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RESEARCH

Seasonal variation in pesticide residue occurrences in surface waters found in Narok and Bomet Counties, Kenya

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Abstract Narok and Bomet are agricultural counties in Kenya which depend on flowing surface waters for farming activities. Agrochemicals have frequently been used to increase agricultural produce in this region. Occasionally, appropriate pesticide utilization measures are not followed. These surface waters are also consumed domestically by humans, livestock, and wild animals thus posing safety concerns to them. The current study sought to evaluate the levels and nature of pesticide residues found in surface waters in the dry and wet seasons of these counties. Eight water samples were collected in July (dry season) and October (wet season) at four different river sites in each of the two counties predetermined by the agricultural activity of its proximate environs. Pesticides extracted by solid phase extraction were analyzed by gas chromatography-mass spectrometry. At least 38 different pesticides were detected in the two counties with the highest concentration being recorded for chlorpyrifos and piperidine in Narok and Bomet counties, respectively. The pesticides chlorpyrifos, cypermethrin, cyfluthrin, and cyhalothrin were more prevalent in Narok County while triazine, semicarbazone, and epinephrine were more prevalent in Bomet County. There were significantly more pesticides detected during the wet season ($P \leq 0.05$). Out of the nine prevalent pesticides detected, four of them posed serious ecotoxicology concerns with risk quotients above 1.0 (high risk); thus, there is a need for more government policy interventions in deterring farming near riparian lands and in training of famers regarding best practice for pesticide applications.

Keywords Pesticides · Seasons · Agrochemicals · Pollution · Ecotoxicological

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Introduction

The demand for more food and nutrition security in Kenya has led to agricultural production stress (Merchant et al., 2022). Efforts to improve land productivity have been affected by climate change and overexploited arable farming lands (Godde et al., 2021). On the other hand, crop and livestock pests continue to reduce agricultural produce, thus the need for use of more pesticides. Narok and Bomet are traditionally agricultural counties in Kenya (Ndolo et al., 2022). Narok is the source of Kenya's wheat and barley food basket (blogs.worldbank.org, 2011). The northwestern part of the county (around the Mau region) is popular for potato growing, making the county one

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of the leading counties in potato production in Kenya (Muthoni et al., 2017). On the other hand, agriculture is by far the dominant economic activity in Bomet County (Bomet.go.ke, 2018). Mixed small-scale farming is practiced throughout Bomet County, with the northern part of the county near Kericho County reserved for tea plantations (Bomet.go.ke, 2018).

The two counties depend on flowing surface water for domestic use, farming, and other uses (Bosire et al., 2022). The Mau Forest, located at the apex of these two counties and neighboring Nakuru County to the north, is the main water catchment area for the region. Several rivers and tributaries originate here and not only feed these two counties, but also the entire southern Rift Valley and Nyanza regions (approximately 30% of Kenya's population) (Lunani et al., 2018) as well as the upper part of Tanzania. This region is of economic importance to the country—with a significant proportion of the country's food being grown here. The Maasai Mara National Game Reserve, which is the country's largest tourist attraction site and which yields billions in terms of income per year (Henseler et al., 2022) from wildlife tourism is also fed by the Mara and Talek (sand river) which all span from the Mau Forest water region. The Nyangores River and her tributaries feed the tea plantations in Bomet and Kericho counties (Kenya's main income earner since independence). The hydrological assessment of rivers in this region is thus not only of human health concern but also of economic importance. To facilitate agricultural production, both large- and small-scale farmers have utilized agrochemicals.

Agriculture extension officers no longer frequent farms, thus leaving farmers to use agrochemicals of their choice. Some of the notable agrochemicals sold in the region for crop and livestock farming include α-cypermethrin, cyhalo (λ-cyhalothrin), almatrix (chlorpyrifos), thunder (beta-cyfluthrin), duduthrin (tebuconazole), rudomil (mefenoxam), emerald (tebuconazole), zetanil (cymoxanil), mistress (cymoxanil), and fixtix (chlorpyrifos) among others (as identified by the authors). Acquisition of these agrochemicals from noncertified suppliers is also common. These suppliers give limited information regarding application dosage, spraying, handling, and cleaning of pesticide containers which can lead to release of these compounds into the environment (Andersson & Isgren 2021; Staudacher et al., 2020). This coupled with the demand for more agricultural produce has led to utilization of toxic chemicals such as class A pesticides, which have been detected in soil samples in the region. Indiscriminate disposal of pesticide containers and spraying near surface waters is also a common phenomenon that could lead to water pollution (Matthews, 2008; Staudacher et al., 2020).

There are two major planting seasons in this region that influence the agrochemicals used. The relatively "dry" January to August season is predominantly for grasses such as maize, barley, and wheat and is more prolific in Narok County. The September to December season is reserved for short crops, is relatively "wet," and is used for planting potatoes and other vegetables. While the grasses require a lot of fertilizer during planting and top-dressing, considerable spraying is used to kill pests, keep away birds, and protect the crops from fungi such as wheat rust diseases (Figueroa et al., 2018). Several pyrethroid organochlorines such as cyfluthrins and cyhalothrins are popular for this application (Marete et al., 2021). Vegetables such as kale, spinach, tomatoes, and coriander that are commonly grown in these areas are prone to pests that are mainly contained by pyrethroids such as duduthrin (tebuconazole) and zetanil (cymoxanil) (Djouaka et al., 2018). Ticks are the most common pests that attack livestock, and Fixtix (chlorpyrifos) is thus used to spray livestock. Tea farming requires sufficient soil fertilizer and several agrochemicals are used (Li et al., 2019). Due to poor spraying methods, there exist high probabilities of these agrochemicals ending up in surface waters, even far away from the target sites.

Poor pesticide application contributes to the presence of these agrochemicals in surface waters. Misinterpretation or ignorance in observing wind direction causes spray drift while application using the wrong water ratio or during inappropriate weather conditions leads to volatilization of pesticides. These pesticides can be transported over a long range, degrading to their residues in the course of their movement (Kalyabina et al., 2021). Loose soil structure such as that observed in Narok County due to overgrazing and deforestation causes them to be washed off or leach onto surface waters. Damalas and Eleftherohorinos (2011) confirmed the presence of pesticide residues in pristine areas far from the target sites. Chukwuka and Ogbeide (2021) also confirmed high levels of pesticides in riparian lands which were far off from farmlands. The concentration of pesticide residues away from the point source was found to decrease exponentially, but appreciable levels have been detected at least several kilometers from the source point (Chukwuka & Ogbeide, 2021). These residues then accumulate in the original sites, while others degrade and their active metabolites undergo reactions with each other to create secondary pesticides (Lushchak et al., 2018).

The Environmental Protection Agency (EPA), World Health Organization (WHO), Pesticides Control and Produce Board (PCPB), and Kenya Bureau of Standards (KEBS) regulate the pesticide standards in human drinking water in Kenya (Lalah et al., 2022). Some pesticides are more detrimental than others even at minute concentrations. There is a need for more radical approaches against pesticide-contaminated potable water in the region especially with increasing cases of cancer, lung, and kidney diseases in these regions (Macharia et al., 2019). Long-term pesticide monitoring is essential in enhancing control at point sources in good time before the pesticide residues are transferred further away. Additionally, regular monitoring of the water bodies during different seasons enables real-time detection of pesticides, thus enabling action to be taken before these pollutants degrade to other residues. For this to happen, there is need for stringent government policies as well as more scientific assessment of the pesticides pollution situational analysis. Such measures will enhance real-time mitigation strategies such as a ban of lethal pesticides or farming methods before significant pollution levels with ecological effects are realized.

Little data from the global south, and more so around Narok and Bomet Counties exists on the exact nature and levels of different pesticide residues in surface waters. Such information is quite significant owing to the numerous people, livestock, and wild animals depending on this water. This study aimed at screening pesticide residues found in surface waters of Narok and Bomet Counties during different seasons in a view of assessing their potential impact on water quality in these regions.

Research methodology

Study region

The research was guided by a randomized two-factorial experimental design—based on seasonality and proximity of samples to the source pollutants. Samples of surface waters were obtained from selected rivers in Narok and Bomet Counties, Kenya (0°37 N and 35°48 E). These counties have a tropical climate with annual precipitation rates of 1300 mm/year and 700 mm/year for Bomet and Narok counties, respectively. The counties are located at an altitude of 900 to 1100 m above sea level. The inhabitants of the counties are predominantly large-scale farmers in Narok and small-scale farmers in Bomet. In Bomet, mixed farming is practiced all throughout the year while in the northern side neighboring Kericho County (in Sotik and Litein sub-counties), tea farming is practiced. Both regions have two seasons per annum, the January–August one is relatively dry, and the September–December one is relatively wet. In Narok, the majority of the farmers produce wheat and barley, usually in the January–August season. The northern part of the county is also used for potato farming while the lower plains are predominantly pastoral lands. The main water for these activities is from the Ewaso Ng'iro, Enkare, and Talek (sand) rivers. All these rivers originate from the Mau Forest (Fig. 1).

Four points were selected from different rivers in the two counties based on proximity to activities that may result in pesticide discharge. The authors acknowledge the limitations of four samples per county in generalization of the exact pollution status. However, the strategic choice of the samples based on their localities provide a significant insight of the situational analysis as far as pesticides are concerned in Narok and Bomet Counties. In Narok County, sampling point A is surrounded by wheat farming activities, B is located with Narok town where anthropogenic activities and small mixed-farming activities occur, C is located beyond the town near a sewerage treatment plant and neighboring several vegetable plantations, and point D is located near a leather tannery in a postoral surrounding. In Bomet County, sampling point A is located in a region containing a lot of maize plantations, points B and C were surrounded by mixed farming activities, while point D was near tea plantations.

Sampling

Both Narok and Bomet Counties have several short-term seasons with different precipition levels which thus affect pesticide levels. However, the dry and wet seasons are more pronounced, and the majority of the farming decisions such as planting, weeding, harvesting, or movement of livestock are made based on these

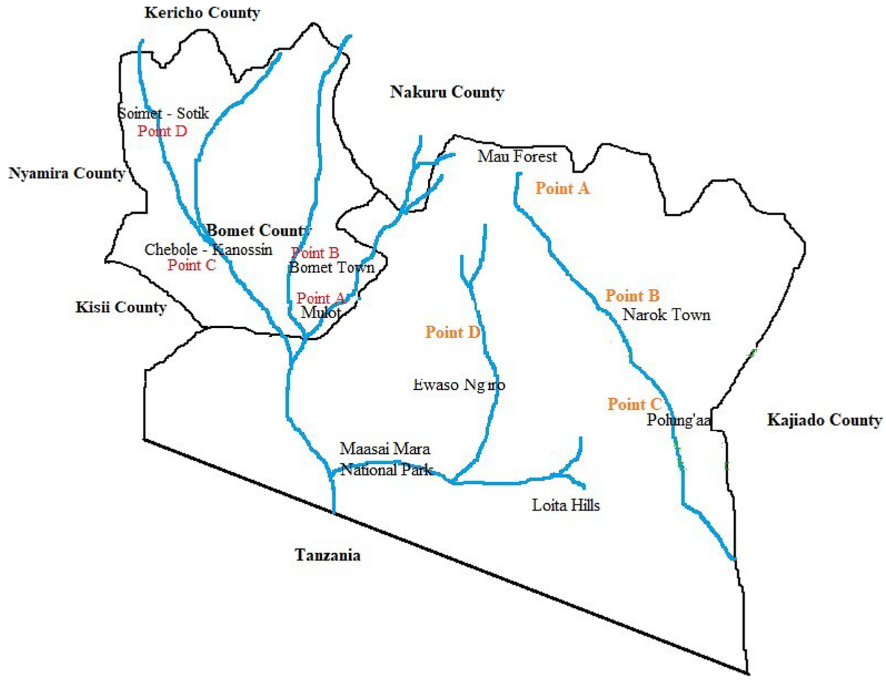


Fig. 1 The sampling sites selected from various rivers in Narok County and Bomet County

two seasons. The samples were obtained in July 2022 and in October 2022 when the dry and wet seasons, respectively, were most pronounced. However, the probabilities for pesticide level fluctuations in between these two seasons are realistic and are expected. The grab sampling method was used to collect 1-l aliquots of the surface water from the sampling points. For each sampling point, triplicate samples were taken, 5 m apart from the central point. The samples were made of polyethylene terephthalate (PET) sealed with high-density polyethylene (HDPE) caps. Physico-chemical properties of the samples were determined in situ using a portable pH meter (Hanna G-114, Shimadzu). Other physico-chemical properties such as the electrical conductivity (EC), dissolved oxygen (DO), and turbidity were also determined. A drop of 1% nitric acid was then added to the samples and they were stored in a cooler box for transfer to the laboratory for analysis.

Extraction

The samples were concentrated using a 3-layered SPE cartridge (HLB Oasis) in an SPE manifold as described by Kern et al. (2009) and Volger (2013). Before sample loading, the cartridges were preconditioned using 1M ammonium acetate and adjusted to pH 6.5–6.9 using 1M ammonia solution and 1M formic acid. The samples were then filtered using 0.25-µm microfilters (Millex-GP Syringe Filter Unit-33-mm-diameter sterile syringe filter with a 0.25-µm pore size; hydrophilic polyethersulfone (PES) membrane-gamma sterilized). The cartridge was conditioned using 5 ml of methanol and then 10 ml of filtered water. The samples were loaded onto the cartridge at a constant flow rate (~5 ml/min). Once a sample volume of 300 ml was loaded, the cartridges were dried and stored at −20 °C until elution. The cartridges were eluted back flush to avoid the sorption of all analytes on the layers. The elution was performed with 6 ml of methanol/ethyl acetate (50:50) containing 2% ammonia, then 3 ml of methanol/ethyl acetate (50:50) containing 1.7% of formic acid, and finally 2 ml of methanol. The extracts were concentrated to a final volume of 0.1 ml under a gentle stream of nitrogen. Methanol was then added to reach a final volume of 1 ml. Samples were centrifuged at 4000 rpm during 30 min, and the supernatant transferred to amber 5-ml vials for analysis.

Analysis

The analysis was carried out according to the method by Otramare et al. (2022). The samples were analyzed using a GC (QP2010 SE series, Shimadzu, Japan) coupled to a time of flight mass spectrometer (ToFMS). The GC column was a BPXS column (30 m by 0.25 mm inner diameter by 0.25 µm film thickness). Helium gas (99.999% purity) was used as the carrier gas at a flow rate of 1 ml/min. Samples were injected in a split mode in a ratio of 10:1. The sample injection temperature and injected volume were 200 °C and 1 µl, respectively. The column initial temperature was 55 °C which increased to 250 °C at a rate of 15 °C/min held for 3 min then increased to 320 °C at a rate of 10 °C/min then held in isothermal mode for 7 min. The column flow rate was 1.08 ml/min with linear velocity 37.8 cm/s at a pressure of 11.3 psi.

Fragmentation was carried out by electron ionization under a field of 70 eV, with the source of the ions and interface being maintained at 200 °C and 250 °C, respectively, at a solvent cut time of 4.5 min. The microscan width was 0.0 at 0.0 kV. Acquisition was in scan mode with the two mass spectra at a range of mass-to-charge ratio of 35–55 with a scan speed of 0.35 s/scan. The best transition was used as a quantifier and the second as a confirmation ion (qualifier). Identification of each compound with their respective limits of quantification (LOQs) were carried out on the basis of its mass-to-charge ratio in comparison to those of National Institute of Standards and Technology (NIST) database (nist.gov, 2022).

The instrument limit of detection (LOD) and limit of quantification (LOQ) of the pesticides were calculated on the basis of signal-to-noise ratio (S/N) which is 3.3 and 10, respectively, according to the International Council for Harmonisation (ICH) guidelines (Lister, 2005). The LODs and LOQs were considered for analysis to minimize the possibility of false positives or negatives. Authentic standards were used for the calibration, which minimized chances for inaccurate compound identification, as retention time as well as mass spectral data were used in this regard. These values are indicated alongside the calibration curves in Appendix 1. The calibration curves of the standards (used 99.999% pure multiresidue pesticide standards, i.e., SPX-MROP-1 (for organophosphate pesticides), SPX-MROC-1 (for organochlorine pesticides), and SPX-MRON-1 (for organonitrogen pesticide), Spex, USA) are indicated in Appendix 1.

Environmental Risk Assessment (ERA) by ecotoxicological risk quotient (RQ)

ERA was conducted to determine and classify the pesticide occurrence based on their RQ. RQ was calculated by dividing the experimental/actual measured pesticide concentration (MC) with the predicted no-effect concentration (PNEC) of the pesticide as described by Tóth et al. (2022) in Eq. 1. The PNEC values were determined from literature sources (Stadlinger et al., 2018; Zheng et al., 2017).

$$RQ = \frac{MPC}{PNEC} \quad (1)$$

If the literature was not available, PNEC values were obtained by Eq. 2 using LC_{50} values obtained from Pesticide Properties Database of the University of Hertfordshire (PPDB, 2021).

$$PNEC = \frac{LC50,\ EC50\ \text{or}\ NOEC}{AF} \quad (2)$$

where assessment factor, AF = 1000 was used whenever only EC_{50} or LC_{50} toxicological data were available from three trophic levels; AF = 100 and AF = 50 were applied when NOEC (no observed effect concentration) was available from one or two various trophic levels, respectively.

$0.01 \leq RQ \leq 0.1$, indicating low risk; $0.1 \leq RQ \leq 1$, where the level of the risk is medium; and $1 \leq RQ$, meaning high risk (Hernando et al., 2006; Zeng et al., 2018).

Data analysis

The data obtained was reported as mean ± standard deviation. A 95% confidence level (CL) was used for significance *p*-value and *t*-value tests. The data obtained was analyzed using MS Excel 2019. Pesticide concentrations were compared to Environmental Quality Standards (EQS), World Health Organization (WHO), and the US Environmental Protection Agency (US EPA) standards. For multiple regression analysis, a confidence level of 0.99 was used.

Results and discussion

At least 35 different pesticides of different groups were observed from surface waters in the 2 counties (Fig. 2). There were herbicides, insecticides, fungicides, acaricides, and nematocides (in order of increasing frequency of occurrence). The surface water from sampling point NB was the most polluted (with a pH of 4.45, turbidity of 6.8 nephelometric turbidity units (NTU), EC of 22.55 μS/cm, and DO of < 3.3%). This point registered at least 6 different pesticides above the LOQ; with chlorpyrifos, a class A pesticide, being detected at concentrations well beyond the safety limits as per US EPA and WHO guidelines for surface waters. Some of the residents at the riparian lands adjacent to the Enkare e'Narok river actually consume the water directly from its source with very little if any treatment measures—posing potentially serious health risks. On the contrary, sampling point BA, which is located at Mulot, was found to have the least pesticide diversity (4 pesticides were detected). The physico-chemical parameters of the region were pH of 5.7, turbidity of 5.5 NTU, EC of 15.5 μS/cm, and DO of < 4.3% indicating better water quality in comparison to NB. The region is predominantly a maize-growing zone thus, explaining the presence of the herbicide epinephrine. Insecticides such as benzeneethanamine, benzodiazepine, and tebuconazole were also detected due to pastoral activities in the region. There were no significant differences in the levels of pesticides in both regions during the dry and wet seasons.

The pesticide distribution was seen to follow the agrochemical use of surrounding environments as predicted in the study design. Consequently, there were more insecticides in Narok (9) compared to those in Bomet County (6; with 3 being detected at the border with Narok, i.e., at Mulot). Out of these insecticides, chlorpyrifos registered the highest concentration and frequency of occurrence due to its popularity in wheat and maize farming. The majority of the insecticides in Narok were pyrethroids or chloro-based residues (chlorpyrifos, cypermethrin, cyhalothrin, bicyclopropane, 2,2,2′,2′-tetrachloro-1,1′-dimethyl, and cyclopropanecarboxylic acid, 3-(2,2-dichloroethenyl)-2,2-dimethyl) contrast to Bomet which recorded only two chloro-based insecticides (furanone and benzodiazepine). All the rest were fluoride, carbamate, and phosphate-based residues. This difference in chemical composition of pesticides can be explained by the differences in

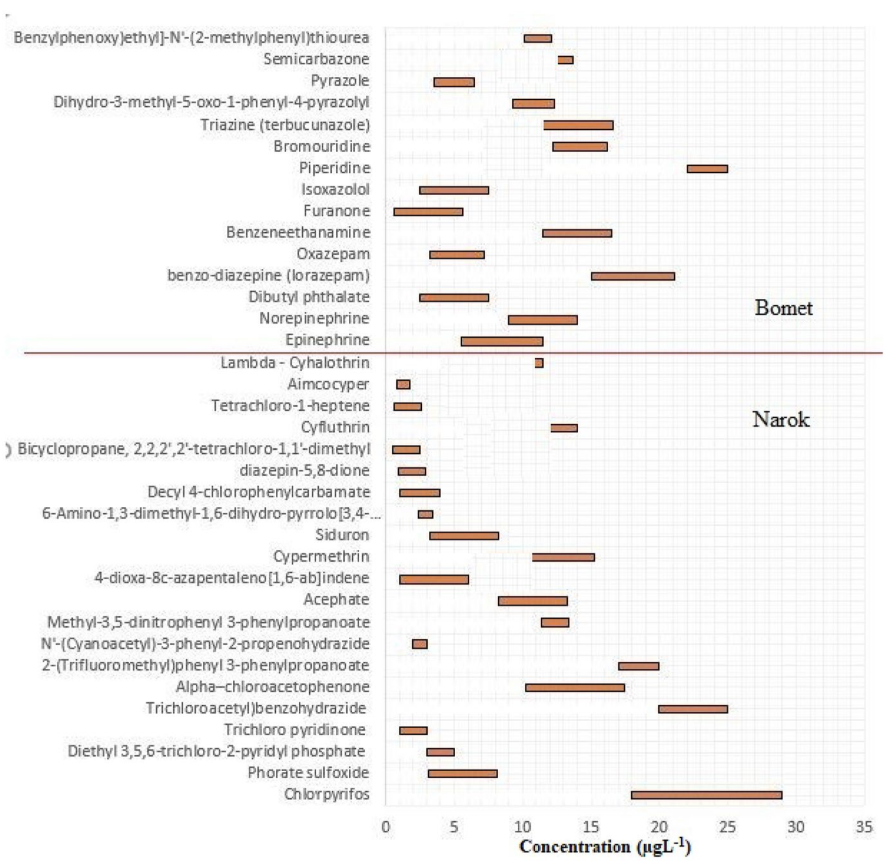


Fig. 2 The pesticide residues detected in the study region

climatic conditions between the two counties which would lead to different insecticide prescription by agrovets. Insecticides used in the relatively drier Narok County are mostly for killing ticks and other pests from livestock due to their low toxicity toward mammals (Zacharia, 2011). A good number of these insecticides are chloro-based. On the other hand, organophosphate insecticides effective against plant-sucking insects such as aphids and mites are required. Abong'o et al. (2018) indicated a great contrast in occurrence of pesticides along the Kericho-Awendo water catchment region. A good number of the pesticides in surface water were found in appreciable levels during the rainy seasons unlike in the dry season whereby most of these residues concentrate in sediments and few residues are left in surface water (Abong'o et al., 2018).

While no previous study was found to evaluate the levels of pesticide residues in surface waters in the two counties, several studies found a high presence of organochlorine pesticide residues in farms and sediments located between Mau and Lake Nakuru. Dieldrin, dichlorodiphenyltrichloroethane (DDT), and dichlorodiphenyldichloroethylene (DDE) residues were detected at levels of up to 2.13, 0.35, and 0.11 mgL^{-1}, respectively (Lincer et al., 1981), arising from the extensive use of these insecticides for horticulture and floricultural purposes. DDT, DDE, and DDD were also detected to the levels of 5.9–30.9 ng g^{-1} in sediments 1 km from Lake Bogoria (central rift valley) and Lake Magadi (south rift valley) (Bettinetti et al., 2011). The present study thus gives an interesting contrast in terms of chloro-based pesticides in Kenya. Whereas several lethal residues of DDD, DDE, and DDT were detected in other Counties, none of these was detected in the surface waters of Narok and Bomet Counties. This could probably be due to the lower sensitivity of the analytical method employed in this study (Table 1).

There were different 22 pesticide residues detected in Narok compared with 16 detected in Bomet County (Table 2). All the pesticide residues were detected in multiple sampling sites, with chlorpyrifos and cypermethrin being more common in Narok County (at least 3 counts each) while benzodiazepine, benzeneethanamine, and triazine were popular in Bomet (3 counts each). Chlorpyrifos and trichloroacetyl-benzohydrazide recorded the highest concentration levels in Narok possibly for its multiple uses as an insecticide, acaricide, and miticide. Otieno et al. (2013) detected chlorpyrifos levels of up to 22.4 and 32.8 ng g^{-1} in water and sediments of Lake Naivasha (found to the north-west side of Narok County) arising from the use of pesticide in flower plantations. Independent t test analysis conducted indicated significant difference in concentration at $P \leq 0.05$ between the seasons with respect to sediment and water samples. The chlorpyrifos levels detected exceeded those set by WHO (10 μgL^{-1}) in drinking water, thus potentially exposing the inhabitants of the region and their livestock to nervous system and body organ disorders. Piperidine—which potentially causes central nervous system (CNS) toxicity in humans (Committee on Acute Exposure Guideline Levels, 2012) had concentration levels of up to 27 μgL^{-1} in Bomet County which are well above the recommended limits (0.74 ppm) by WHO in drinking water (carlroth.com, 2022).

Other pesticide residues detected in high concentrations include alpha-chloroacetophenone (16.2 μgL^{-1}) 2-(trifluoromethyl)phenyl 3-phenylpropanoate (27.0 μgL^{-1}), benzodiazepine, and benzeneethanamine. Alpha-chloroacetophenone which is more popular in the preparation of tear gas "riot control chemical" was detected in appreciable levels in Narok. 2-(Trifluoromethyl)phenyl 3-phenylpropanoate or fluorinated PEP as it is usually abbreviated is effective toward repelling beetles and belongs to a class of emerging toxic non-biodegradable compounds known as per- and polyfluorinated alkyls (PFAs). These "forever chemicals" have long half-lives and their impacts in the environment can be felt for a long period of time. The permissible limit for their residues is 0.1 μgL^{-1} illustrating heavy pollution by the compounds in Ewaso Ng'iro. Ebele et al. (2017) detected several classes of diazepines including bromazepam, clonazepam, and diazepam in surface waters to maximum concentrations of 42, 198, and 335 ngL^{-1}, respectively, relatively higher than those detected in the Chebole-Kanossin region of Bomet County. Oxazepam is a close derivative of benzodiazepine and was also detected up to 1.73 ± 1.62 μgL^{-1} at the same sampling point. These compounds are rated as being highly persistent in water and can last for up to 119–328 days without degrading (Löffler et al., 2005). Benzeneethanamine is relatively insoluble in water and its presence in surface water would depict extensive water pollution, especially by nonpolar substances that would solubilize it. Due to its chemistry, the compound can be linked to other more polar groups such as

Table 1 A comparison of chloro-based pesticide residues in Kenya and N. Tanzania

Sites	Season	pp′DDT (ng g^{-1})	pp′DDD (ng g^{-1})	pp′DDE (ng g^{-1})	ΣDDT (ng g^{-1})	References
Bomet surface waters	Dry	BDL	BDL	BDL	BDL	**Present study**
	Rainy	BDL	BDL	BDL	BDL	
Narok surface waters	Dry	BDL	BDL	BDL	BDL	**Present study**
	Rainy	BDL	BDL	BDL	BDL	
Lake Nakuru	Dry	BDL	2.3	7.5	9.8	Mavura and Wangila (2004)
	Rainy	13.6	BDL	2.2	15.8	
Lake Victoria (southern basin)	Dry	–	–	–	BDL-12	Kishimba et al. (2004)
	Rainy	–	–	–	BDL-131	
Kericho-upper Nyando sub-catchment	Rainy	96.124 ± 3.052	92.025 ± 2.251	96.101 ± 2.015	–	Abong'o et al. (2018)
Lake Natron (N. Tanzania, southern border of Narok County)	Dry	0.4–0.6	0.9–1.5	4.6–15.9	5.9–18.0	Bettinetti et al. (2011)
Lake Bogoria	Dry	0.4	0.7	10.8	12.0	Bettinetti et al. (2011)
Bomet surface waters	Dry	BDL	BDL	BDL	BDL	Present study
	Rainy	BDL	BDL	BDL	BDL	
Narok surface waters	Dry	BDL	BDL	BDL	BDL	Present study
	Rainy	BDL	BDL	BDL	BDL	

sulfates and phosphates. An average of 7.22 ± 5.82 μgL^{-1} of benzeneethanamine was detected in the Chebole-Kanossin region. The region is popular for mixed farming throughout the year, thus explaining the origin of the residues in the water.

Acaricides are gradually finding more populace in Kenya due to the increasing resistance of ticks such as *Rhipicephalus* (*Boophilus*) *decoloratus* and *Rhipicephalus* (*Boophilus*) *microplus*, which transmit the pathogens causing babesiosis (*Babesia bigemina* and *Babesia bovis*), anaplasmosis (*Anaplasma marginale*), and *Theileria parva* (East Coast fever) (Githaka et al., 2022; Vudriko et al., 2016). Some of the acaricides detected in the two counties included phorate sulfoxide, tetrachloro-1-heptene, benzeneethanamine, and isoxazolol (1.50 ± 1.32 μgL^{-1}). There have been fatal and severe postharvest losses, especially in maize due to aphids and other pests leading to increased pesticide usage in the Rift valley, Kenya (Koskei et al., 2020). Phorate sulfoxide which is also used as a nematocide (sometimes a herbicide too) is one of the common pesticides extensively used to control various pests including the Mexican bean beetle, corn rootworm, mites, corn borers, wireworms, white grubs, cornleaf aphids, seedcorn beetles, leafminers, thrips, black cutworms, leafhoppers, white flies, nematodes, southern corn rootworm, and flea beetle larvae, among others. Tetrachloro-1-heptene, which has been effectively used, usually with dieldrin against the pest leaf miner, the larvae of the *Cerambycoidean* beetle and *Leptispa pygmaea* (Baly) (Bhardwaj & Rana, 2011), was also detected in minute traces point NC (0.30 ± 0.30 μgL^{-1}). Isoxazolol is a multifunctional pesticide with the potential of an acaricide, fungicide, and insecticide. The residues of isoxazolol were detected in point Bomet B. Though these levels were below the WHO standards of isoxaloles in water, cumulative ingestion of the residues can cause seizures and lethargy, especially in pets such as dogs (Palmieri et al., 2020). Welimo et al. (2021) detected three different acaricides from surface waters in Ewaso Nyiro river, Kajiado County, i.e., cypermethrin (3834 ± 80.2 to 11,972 ± 74 μg/L), amitraz (3884 ± 25.3 to 12,236 ± 145.4 μg/L), and deltamethrin (3879 ± 33.2 to 12,298 ± 82.1 μg/L).

Table 2 Distribution of the prevalent pesticide`s within the study region

Pesticide	Use[a]	Season	Most prevalent location[b]	Concentration of samples > LQ[c] (μgL^{-1})								Cases > LOD
				Narok				Bomet				
				NA	NB	NC	ND	BA	BB	BC	BD	-
Chlorpyrifos	I	Dry	NB	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	3
		Wet	-	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	
Alpha-chloroacetophenone	F	Dry	NB	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	2
		Wet	-	<LQ	<LQ	16.2	<LQ	<LQ	<LQ	<LQ	<LQ	
Trichloroacetylbenzohydrazide	F	Dry	NB	<LQ	<LQ	3	<LQ	<LQ	<LQ	<LQ	<LQ	2
		Wet	-	<LQ	28.2	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	
Acephate	H	Dry	ND	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	2
		Wet	-	<LQ	<LQ	13.3	<LQ	<LQ	<LQ	<LQ	<LQ	
Cypermethrin	I	Dry	ND	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	4
		Wet	-	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	
Siduron	H	Dry	NA	<LQ	<LQ	<LQ	3.32	<LQ	<LQ	<LQ	<LQ	2
		Wet	-	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	
Decyl 4-chlorophenylcarbamate	F	Dry	NA	<LQ	<LQ	<LQ	<LQ	<LQ	1	<LQ	<LQ	2
		Wet	-	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	
Diazepin-5,8-dione	I	Dry	NA	<LQ	<LQ	<LQ	0.9	<LQ	<LQ	<LQ	<LQ	2
		Wet	-	<LQ	<LQ	<LQ	0.03	<LQ	<LQ	<LQ	<LQ	
Cyfluthrin	H	Dry	NC	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	3
		Wet	-	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	
Aimcocyper	I	Dry	NC	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	2
		Wet	-	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	
Lambda-cyhalothrin	I	Dry	NC	<LQ	<LQ	<LQ	<LQ	<LQ	0.01	<LQ	<LQ	3
		Wet	-	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	
Epinephrine	H	Dry	BC	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	3
		Wet	-	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	
Norepinephrine	I	Dry	BC	<LQ	<LQ	<LQ	<LQ	<LQ	9.98	<LQ	<LQ	2
		Wet	-	<LQ	<LQ	<LQ	<LQ	<LQ	5.27	<LQ	<LQ	
Benzodiazepine (lorazepam)	I	Dry	BC	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	4
		Wet	-	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	
Oxazepam	A	Dry	BC	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	2
		Wet	-	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	

Table 2 (continued)

Pesticide	Use[a]	Season	Most prevalent location[b]	Concentration of samples > LQ[c] (μgL^{-1})								Cases > LOD
				Narok				Bomet				
				NA	NB	NC	ND	BA	BB	BC	BD	-
Benzeneethanamine	A	Dry	BC	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	3
		Wet	-	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	
Triazine (tebuconazole)	F	Dry	BB	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	3
		Wet	-	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	
Pyrazole	I	Dry	BD	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	3.5	2
		Wet	-	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	
Semicarbazone	H	Dry	BD	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	3
		Wet	-	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	

[a] *I* insecticide, *F* fungicide, *H* herbicide, *A* acaricide)

[b] *NA* Narok-Mau, *NB* Narok-Town, *NC* Narok Polung'aa, *ND* Narok-Ewaso Ng'iro, *BA* Bomet-Mulot, *BB* Bomet-Town, *BC* Bomet-Chebole, *BD* Bomet-Soimet

[c] <LQ means below LOQ value

Effect of seasonality on pesticide occurrence and levels

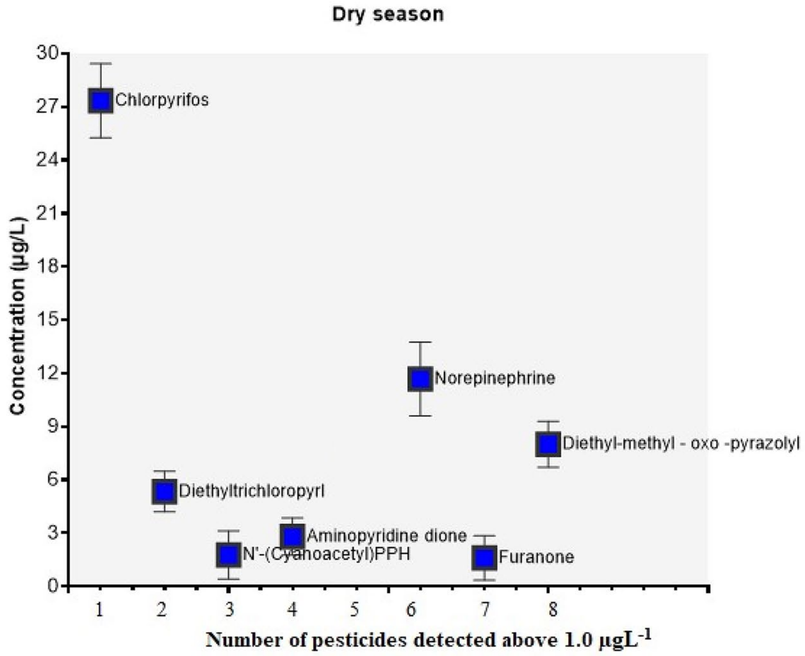
The wet season was found to have significantly more ($P \leq 0.05$) number of pesticide samples compared to the dry season for both counties, i.e., 15 against 7 counts. This may be attributed to more precipitation during the wet season leading to higher surface runoff and increased suspended residues in the surface waters thereof (Kruć-Fijałkowska et al., 2022). Some of the pesticides were only detected in one season while indicating levels BDL in the other season (Fig. 3). Some of the notable residues detected during the dry season include chlorpyrifos, cyfluthrin, furanone, and norephrine. The findings concurred with those of Liu et al. (2018) who detected more chlorpyrifos in the Yellow River during the dry season—citing volatilization as the key reason for the increased concentration during the dry season. Nyantakyi et al. (2022) found out varying seasonal concentrations with pesticides during rainy and dry seasons in River Tano, Ghana. In the study, the residues of cypermethrin and profenofos were found to be higher during the rainy season unlike lindane whose concentration was higher during the dry season.

There were more pesticides detected during the wet season since this season had more plant varieties (majority of the vegetables) compared to the dry season (traditionally reserved for maize and wheat). There are no significant changes in the applications and dosages of livestock pesticides in both counties ($P \leq 0.05$). Several studies conducted within the tropical region are also in support of more pesticide discharge and thus detection during rainy seasons (Carazo-Rojas et al., 2018; Sharma et al., 2019; Jayasiri et al., 2022). Rainfall is known to directly affect dilution and transport of pesticide residues in surface waters (Oltramare et al., 2022). In the current study, we could not elucidate any specific pesticide applied during either of the seasons alone, indicating that all the pesticides were applied on a needs basis.

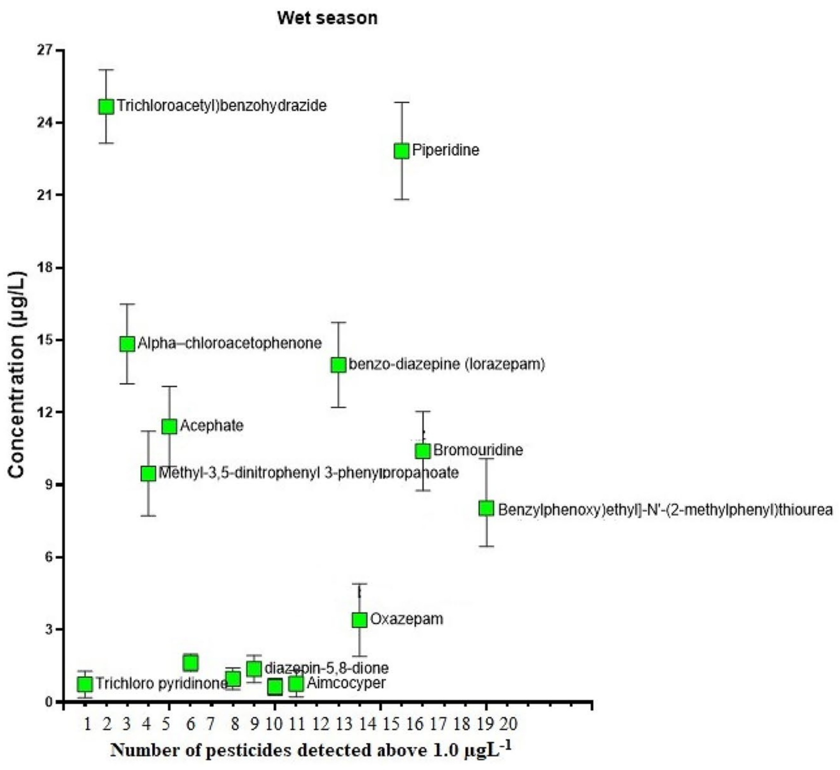
Correlation between location and season in pesticide occurrence and levels

The pesticide occurrence and concentration levels were not found to have any direct mathematical relation with the region of occurrence and the season (Fig. 4). A multivariate scatter plot indicated only 6 out of the 36 pesticides correspond to a positive

Fig. 3 Variation in pesticide residues between the dry season **a** and the wet season **b**



(a)



(b)

linear regression line of slope 0.99. The occurrence and the levels of pesticides detected can be ascribed to result from the proximate farming or anthropogenic activity—as the study had hypothesized. Three pesticides were detected in both seasons in Narok, i.e., chlorpyrifos, cypermethrin, and cyfluthrin, while triazine was detected in both seasons in Bomet. No pesticide was found in both counties probably due to the climatic differences coupled with different farming practices in the two counties. From Fig. 4, piperidine and chlorpyrifos were present at higher concentrations and were found to belong to different population ($P \leq 0.05$).

Ecotoxicological assessment of the pesticides

The identified prevalent class II and class III pesticides were further subjected to ERA for determination of the potential risks to people and other animals in these regions. There were 4 such pesticides in Narok County, i.e., chlorpyrifos, cyperthrin, cyfluthrin, and cyhalothrin (all pyrethroids). The high occurrence of these pesticides in appreciable amounts in Narok County surface water is attributed to the popularity of these pesticides in wheat growing as well as killing ticks on livestock. Sampling point Bomet C had two counts above the LOD for

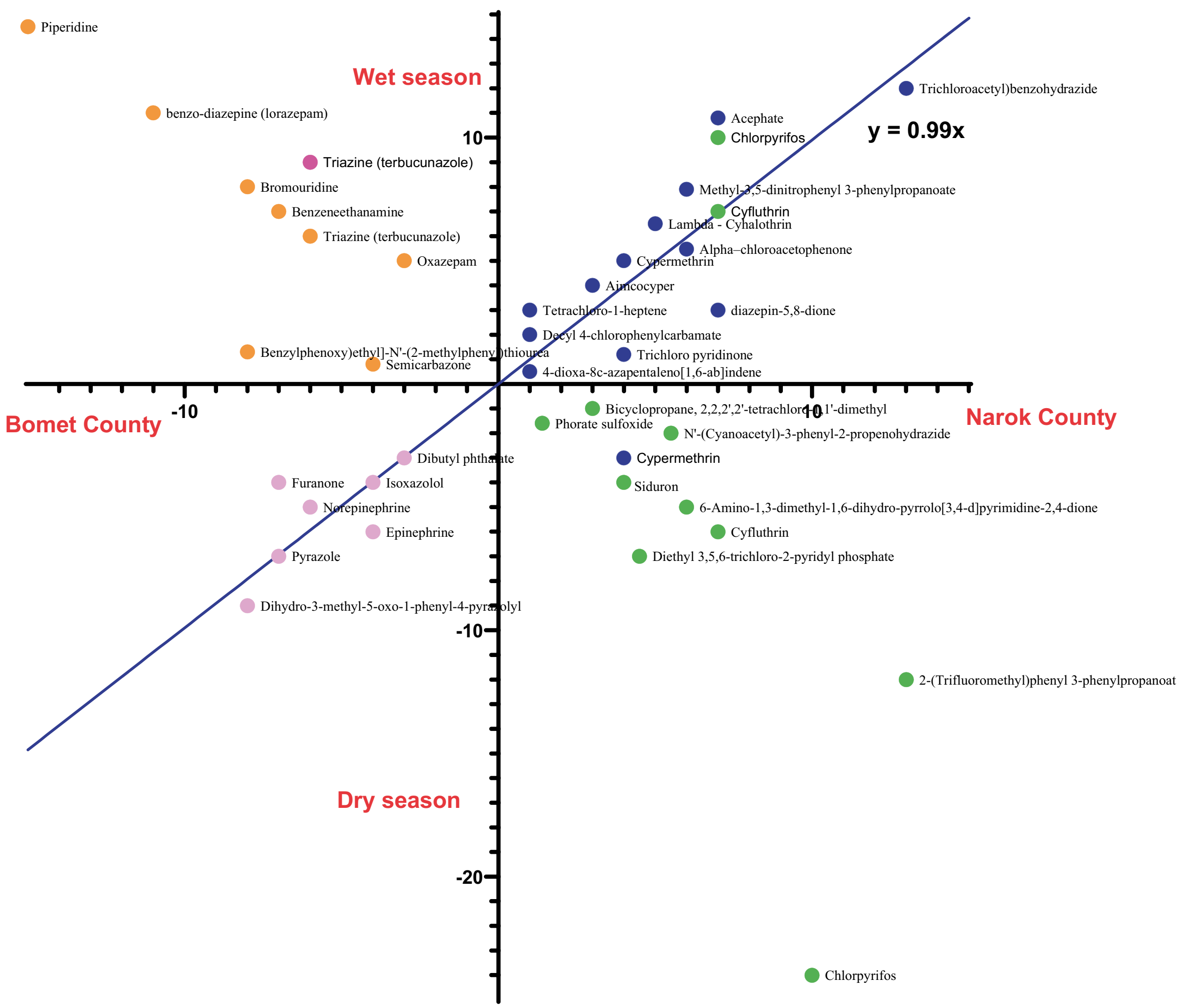


Fig. 4 The correlation between the pesticide occurrence and levels versus location and seasons

these residues while all the others only registered a single count above the LOD of these prevalent pesticides. Sampling point A is located upstream where there are minimal point source pollutants other than from wheat farming. On the other hand, at point B, there are more mixed farming and anthropogenic activities in addition to the pollution from point A. The topographical appearance of point B (relatively flat) also increases the residual flow time of the river as opposed to the other points which are geographically inclined. Chlorpyrifos was found to cause a high risk to the ecology with RQ values of 69.13 (Table 3). The high levels of chlorpyrifos are a great concern to the aquatic animals (and fish), invertebrates, as well as people in that region. Exposure of aquatic animals to chlorpyrifos to a limit of 5 ppm is lethal enough to cause behavorial and histological changes within just 10 days of exposure (Stalin et al., 2019). The residues lead to mortality of earthworms and other soil invertebrates (Krishnaswamy et al., 2021) with essential roles to agriculture while causing nervous disorders in humans. Cyfluthrin toxicity has been found to have severe kidney and liver effects in rats and higher mammals (Yilmaz et al., 2015). Like cyfluthrin, exposure to cyhalothrin even in minute concentrations is known to cause nausea and severe headache and triger vomitting (Hanson et al., 2018). Cypermethrin had an RQ value of 0.00 and was found to be of low risk in the study region.

In Bomet County, epinephrine, benzodiazepine, benzenethanamine, triazine, and semicarbazone class II and III pesticides were found to be prevalent and in appreciable concentrations. Benzeneethanamine and triazine were found to be of high ecotoxicological risks (RQ values of 263.0 and 2.26, respectively). Like other benzene derivatives, benzeneethanamine is quite lethal (thus the low PNEC values) and is a potential source for brain dysfunction, autism, and ulcerative colitis carcinogens (National Center for Biotechnology Information, 2023). Epinephrine is a fluoro-based herbicide effective in killing weeds especially in vegetable farming as well as in animal feed additives. The study ranked this residue as being of high risk—with potential for causing CNS disorders and Parkinson's disease after prolonged exposure in humans while causing vascular and metabolic effects to other mammals such as dogs (Hjemdahl et al., 1979). Semicarbazone is an effective herbicide with several "more effective" derivatives that have gained more popularity such as metaflumizone. Metaflumizone is a common herbicide and insectide for cabbages (*Brassica oleracea* Linne) which is lethal against important lepidopterous pests and certain pests in the orders *Coleoptera*, *Hemiptera*, *Hymenoptera*, *Diptera*, *Isoptera*, and *Siphonaptera* (Chatterjee & Gupta, 2013). The pesticide has prolonged residual time on cabbage leaves and the soil

Table 3 The ecotoxicities and risk quotients of prevalent pesticides in the study regions

Location[a]	Pesticide concentrations (μgL^{-1})								
	Chlorpyrifos	**Cypermethrin**	**Cyfluthrin**	**Cyhalothrin**	**Epinephrine**	**Benzodiazepine**	**Benzeneethenamine**	**Triazine**	**Semicarbazone**
NA	28.18	BDL[b]	BDL	BDL	BDL	BDL	BDL	BDL	BDL
NB	13.30	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
NC	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
BA	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
BB	BDL	BDL	BDL	BDL	BDL	17.07	BDL	BDL	BDL
BC	BDL	BDL	BDL	BDL	BDL	12.9	13.15	BDL	BDL
BD	BDL	BDL	BDL	BDL	BDL	BDL	BDL	9.57	BDL
Mean	20.74	BDL	BDL	BDL	BDL	9.16	13.15	9.57	BDL
Std. Dev	10.52	BDL	BDL	BDL	BDL	2.36	BDL	0.00	BDL
PNEC	0.30	33.8	0.30	0.45	0.04	9.32	0.05	4.24	0.30
RQ	69.13	BDL	BDL	BDL	BDL	0.98	263.0	2.26	BDL

[a]*NA* Narok-Mau, *NB* Narok-Town, *NC* Narok Polung'aa, *ND* Narok-Ewaso Ng'iro, *BA* Bomet-Mulot, *BB* Bomet-Town, *BC* Bomet-Chebole, *BD* Bomet-Soimet

[b]*BDL* below detectable limits/below limit of detection (LOD)

leading to ecotoxicity to people and soil invertebrates (Chatterjee & Gupta, 2013). Long-term exposure to the pesticide causes mutagenicity (Hempel et al., 2007). Baynes and Riviere (2010) proved long-term exposure to atrazine could cause nephrotoxicity.

Each of these pesticides may have lethal and far-reaching ecological effects to nontarget species. Chlorpyrifos has detrimental effects on water and soil bacteria, fungi, and actinomycete which play important ecological functions including soil mineralization (Wołejko et al., 2022). Extensive use of chlorpyrifos has also been attributed to disruption of biogeochemical cycles (Dar et al., 2019). Prolonged exposure of this pesticide leads to inhibition of the choline esterase enzyme, thus leading to immunological, hematological, renal, ocular, dermal, and psychological effects in humans (Dar et al., 2019; Nandi et al., 2022). Both chlorpyrifos and cyfluthrin have adverse effects on gene expression and can alter the primary human astrocytes leading to neurotoxicity (Mense et al., 2006). Wendt-Rasch et al. (2003) observed a rapid decline in population of crustacean zooplankton upon cypermethrin exposure above a concentration of 0.13 μgL^{-1}. In humans, long-term exposure to cypermehtrin leads to neurodegradation as this pesticide has an ability to interfere with neurotransmitters (Sing et al., 2012). λ-Cyhalothrin residues have been associated with abdominal pain, mouth ulcers, increased secretions, and dysphagia in humans (Djouaka et al., 2018; Bradbery et al., 2005). Prolonged exposure to epinephrine has been associated with proteome larval metamorphosis in zooplanktons (Di et al., 2020). Brodin et al. (2017) have illustrated severe and repeated alteration in the behavorial traits of planktivorous fish. Bioaccumulation of benzene-ethanamine in humans has been attributed to variation in *Monascus* pigments (Chen et al., 2018). Atrazine has been found to bioaccumulate in benthic aquatic species to cause far-reaching and lethal effects to these organisms. Bioaccumulated concentrations of < 100 μg atrazine/L quantitative weight of evidence (QWoE) leads to infertility in fish (Hanson et al., 2019). Semicarbazone has been proven to have an effect on enzymes such as amine oxidases, lysyl oxidase, and glutamic acid decarboxylase (GAD) leading to anti-estrogenic effects in fish (Xing et al., 2021).

The potential human risks arising from these pesticides may be significant and far-reaching. Exposure to the pesticides may lead to interferences with the human metabolism, immune, dermal, hematological, and gene functions. Pesticide effects can be both acute and chronic to humans, based on the level of exposure to these pesticides. Organophosphate pesticides such as chlorpyrifos are more severe as indicated in the RQ levels in Table 3. Organophosphate toxicity is the key to the development of Parkinson's disease (Nakamagoe et al., 2009). Despite being more popular in Kenya, pyrethroids such as cypermethrin and cyfluthrin are also fatal to humans at high levels of concentration and can cause neurotoxicity through "pyrethroid poisoning" (Hołyńska-Iwan & Szewczyk-Golec, 2020). By extension, the effect of the pesticides on humans may negatively affect the quality time used for agricultural activities as well as requiring resources used in seeking medication.

Conclusions

At least 38 different pesticide residues were detected in surface waters of the two counties. The majority of the pesticides detected in Narok were chloro-based herbicides and insecticides such as chlorpyrifos, cypermethrin, cyfluthrin, and cyhalothrin. In Bomet County surface waters, the majority of the pesticides were fluoro-, azo-, and phosphate-based residues such as triazine, semicarbazone, and epiphrine. Seven of the 15 pesticides were more prevalent during the rainy season. Several prevalent pesticides exhibited high risks to surface water ecologies with four out of the nine prevalent residues detected having RQ values above 1.0.

The study recommends government policy formulations on more farmer education on pesticide application, stringent measures imposed on agrochemical suppliers, and restricted farming in riparian lands. There is a need for more long-term studies with a wider spatial and temporal coverage of the two counties as well as other counties in Kenya. This would ensure real-time detection of the pesticides before they degrade to fatal residues and inform appropriate mitigation measures. There is a need to enforce implementation of pesticide application methods through "Nyumba Kumi leaders"—the local village leaders. A workshop for these leaders and other farmers on good pesticide application measures is crucial. Additionally, the agricultural extension officers in the counties need to be conversant with contemporary farming methods that provide alternative and greener pesticides.

Appendix 1: Calibration curves (Figs. 5, 6, 7, 8, 9, 10, 11, 12 and 13)

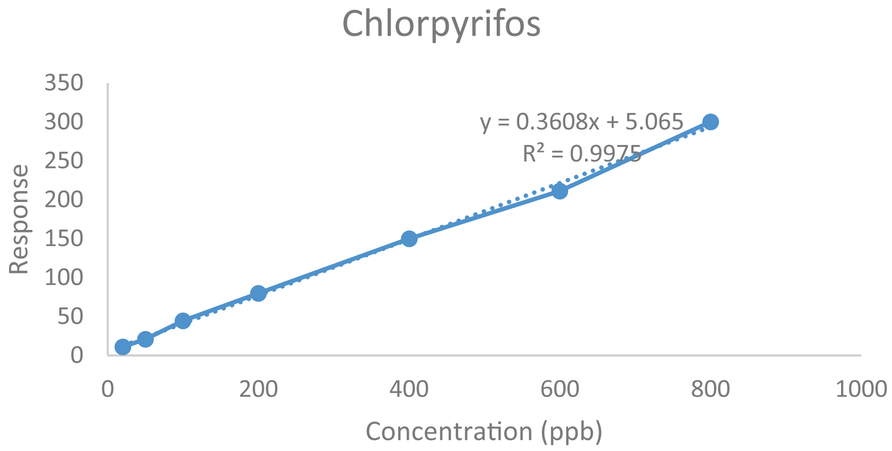


Fig. 5 The calibration curve used for chlorpyrifos

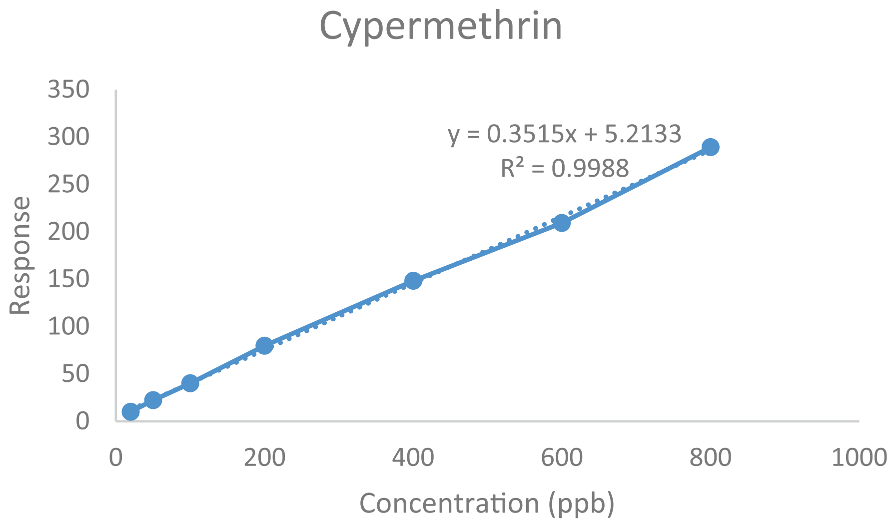


Fig. 6 The calibration curve used for cypermethrin

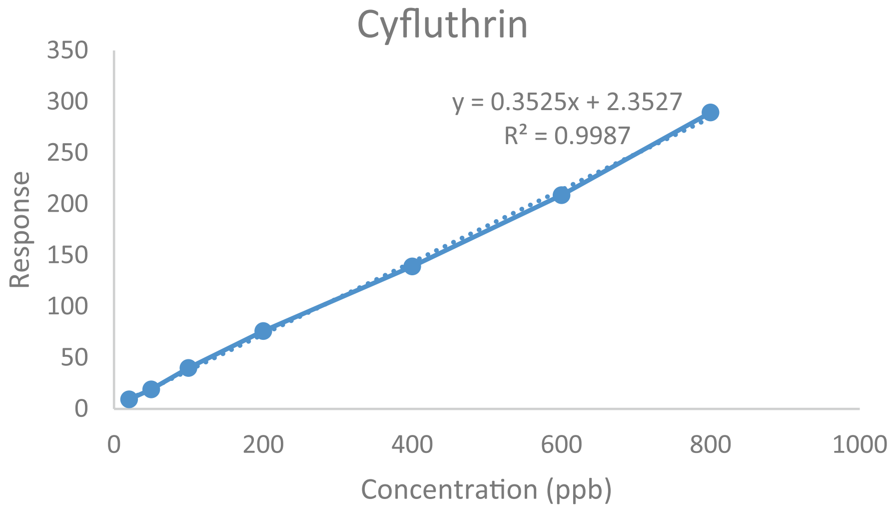


Fig. 7 The calibration curve used for cyfluthrin

Fig. 8 The calibration curve used for cyhalothrin

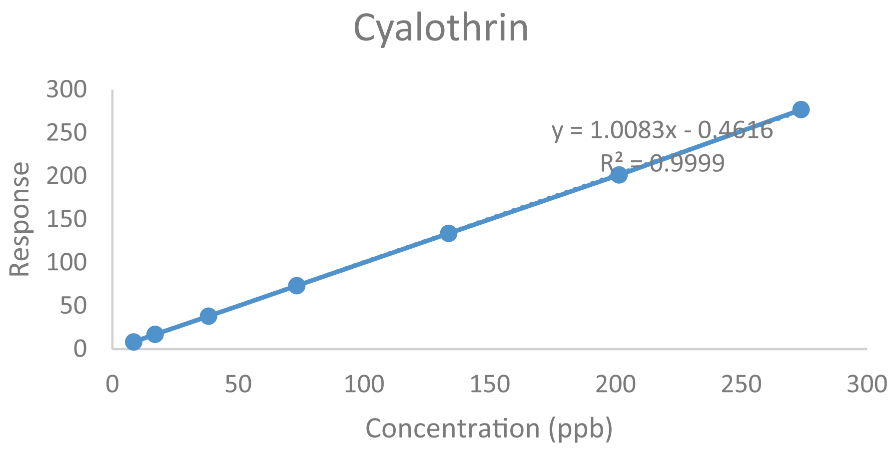


Fig. 9 The calibration curve used for epinephrine

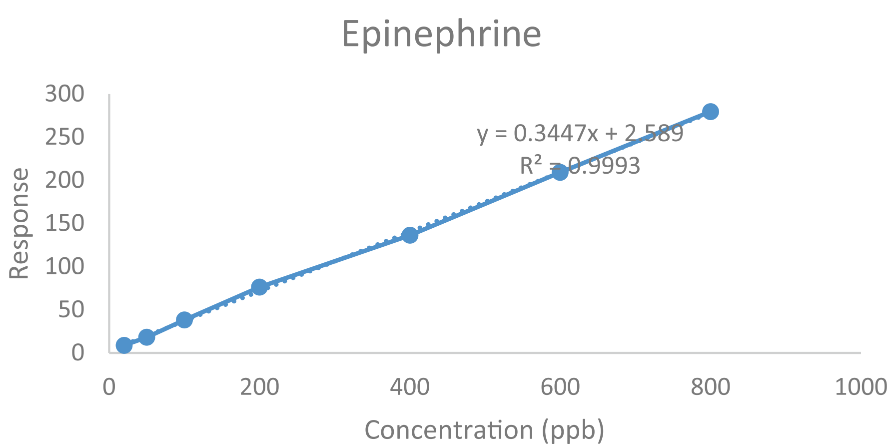


Fig. 10 The calibration curve used for benzenediazepine

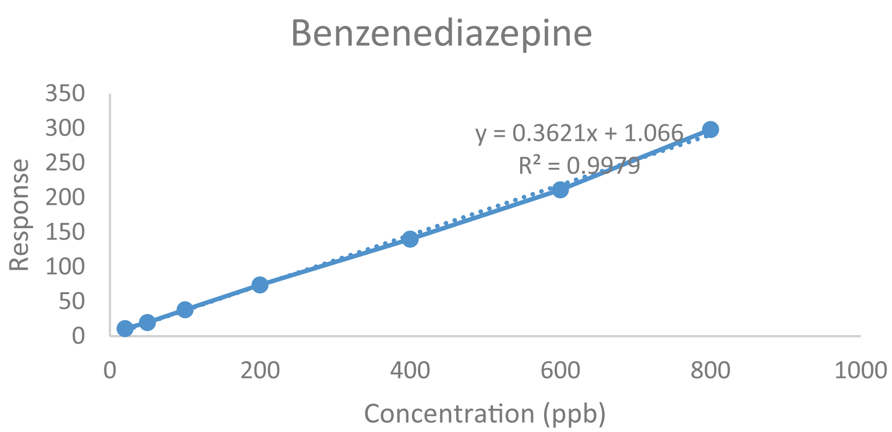


Fig. 11 The calibration curve used for benzeneethanamine

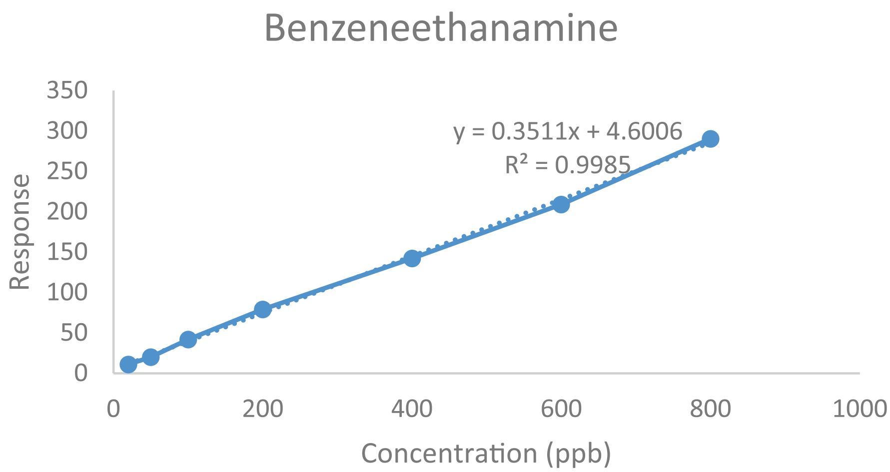


Fig. 12 The calibration curve used for triazine

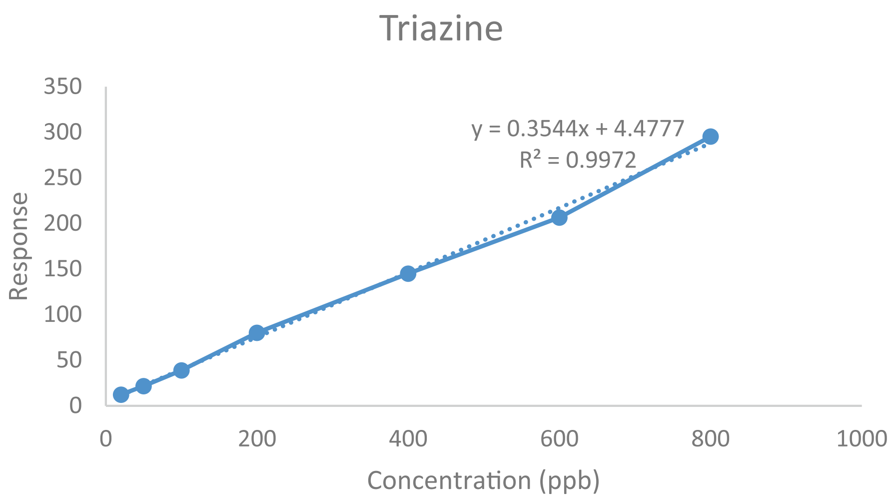
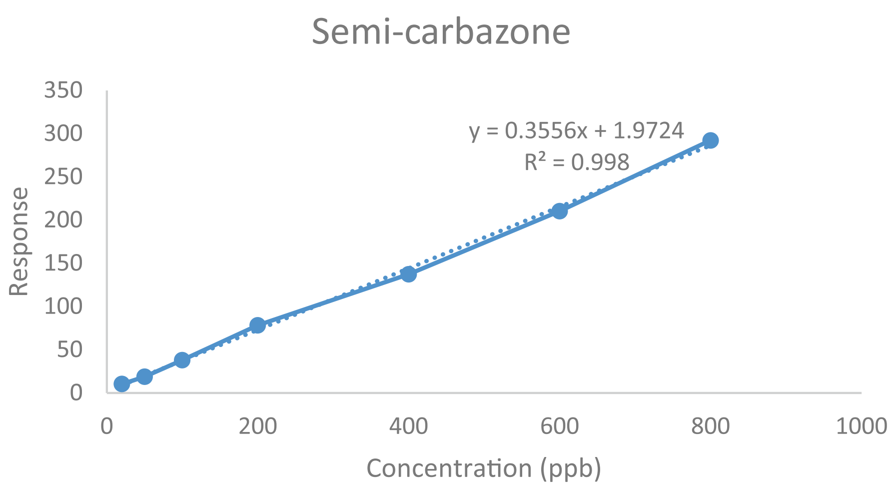


Fig. 13 The calibration curve used for semicarbazone



Appendix 2: Table of LODs and LOQs

#	Pesticide	LOQ (ppb)	LOD (ppb)
1	Chlorpyrifos	35.66	10.70
2	Cypermethrin	39.28	11.78
3	Cyfluthrin	43.33	13.00
4	Cyhalothrin	47.96	14.39
5	Epinephrine	44.95	13.49
6	Benzodiazepine	36.30	10.89
7	Benzeneethanamine	36.04	10.81
8	Triazine	32.56	9.57
9	Semicarbazone	38.98	11.69

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Author contribution Bakari Chaka, Aloys Osano, Wesley Omwoyo, and Patricia Forbes wrote the main manuscript text. Bakari Chaka, Aloys Osano, and Patricia Forbes prepared all the figures. Bakari Chaka, Aloys Osano, and Wesley Omwoyo prepared the tables. Bakari Chaka and Patricia Forbes analyzed the discussions. All the authors reviewed the manuscript.

Data availability All the data used in this work are within the manuscript. Any further data will be provided upon request.

Declarations

Competing interests The authors declare no competing interests.

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