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Pesticide Contamination of Surface and Groundwater in an Ethiopian Highlands' Watershed

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Abstract: Agricultural intensification in sub-Saharan African countries has significantly increased pesticide applications. Information on pesticide residues and their transport in groundwater and streams is needed to properly manage and reduce any harm to the ecosystem and environment. This information is lacking in the volcanic soils of Ethiopian highlands. Therefore, this study was conducted to assess pesticide concentrations in ground and surface water and their risk to humans and aquatic life. The 9 km² rural watershed Robit Bata in the Lake Tana Basin was selected. Crops were grown under rainfed and irrigated conditions. Pesticide use was assessed, and groundwater samples were collected from eight wells and surface water samples at the outlet twice in the rain phase and once in the dry phase. Samples were analyzed for chlorpyrifos, dimethoate, (α and β) endosulfan, profenofos, NO₃⁻, and pH. Chlorpyrifos and endosulfan, which are strongly adsorbed and slowly degrading pesticides, were found in nearly all surface and groundwater samples, with maximum concentrations in surface water of 8 $\mu\text{g L}^{-1}$ for chlorpyrifos and 3 $\mu\text{g L}^{-1}$ endosulfan. Maximum groundwater concentrations were only slightly lower. The weakly adsorbed and fast degrading pesticides, dimethoate, and profenofos were detected only in the rain phase after spraying in the groundwater, indicating preferential transport to groundwater at depths of up to 9 m. The average concentration was 0.38 $\mu\text{g L}^{-1}$ for dimethoate in surface waters and 1.24 $\mu\text{g L}^{-1}$ in groundwater. Profenofos was not detected in surface water. In the groundwater, the average concentration was 0.05 $\mu\text{g L}^{-1}$. Surface water concentrations of chlorpyrifos and endosulfan were highly toxic to fish. The World Health Organization banned these pesticides worldwide. It should be phased out for use in Ethiopia to safeguard the ecological health of Lake Tana, which is rich in biodiversity and endemic fish species.

Keywords: pesticide; groundwater; surface water; eco-toxicity; Ethiopian highlands; sub-Saharan Africa; lake pollution; risk; fish



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1. Introduction

Freshwater contamination is a concern worldwide [1]. Natural and anthropogenic organic substances employed in medicine, industry, agriculture, and households are constantly released into the environment, potentially harming both ecosystem functions and human health [2,3]

In North America, contamination from agriculture has been falling than industrial and urban sources [4]. Consequently, although the water quality has been improving, the share of nonpoint agriculture pesticide pollution of ground and surface water has been

unchanged [4]. In contrast, both point and nonpoint sources increase water resource contamination in developing countries [2,5,6]. Particular intensifying agricultural production with increased use of fertilizers and pesticides has greatly impacted water quality. At the same time, the use in crop production of insecticides, fungicides, herbicides, rodenticides, molluscicides, and nematocides is crucial in achieving the United Nations (UN) sustainable goal of zero hunger [7,8]. Without pesticides, there would be a 78% loss in fruit production, a 54% loss in vegetable production, and a 32% loss in cereal production [9]. Insects alone would destroy 50% of the crops in sub-Saharan Africa [10]. However, only a small portion of the used pesticides control pests. Most of the pesticides applied are degraded. A small but significant amount harm non-target plants and cause environmental pollution [9].

In Ethiopia, nearly all farmers use pesticides with an average application rate of $0.23 \text{ kg A.I. ha}^{-1}$ [11]. When pesticides were introduced 60 years ago, herbicides were only applied on wheat and tef [12]. Recently pesticide use has been more widespread, especially to combat the fall armyworm (*Spodoptera frugiperda*) in maize and cash crop like khat [13–15].

Pesticide research in Ethiopia has been concerned with the pesticide use of farmers [16], the safety of pesticide spraying [17–21], the effect on crops [15,22], accumulation in the food chain and ecological health [23–25], and contamination of water resources [26–30].

The limited studies investigating pesticide concentration in surface and groundwater were in southeast Ethiopia, focusing on the Great Rift Valley. In Lake Ziway, up to $9.1 \mu\text{g L}^{-1}$ carbendazim was recorded, and the assessed risk indicated a chronic health risk to fish [30]. Concentrations reported in other studies [26,27,29] were all above the maximum allowed concentrations in drinking water in Europe [31]. Mekonen et al. [28] investigated concentrations in drinking water from various sources, including well water, and reported widespread contamination. One well water sample had a Malathion concentration of $100 \mu\text{g L}^{-1}$.

The impact of past and recent pesticide applications on surface and groundwater concentration has not been investigated yet in the northern Ethiopian highlands. An assessment is urgently needed as the source of 90% of the public drinking water is groundwater [32], 70% of which is shallow [33]. Surface water is often used in areas without public water points. In addition, pesticides affect ecological health as well. Therefore, the objective was to evaluate pesticide concentrations in surface and shallow groundwater of rural watersheds in northern Ethiopian highlands and assess human and ecological pesticide risks. The research was carried out in the Lake Tana basin in the northern highlands. The 3000 km² Lake Tana is the largest freshwater body in Ethiopia, with an average depth of 9 m [34]. It is one of the UNESCO-registered biospheres. It is the home of unique fish species like barbs, an endemic cyprinid specie flock [35,36].

2. Materials and Methods

2.1. Description of the Study Area

The 9-km² Robit Bata watershed is in the Lake Tana basin in the headwaters of the Blue Nile in the northern highlands (Figures 1 and 2a). The average annual rainfall over the last ten years was 1420 mm a^{-1} , of which 80% fell in the rain phase from June to the end of September. The average annual temperature is 21°C and varies between 11°C to 27°C . The watershed is representative of the Lake Tana Basin, where the precipitation ranges from 1200 to 1600 mm and an average temperature of 22°C [37].

Robit Bata is part of the northwestern plateau of Ethiopia, composed of Tertiary basalt, Quaternary olivine basalts, and Quaternary lacustrine and alluvial deposits [38]. Robit Bata is southeast of Lake Tana and is situated on the Quaternary lacustrine and alluvial deposits that are underlain by quaternary olivine basalts. These basalts are commonly fractured (Figure 2b). The surface soils are highly conductive. The rainfall intensity exceeds the soil infiltration capacity less than 2.5% of the time [39].

Integrated crop and livestock agriculture is practiced in the watershed [40]. Thirty-eight percent of the total land area was cultivated with millet, 35% with maize, and 13%

with Khat. Khat is a mild narcotic perennial small bush irrigated during the dry phase [15]. The remainder of the land was not cultivated and consisted of grass and bushland that were too wet or stony for crop production.

The upper part of the watershed is severely degraded with shallow Eutric Cambisols and Luvisols soils over bedrock; the middle and lower portions of the watershed are Alisols up to 15 m in depth [41]. These soils have a clay loam texture with an average organic carbon content of 1.6 mg L^{-1} [41,42]. They are underlain in the lower portion by the regolith layer. Water loss from the upper part is mainly caused by saturated excess overland flow. In the middle and lower part, rainwater infiltrates and recharges a hillslope aquifer. The aquifer forms at the beginning of the rain phase in June and lasts about three months after the rain ends (December) due to the high base flow draining the aquifer. The hillslope aquifer drains fast due to the high transmissivity of $700 \text{ m}^2 \text{ day}^{-1}$ [43] and 5–8% slopes. From January to May, the groundwater can only be found near the fault lines where most wells are located [39,44].

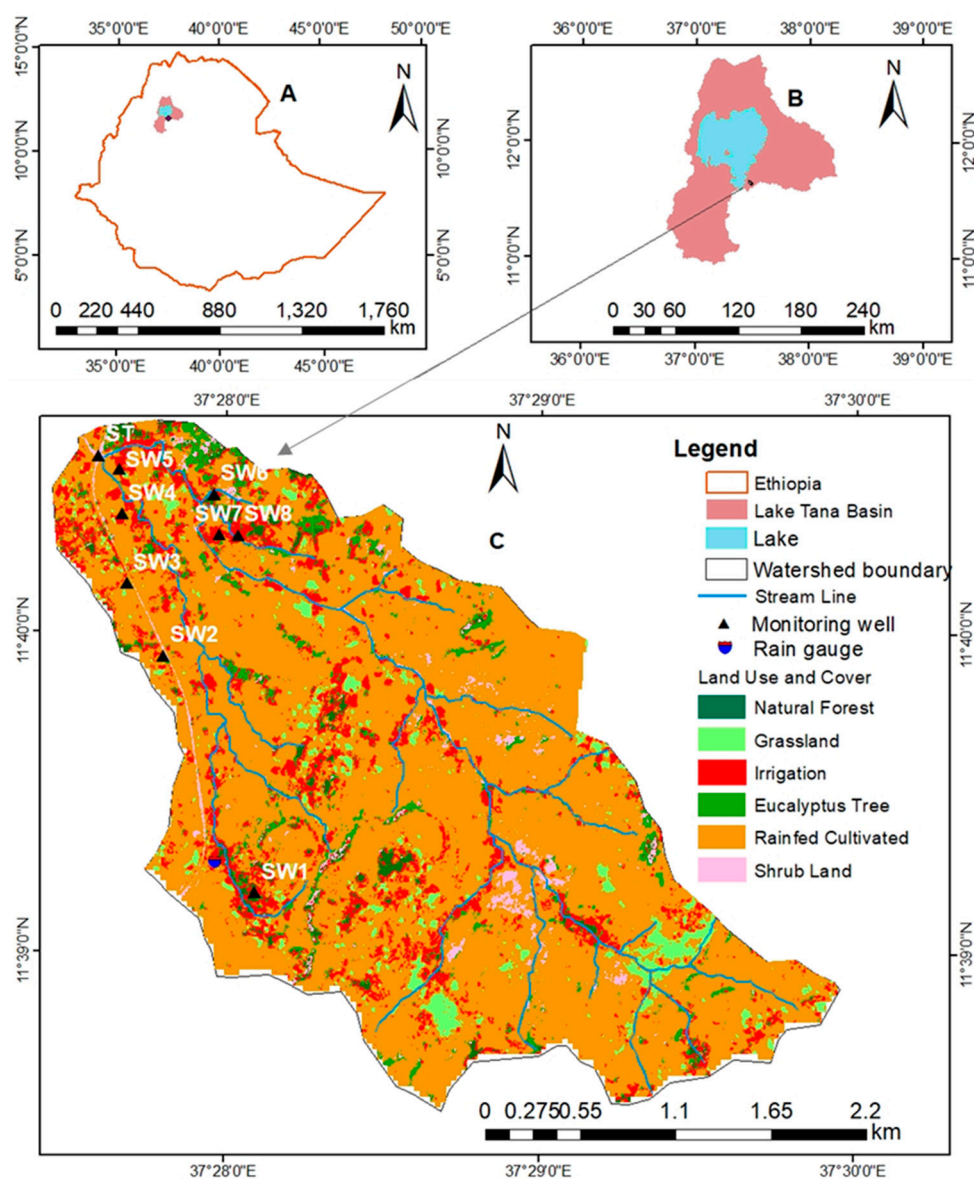


Figure 1. Location of Robit Bata watersheds in Lake Tana basin. (A) Lake Tana basin, (B) location of Robit Bata within Lake Tana basin, and (C) land use and cover maps, with monitoring wells in Robit Bata watersheds. SW1-SW8 are the sampling well identifiers, and ST is the outlet.

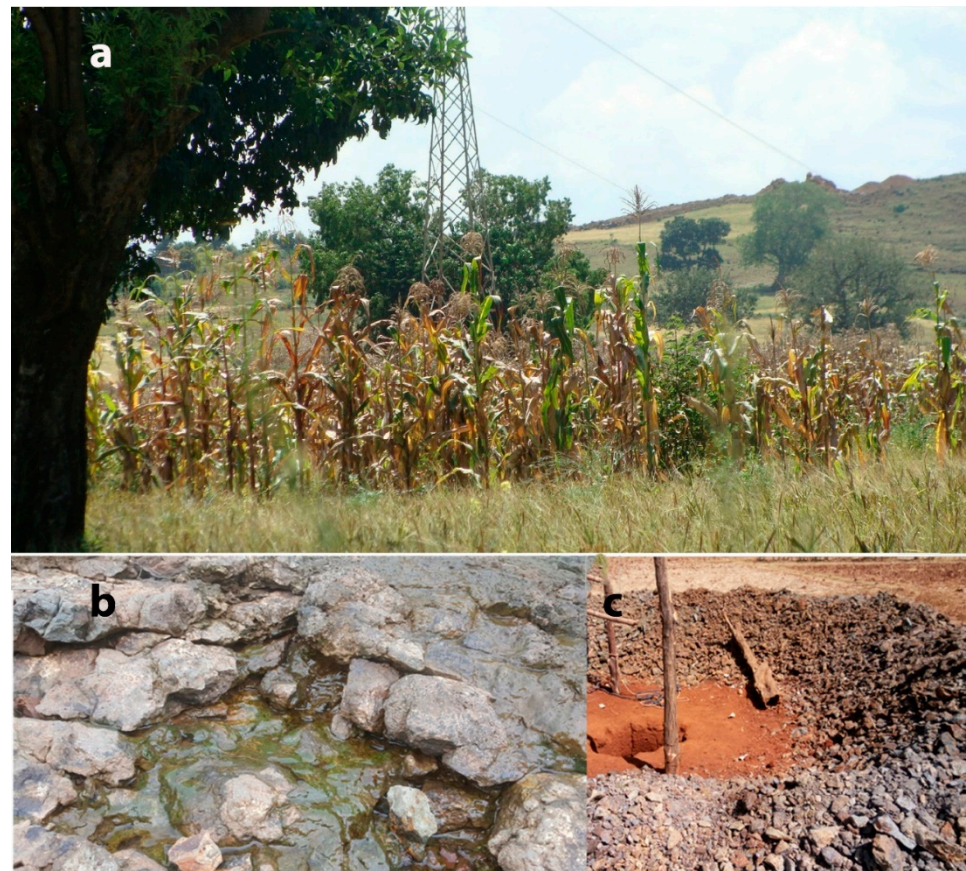


Figure 2. The Robit Bata watershed: (a) landscape view; (b) fractured quaternary basalt bedrock; (c) excavated soil from a well. The stones in the foreground are from the regolith layer.

2.2. Data Collection

Groundwater table depth, stream discharge, pesticide concentrations, and other water chemical constituents were measured. Additionally, data were collected on pesticide use by the farmers and awareness of the community on the implications of pesticide use on their health.

2.2.1. Pesticide Application Data Collection

Eighty-nine smallholder farms were surveyed in 2017 in collaboration with Feed the Future of Innovation Lab for Small-Scale Irrigation. The pesticide type, the amount applied, the crop, and the number of applications were gathered.

The awareness of pesticide use on human health and the environment was assessed in 2019 in a collaborative meeting between local farmers and personnel of the Bureau of Water Resources, Bureau of Agriculture, Environment protection agency, and Forest and Wildlife Conservation and Development Authority. Information was obtained on safety procedures during pesticide application and equipment handling, awareness of off-target transport, and the occurrence of chronic illnesses.

2.2.2. Water Sample Collection

Eight shallow hand-dug wells with depths varying between 6 to 15 m were randomly selected for the sampling (SW1 to SW8 in Figure 1C) from a larger set [39]. Twenty-four water samples were collected from these wells using a bailer and fifteen from the stream at the watershed outlet. The budget available limited the number of wells sampled. The groundwater sampling was on 5 July, 15 August in the rain phase, and 29 November in the dry phase in 2018. The stream was sampled during runoff events on 2 July and 12 August in the rain phase and 29 November in the dry phase in 2018. Five samples were collected

from the stream during the runoff event at a 20 min interval of storm event flow. In the dry phase, five samples were collected from the base flow.

The depth of the groundwater table was measured at the time of sample collection. The stream discharge starting in 2017 was published in [42]. Using grab sampling, water samples were collected in 500 mL amber glass bottles with glass lids, which were cleaned according to the standard protocols of the American Public Health Association [45]. Additional water samples were taken in 300 mL polyethylene plastic bottles to determine the dissolved P and N – NO₃[−] concentrations. After collection, samples were put in coolers with ice packs and transported to the Quality Monitoring and Pesticide Testing Laboratory of the Abbay Basin Authority [46] 15 km away.

2.3. Risk Assessment

2.3.1. Aquatic Life Risk Assessment of Pesticides in Surface Water

Various indices have assessed water quality in the Nile basin [47,48]. The acute and chronic risk quotient (RQ) for aquatic life and human health due to pesticide application were most appropriate for use here. The RQ for aquatic life was calculated using the stream pesticide concentration in Robit Bata. The procedure, specifically developed for Ethiopia by Deneer et al. [49] and Adriaanse et al. [50], is based on methods in Europe and USA. It has been employed to quantify aquatic life risks of pesticides in lakes and rivers in the Great Rift Valley in Ethiopia [16,29,51]. The acute risk quotient for fish, $RQ_{acu, fish}$, the invertebrate acute risk, $RQ_{acu, invbrat}$, and the chronic risk for fish, $RQ_{chronic, fish}$ are defined as follows:

$$RQ_{acu, fish} = UF_{acu} \frac{C}{LC_{50}} \quad (1)$$

$$RQ_{acu, invbrat} = UF_{acu} \frac{C}{EC_{50}} \quad (2)$$

$$RQ_{chronic, fish} = UF_{chr} \frac{C}{NOEC} \quad (3)$$

where UF is a safety factor to account for uncertainty; for acute risk is $UF_{acu} = 100$ and $UF_{chr} = 10$ for chronic exposure [49], C is the measured concentration of the pesticide, LC_{50} is the median lethal concentration, EC_{50} median effective concentration, and $NOEC$ is no-observed effect concentrations. The values for these parameters are listed in the properties database of the University of Hertfordshire [52] and reproduced in Table S1 in the Supplementary Materials B. The calculated probable risks were categorized as $RQ < 1$: negligible to low risk; $1 < RQ < 10$: possible risk, and $RQ > 10$: high risk to aquatic organisms [49].

2.3.2. Human Health Risk Assessment of Pesticides in Groundwater

Since groundwater is used for drinking water, possible risks to human health were evaluated. The risk quotient (RQ) for humans was estimated based on the pesticide concentration recorded in water from the wells akin daily orally (μg of pesticide per day) of each pesticide [49] and divided by the acceptable daily intakes chronic (ADIC), viz,

$$EDI = C \text{ DWC} \quad (4)$$

$$ADIC = UF \text{ ADI BW} \quad (5)$$

$$RC_{chronic} = \frac{EDI}{ADIC} \quad (6)$$

where EDI is the estimated daily pesticide intake ($\mu\text{g d}^{-1}$); C is the concentration of the pesticide ($\mu\text{g L}^{-1}$); DWC is the daily water consumption which is 2 L d^{-1} for adults, 1 L d^{-1} for a child and 0.75 L d^{-1} for an infant [53] $ADIC$ is the acceptable daily pesticide intake chronic that will not result in adverse effects at any stage in life span which is calculated from ADI values. ADI values were retrieved from the Pesticide Properties Database Joint

FAO/WHO Meeting on Pesticide Residues [54]. *UF* is the uncertainty factor set to 0.1, and *BW* is the body weight. The adult body weight was 60 kg, 10 kg for a child, and 5 kg for an infant [53]. If $RQ > 1$ indicates that the exposed population is possibly at risk.

2.4. Statistical Analysis

Pesticide concentrations in shallow groundwater wells and the stream were statistically evaluated among the dry and rain phases. Since the concentrations were not normally distributed, the non-parametric Kruskal–Wallis one-way ANOVA test was used. A probability level $\alpha = 0.05$ was set for differences to be significant. Version 4.2 of the R Project for Statistical Computing was used for the analysis.

2.5. Chemical Analysis Methods

The pH and EC were measured on-site using Yellow Springs Instrument (YSI) ProDSS (digital sampling system) multi-parameter.

The nitrate and dissolved phosphorus samples were filtered through Whatman filter paper with a pore size of $0.45\ \mu\text{m}$ and stored below $4\ ^\circ\text{C}$ until analyzed within three days. The standard Palin test method was used to analyze nitrate and phosphate using the photometer 7100. The detailed procedure is described in the Palintest Operation Manual [55].

Samples for pesticide analysis were filtered using Nylon membrane filters with a diameter of 47 mm and $0.45\ \mu\text{m}$ nominal pore size. After filtration, pesticides were extracted using solid-liquid extraction based on USEPA, standard method 1699 [56]. The samples passed through Sep-Pak[®] (Waters Corporation, Milford, MA, USA) vac 6 cc (500 mg)/6 mL C 18 cartridges with a flow of $7\ \text{mL min}^{-1}$ by installing on a vacuum manifold. Then the cartridges matrix containing an extracted compound was dried under vacuum for 10 min to remove water moisture. After removing moisture, pesticides were clean-up from the cartridge using HPLC grade dichloromethane (DCM) and methanol. 1.5 mL of dichloromethane and 0.5 mL of methanol were used to elute pushing through the cartridge. Afterward, the eluent was evaporated to near dryness. Then residue extract was reconstituted in 200 μL using acetonitrile and ready for analysis by the gas chromatographic (GC).

The pesticides were analyzed using a gas chromatograph (GC) 7890B Agilent Technologies, Inc., Santa Clara, CA, USA, equipped with Agilent 7000C mass spectrophotometer triple quad and controlled by mass hunter acquisition software. GC was equipped with two HP-5 15 m capillary columns, 0.25 mm internal diameter, and 0.25 μm film was used in the separation of pesticides compound. The oven temperature program was initially at $60\ ^\circ\text{C}$ hold for 1.0 min, ramp at $50\ ^\circ\text{C min}^{-1}$ until $160\ ^\circ\text{C}$, then ramp at $10\ ^\circ\text{C min}^{-1}$ until $300\ ^\circ\text{C}$ and hold for 1 min. We used helium as a carrier gas and nitrogen as a makeup gas with a 99.999% purity grade. The helium flows in the first column at $1.2\ \text{mL min}^{-1}$ and in the second column at $1.5\ \text{mL min}^{-1}$. A 2 μL volume aliquot of sample was injected into an inlet at a temperature of $280\ ^\circ\text{C}$ by spitless injection mode. The transfer line temperature from the GC to MS was $280\ ^\circ\text{C}$, the quadrupole at $180\ ^\circ\text{C}$, and the MS ion source at $300\ ^\circ\text{C}$. The MS operated in electron-ionization (EI) mode.

2.6. Quality Control and Assurance

Validation techniques for the analytical method, including calibration curves and recovery analysis, are described in [57]. A pure standard compound of the pesticides purchased from Sigma Aldrich, St Louis, MO, USA, were analyzed for pesticide quantification. Using acetonitrile mixed, a standard solution was prepared at six different concentrations ranging between 0.1 to $100\ \mu\text{g L}^{-1}$. The observed linear relationships R^2 between the ratios of the peak area and corresponding concentrations were 0.99 for all pesticides in standard solution.

A limit of detection (LOD) and a limit of quantification (LOQ) were calculated for each pesticide, according to Currie, L.A. [58]. The minimum level of detection of all pesticides was below $0.003\ \mu\text{g L}^{-1}$. By analysis of spiked samples, we evaluated method performance.

The repeatability was determined by calculating the relative standard deviation (%RSD). It was obtained by preparing and analyzing four spike samples at a concentration of $20 \mu\text{g L}^{-1}$. The value was between 5.2 to 19%. These values agree with the guidelines limit of USEPA [56]. The percent of recovery (%R) ranges from 86.7 to 105 (Table S2 in the Supplementary Materials A).

3. Results

3.1. Pesticide Use

Farms surveyed pesticide type and percentage applications are summarized as a bar plot in Figure 3, and the detail, including crop types and application rate, are documented in Supplementary Materials B. Twelve pesticides were used by 89 smallholder farmers (Figure 3). Megaban (chlorpyrifos) to control aphids was used on all farms. Some pesticides with different common names had the same active ingredients. Five principal active ingredients were identified. They were chlorpyrifos, dimethoate, profenofos, endosulfan α and β endosulfan (Table 1). Khat was sprayed heavily throughout the year. Pesticides with chlorpyrifos as an active ingredient were applied eight times from June through January, profenofos was used four times during June and July, and Endosulfan three times from October to December. Maize was sprayed with chlorpyrifos, dimethoate, and profenofos during the rain phase from June to July. Application rates were around the recommended rates (Table 1).

The physical and chemical properties of the active ingredients are given in Table 2, retrieved from the Pesticide Properties Database (PPDB University of Hertfordshire, Hertfordshire, [52]. The data in parenthesis are from [59]. Although there are differences between the two sources, the general ranking in degradation rate and adsorption strength is maintained. Chlorpyrifos had the longest half-life of over a year. Endosulfan had the next longest half-life of a little over a month. The other two pesticides had half-lives of less than a week, and concentrations in the field after application decreased by 50% each week, provided that the Ethiopian conditions reflect the values in the table. Endosulfan was the strongest adsorbed to the soil, followed by chlorpyrifos and profenofos. Other properties mentioned in Table 2 do not greatly affect the transport of pesticides.

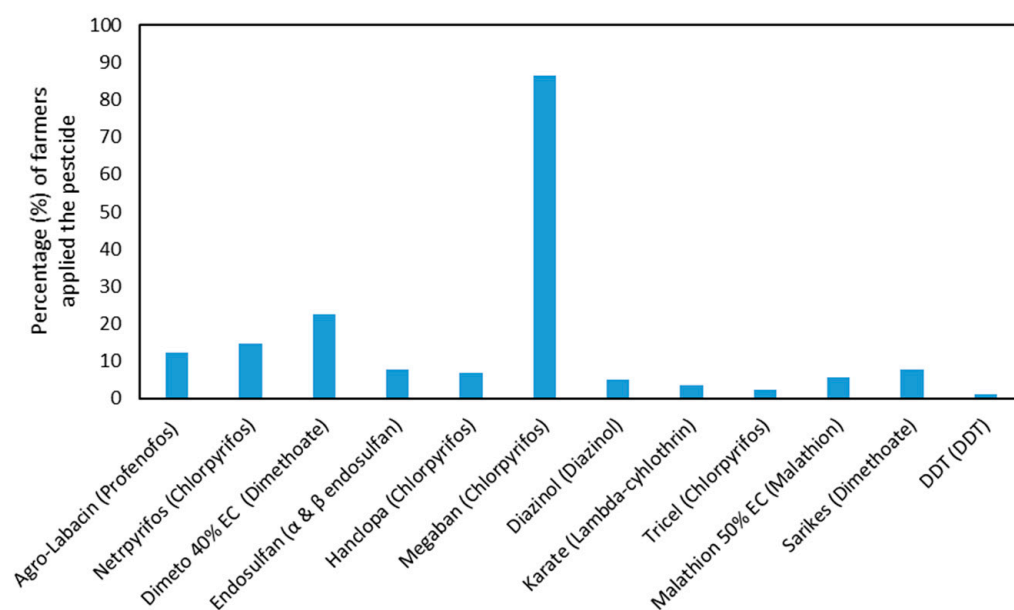


Figure 3. Pesticide applied by small farm holder farmers and percentage of farmers used the pesticide to one of the crops either in irrigation or rainfed agriculture.

Table 1. Application rate and use of the major active ingredients in the applied pesticides during irrigation and rainfed cropping for different crops.

Pesticide	Type of Crop	Time of Application	Frequency	Farmers Application Rate (L ha ⁻¹)	Active Ingredients per Application (kg ha ⁻¹)	Recommended Active Ingredients (kg ha ⁻¹)
Chlorpyrifos	Maize	Jun.–Jul.	1	1.05	0.50	0.12
	Khat	Jun.–Jan.	8	2.13	1.02	0.82
	Onion	Jun.–Jul.	1	0.92	0.44	0.48
	Cabbage	Oct.–Dec.	1	0.78	0.37	0.48
	Garlic	Oct.–Dec.	1	0.63	0.30	0.48
Dimethoate	Maize	Jul.	1	2.00	0.80	0.26
	Khat	Jun.–Jul.	4	2.50	1.00	0.32
	Tomato	Oct.–Dec.	1	1.32	0.53	0.32
	Onion	Oct.–Dec.	1	0.75	0.30	0.32
	Garlic	Oct.–Dec.	1	0.75	0.30	0.32
Profenofos	Maize	Jul.	1	1.14	0.57	0.55
Endosulfan (α and β)	Khat	Nov.–Jan.	2	3.12	1.09	0.81
	Tomato	Oct.–Dec.	1	2.30	0.81	0.81

Table 2. The physical and chemical properties of active ingredients in farmer-applied pesticides in the Robit Bata watershed. Data were extracted from Pesticide Properties Database (PPDB) University of Hertfordshire, UK. Numbers in parentheses are from FAO [59].

Physical and Chemical Properties	Pesticides			
	Chlorpyrifos	Dimethoate	Profenofos	Endosulfan (α and β)
Substance Group	OPP	OPP	OPP	OCP
Molecular mass	351	229	374	407
Solubility in water @20 °C (mg L ⁻¹)	1.05	25,900	28	0.32
Vapor pressure (mPa @20 °C)	1.43	0.25	2.53	0.83
Soil degradation DT ₅₀ (days) (lab at 20 °C)	386	2.5 (4–122)	7	39 (60–800)
Aqueous hydrolysis DT ₅₀ (days)	53.5	68	14.6	20
Sorption: K _{OC} (m ³ Mg ⁻¹)	5509	28.3 (10)	2016	11,500 (2500)
Mobility	slightly	high/moderate	slightly	Slightly/hardly
K _d for 2% organic matter (m ³ Mg ⁻¹)	66	0.34	24	138
Avg displacement cm a ⁻¹ for a soil with $\rho = 1.2$; $\theta = 0.3$; and 500 mm a ⁻¹ recharge	<1	70	2	<1

3.2. Concentration of Pesticides in Groundwater

Four active ingredients of the 12 pesticides were detected in the groundwater (Figure 4 and Table 1) for eight wells and the three sampling dates: 5 July at the beginning of the rain phase when the water table started to rise; 15 August near the end of the rain phase when groundwater level was closest to the surface, and 29 November in the dry phase when the rain had ceased and groundwater levels were near base levels. Dimethoate applied at a rate of 0.8 kg per hectare in July to control fall armyworm on maize was detected only in August and was below detection levels in early July and November (Figure 4). It behaved like nitrate in the same watershed that peaked only after the fertilizer application and decreased to base levels within two months [60]. Profenofos that was applied to maize in June and July at the relatively low rate of 0.57 kg ha⁻¹ by a small number of farmers (Figure 3) was only detected in a few wells during the rain phase. It was not detected in groundwater during the dry phase. Chlorpyrifos was found in almost all wells on three sampling dates (Figure 4). It was applied once in the rain phase by all farmers on nearly 306 ha (a third of the watershed) and eight times to 100 ha khat. Endosulfan applied to khat and tomato during the dry phase was detected in both wet and dry phases. The endosulfan and chlorpyrifos concentrations in groundwater were not statistically different between the rain and dry phases ($p > 0.05$, Kruskal–Wallis test. Except for profenofos, the mean

recorded concentrations of pesticides were above the European union drinking water limit of $0.1 \mu\text{g L}^{-1}$ [31] and were below the World Health Organization (WHO) limit [61].

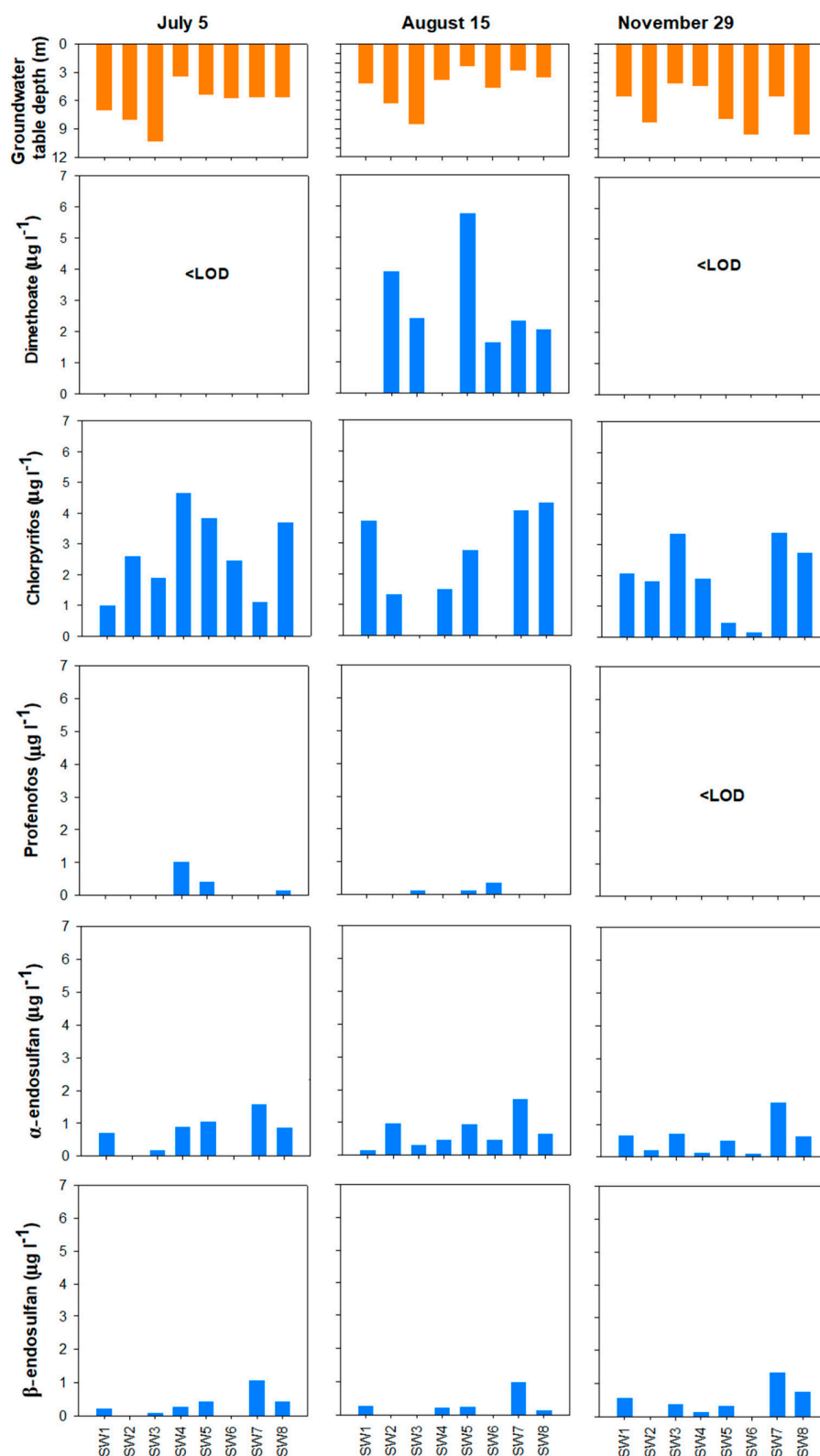


Figure 4. Pesticide concentrations in wells SW1–SW8 during dry and rain phases. The well locations are given in Figure 1.

Three main factors should be considered to explain these concentration patterns: (1) time and amount of pesticide applied, (2) transport from the surface to the groundwater, and (3) degradation during transport. A complication in the analysis is that the same water is not sampled from one sampling period to the next as water moves down in these sloping hillside aquifers. The sampled water originates from uphill and contains the leachate from fields uphill. Therefore, the sampling frequency and groundwater movement do not allow for quantitative analysis.

3.2.1. Transport from Surface to Groundwater

Although three pesticides were labeled slightly mobile, all pesticides were found in the groundwater. This was not expected based on the equilibrium convective dispersive transport, as shown below.

Assuming that the equilibrium convective dispersive transport is valid, the annual average distance the pesticide would move can be expressed as [62].

$$d = \frac{R}{\theta + \rho k_d} \quad (7)$$

$$k_d = 0.6 f_{OM} K_{OC} \quad (8)$$

where d is the average annual displacement of the pesticide, R is the annual recharge, θ is the moisture content at field capacity, ρ is the bulk density of the soil, k_d is the adsorption partition coefficient, f_{OM} is the organic matter content of the soil, and K_{OC} is the octanol carbon partition coefficient.

For example, the K_{OC} of chlorpyrifos is 5509 (Table 2). For a typical degraded soil with 2% organic matter [42], using Equation (7), the adsorption partition coefficient $k_d = 66 \text{ m}^3 \text{ Mg}^{-1}$ (Table 2). Recharge in the Robit Bata watershed is around 50 cm [39]; the soil bulk density is 1.2 Mg m^{-3} ; the field capacity is assumed to be $0.3 \text{ cm}^3 \text{ cm}^{-3}$. Using Equation (6), we find that the annual displacement is less than 1 cm under the assumption that the traditional equilibrium convective-disperse transport is valid (Table 2). Based on this theory, dimethoate with the smallest K_{OC} and a $k_d = 0.34$ moves the farthest at under 1 m a^{-1} (Table 2). Thus, even dimethoate displacement was less than the average groundwater depth of almost all wells. We did not include dispersion in these calculations. Therefore, due to dispersion, some dimethoate may reach the groundwater ahead of the front. However, for the three other pesticides, the dispersion certainly cannot explain the high concentrations of these pesticides in groundwater (Figure 4). Therefore, we can conclude that the equilibrium transport of pesticides did not occur during transport in the Ethiopian highlands in the rain phase. Instead, non-equilibrium adsorption and preferential flow, where the infiltration water bypasses most of the soils, is the main transport mode of pesticides. Dimethoate was also applied to the irrigated vegetables during the dry phase. Still, it did not reach the groundwater indicating that under irrigation, the transport might be more consistent with equilibrium transport.

3.2.2. Degradation

The short half-life of dimethoate and profenofos (i.e., Table 2) explains that the pesticides detected in groundwater in the rain phase were undetected in the dry phase (Figure 4). Another factor that could explain the non-detects is the lateral flow transporting pesticides to the river. However, if lateral transport was the only factor, wells closest to the stream should not have been pesticide free.

The chlorpyrifos and α and β endosulfan were found in the groundwater in the dry and rain phase. Both are resistant to microbial degradation, but endosulfan hydrolysis in water with a half-life of 20 days (Table 2). It suggests that these two chemicals are adsorbed to the soil in the aquifer near the wells. Otherwise, endosulfan would not have been found due to the rapid disappearance in water.

3.2.3. Relationship with Other Variables

To further explain the interaction of transport and degradation, we plotted in Figure 5 the pesticide active ingredient concentrations in the groundwater as a function of the groundwater depth, pH, and nitrate and phosphorus concentrations at the sampling time. Very few significant statistical relationships were found (Table 3). As mentioned, the degradation of dimethoate and profenofos determined their concentration; hence, a relationship to other variables was not expected. Only chlorpyrifos showed relationships with depth to groundwater, nitrate, and phosphorus, which indicates that preferential transport mainly determines the concentration in groundwater. This was expected since the degradation is slow for this chemical. The statistical relationship between endosulfan and pH might be spurious as higher pH is related to faster disappearance [63], while Figure 5C shows the opposite effect for α -endosulfan.

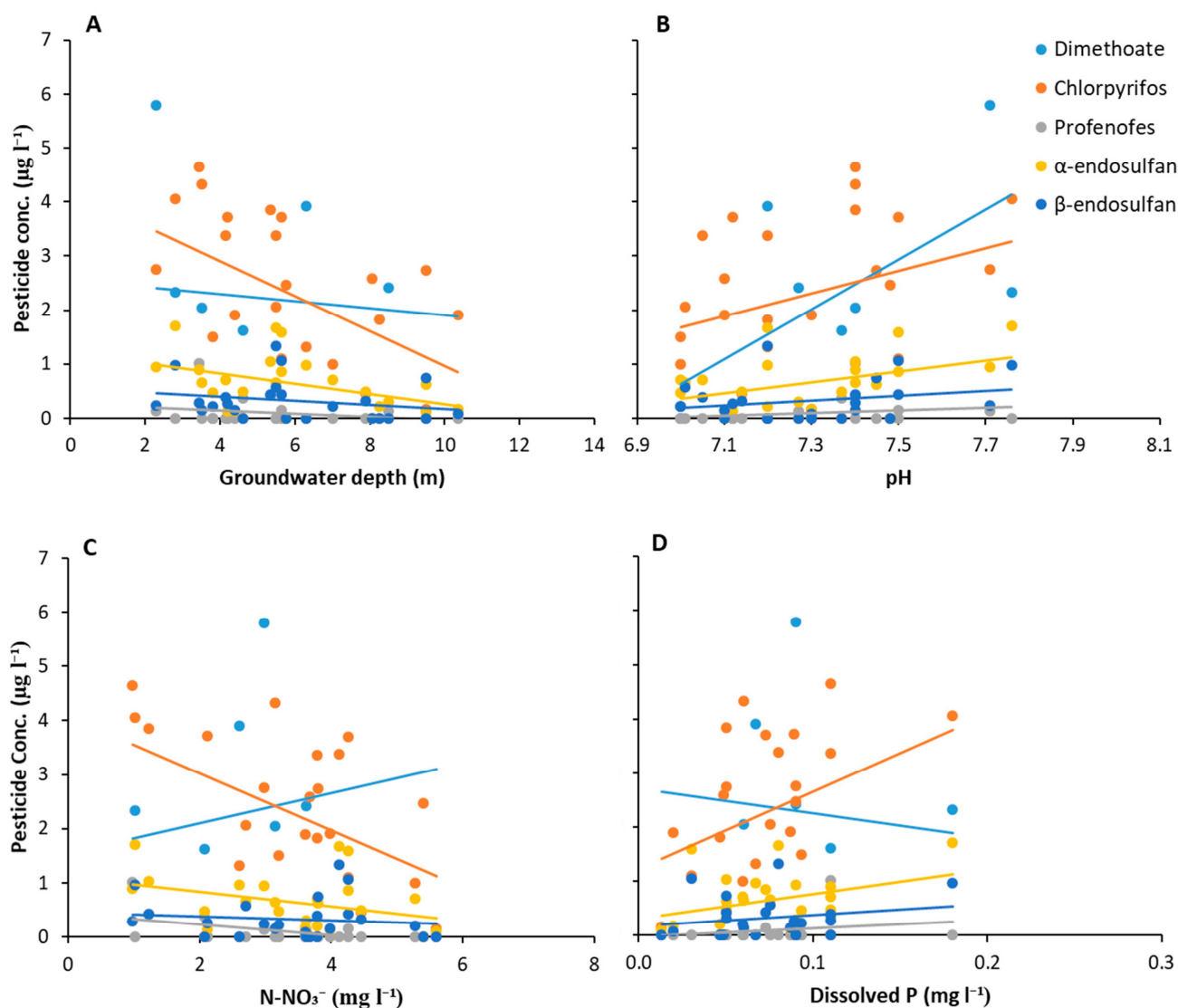


Figure 5. Pesticide concentration in groundwater as a function of groundwater depth, pH, dissolved phosphorus, and nitrate concentrations. The regression lines have the same color as the symbols. The statistics of the regression lines are provided in Table 3.

3.3. Concentrations of Pesticides in Surface Water

Dimethoate applied in July to control fall armyworm on maize was only detected in August and was below the detection limit in early July and November (Figure 6 and Table 4). Profenofos was not detected at all in the surface waters. Thus, dimethoate application in

the dry phase on the irrigated horticultural crops (Table 1) did not result in surface water pollution. It indicates that drift from pesticide applications, as noted elsewhere [64,65] in surface water, does not occur when hand sprayers are being used despite the that irrigated areas were located less than 20 m from the stream (Figure 1). It also confirms that overland flow was the cause of the pesticide concentration in the creek since overland flow only occurs during the rain phase

Table 3. Statistical significance test for the slope of the linear regression line using the *t*-test.

Variables	Act. Ingredients	R ²	Slope Coef (β)	<i>t</i> -Test	<i>p</i> -Value
Depth to groundwater	Chlorpyrifos	0.23	−0.3	−2.79	0.01
	Dimethoate	0.08	0.25	0.13	0.10
	Profenofos	0.04	−0.02	−1.58	0.20
	α-endosulfan	0.15	−0.14	−2.23	0.13
	β-endosulfan	0.07	−0.05	−1.57	0.16
pH	Chlorpyrifos	0.06	2.10	1.50	0.13
	Dimethoate	0.01	0.73	0.27	0.78
	Profenofos	0.02	0.52	1.16	0.26
	α-endosulfan	0.15	1.09	2.23	0.05
	β-endosulfan	0.11	0.69	1.40	0.06
N-NO ₃ [−]	Chlorpyrifos	0.21	−0.6	−2.50	0.02
	Dimethoate	0.05	0.16	0.57	0.15
	Profenofos	0.05	0.07	1.40	0.16
	α-endosulfan	0.12	0.12	1.80	0.04
	β-endosulfan	0.10	0.10	1.70	0.07
Dissolved_P	Chlorpyrifos	0.12	2.30	2.60	0.04
	Dimethoate	0.05	1.30	1.50	0.13
	Profenofos	0.05	1.53	1.14	0.26
	α-endosulfan	0.06	4.80	1.40	0.12
	β-endosulfan	0.02	3.00	1.80	0.29

Table 4. Mean, minimum (min.) and maximum (max.) concentrations (μg L^{−1}), and detection frequencies of the studied pesticides in water samples from shallow wells and streams.

Pesticide	Groundwater						Surface Water					
	Date	DF (%)	Min	Mean	Max	Sig. <i>p</i>	Date	DF (%)	Min	Mean	Max	Sig. <i>p</i>
Dimethoate	5-Jul.	-	<LOD	-	<LOD	-	2-Jul.	0	<LOD	-	<LOD	-
	15-Aug.	75	<LOD	1.75	5.79		12-Aug.	60	<LOD	0.38	1.03	
	29-Nov.	-	<LOD	-	<LOD		29-Nov.	0	<LOD	-	<LOD	
Chlorpyrifos	5-Jul.	100	1.01	2.15	4.65	0.19	2-Jul.	80	<LOD	2.50	3.60	0.03
	15-Aug.	50	<LOD	2.21	4.33		12-Aug.	80	<LOD	3.15	7.73	
	29-Nov.	75	<LOD	1.91	3.12		29-Nov.	100	0.41	0.58	0.87	
Profenofos	5-Jul.	38	<LOD	0.07	1.02	0.03	2-Jul.	-	<LOD	-	<LOD	-
	15-Aug.	25	<LOD	0.03	0.37		12-Aug.	-	<LOD	-	<LOD	
	29-Nov.	-	<LOD	-	<LOD		29-Nov.	-	<LOD	-	<LOD	
α-endosulfan	5-Jul.	75	<LOD	0.65	1.59	0.28	2-Jul.	100	0.48	0.69	0.87	0.02
	15-Aug.	100	0.14	0.51	1.71		12-Aug.	80	<LOD	1.02	2.61	
	29-Nov.	75	<LOD	0.28	1.67		29-Nov.	80	<LOD	0.41	1.69	
β-endosulfan	5-Jul.	100	0.21	0.31	1.06	0.48	2-Jul.	100	0.13	0.30	0.51	0.01
	15-Aug.	80	<LOD	0.34	1.33		12-Aug.	80	<LOD	0.64	1.71	
	29-Nov.	80	<LOD	0.29	0.97		29-Nov.	80	<LOD	0.24	0.76	

The strongly adsorbed pesticides, chlorpyrifos α- and β-endosulfan, were found in the surface water during the three sampling periods (Figure 6). The chlorpyrifos concentrations were significantly greater than endosulfan (Figure 6, Table 4) due to its widespread use (Table 1). Moreover, the concentrations of α-endosulfan were greater than the β-isomer, related to the stronger sorption of the β-isomer than the α-isomer (log KOCα 3.6; log KOCβ 4.3; [66]. The difference in adsorption strength implied that the α-isomer has greater potential for aquatic transport. It also caused the enrichment of β-endosulfan in sediment

compared to the α -isomer [29,67–69]. Re-mobilization experiments conducted by Peterson and Batley [66] confirmed that α -endosulfan was more readily desorbed from sediments than the β -isomer.

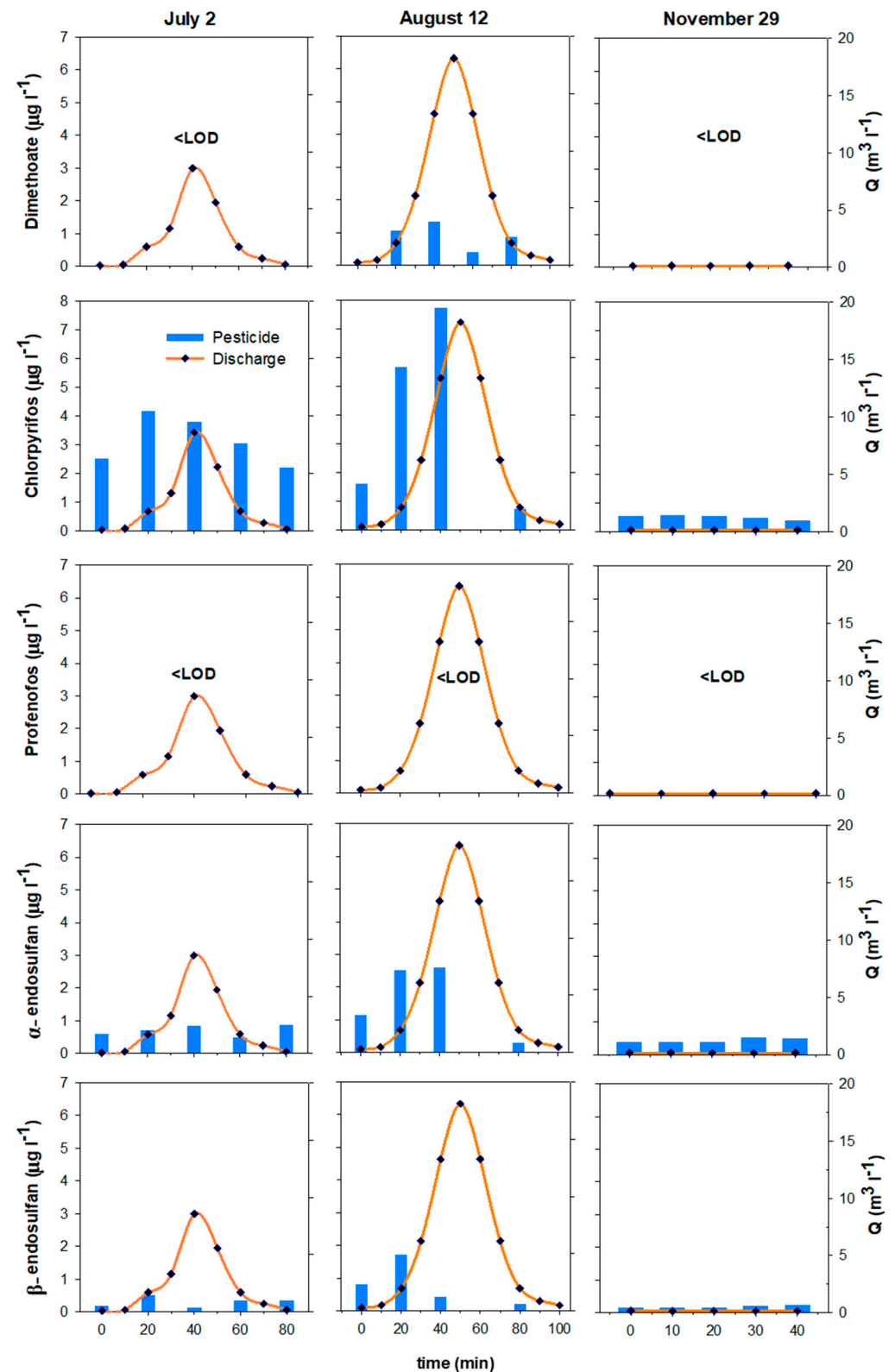


Figure 6. Stream water pesticide concentrations at watershed outlet during a runoff event in the rain phase (2 July and 12 August) and dry phase (29 November). The rain on 2 July was 20 mm and 36 mm on 12 August.

The chlorpyrifos α - and β -endosulfan concentrations were significantly less during the dry phase than during the rain phase ($p > 0.05$, Kruskal–Wallis test, Table 4; Figure 6). Low concentrations during the dry phase indicate that the baseflow concentrations were small, despite the elevated groundwater concentrations, which remained nearly the same over the three sampling periods. Thus the high concentrations during the rain phase were caused by direct runoff originating from the rainfed or irrigated land where the pesticides were applied. The elevated concentration in the direct runoff also explains that pesticide concentration in the discharge is greater for the rising limb when the overland flow is a relatively larger portion of the streamflow than for the falling limb when base flow dominates (Figure 6); [70–72]. Duffner et al. [73] also observed in a tropical sloped watershed that peak concentration occurred during the rising limb of the hydrograph.

4. Discussion

4.1. Comparison with Published Pesticide Concentrations in Groundwater and Surface Water

Pesticide concentrations in surface water observed in our study are less than the maximum concentrations reported worldwide [9,74]. Our concentrations are in the same range as recorded for the Yavatmal region in India [75], with a mean groundwater endosulfan concentration of $0.78 \mu\text{g L}^{-1}$, in Iran [76] ($0.54 \mu\text{g L}^{-1}$ endosulfan and $2.6 \mu\text{g L}^{-1}$ profenofos) and in Spain [77], with a $2.3 \mu\text{g L}^{-1}$ dimethoate concentration.

In surface water in sub-Saharan Africa, the mean endosulfan concentration in Nyando River in Kenya was $0.64 \mu\text{g L}^{-1}$ [78], $0.13 \mu\text{g L}^{-1}$ in Lake Victoria [79], and $1.65 \mu\text{g L}^{-1}$ in Agoo River in Nigeria [80]. Chlorpyrifos concentration detected in Lake Naivasha in Kenya averaged $8 \mu\text{g L}^{-1}$ [81], and in the Ankobra River in Ghana, $2.00 \mu\text{g L}^{-1}$ [82]. Our measured concentrations were relatively greater than the mean endosulfan concentration of $0.064 \mu\text{g L}^{-1}$ in Lake Bosomtwi, Ghana [83], $0.14 \mu\text{g L}^{-1}$ in South Africa [84], and $0.13 \mu\text{g L}^{-1}$ in the NyandoSondur-Miriu river, Kenya [85]. A concentration of $0.7 \mu\text{g L}^{-1}$ chlorpyrifos was reported for South Africa. The few studies in rural watersheds with crop production in the Ethiopian highlands reported surface water concentrations surface water within the same order. Merga et al. [29] measured in Lake Ziway in the Great Rift Valley, average endosulfan concentrations of $1.1 \mu\text{g L}^{-1}$ are similar to our findings. Chlorpyrifos mean concentrations were less by a factor of five, and dimethoate was three times less. Unlike our study, profenofos were found in surface water in Lake Ziway [26]. Teklu et al. [30] recorded $0.14 \mu\text{g L}^{-1}$ endosulfan in the Meki River, a tributary of the Lake Ziway.

We found two studies on pesticide concentration in groundwater in sub-Saharan Africa [28,82]. Mekonen et al. [28] observed groundwater organophosphate concentrations in central Ethiopia that were six times greater than in our study. Affum et al. [82] detected the maximum chlorpyrifos concentration in an agricultural catchment dominated by cocoa crops in the Ankobra Basin, Ghana, of $2.1 \mu\text{g L}^{-1}$. They were of the same order as our concentrations in Table 4.

4.2. Farmers' Awareness of Pesticides Use and Management

During the discussion between farmers and agencies personnel, farmers confirmed that they are unaware of the off-target transport of pesticides to surface and groundwater and its impact on the environment. When spraying pesticides, they do not keep a safe distance from rivers and shallow hand-dug wells. They usually clean up spray materials in the stream or near the hand-dug wells used for drinking, livestock, and irrigation (Supplementary Materials B). Sometimes, they receive pesticides from an illegal importer not registered with the Ministry of Agriculture. Moreover, both participants, i.e., farmers from local communities and experts, underlined that the retailers could not provide information on pesticides.

Pesticide applicators responded that they did not receive training on pesticide use and management and did not think pesticides could affect human health during spraying. It was also established that farmers in the study area did not use personal protective

equipment (PPE). Farmers usually use empty pesticide containers to store food. Pesticides are kept anywhere in the house, including in kitchens and bedrooms. The lack of PPE, appropriate storage places, and disposal of containers of agro-chemicals pose a great threat to human and livestock health [7].

Our observations in the field survey of farmer practices agree with several studies on pesticide use and management in Ethiopia. These studies also showed a lack of knowledge on safety precautions, management, and use of pesticides [17–20]. Importantly, the survey by Mengistie et al. [21] demonstrated that retailers did not give instructions on properly using pesticides. More than 90% of retailers did not have a background in the use of agro-chemicals.

4.3. Risk Assessment

The acute and chronic risks quotient (RQ) for adults, children, and infants was based on the observed groundwater concentrations because groundwater wells are the drinking water source in most households. The eco-toxicological risk assessment employed the observed surface water concentrations to calculate RQ for the aquatic invertebrate and fish in Lake Tana.

4.3.1. Human Health Risk Assessment of Pesticides in Groundwater

Dimethoate concentrations found in the August water sample had chronic risk quotients greater than 1 for infants indicating possible adverse health effects (Figure 7) if these pesticides occurred all year long in the wells. For adults, the RQ was less than 1 in all wells. The possible chronic risk of dimethoate from groundwater sources was also reported for orchards in the valley of Neuquen river, Argentina [86]. The chronic risk coefficients of chlorpyrifos, profenofos, and endosulfan were all below 1 in our study (Figure 7). None of the active ingredients caused an acute risk. It is important to recognize that the number of analyses was small due to cost constraints and that the climate was sub-humid. Thus, the human health risks of these studies should be further investigated.

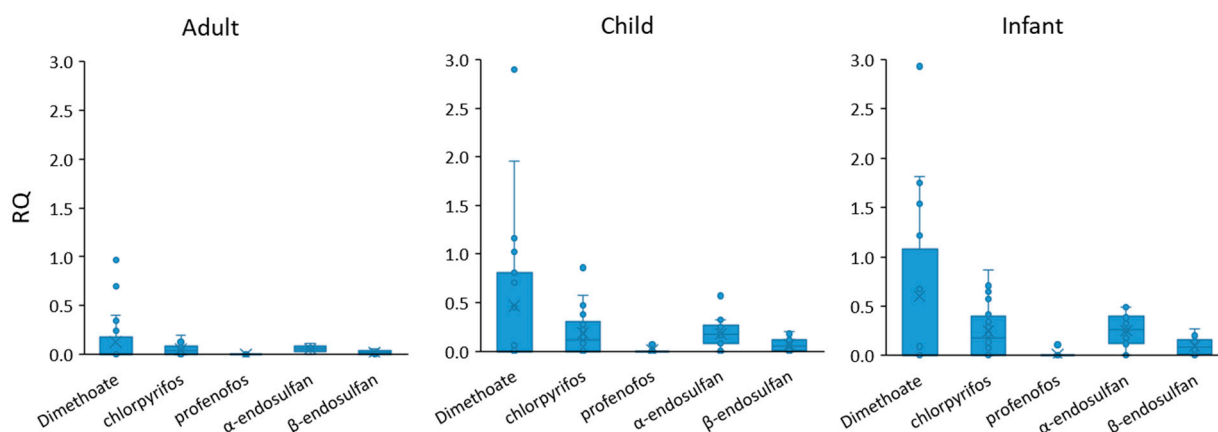


Figure 7. Boxplot of the risk quotient for pesticides in the groundwater sources consumed by adults, children, and infants via the oral pathway in the study catchment.

4.3.2. Eco-Toxicity Risk Assessment of Pesticides in Surface Water

Chlorpyrifos, dimethoate, and endosulfan concentrations at the watershed outlet were employed to assess the eco-toxicity using Equations (1) and (2). The results show that chlorpyrifos concentrations (Table 4, Figure 6) were acutely toxic for aquatic invertebrates, with RQ values varying between 121 and 5680 (Table 5). The chlorpyrifos concentrations were also a chronic toxic for fish with RQ > 405. In addition, the observed endosulfan concentrations had acute and chronic toxicity to fish, with chronic RQ values ranging from 560 to 5680 for the α isomer and 520–4140 for the β isomer (Table 5). These RQ values were much greater than the lower boundary of 10 of the high-risk category. Dimethoate did not exhibit an eco-toxicological risk, and profenofos were not observed in surface water.

Table 5. Eco-toxicological risk assessment of pesticides detected in streams.

Pesticide	Aquatic Invertebrate				Fish			
	Acute		Chronic		Acute		Chronic	
	RQ Range	%RQ > 1	RQ Range	%RQ > 1	RQ Range	%RQ > 1	RQ Range	%RQ > 1
Dimethoate	0.01–0.20	0	0.03–0.85	0	0.01–0.10	0	0.01–0.87	0
chlorpyrifos	121–5680	100	0.26–9.20	67	1.56–2.30	100	1.87–405	100
α -endosulfan	0.01–0.65	0	-	-	14–94	100	560–5680	100
β -endosulfan	0.03–0.47	0	-	-	11–57	100	520–4140	100

The severe eco-toxicity risk of endosulfan and chlorpyrifos in surface water for aquatic organisms in Ethiopia was confirmed by other recent studies [29,30]. In addition, the toxic effect is not limited to Ethiopia [87]. In sub-Sahara Africa, for example, in the Ankobra River Basin with intensive cocoa production, the chlorpyrifos concentration was reported as toxic to fish, algae, and aquatic invertebrates [82]. Finally, endosulfan and chlorpyrifos concentrations in the Mae Sa River in mountainous Thailand [88] and the Ebro River Delta in NE Spain [89] were harmful to aquatic organisms.

The implication of this and other studies is that pesticide concentrations of chlorpyrifos and endosulfan (α and β) in streams in Ethiopia are highly toxic for invertebrates and fish. The risk analysis indicates that the ecological health of lakes is threatened severely. The Ethiopian government should consider following the lead of other countries by replacing the use of these two pertinent chemicals with pesticides that have a shorter half-life and do not harm the lake ecology. It is estimated that the livelihood of a million people depends on Lake Tana alone.

5. Conclusions

This study evaluated pesticide concentrations in surface and groundwater. Concentrations were measured, and a risk assessment was conducted in a small agricultural watershed in Lake Tana Basin in the Ethiopian highlands.

Five active ingredients, dimethoate, profenofos, chlorpyrifos, and endosulfan (α and β), were detected in the groundwater and four in surface water. Profenofos, a weakly adsorbed and fast-degrading pesticide, was found only in the groundwater after application in the rain phase. Dimethoate, a fast-degrading, weakly adsorbed pesticide, was only detected during the rain phase. Chlorpyrifos and endosulfan (α and β), both strongly adsorbed, were detected in 80% of the groundwater samples taken during rain and dry monsoon phases. The mean recorded concentrations of pesticides were above the 1998/39/European Union Council Directive limit for drinking water. The pattern of observed concentration indicated that the pesticides were transported rapidly to the groundwater through preferential flow paths under non-equilibrium sorption conditions. Surface runoff was the main transport mode for the strongly adsorbed to Lake Tana.

Chlorpyrifos and endosulfan (α and β) concentrations indicated that these pesticides were extremely toxic to the invertebrates and fish. They can affect the ecological health of the lake and, thereby, the people's livelihood, which depends on the lake. Together with the research findings of high concentrations of these two pesticides in Ethiopian lakes, the Ethiopian government should consider banning these pesticides in accordance with the WHO guidelines. At the same time, these pesticides are essential for crop production, and restricting their use will negatively affect food security. It is, therefore, vital that alternatives are developed to prevent loss in crop yield.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w14213446/s1>, Supplementary Materials A: Table S1: Eco-toxicological endpoint concentration data of studied pesticides. Table S2: The mean percent recovered (%R) and relative standard deviation (%RSD) for spiked pesticides in water samples and method limit of detection (LOD) and quantification (LOQ) analyzed using GC-MS Supplementary Materials B: an excel file with the Detail information surveyed on pesticide type, application rate, and the crop types practiced by the small farm holders.

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