Original Research Article

PESTICIDE RESIDUE LEVELS IN SOIL, WATER AND SELECTED VEGETABLES IN EWASO NAROK WETLAND, LAIKIPIA, COUNTY, KENYA

ABSTRACT

Soil, water, kales and tomatoes from Ewaso Narok wetland were collected during wet and dry seasons and analyzed for 15 pesticide residues. Multi-residues method (QuEChERS EN) was used for sample preparation and Liquid chromatography-tandem mass spectrometry (LCMS/MS) used for analysis. Soil was highly contaminated compared to water, kales and tomatoes. Banned (Aldicarb, azinphos methyl) and restricted (diazinon, chlorpyrifos and fenpropathrin) pesticide residues were detected in sample matrices in different concentrations. Residues levels that exceeded the European Union (EU) maximum residues limit (MRLs) were found in kales (triadimefon, cyproconazole I and II, fenpropathrin), tomatoes (cyproconazole I and II, fenpropathrin and spiroxamine) and water (aldicarb). All the pesticide residues concentrations were within the recommended levels of the World Health Organization (WHO) and Agricultural Food Organization (FAO). Residue levels were significantly high in the upstream and midstream during wet and dry seasons. Temperatures, conductivity (EC), pH, salinity, total dissolved solids (TDS) and dissolved oxygen (DO) were measured to assess soil/water quality. All the physico-chemical parameters were within the recommended levels. Though most residue levels were below the EU-MRLs, MCLs and within the toxicological levels (LD_{50}), the negative effects of the long term exposure to the wetland biodiversity and human health is real and should not be ignored. Farmers need to embrace Good Agricultural Practices (GAP) in order to reduce over-reliance on pesticide use in the wetland.

Keywords*; Pesticide residues, vegetables, Ewaso Narok wetland, LCMS/MS, QuEChERS*

1. INTRODUCTION

Pesticide use in agriculture is vital for the improved sustainability of food supply globally. However, high residue levels in food is a major global concern. Pesticides distribution from targeted sites follows different routes during spraying and enables toxic chemicals to reach beneficial and non-target organisms in the environment (1, 2,3). The distribution of residues in the environment is dependent on a combination of factors namely; pesticides rates of application and inherent chemical properties [4]. Knowledge of chemical properties of pesticide in terms of water solubility, persistent and soil sorption is vital in tracing environmental chemical mobility and evaluating the likely environmental risk associated to a particular applied pesticides [5]. To ensure safety, adherence to specific pesticide time intervals (re-entry interval) or (pre-harvest interval) is important [6]. Failure to adhere to the time intervals is a recipe to increased human pesticide exposure [7]. Unpredictable weather patterns and effects of climate change has led to independence on rain-fed agriculture [8]. As a result, important ecological sites such as natural wetlands continue to witness fastest agricultural growth due to the availability of fertile land and water for irrigation in the recent past.

Ewaso Narok wetland is a major source of horticultural produce in Kenya. Because of the vulnerability of horticultural crops to pests attack, a range of pesticides are used to reduce crop losses from pests and diseases, ensuring improved harvest and better returns on investment [9,10]. Modern pesticides such as organophosphates, carbamates, pyrethroids, azoles are commonly used. Though the pesticides are preferred due to their low persistence in the environment, some are highly toxic and poisonous thus could harm human and environment [11]. Some pesticides have been associated with human blindness, liver complications, cancer, reduction of sperms, infertility, increased cholesterol levels, high infant mortality rates, metabolic and genetic disorder [12]. With the extensive pesticide use in the wetland, the level of residues in soil, water and vegetables were investigated during wet and dry seasons. The seasonal variation was used to determine the agricultural practices that are employed by farmers to protect the crops irrespective of the potential hazards and risks that follow human exposure and consumption of contaminated vegetables. Accessibility to safe drinking water is a basic need for all for better health and sustainable development goals (SDGs) [13]. Ewaso Narok wetland is a major source of water for both domestic and agriculture in the region. Agriculture and other anthropogenic activities within the wetland have great impact on the quality of water of Ewaso Narok River. The chemical and biological quantity in the water cannot be ignored in comparison to expected water drinking quality. Furthermore, WHO recommends regular monitoring of water quality for temporal changes of vital physico-chemical characteristics (pH, temperature, conductivity, dissolved solids, dissolved oxygen, salinity etc) in agricultural areas especially after heavy rains [14].This study also evaluated the physico-chemical parameters (pH, temperature, conductivity, salinity, total dissolved solids, dissolved oxygen and salinity) of both soil and water to determine soil/water quality of Ewaso Narok wetland and its suitability for human use or associated risks. The European Union regulation sets a limit of the total and individual concentration of the pesticides in drinking water at 0.5µg/L and 0.1µg/L, respectively [15].

2. MATERIALS AND METHODS

Ewaso Narok wetland found in arid and semi-arid part of Laikipia County Kenya, lies between 36°12’17’’E to 36°45’16’’E and 0°28’51’’N and 0°7’28’’S with altitude ranging from 1780 to 1835m above the sea level. Soil, tomatoes, kales and water used in this study were collected in June (wet season) and October (dry season), 2016. The samples were collected in triplicates from 15 purposively selected grids superimposed on the study area following an (X) pattern. Both kales and tomatoes were blended and 50g weighed and placed separately in a sealed well labeled plastic containers. Water samples were collected from the Ewaso Narok River at the upstream, mid-stream and downstream using grab method as described by [16]. Ten (10) water samples were grabbed from each sampling site after every 5 minutes and placed into a clean bucket to form a composite sample. 500mL water samples from each site was measured and kept into a well labeled dark glass bottles. All the samples were kept in ice-packed cooler box at $4^{o}C$ and transported to the laboratory where they were kept at $-86^{o}C$ before extraction. Electrical conductivity (EC), temperature, pH, salinity and TDS were measured in-situ during sampling using a professional digital multimeter for pH/EC/TDS mobile measurements (made in Germany), model multi 3420 SET H 2FD46H. The measurements were taken by selecting a target probe. The probe was submerged into the sample solution after re-calibration with a blank solution (de-ionized water) and readings taken after stabilization. Plastic bottles were used to minimize any electromagnetic interferences. Soil salinity was measured based on a dilution value of 1:5. Dissolved oxygen (D.O) was determined using Winkler titration method according to Environmental Chemistry of Boston Harbor-IAP 2006 [17].

Samples were prepared according to QuEChERS EN method as described by [18]. 10 g of soil, kales and tomatoes were separately weighed into clean 50ml falcon tubes, 10ml water and 10ml acetonitrile were added to each tube. The mixtures were vigorously shaken for 1 minute and vortexed for 1 minute. QuEChERS salt pouch containing a mixture of 4g magnesium sulphate, 1g sodium chloride, 1g sodium citrate and 0.5g sodium hydrogencitrate sesquihydrate were added to the tubes to promote phase separation. The tubes were shaken and vortexed for 1 minutes and centrifuged for 5minutes at 4000 rpm. The upper organic layers (acetonitrile extract) containing pesticide residues were then transferred into clean tubes for sample clean-up procedure. For cleanup, 3ml of the acetonitrile extracts of each samples were transferred to well label clean tubes containing 900 mg magnesium sulphate/ 150 mg PSA. The mixtures were shaken for 30 seconds and centrifuged for 3 minutes at 3000 rpm. For tomatoes and kales extracts, graphitized carbon black (GCB) was added, shaken for 30 seconds and centrifuged for 3000 rpm for 5 minutes to remove the highly pigmented chlorophyll. For water samples, 10 mL were added into a clean 50ml falcon tube followed by 10ml of acetonitrile. The mixture was vigorously shaken for 1 minute and vortexed for 1 minute. Contents of QuEChERS salt pouch was added to the tubes to promote phase separation.

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Pesticide analysis was performed using Waters Acquity UHPLC (ultra-high performance liquid chromatography) system (Waters, Milford, MA, USA) using UHPLC BEH C18, 2.1 × 50 mm, 1.7 µm column, which was equipped with a guard pre-column. The flow rate was 0.45 ml/min, the injection volume was 5 µl and the column was operated at 30°C. A binary mobile phase was composed of (A) 10mM ammonium formate in water and (B) 10mM ammonium formate in methanol. A mobile phase gradient started at 2% B (0.0-0.25 min) and increased to 99% B at 12.25 min (curve 6), was held until 13 min and concluded by column equilibration at initial condition for 4 minutes for a total run time of 17 minutes. The UHPLC system was interfaced to a Xevo TQ triple quadrupole mass spectrometer (Waters, Milford, MA, USA). The MS determination was performed in positive electrospray mode with monitoring of the two most abundant MS/MS (precursor/ product) ion transitioning using scheduled multiple-reaction monitoring (MRM) program for 60seconds for each analyte with an electrospray ionization operated both in positive ion mode. Source conditions were set as follows: ion source temperature 150°C, capillary voltage 1.5kV, desolvation temperature 500°C. Nitrogen was used as desolvation and cone gas, desolvation and cone gas flows were set at 800 and 150 l/h, respectively. Argon was used as a collision gas and the flow rate was set at 0.12 ml/min. Stock standard solutions (1mg/mL) were prepared by weighing dissolving them in a high performance liquid chromatography (HPLC) grade acetonitrile. They were kept in the dark at -20^{o}C. Linearity of calibration curves were evaluated from peak area calculations after five injections of standards prepared at the concentrations 50, 100, 150, 200 and 250ug/L. LOD was calculated from the RSD of the mean detector responses of five replicate injections using the formula LOD=3 x RSD x concentration (when the blank response is zero).

3 RESULTS AND DISCUSSION.

For all the analytes, the percent recovery ranged from 83.5-97.5 (soil), 73.6-96 (water), 75.4-89.1(kales) and 75-92% (tomatoes). Confirming reliability and accuracy of the QuEChERS method and UHPLC-MS/MS. The %RSD ranged between 0.69%-10.81percent. Regression coefficient (r^2) ranged between 0.961 and 0.999 with most analyte giving a regression coefficient of determination ($r^2 \geq 0.99$) adequate for residues analysis [19]. Over the calibration range (0.1-500) µg/L all the calibration curves were linear. The baseline chromatographic resolution of ≥1.5 from the other sample components was also found, indicating a suitable chromatographic conditions (column type, flow rate and detection mode) chosen for selectivity as reported by [20] and [21]. The LOD values obtained ranged from <0.1 to 0.241 which were below the maximum residue limits (MRLs) of the respective pesticides.

Table 1: Seasonal variation in the physico-chemical characteristics of soil in Ewaso Narok wetland during Wet and Dry seasons

Physico-chemical characteristics	***Seasons***		
	Wet	**Dry**	**p-value**
Temperature (^0C)	22.68^a±0.13	24.17^b±0.10	<0.001
pH	6.64^a±0.05	7.16^b±0.07	<0.001
Conductivity (µS/cm)	186.79^a±18.12	340.05^b±31.02	<0.001
Salinity (psu)	0.21^a±0.03	0.16^a±0.01	0.066
Total Dissolved Solids (mg/L)	199.46^b±26.92	115.63^a±7.78	0.006

Table 2: Seasonal variation in the physico-chemical characteristics of water in Ewaso Narok River during Wet and Dry Seasons

Sample	***Physico-chemical characteristics***	***Seasons***		***p-values***
		Wet	**Dry**	
Up-stream water samples	Temperature	20.87±0.20	21.67±0.18	ns
	pH	6.80±0.05	6.87±0.05	ns
	Conductivity (EC)	144.17±3.76	158.40±3.41	ns
	Salinity	0.39±0.12	0.06±0.13	ns
	TDS	157.80±9.06	165.30±9.09	ns
	Dissolved Oxygen (D.O)	90.60±1.14	88.60±1.16	ns
Mid-stream water samples	Temperature	20.96±0.22	21.37±0.20	ns
	pH	6.62^a±0.06	6.95^b±0.08	0.009
	Conductivity (EC)	147.60^b±3.63	136.90^a±4.02	0.0003
	Salinity	0.25±0.01	0.08±0.01	ns
	TDS	151.53±8.23	180.77±8.34	ns
	Dissolved Oxygen (D.O)	87.87±1.54	88.47±1.71	ns
Down-stream water samples	Temperature	21.00^a±0.30	22.20^b±0.31	0.043
	pH	6.65±0.06	6.87±0.04	ns
	Conductivity (EC)	139.73±6.49	186.50±6.44	ns
	Salinity	0.12±0.01	0.11±0.01	ns
	TDS	150.43±5.08	167.70±6.02	ns
	Dissolved Oxygen (D.O)	87.33±0.69	87.00±0.55	ns

ns- no significance difference (p>0.05)Physico-chemical characteristics (temperature,

Physico-chemical characteristics (Temperature, pH, conductivity (EC), salinity, total dissolved solid (TDS) and dissolved oxygen (DO)) were measured in the soil and water during wet and dry seasons. Significantly higher values of temperature, pH and conductivity were recorded for the soil during the dry season than the wet season. (Table 1). While significantly higher values for the TDS was recorded for the soil during the wet season compared to dry season. However, soil salinity levels had no significance different for the two seasons ($p>0.05$). Soil temperature ranged between 22.0-24.7 ^oC with an average of 23.4^oC, pH ranged between 6.30-7.48 with an average of 6.90, EC ranged between 98.5-571µS/cm with an average of 263.4 µS/cm, salinity ranged between 0.11-0.44 psu with an average of 0.18psu while TDS ranged between 80.7-456 mg/L with an average of 157.5mg/L for the entire study period. The water pH for both wet and dry seasons ranged from 6.62-7.12 with an average of 6.79. Water temperature ranged from 20.6-22.8 ^oC with an average of 21.5^oC, EC ranged from 135.7-204 µS/cm with an average of 157.2µS/cm. Water salinity measured during wet and dry season had a range of 0.05-0.17 psu with an average of 0.14psu, TDS in water ranged from 130.8-194.1mg/L with an average of 163.5mg/L while D.O ranged from 80.7-96.1% with an average of 88.3%. (Table 2). [22] in a similar study in Njoro Sub-County, Kenya, reported physico-chemical characteristics of river Mauche and Njoro in the range of; temperature (16.3-24.7)^oC, pH (7.51-8.17), EC(310-3360)µS/cm, DO (5.83-7.27)mg/L and TDS (70-150)mg/L. The reported values in this study for water pH, and TDS during wet and dry seasons were all within the World Health Organization (WHO) and Kenya Bureau of Standards (KEBS) recommended limits [23] and [22]. For untreated water pH, the recommended limits are in the range of WHO/ KEBS (6.5-8.5), TDS range; WHO (600mg/L) and KEBS (1200mg/L). Temperature and EC have no specified limits for both WHO and KEBS.

Fifteen (15) pesticide residues were found to be present in the sample matrices in Ewaso Narok wetland. Pesticide residue levels in soil, kales and tomatoes in Ewaso Narok wetland for the wet (June, 2016) and dry (August, 2016) seasons (Table 3). There was a significant difference ($p<0.05$) in the pesticide residue levels in soil, kales and tomatoes during both wet and dry seasons except for diazinon ($t=0.523$), pyrimethanil ($t=0.096$) and spiroxamine ($t=0.338$) that showed no significant differences in soil, kales and tomatoes for the wet and dry seasons. Significantly higher residue levels were observed in soil in the range of 0.25-640 µg/L (wet season) and 4.31-1000.21 µg/L (dry season). However, the levels of pesticide residues in both kales and tomatoes were not significantly different from one another. (Table 3). Residue levels in kales ranged from 1.22-132.98 µg/L (wet season) and 1.37-149.86 µg/L (dry season). In tomatoes residue levels ranged from 0.70-117.76 µg/L (wet season) and 0.30-135.75 µg/L (dry season). There was a significant difference ($p<0.05$) in the levels of aldicarb, triadimefon, metalaxyl, cyproconazole II and pyrimethanil in the water during wet and dry seasons. (Table 4). Significantly higher levels were recorded in the upstream and midstream in both wet and dry seasons. Relatively high concentration ranges were noted in the upstream for aldicarb (2.93-4.33) µg/L, triadimefon (1.38-2.28) µg/L and cyproconazole II (2.12-3.51) µg/L. Residue levels were slightly lower in the mid-stream than in the upstream for the two season except for aldicarb (5.85) µg/L and bifenazate (0.25) µg/L for the wet season, metalaxyl (0.20) µg/L and pyrimethanil 0.30µg/L for the dry season. In the wet season, the residue loads ranged from; upstream (0.18-4.33)µg/L, mid-stream (0.15-5.85)µg/L, down-stream (0.13-2.75) µg/L. While in the dry season, residue loads ranged from; upstream (0.09-2.93) µg/L, mid-stream (0.12-2.20)µg/L and downstream

(0.14-1.45)µg/L. Residues levels exceeded the maximum contamination limit (MCL) in drinking water which is set at 0.5µg/L (sum total pesticides concentrations) and 0.1µg/L (concentration of individual pesticide) by EU.

Table 3: The mean seasonal variation of 15 pesticide residues in soil, kales and tomatoes from Ewaso Narok wetland during the wet and dry seasons.

Pesticides	***Season***	***Soil (µg/L)***	***Kales (µg/L)***	***Tomatoes (µg/L)***	***P-value***
Triadimefon	Wet	618.79±117.24[b]	132.98±5.56[a]	117.76±4.79[a]	0.003
	Dry	1000.21±50.12[b]	149.86±3.07[a]	131.42±1.37[a]	<0.001
Metalaxyl	Wet	640.18±49.33[b]	96.29±7.11[a]	91.96±7.28[a]	<0.001
	Dry	800.23±15.25[c]	108.52±4.49[a]	135.75±6.64[a]	<0.001
Azoxystrobin	Wet	167.75±47.87[b]	49.83±13.47[a]	40.13±11.26[a]	0.039
	Dry	450.49±56.89[c]	56.16±8.29[a]	86.15±9.27[b]	<0.001
Azinphos methyl	Wet	29.46±6.20[b]	14.44±2.53[a]	12.54±2.21[a]	0.049
	Dry	100.09±4.66[c]	16.16±1.31[b]	34.42±2.02[a]	<0.001
Buprofezin	Wet	5.19±1.30[b]	2.76±0.69[ab]	1.02±0.32[a]	0.040
	Dry	6.36±2.19[b]	3.11±0.63[ab]	1.17±0.21[a]	0.005
Cyproconazole I	Wet	193.87±50.70[b]	59.00±18.06[a]	54.04±19.68[a]	0.040
	Dry	437.49±26.26[c]	66.50±14.48[a]	82.15±13.96[b]	<0.001
Cyproconazole II	Wet	261.75±9.18[b]	71.75±10.89[a]	80.08±2.87[a]	<0.001
	Dry	420.64±5.38[b]	80.86±7.94[a]	92.09±2.42[a]	<0.001
Diazinon	Wet	2.17±0.66	1.68±0.69	1.13±0.46	0.523
	Dry	5.66±0.60[b]	1.90±0.13[b]	0.30±0.12[a]	<0.001
Fenpropathrin	Wet	207.91±74.18[b]	27.03±8.49[a]	16.82±4.71[a]	0.035
	Dry	480.69±47.69[c]	30.46±5.75[b]	19.34±2.30[a]	<0.001
Chlorpyrifos	Wet	3.52±0.38[b]	1.22±0.19[a]	0.70±0.06[a]	<0.001
	Dry	4.31±0.25[b]	1.37±0.27[b]	0.81±0.02[a]	<0.001
Bifenazate	Wet	37.47±0.41[b]	16.13±0.01[a]	12.30±0.12[a]	<0.001
	Dry	45.90±0.37[c]	18.18±0.05[b]	24.15±0.08[a]	<0.001
Paclobutrazole	Wet	9.34±1.01	<LOD	<LOD	-
	Dry	21.45±0.72[a]	<LOD	<LOD	-
Pyrimethanil	Wet	365.82±154.16	88.83±36.51	46.28±17.31	0.096
	Dry	448.13±120.67[b]	62.87±15.41[a]	42.31±20.11[a]	0.001
Spiroxamine	Wet	128.37±56.06	55.79±24.56	51.57±23.13	0.338
	Dry	357.25±21.15[b]	144.96±3.07[c]	105.42±1.37[b]	<0.001
Aldicarb	Wet	10.39±0.76[b]	6.89±0.90[a]	5.23±0.75[a]	0.011
	Dry	32.73±0.49[a]	7.76±0.82[a]	8.01±0.58[a]	<0.001

Mean values followed by the same small letter within the same row do not differ significantly from one another (one-way ANOVA, SNK-test =0.05). LOD (limit of detection)

Table 4: Mean concentrations (±SE) of pesticide residues in Ewaso Narok river water (n=3) for the wet season and dry seasons, respectively

Pesticide residues	***Seasons***	***Upstream µg/L***	***Mid-stream µg/L***	***Down-stream µg/L***	***P-value***
Aldicarb	Wet	4.33 ± 0.04^{b}	5.85 ± 0.03^{b}	2.56 ± 0.02^{a}	<0.01
	Dry	2.93 ± 0.02^{b}	2.20 ± 0.01^{b}	1.08 ± 0.01^{a}	<0.01
Triadimefon	Wet	2.28 ± 0.05^{b}	2.15 ± 0.03^{b}	0.91 ± 0.03^{a}	<0.01
	Dry	1.38 ± 0.01^{b}	1.01 ± 0.00^{b}	0.39 ± 0.03^{a}	<0.01
Metalaxyl	Wet	0.25 ± 0.03^{a}	0.15 ± 0.01^{a}	0.37 ± 0.02^{b}	<0.01
	Dry	0.15 ± 0.01^{a}	0.20 ± 0.02^{a}	0.29 ± 0.01^{b}	0.01
Cyproconazole II	Wet	3.51 ± 0.15^{b}	3.30 ± 0.03^{b}	2.75 ± 0.02^{a}	<0.01
	Dry	2.12 ± 0.01^{c}	1.55 ± 0.01^{a}	1.45 ± 0.01^{a}	<0.01
Bifenazate	Wet	0.23±0.03	0.25±0.01	<LOD	-
	Dry	0.14±0.01	0.12±0.00	<LOD	-
Pyrimethanil	Wet	0.18 ± 0.02^{b}	0.18 ± 0.01^{b}	0.13 ± 0.02^{a}	0.044
	Dry	0.09 ± 0.01^{a}	0.30 ± 0.01^{b}	0.14 ± 0.01^{a}	<0.01

Mean values followed by the same small letter within the same row do not differ significantly from one another (one-way ANOVA, SNK-test =0.05), LOD – limit of detection

Discussion

The presence of pesticide in the soil may be due to the chemicals ability to bind strongly to the soil particles. This makes them unavailable for leaching through the soil or giving off vapour in the environment. A similar study conducted by [2] in Laikipia, Kenya reported different levels of pesticide residues in agricultural farmlands. The levels of azinphos methyl, buprofezin, diazinon, chlorpyrifos, bifenazate, paclobutrazole and aldicarb in the soil were ≤ 100 µg/L for both wet and dry seasons, respectively. This could be attributed to pesticide loss through leaching into the soil resulting from chemical's moderate to high solubilities and short half-life. [24] in a similar study conducted in Pakistan, reported several pesticide residues in farmland in varying degrees of concentrations. The notable residue was chlorpyrifos present in 16 soil samples with a mean concentration of 0.486mg/Kg [24]. The presence of highly hazardous chemicals (aldicarb, azinphos methyl, chlorpyrifos, fenpropathrin and diazinon) and high concentrations of residues in the soil poses potential food and environmental safety risks in Ewaso Narok wetland that should not be ignored. Some of these chemicals can kill untargeted useful soil organisms while others are easily taken up by plants and may bioaccumulate in higher mammals as described by [25].

Most residue levels in kales and tomatoes irrespective of the seasonality were below the se EU-MRL. This shows that most pesticide residues reported in this study do not pose any immediate health risk to human. Paclobutrazole was only detected in soil collected during the two seasons and not in vegetables or water samples pointing to a possible historical use [26]. The demand for quality and good return on investment for farmers has led to the use of various pesticide chemicals on crops. Some of these chemicals when used frequently may accumulate in various food crops leading to subsequent bioaccumulation in people who consume such food. A number of previous studies have reported various levels of pesticide residues in vegetables raising food safety concerns. [27] in a study conducted in Chile on the pesticide residues in leafy vegetable, reported a mean range of 0.54-2.25 mg/kg. In other studies by Golge and Kabak (2015), the levels of chlorpyrifos and azoxystrobin in oranges was reported in the range of 10-90 and 20-30µg/L, respectively. While [28] reported the levels of diazinon in rice paddies in the range of 480-923.7 µg/L. [29] in a similar study reported high level of bifenazate (60 µg/L) in tomatoes after 15 days of treatment with 4060 µg/L of bifenazate pesticide. [30] on the other hand, reported the levels of metalaxyl, pyrimethanil, triadimefon, azoxystrobin and buprofezin in tomatoes in the range of 0-170 µg/L. Since some pesticides are easily absorbed by the plant surface into the plant transport system while some stay on the plant surface, it is important to understand the chemistry of pesticide chemical prior to use. Pesticides undergo various degradation processes such as volatilization, photolysis and microbial degradation in environment [31]. All these processes play a role in either reduction of the original pesticide concentration or introduction of new metabolites

Most residues were within the recommended maximum residue limits (MRLs) in both kales and tomatoes considering concentration range during wet and dry seasons. However, cyproconazole I and II, fenpropathrin, pyrimethanil and spiroxamine had their levels exceeding the EU-MRLs in kales (K) and Tomatoes (T). Highly toxic chemicals were also detected though in small quantities; Aldicarb (6.89 µg/L and 9.76 µg/L) and azinphos methyl (14.44 and 36.16 µg/L) during wet and dry seasons, respectively. MRLs are values set at the highest levels of residues expected to be in food when pesticides are used according to Good Agricultural Practices (GAP), hence they are set below the levels considered safe for humans [32]. However, MRLs are not safety limits as residues can be higher in food than the MRL but still considered safe for consumption. MRLs are subjects to legal requirements in most countries. Safety is therefore assessed in comparison with tolerable daily intake (TDI) for short term exposure and acute reference dose (ARfD) based on the body weight of the consumer. Most pesticides determined in this study had no set MRL for kales except triadimefon and cyproconazole, few (fenpropathrin, pyrimethanil and spiroxamine) with (*) were under review. High residues levels in food above the set MRLs raises food safety concerns. However, this cannot be used as a basis of rejecting kales and tomatoes with high residues levels above the MRLs without considering the TDI that can lead to bioaccumulation in human due to long exposure and ARfD which largely depend on the body weight of the consumer.

Aldicarb and azinphos methyl use in vegetables are restricted or banned by World Food Organization (WHO), Agricultural Food Organization (FAO) and European Union (EU) among other countries [33]. This follows their extremely toxic nature making their presence in soil, kales and tomatoes a major health concern. In addition, chlorpyrifos, paclobutrazole, fenpropathrin and diazinon use is restricted only to ornamental plants due to their highly hazardous nature (HHPs) [34]. With a concentrations below the EU-MRLs, these chemicals pose no immediate environmental and human health risk though bioaccumulation risks are possible. Table 5 shows the levels of pesticide residues contamination of Ewaso Narok river waters. The presence of residues at the upstream is an indication that some of the residues originated from the river catchments areas considering variety of different land uses in the region [35]. Aldicarb, metalaxyl and triadimefon are highly susceptible to transport in dissolved phase. However, high concentration of cyproconazole in water could be attributed to its high tendency of leaching into the underground water since it is sparingly soluble in water. Pyrimethanil and bifenazate have very low water solubilities hence poor leaching properties to underground water. In addition, bifenazate is highly volatile and can easily be transported by wind in vapour phase according to new pesticide fact sheet hence, low detection in the water. Aldicarb is an extremely hazardous chemical (class 1a), thus, presence of aldicarb at the upstream (4.33 µg/L) and mid-stream (5.85 µg/L) is a great risk to the aquatic system (WHO, 2017; WHO, 2003). Though, the levels are below the toxicological limits (LD_{50}) of 0.93mg/Kg and do not pose any immediate health risks, possible bioaccumulation in higher organisms resulting from long time exposure cannot be ignored. Triadimefon, metalaxyl and cyproconazole II are slightly hazardous chemicals (class III), in addition, having LD_{50} values of 602, 670 and 1020mg/Kg, respectively makes their presence safe in water. Bifenazate is practically non-toxic chemical (class IV) with an LD_{50} >5000mg/Kg according to new pesticide fact sheet by United States Environmental Protection Agency (EPA). A similar study conducted by [37] in rivers Yala and Nzoia in Lake Victoria reported traces of pesticide in water in the range of (0.05-59.01) and (ND-24.54) µg/kg for the wet and dry seasons, respectively.

Conclusions

From the results of this study **the l**evels of triadimefon and bifenazate in kales, cyproconazole (I and II), fenpropathrin and spiroxamine in kales and tomatoes exceeded the recommended the EFSA-MRLS for the wet and dry seasons. Banned (aldicarb and azinphos methyl) and restricted (chlorpyrifos, diazinon and fenpropathrin) pesticides were detected in soil, water, kales and tomatoes indicating their continual use on vegetables within the wetland and its environment against international regulations. However, despite the levels of some residues exceeding the EFSA-MRLs, all the levels were below the experimental toxicological levels (LD_{50}), acceptable daily intakes (ADIs) and acute reference doses (ARfD). This means that both tomatoes and kales from Ewaso Narok wetland do not pose immediate human health issues based on their pesticide residue levels. However, most pesticides when consumed by lover organisms in the food chain, may bioaccumulate in the higher mammals including Humans leading to human health problems in future. Some of the pesticides are highly toxic and harmful to birds and insects including pollinators. Their presence in the ecosystem such as wetland, may lead to devastating effects to the wetland natural functionalities especially when the important food chain is disrupted as a result of the death or disappearance of an important species in the ecosystem. To minimize the over-reliance on synthetic pesticide use and to improve on pesticide handling techniques, farmers from Ewaso Narok wetland should be encouraged to embrace Good Agricultural Practices (GAP) and Integrated Pest Management (IPM). Training of farmers on sound pesticide management practices and the use of agricultural extension services is important. Constant surveillance of the banned and restricted compounds such as aldicarb, azinphos methyl, chlorpyrifos, fenpropathrin and diazinon is important to ensure protection of Ewaso Narok wetland ecosystem.

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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