addition of 10 ml ACN to the homogenized sample
Shaking the mixture intensively for 1 min
Step-2
Adding 6 g anhydrous MgSO4 and 1.5 g sodium acetate to the mixture
Shaking the mixture intensively for 1 min
Vortexing the mixture for 5 min at 3200 rpm to separate supernatants
Step-3
Transferring 6 ml supernatant to a clean-up tube
Adding 900 mg MgSO4, 300 mg PSA, and 150 mg GCB on the supernatant solution
Vortexing the mixture for 3 min
Centrifugation of the mixture at 3500rpm for 1 minute
Step-4
A cleaned extract was transferred to a vial passing through a syringe filter, plugged it, and tightly bound the vials with Teflon
Kept it in deep freeze until the GC/MS analyses
Step-5
Analysis of the analytes using the GC-MS techniques

60 °C for 1 min, then increased to 120 °C at a rate of 10 °C/min, and then raised to 220 °C at a rate of 5 °C/min. Subsequently, the temperature was increased to 250 °C at a rate of 8 °C/min (and held for 10 min), and finally, it was increased to 290 °C at a rate of 20 °C/min and held for 2 min. as used by Shalaby et al. (2021). The GC separated the pesticide residues based on their boiling points, volatility, and polarity, and the MS operated in selected ion mode (SIM) identified the pesticides according to the chromatographic retention times and monitoring of the ion transitions listed in Supplemental Information in Table S4.

The working standard solutions with seven concentration levels were analyzed using GC–MS/MS to validate the efficiency of the method. The method was validated by

calculating the linearity of the calibration curve (R^2), the limit of detection (LoD), the limit of quantitation (LoQ), the % mean recovery of the analytes (%R), and the relative standard deviation (RSD). Various volumes of stock solutions (1 mg/mL) were taken and diluted in acetonitrile to produce a working standard of 1, 2, 5, 10, 20, 30, and 50 µg/mL, respectively. The linearity coefficient (R^2) and the polynomial equation were automatically computed after the GC–MS analysis. The LoD and LoQ were calculated by dividing the standard deviation of the y-intercept (standard error) by the slopes of the calibration curve (the x coefficient of the polynomial equation).

$$\mathrm{LoD} = \frac{3.3 * \mathrm{SD}}{\mathrm{Slope}} \tag{1}$$

$$\mathrm{LoQ} = \frac{10 * \mathrm{SD}}{\mathrm{Slope}} \tag{2}$$

The %R (accuracy) was calculated by dividing the concentration of pesticides recovered to the concentration added into the samples.

$$\mathrm{Recovery}(\%) = \frac{\text{Conc. in spiked} - \text{conc. unspiked (mg/kg)}}{\text{Concentration added (mg/kg)}} \times 100 \tag{3}$$

The % RSD (precision) was calculated by dividing the standard deviation (SD) of the replicates to the mean % recovery value of the replicates.

$$\%\mathrm{RSD} = \frac{\mathrm{SD}}{\%\mathrm{Rmean}} \times 100 \tag{4}$$

The %R Values ranged from 70% to 120, and the % RSD values less than 20% were scientifically acceptable (Li et al. 2020).

Quality Control in Pesticide Analysis

Each sample of the cabbage and fish was labeled, including the samples' harvest and collection date, the name of the farmers supplied the samples and their villages in the subdistrict, and the analysis required. Care was taken to avoid contamination of the samples during sampling, transporting, storing, and analyses. This is to avoid a false positive and false negative analysis results as used by FSSAI (2015). Thus, all test tubes and all equipment used in contact with the samples were washed with detergents and conditioned using methanol and distilled water in a 5:3 ratio to avoid possible contaminants.

A reagent blank (negative control) was prepared by pipetting 10 ml distilled water, and then, the analytes were extracted following the steps mentioned in Table 4. Then, one of the cabbage samples was homogenized and split into two halves, for unspiked and spiked sample analysis. The unspiked portion was added into each of the three 50-ml centrifuge tubes and extracted following the steps used by Adeniyi et al. (2016). The positive controls (spiked samples) of the cabbage were prepared by adding 15 g of homogenized cabbage into each of the three 50-ml centrifuge tubes, and then, 2, 5, and 10 µg/ml working standard solutions were added into each of the centrifuge tubes, vortexed, and allowed to sit for 30 min. Then, the analytes were extracted from the spiked samples following the steps used by the unspiked samples. Then, the triplicates of the unspiked and spiked samples of cabbage were analyzed using the GC/MS, and the difference in concentration was computed to validate the efficiency of the technique. Similarly, the unspiked fish samples were prepared by adding 5 g of homogenized fish into each of the three 50-ml centrifuge tubes. The spiked fish samples were prepared by adding 5 g of homogenized fish samples of the same source into each of the three 50-mL centrifuge tubes and then adding 2, 5, and 10 µg/mL working standard solution on the spiked samples, respectively, vortexing, and allowing it to sit for 30 min. Then, the spiked and unspiked samples were extracted following the steps summarized in Table 5.

Human Health Risk Assessment

The pesticide residues in the samples were calculated and compared with standards of maximum residual limit (MRLs) and acceptable daily intake (ADI) (PPDB 2024). The estimated daily intake (EDI) of the pesticides was computed by multiplying the concentration of each of the pesticides in the samples and the daily food consumption assumptions of individual consumers and then dividing it to their body weight. The formula used to calculate the EDI of the pesticide residues in the samples was:

$$\begin{aligned} EDI &= \sum \{A\,x\,B\}/C \\ A &= \text{food consumption } (kg/person/day) \\ B &= \text{pesticide concentration } (mg/kg\,food) \\ C &= \text{body weight } (kg) \end{aligned} \tag{5}$$

The Ethiopia dietary guideline described that 100 – 170 g of vegetables/ day /person was the daily intake standard of the country, and 35 g / day/person was the intake of cabbage (Federal Government of Ethiopia et al. 2022). Thus, 35 g/day/ person was taken as the daily intake in this study. Though different studies confirmed that 68.5 g/person/day was used to estimate the daily fish food intake in Egypt (Akoto et al. 2016; Shalaby et al. 2019), 30 g/day/person was used to assess the EDI, taking 60 kg as adult body weight (WHO and FAO 2009; Yohannes et al. 2014). The EDI was focused on a specific population group living in Fogera

District, around the lake and rivers. The EDI was compared with ADI to level the health risks of each pesticide residue to humans (European Food Safety Authority 2022). The hazard quotient (HQ) of each pesticide residue was summed up to estimate the hazard index (HI) and the health risks (HR).

$$HQ = EDI/ADI \quad (6)$$

The HQ summed up to give a hazard index (HI)

$$HI = \sum HQ \quad (7)$$

HQ = 1 and HI = 1 is the threshold. If the HQ or HI is greater than 1, it is believed that it will cause a health risk to consumers. The ADI of the pesticides was taken from the European Food Safety Authority (EFSA 2020). The toxicity quotient (TQ) and the pesticide toxicity index (PTI) were estimated by dividing the maximum concentration of a pesticide in the cabbage to its corresponding MRL and summing up the TQ, respectively.

$$TQ = C/MRL \quad (8)$$

$$PTI = \sum TQ \quad (9)$$

where C is the maximum concentration of individual pesticide residue (mg/kg); TQ is the toxicity quotient; MRL is the maximum residual limit (mg/kg); and PTI is the pesticide toxicity index. If PTI is lower than 1, the concentrations of the pesticides are not at the level to cause risk to human health (Chaikasem and Roi-et 2020).

Statistical Analysis

The results of the GC–MS were computed using Excel and SPSS to quantify the pesticide residues and define their implications on the health of humans and the ecosystem. Descriptive statistics were used to calculate the mean, range, frequency, and percentage of the detected pesticides and the samples contaminated. One-way ANOVA was performed to compare the concentration of pesticides in cabbage from the three sites, and independent t-test was used to compare the pesticide residues in fish of the two ponds.

Results

Analytical Method Validation

The method validation was carried out for 50 pesticides for both the cabbage and fish samples, and its results (linear correlation coefficient, LoD, LoQ, and % recoveries) in the cabbage and fish samples were summarized and are presented in Table 6. The results of method validation confirmed that the R^2 values of the 38 pesticides in both cabbage and fish samples were > 0.99. The % recoveries of the pesticide residues in the cabbage samples ranged between 70.4% (Endosulfan sulfate) and 116.1% (Hexachlorobenzene), and the corresponding %RSD was < 15%. Similarly, the % recoveries of pesticides in the fish samples ranged between 74.66% (Cypermethrin I) and 119.72% (DDT-p,p'), and the % RSD was < 14%. If the linearity is > 0.99, the mean recovery is in the range between 70 and 120%, and the % RSD is ≤ 20%, the analytical method is suitable and acceptable for the multi-residue analysis (European Commission, 2017; FSSAI 2017; Mekonnen et al. 2021; Park et al. 2022).

The LoDs of the pesticides ranged from 0.0017 mg/kg to 0.0240 mg/kg, and the LoQs ranged from 0.0053 mg/kg to 0.0728 mg/kg in Endrin aldehyde and DDE-p,p', respectively. Therefore, this method is appropriate for the analysis of the target pesticides in both cabbage and fish samples. A chromatogram showing the analysis of pesticides in calibrated mixed pesticide standards is presented (Fig. 2).

Analysis of Pesticide Residues

To level human health risks of pesticide residues in sampled cabbages, the pesticides were identified and quantified. A chromatogram showing the results of analysis of the pesticide residues in a cabbage sample is presented in Fig. 3.

Among the detected pesticides in sampled cabbages and fish, 44.44% were organochlorine pesticides, as shown in the pie chart (Fig. 4).

The pesticides detected and quantified in cabbage are presented in Table 7. To estimate the human health risks of pesticide residues in sampled cabbages, the EDI of each pesticide was compared with their corresponding ADI and MRL values (European Food Safety Authority et al. 2022; WHO 2024). The information in Table 7 included the EDI, ADI, HQ, MRL and HI of the pesticides in the cabbage samples.

As shown in Table 7, the mean concentration of 25 out of 28 pesticides exceeded the MRL values of the pesticides. The calculated EDI of Disulfoton, Endrin, Endrin aldehyde, and Endrin ketone was greater than their corresponding ADI. Though the HQ of most pesticide residues in the cabbage samples was less than 1, the sum total concentrations of the pesticide residues exceeded the acceptable limit of the pesticide residues.

Among the 22 cabbage samples collected, 4, 3, and 13 were from Abuha Kokit, Kuhar Michael, and Shina subdistricts, respectively. The mean pesticide residue concentration of the sub-districts is summarized in Table 8.

The ANOVA test results confirmed that there was no significant mean difference in the concentration of the pesticide residues in the cabbage samples across the sampling sites (annexed in appendix V).

Table 6 Results of the analytical method validation of the parameters for samples of cabbage and fish. *Source*: the analysis results of this study

Compound	Class	R^2	LoD (mg/kg)	LoQ (mg/kg)	Cabbage		Fish	
					%R mean	%RSD	% R Mean	%RSD
Aldrin	Organochlorine	0.999	0.004	0.012	111.000	0.000	111.000	0.000
Bendiocarb	Carbamates	0.996	0.006	0.019	94.900	0.004	94.900	0.000
BHC-alpha (benzene hexachloride)	Organochlorine	1.000	0.004	0.011	108.000	0.001	108.000	0.011
BHC-beta	Organochlorine	1.000	0.004	0.011	109.000	0.003	109.000	0.000
BHC-delta	Organochlorine	1.000	0.004	0.011	107.000	0.002	107.000	0.026
BHC-gamma (Lindane, gamma HCH)	Organochlorine	1.000	0.004	0.011	108.000	0.000	108.000	0.011
Bromophos-ethyl	Organophosphates	0.998	0.006	0.017	94.200	0.000	94.200	0.000
Chlordane-cis (alpha)	Organochlorine	0.998	0.006	0.018	77.000	0.000	77.000	0.000
Chlordane-trans (gamma)	Organochlorine	0.998	0.006	0.017	75.700	0.000	75.700	0.000
Chlorpyrifos-methyl	Organophosphates	0.999	0.009	0.028	75.900	0.005	75.900	0.019
Cyfluthrin II {CAS # 68,359–37-5}	Pyrethroids	0.992	0.013	0.039	90.600	11.300	112.000	1.390
Cypermethrin I (Zeta)	Pyrethroids	1.000	0.011	0.033	78.200	9.740	74.700	2.450
DDD-o,p'	Organochlorine	0.999	0.003	0.009	106.000	4.930	109.000	0.021
DDE-o,p'	Organochlorine	0.999	0.002	0.007	107.000	3.210	116.000	3.480
DDE-p,p'	Organochlorine	0.999	0.024	0.073	75.300	8.370	116.000	0.263
DDT-o,p'	Organochlorine	0.999	0.003	0.009	106.000	4.940	109.000	3.240
DDT-p,p'	Organochlorine	0.997	0.005	0.015	82.000	3.380	120.000	0.048
Deltamethrin	Pyrethroids	1.000	0.011	0.032	70.600	7.150	76.200	6.850
Diazinon	Organophosphates	1.000	0.004	0.013	92.800	0.003	92.800	0.000
Dimethoate	Organophosphates	0.999	0.004	0.011	91.700	0.000	91.700	0.000
Disulfoton	Organophosphates	1.000	0.004	0.011	103.000	0.036	103.000	0.180
Endosulfan I (alpha isomer)	Organochlorine	0.998	0.003	0.010	107.000	0.000	107.000	0.000
Endosulfan II (beta isomer)	Organochlorine	0.999	0.003	0.008	111.000	5.240	112.000	0.196
Endosulfan sulfate	Organochlorine	1.000	0.008	0.026	70.400	12.500	81.900	0.141
Endrin	Organochlorine	0.998	0.002	0.007	115.000	5.330	114.000	5.140
Endrin aldehyde	Organochlorine	0.998	0.002	0.005	99.400	4.090	102.000	5.850
Endrin ketone	Organochlorine	1.000	0.020	0.061	117.000	4.310	115.000	1.930
Fenitrothion	Organophosphates	1.000	0.005	0.016	84.500	0.001	84.500	0.003
Fenthion	Organophosphates	1.000	0.005	0.016	83.000	0.002	83.000	0.000
Heptachlor	Organochlorine	1.000	0.004	0.011	106.000	0.000	106.000	0.000
Heptachlor exo-epoxide (isomer B)	Organochlorine	0.999	0.004	0.012	109.000	0.000	109.000	0.000
Hexachlorobenzene	Organochlorine	1.000	0.004	0.012	116.000	0.000	116.000	0.000
Malathion	Organophosphates	0.999	0.007	0.021	113.000	6.920	117.000	0.459
Parathion	Organophosphates	0.999	0.007	0.020	88.200	2.290	93.400	0.445
Parathion-methyl	Organophosphates	1.000	0.010	0.029	75.800	0.002	75.700	0.004
Piperonyl-butoxide	Heterocyclic	0.999	0.009	0.027	107.000	10.400	115.000	0.054
Profenofos	Organophosphates	0.998	0.014	0.041	82.300	3.540	89.400	0.217

Similar to the pesticide residues in cabbage samples, the pesticide residues in fish samples were also identified and quantified using GC–MS/MS. A chromatogram showing the results of one of the fish samples (FS-1-2A) is presented in Fig. 5.

The EDI, ADI, HQ, and HI of 28 pesticide residues quantified in the fish samples were also summarized and are presented in Table 9. Among the 28 pesticide residues quantified in the fish samples, the HQs of six of the pesticides exceeded the daily acceptable limit.

The results of the independent samples t-test between fish samples of the two ponds confirmed that there was no significant mean difference in the pesticide residue concentration between the two groups of fish samples of the two ponds. The mean pesticide residue concentration in fish of pond 1 (M = 2.866, SD = 2.991) was slightly higher than the pesticide residue concentration in fish of pond 2 (M = 2.784, SD = 3.037). However, the magnitude of the difference in mean (mean difference = 0.082, 95% CI:

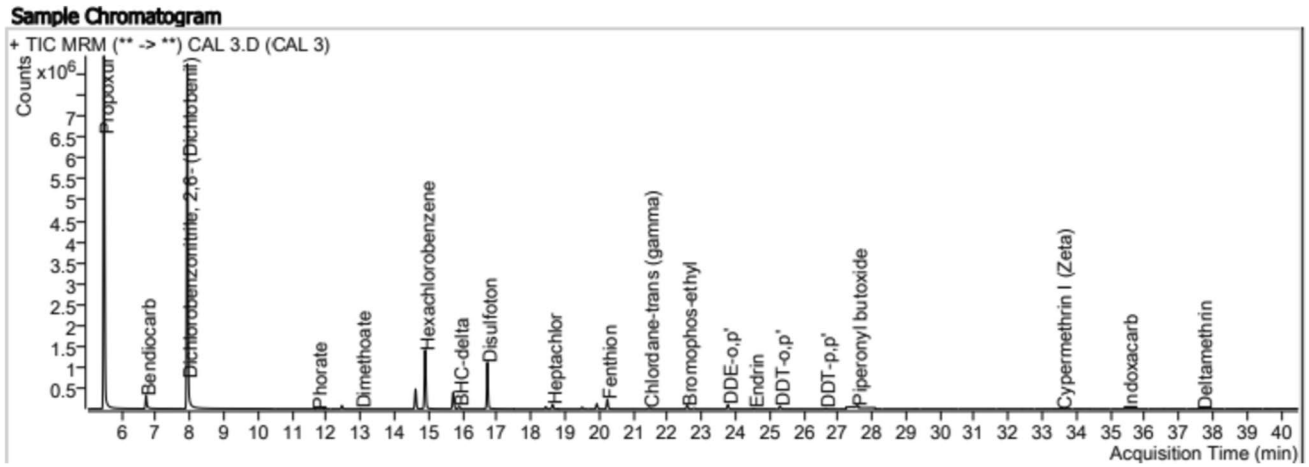

Fig. 2 Selected ion chromatograms showing results of analysis of calibration No 3 (5 µg/mL), *Source*: analysis results of this study

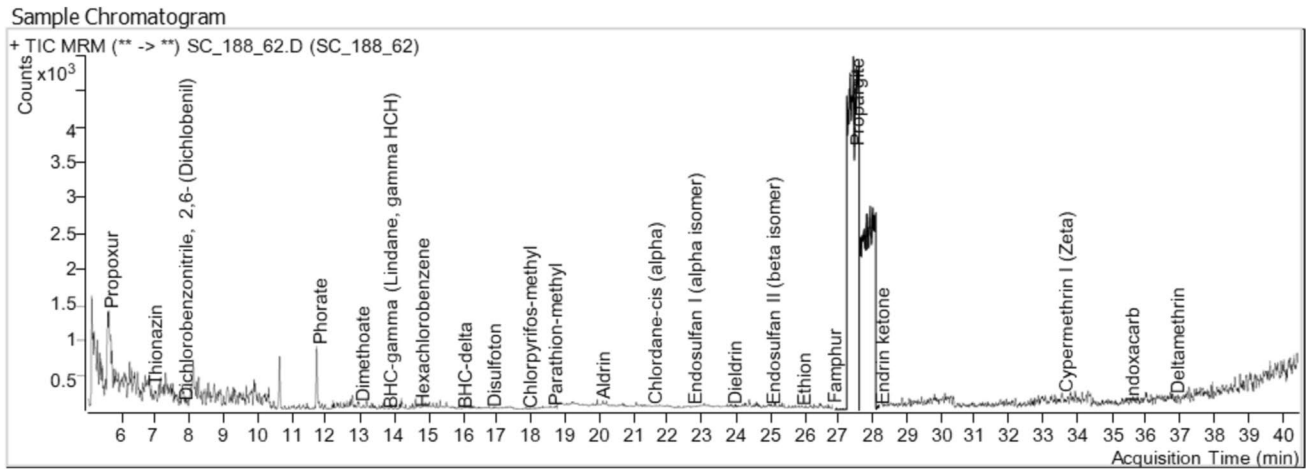

Fig. 3 Selected ion chromatograms showing of pesticides in cabbage sample SC_188_62. *Source*: the analysis results of this study

0.11569 to 0.30617) between the two groups of fish in the ponds was not significant (Table 10).

Discussion and Implications

Among the pesticide residues detected in the 22 cabbage samples, the concentrations of 25 of the 28 pesticide residues exceeded the MRLs. This indicated that the pesticide residues in cabbage samples were above the legally recommended concentration set by the Codex Alimentarius Commission (Department of Agriculture Food and the Marine Laboratories, 2015). In addition to the 25 pesticides, 18.2% and 90.9% of the cabbage samples contained parathion and Cypermethrin I beyond the corresponding MRLs, respectively. The toxicity quotients (TQs) of pesticide residues in cabbage samples apart from piperonyl-butoxide were greater than the threshold. The comparison of the EDI and their corresponding ADIvalues of the pesticide residues in the cabbage confirmed that they are at the level of causing health risks to consumers. The HQ of individual pesticides such as Disulfoton (1.24), Endrin (1.22), Endrin aldehyde (3.44), and Endrin ketone (13.66) exceeded the acceptable limit and could expose the consumers to various health risks. In general, the HI (22.32) of the pesticide residues in the cabbage samples was much higher than the acceptable limit and could expose consumers to health risks. A similar study on vegetables cultivated near Lake Ziway confirmed that the total HQs of the pesticide residues in onion exceeded the acceptable limit (Demsie et al. 2024). A similar study conducted in the river basin of Thailand confirmed that the cumulative risk indices of pesticides in vegetables are higher than the individual risk index (Chaikasem and Roi-et 2020). In addition to cabbage, various vegetables, including tomato,

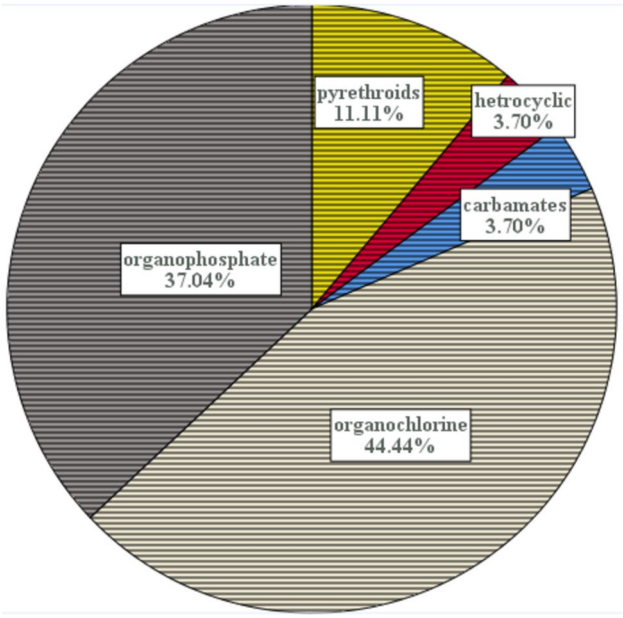

Fig. 4 Composition of the pesticides detected in the samples of cabbage

onion, garlic, and pepper, which are sprayed with highly toxic pesticides in this study area, are also supplied to consumers (Abaineh, et al. 2024a).

Moreover, more than 44% of the pesticides residues in both cabbage and fish samples were organochlorine pesticides. The mean concentration of organochlorine pesticides ranged from 0.266 to 4.683 mg/kg in cabbage samples and from 0.492 to 10.174 mg/kg in fish samples. The chlorinated pesticides are persistent, nonpolar, and lipophic and bioconcentrated in the body of humans and remain for 50 years (Hassaan and Nemr 2020). The ratio of parent DDT to DDD and DDE (DDT ÷ (DDD + DDE)) in cabbage and fish was 3.320 and 3.490, respectively. This is an important evidence for recent applications of DDT in the study area (Cembranel et al. 2017; Mwevura et al. 2002). Organophosphates were the other commonest contaminants identified in both cabbage and fish samples. More than 37% of the pesticides detected in cabbage and fish samples were organophosphates. The concentrations of organophosphate pesticides in cabbage samples ranged from 0.034 to 4.530 mg/kg and in fish samples from 0.157 to 9.3752 mg/kg. The higher concentrations of organophosphates and Carbamates in the samples were another evidence for the recent application of these pesticides. Organophosphates and carbamates are less persistent in the environment compared to organochlorine pesticides. In the cabbage samples, 92.86% of pesticide residues, 96.43% of the maximum pesticide residues, and 17.86% of the EDI of pesticide residues exceeded the MRL, TQ, and ADI, respectively. A similar study conducted in Ghana showed that 66.67% of the cabbage samples contained pesticide residues exceeding the MRL (Lee and Choi 2020). Similarly, 81% of vegetables in Central Vietnam were contaminated with pesticide residues, and farmers producing the vegetables were suffering from pesticide-related respiratorial and gastrointestinal disorders (Ngoc et al. 2020; Chau Nguyen et al. 2022).

Similar to the pesticide residues in cabbage samples, the 28 pesticide residues in the fish samples were also quantified, and the EDI was compared with the corresponding ADI of each pesticide. However, there was no well-established MRL of the pesticides for fish to calculate the toxicity quotient (TQ) and level of the pesticide toxicity index (WHO 2024). The HQ values of the six pesticides, namely Bendiocarb (2.63), Diazinon (1.31), Disulfoton (2.12), Endrin (2.19), Endrin aldehyde (6.07), and Endrin ketone (25.43), were more than the acceptable limit. The concentrations of the parent DDT and its metabolites in fish samples in this study (8.187 mg/kg) were much more than the pesticide residues in fish samples from Lake Tana (0.0712 mg/kg), and all the samples of fish in this study were contaminated with organochlorine pesticides. Agmas and Adugna (2022) confirmed that only 37.84% of the fish samples were contaminated with organochlorine pesticides. The study of Zelalem et al. (2023) also concluded that consumption of fish harvested from lake Tana did not have any health risk to consumers (Zelalem et al. 2023). However, a study by Zelalem et al. (2023) did not include the pesticides detected in this study except Diazinon, Malathion, Parathion, and Piperonyl-butoxide. Similar studies conducted in the Central Rift Valley Lakes of Ethiopia confirmed that the concentration of pesticide residues in the fish samples was lower than the pesticide concentration of the present study (Yohannes et al. 2014). In line with the present study, 100% of the fish samples in Middle Volta basin and 80% of the freshwater fish samples in Srilanka were contaminated by organochlorine pesticides (Gbeddy et al. 2012; Kankanamge et al. 2018). The lateral land use practices, the overall size of the water bodies, its size to catchment ratio and the inherent runoff potential, vulnerability to flooding, the duration of inflow of water in the year, the buffer zone vegetation cover, and sensitivity to pollutants are important determinants of water pollution (Hirpo 2018; Macfarlane and Bredin 2017;). As the size of the water body and the inflow of water increase, its buffering capacity increases (Macfarlane et al. 2014). Hence, the pollutant buffering capacity of the tributary rivers and Lake Tana is higher than small-sized fish ponds.

There were more than 38 permanent and 24 seasonal fish ponds in Fogera District, including the Woreta town. The District is the primary area in the region for fish cultivation in farmers' individual ponds. However, the ponds are more likely to be polluted by agricultural pesticide spray drift and during flooding. The pesticides could pose ecological risks to the fish and other aquatic organisms and lower their

Table 7 Pesticide residues detected and quantified in the cabbage samples of Fogera district and its health implications. *Source*: European Food Safety Authority et al., 2021; WHO 2024 and the analysis results of this study

Cabbage	R^2	Mean (mg/kg)	SD	MRL (mg/ kg bw)	TQ (C/MRL)	EDI(mg/kg bw)	ADI(mg/ kg bw)	HQ	HR
Aldrin	0.999	ND	ND	ND	ND	ND	ND	ND	ND
Bendiocarb	0.996	1.020	0.103	0.010	105.000	0.001	0.004	0.150	No
BHC-alpha (benzene hexachloride)	1.000	0.686	0.000	0.010	68.600	0.000	0.005	0.080	No
BHC-beta(benzene hexachloride)	1.000	0.684	0.049	0.010	69.500	0.000	0.005	0.080	No
BHC-delta	1.000	0.464	0.060	0.010	48.200	0.000	0.005	0.060	No
BHC-gamma (Lindane, HCH)	1.000	0.686	0.000	0.010	68.600	0.000	0.005	0.080	No
Bromophos-ethyl	0.998	1.280	0.157	0.010	134.000	0.001	0.003	0.233	No
Chlordane-cis	0.998	ND	ND	ND	ND	ND	ND	ND	ND
Chlordane-trans	0.998	ND	ND	ND	ND	ND	ND	ND	ND
Chlorpyrifos-methyl	0.999	1.240	0.126	0.010	128.000	0.001	0.010	0.070	No
Cyfluthrin II {CAS # 68,359–37-5}	0.992	6.280	0.771	0.080	82.600	0.004	0.040	0.093	No
Cypermethrin I (Zeta)	1.000	1.400	0.139	1.000	1.470	0.001	0.050	0.016	No
DDD-o,p'	0.999	0.645	0.065	0.050	13.300	0.000	0.010	0.040	No
DDEop	0.999	ND	ND	ND	ND	ND	ND	ND	ND
DDE-p,p'	0.999	0.266	0.063	0.050	7.740	0.000	0.010	0.020	No
DDT-o,p'	0.999	0.645	0.065	0.050	13.300	0.000	0.010	0.040	No
DDT-p,p'	0.997	2.380	0.352	0.050	50.300	0.001	0.010	0.140	No
Deltamethrin	1.000	1.130	0.125	0.100	12.300	0.001	0.010	0.070	No
Diazinon	1.000	0.264	0.000	0.010	26.400	0.000	0.000	1.000	yes
Dimethoate	0.999	ND	ND	ND	ND	ND	ND	ND	ND
Disulfoton	1.000	0.636	0.001	0.010	63.900	0.000	0.000	1.330	Yes
Endosulfan I	0.998	ND	ND	0.050	ND	ND	ND	ND	ND
Endosulfan II (beta isomer)	0.999	0.825	0.083	0.050	17.300	0.001	0.006	0.083	No
Endosulfan sulfate	1.000	1.300	0.156	0.050	27.600	0.001	0.006	0.133	No
Endrin	0.998	0.419	0.042	0.010	44.400	0.000	0.000	1.000	Yes
Endrin aldehyde	0.998	1.180	0.119	0.010	123.000	0.001	0.000	3.500	Yes
Endrin ketone	1.000	4.680	0.850	0.010	675.000	0.003	0.000	13.500	Yes
Fenitrothion	1.000	1.180	0.085	0.010	120.000	0.001	0.005	0.140	No
Fenthion	1.000	1.150	0.083	0.010	117.000	0.001	0.007	0.100	No
Heptachlor	1.000	ND	ND	0.010	ND	ND	ND	ND	ND
Heptachlor exo-epoxide	0.999	ND	ND	0.010	ND	ND	ND	ND	ND
Hexachlorobenzene	1.000	ND	ND	0.010	ND	ND	ND	ND	ND
Malathion	0.999	0.212	0.178	0.020	34.200	0.000	0.030	0.003	No
Parathion	0.999	0.034	0.072	0.050	5.600	0.000	0.001	0.000	No
Parathion-methyl	1.000	1.310	0.095	0.010	133.000	0.001	0.003	0.267	No
Piperonyl-butoxide	0.999	1.370	0.139	8.000	0.177	0.001	0.160	0.005	No
Profenofos	0.998	4.530	0.744	0.010	570.000	0.003	0.030	0.087	No
Health risk index (HI)								22.320	

nutritional values (Bashir et al. 2020; Johnson et al. 2013). Studies confirmed that the level of organochlorine pesticides in Lake Tana, Hawassa, and Ziway could pose risks to the fish and consumers (Agmas and Adugna 2022; Teklu 2016; Yohannes et al. 2013). The concentrations of most pesticide residues in the ponds were lower than the ADI; however, the sum total of the HI (43.07) of pesticide residues in fish of the ponds was much higher than the acceptable limit. An assessment conducted in Lake Chad to level the human health risk from the consumption of four species of fish confirmed that the concentration of organophosphates was higher in Nile tilapia than in other species of fish, and the concentrations of pesticide residue in the fish species exceeded the tolerance limit (Akan et al. 2014). Though the per capita fish consumption in Ethiopia is the lowest in Africa, its consumption around Lakes and rivers reached

Table 8 Mean pesticide residue concentration in cabbage samples collected from three sub-districts. *Source*: the analysis results of this study

Pesticides	Mean concentration of pesticide residues per sub-district (mg/kg)		
	Abuha Kokit	Kuhar Michael	Shina
Bendiocarb	1.054	1.054	1.007
BHC_alpha	0.686	0.686	0.686
BHC_beta	0.694	0.694	0.679
BHC_gamma	0.686	0.686	0.686
BHC-delta	0.482	0.402	0.471
Bromophos_e	1.225	1.336	1.277
Chlorpyrifos_m	1.280	1.280	1.223
CyfluthrinII	6.573	6.583	6.138
Cypermethrin I	1.450	1.448	1.383
DDDop	0.665	0.665	0.635
DDEpp	0.248	0.271	0.270
DDTop	0.665	0.665	0.635
DDTpp	2.515	2.096	2.403
Deltamethrin	1.171	1.140	1.110
Diazinon	0.264	0.264	0.264
Disulfoton	0.635	0.637	0.637
Endosulfan II	0.849	0.849	0.813
Endosulfan sulfate	1.359	1.369	1.268
Endrin	0.433	0.436	0.412
Endrin aldehyde	1.220	1.213	1.162
Endrin ketone	4.745	4.760	4.651
Fenitrothion	1.196	1.196	1.169
Fenthion	1.167	1.167	1.141
Malathion	0.190	0.179	0.224
Parathion	0.020	0.007	0.043
Parathion-methyl	1.334	1.334	1.304
Piperonyl-butoxide	1.414	1.413	1.350
Profenofos	4.682	4.561	4.484

21 kg/year (Breuil and Grima 2014), which is nearly double to the daily consumption assumption of this study. Studies conducted in the Central Rift Valley Lakes of Ethiopia confirmed that persistent pesticide residues are risks to fish and consumers (Negatu and Dugassa, 2021; Yohannes et al. 2014). This study confirmed that consumers are more likely to be exposed to the effects of pesticide residues if they consume fish harvested from ponds than larger water bodies.

Among the pesticides detected in cabbage and fish samples, Disulfoton, Parathion-methyl, and Bromophos-ethyl were extremely to highly hazardous to life with LD_{50} of 2.6, 14, and 71 mg/kg body weight, respectively (WHO 2020). The mean concentrations of the extremely to highly hazardous pesticides in the samples might pose adverse effects to invertebrates and fish larvae. Among the pesticides in the samples, Bendiocarb, Cypermethrin I, DDT, Deltamethrin, Diazinon, Endosulfan, Fenitrothion, Fenthion, and various BHC isomers are all moderately hazardous (class II) and might cause adverse effects on consumers and aquatic organisms (WHO 2020). The pesticides have an effect on aquatic organisms at all levels (autotrophs, microbes, invertebrates, and fish), including humans consuming the resources (Gulliya et al. 2021). Organochlorine pesticides are persistent in water for longer periods of time as they are low water soluble and are bioconcentrated and bioaccumulated in living organisms, particularly in organisms rich in lipids (Kedari 2020). Convulsions, hypersensitivity, dizziness, vision impairment, fear, respiratory disease, cancer, nervous system disorder, system failures, and asthma could be resulted from long-term pesticide poisoning (Emmanuel et al. 2021; Kedari 2020; Lee and Choi 2020). The sum total hazard index of all the cabbage and fish samples in the present study is higher than the acceptable limit set by the European Union (European Food Safety Authority, Cabrera and Pastor, 2021; PPDB 2024). The combined effects of pesticide

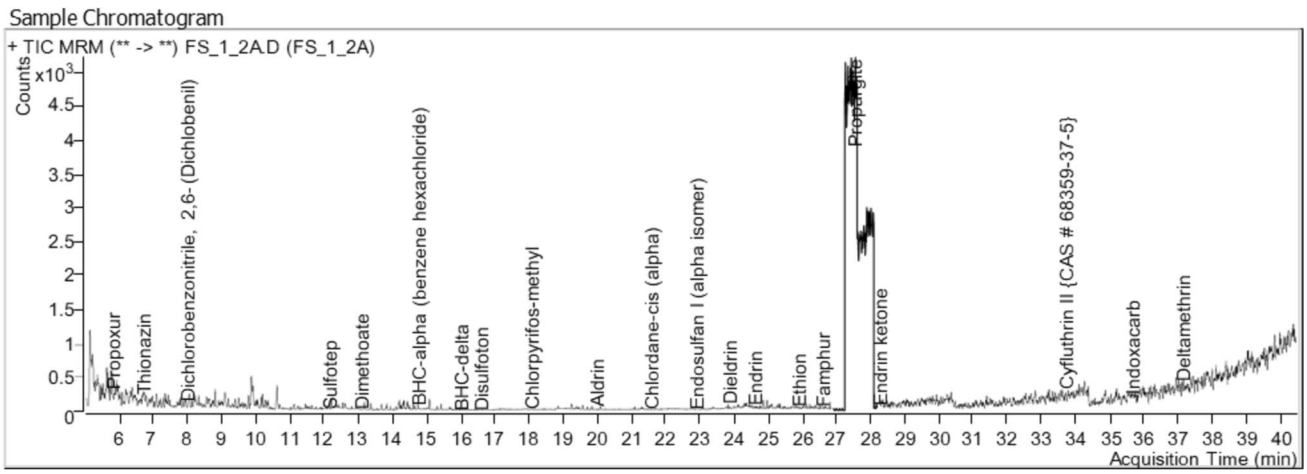

Fig. 5 Selected ion chromatogram showing results of pesticide residues in fish samples. *Source*: results of this study

Table 9 Amount of pesticide residues in fish samples from ponds and its health implications. *Source*: European Food Safety Authority et al., 2021 and the analysis results of this study

Compound	R^2	Mean (mg/kg)	SD	EDI (mg/ kg bw)	ADI (mg/ kg bw)	HQ (EDI/ADI)	Health risk(HR)
Aldrin	0.999	ND	ND	ND	ND	ND	ND
Bendiocarb	0.996	2.107	0.000	0.001	0.000	2.634	Yes
BHC-alpha (benzene hexachloride)	1.000	1.373	0.001	0.001	0.005	0.137	No
BHC-beta	1.000	1.389	0.000	0.001	0.005	0.139	No
BHC-delta	1.000	0.964	0.001	0.001	0.005	0.096	No
BHC-gamma (Lindane, HCH)	1.000	1.373	0.001	0.001	0.005	0.137	No
Bromophos-ethyl	0.998	2.673	0.000	0.001	0.003	0.446	No
Chlordane-cis (alpha)	0.998	ND	ND	ND	ND	ND	ND
Chlordane-trans (gamma)	0.998	ND	ND	ND	ND	ND	ND
chloropyrifos-methyl	0.999	2.561	0.001	0.001	0.010	0.128	No
Cyfluthrin II {CAS # 68,359–37-5}	0.992	13.164	0.033	0.007	0.040	0.165	No
Cypermethrin I (Zeta)	1.000	2.926	0.042	0.002	0.050	0.029	No
DDD-o,p'	0.999	1.331	0.002	0.001	0.010	0.067	No
DDE-o,p'	0.999	ND	ND	ND	ND	ND	ND
DDE-p,p'	0.999	0.492	0.042	0.000	0.010	0.025	No
DDT-o,p'	0.999	1.331	0.002	0.001	0.010	0.067	No
DDT-p,p'	0.997	5.032	0.004	0.003	0.010	0.252	No
Deltamethrin	1.000	2.350	0.137	0.001	0.010	0.118	No
Diazinon	1.000	0.527	0.000	0.000	0.000	1.319	Yes
Dimethoate	0.999	ND	ND	ND	ND	ND	ND
Disulfoton	1.000	1.272	0.004	0.001	0.000	2.121	Yes
Endosulfan I (alpha isomer)	0.998	ND	ND	ND	ND	ND	ND
Endosulfan II (beta isomer)	0.999	1.702	0.010	0.001	0.006	0.142	No
Endosulfan sulfate	1.000	2.706	0.018	0.001	0.006	0.226	No
Endrin	0.998	0.876	0.019	0.000	0.000	2.189	Yes
Endrin aldehyde	0.998	2.428	0.008	0.001	0.000	6.069	Yes
Endrin ketone	1.000	10.174	2.626	0.005	0.000	25.434	Yes
Fenitrothion	1.000	2.391	0.000	0.001	0.005	0.239	No
Fenthion	1.000	2.140	0.674	0.001	0.007	0.153	No
Heptachlor	1.000	ND	ND	ND	ND	ND	ND
Heptachlor exo-epoxide (isomer B)	0.999	ND	ND	ND	ND	ND	ND
Hexachlorobenzene	1.000	ND	ND	ND	ND	ND	ND
Malathion	0.999	0.161	0.110	0.000	0.030	0.003	No
Parathion	0.999	0.157	0.391	0.000	0.001	0.131	No
Parathion-methyl	1.000	2.668	0.000	0.001	0.003	0.445	No
Piperonyl-butoxide	0.999	2.829	0.004	0.001	0.200	0.007	No
Profenofos	0.998	9.375	0.622	0.005	0.030	0.156	No
Hazard Index (HI)						43.071	Yes

residues have more synergetic health effects than the sum total of the individual pesticide residues (Dakuyo et al. 2020; Shalaby et al. 2019). Among the pesticides detected, DDT, Endosulfan, HCH, and Lindane are banned, and parathion and parathion-methyl are permitted for restricted use via informed consent of the importer and exporter countries (WHO 2020). The human health risks of pesticide residues from the consumption of vegetables might be severer than what was observed in the present study. The commonly produced and used vegetables in the District have been sprayed with toxic pesticides in a similar fashion to cabbage and supplied to consumers.

The concentrations of pesticide residues in fish samples are important bioindicators about intensity of cultivation and pesticide use in the catchment and surface water pollution (Akan et al. 2014; Ntow 2005; Sarrazin et al. 2022). The

Table 10 Pesticide residue concentration mean difference between fish samples of the two ponds

Variables		Levene's test for equality of variances				t-test for equality of means						
		Mean	SD	F	Sig	T	Df	Sig. (2-tailed)	MD	Std. Er. Diff	95% CID	
											L	U
P	P1(28)	2.87	2.99	0.00	0.95	0.10	56.00	0.92	0.08	0.79	-1.50	1.67
	P2 (28)	2.78	3.04			0.10	55.99	0.92	0.08	0.79	-1.50	1.67

L = lower; U = upper; MD = mean difference, source: the analysis results of this study; P = pesticides; WF = weight of Fish samples

main reason for surface water pollution in the study area was over and misuse of pesticides, and mixing the pesticides and washing the spraying equipment near water bodies (Abaineh et al. 2023). The results of the independent t-test confirmed that there was no significant difference between concentrations of pesticide residues in the fish of the two ponds.

Most farmers in the study area cultivated three times per year, sprayed more than 14 kg pesticides and up to 26 times per a cropping season (Abaineh, et al. 2024a). The effects of pesticide residues were ever increasing and might cause adverse effects on the fish and humans consuming the fish. Obsolete and banned pesticides are still used by formers to control pests and to give a shiny appearance to khat leaves (Pesticide Action Nexus Association, 2020; Weyesa 2021). There are huge amounts of obsolete pesticides in stores in Ethiopia (Mengistie 2016; Shegen 2016), and farmers buy such pesticides, including DDT and Endosulfan, from the open market and use them for the intended purpose (Negatu et al. 2016; Wolde and Abirdew 2019). So selecting the appropriate pesticide types and applying them following the recommended application practices are important precautions to save aquatic organisms in general and the fish in the ponds in particular (Murthy et al. 2013). A minimum pesticide-free buffer zone between water bodies and farmlands is also important to reduce the effects of pesticide residues on aquatic ecosystems(Abaineh et al. 2024b; Macfarlane et al. 2014).

Conclusion and Recommendation

The findings of this study revealed that all the cabbage and fish samples were contaminated with pesticide residues and were a source of risks to humans, as it exceeded the allowable limit. Pesticide residues include Bendiocarb, Disulfoton, Endrin, Endrin ketone, Diazinon, and Endrin aldehyde that were found in the cabbage, and fish samples are higher than what is supposed to be safe to consume daily. The sum total HQ of pesticides in the cabbage (22.30) and in the fish (43.07) was much higher than the threshold value (1.00). Vegetables and fish were contaminated with extremely hazardous pesticides, and most of them were organochlorine, which can remain in the body for a long time and has a variety of negative impacts on humans and other organisms' physiology. Fish taken from the fish ponds of the District might cause higher health risks to consumers than fish harvested from rivers and Lake Tana. This study confirmed that the application of agricultural pesticides around ponds is a potential threat to fish cultivation. Therefore, establishing an efficient system of monitoring for the pesticide supply chain and application procedures, choosing the appropriate pesticide types, and timing spraying are crucial steps in mitigating the negative effects of pesticides on humans and the ecosystems.

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Data Availability The data needed for the study can be available up on reasonable request from the corresponding author.

Declarations

Conflict of interest All the authors declared that there was no relevant financial or non-financial interest.

Consent to Publish The authors agreed to publish the manuscript in an open-access journal at no cost to the authors or benefit from a discounted article publishing charge.

Consent to Participate All participants of the study were properly informed and agreed to participate without any pressure or coercion.

Ethical Approval This research work is part of dissertation research entitled Risks of Agricultural Pesticides on Aquatic Biodiversity and Consumers: A Case of Fogera District of Lake Tana Biosphere Reserve, Ethiopia. The main objective of the research work is to assess the knowledge, attitudes, and practices (KAPs) of farmers and consumers about the effects of pesticide residues and determine the level of risks of pesticide residues to aquatic biodiversity and human. The study was an ethical free, and the school of fisheries and wildlife of Bahir Dar University has given the ethical clearance letter to undertake the study by a ref. No FASc 1013/15. The letter is attached separately as supplementary information.

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