Pesticide Residue Levels in Water and Sediment from River Thiba, Kirinyaga County, Kenya.

Victor K. Korir*, Deborah A. Abong'o., Joyce G.N. Kithure., Vincent O. Madadi

Department of Chemistry, Faculty of Science & Technology, University of Nairobi

***Corresponding Author**

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ABSTRACT

The study assessed the physicochemical parameters and pesticides residue levels in water and sediment samples from Thiba River Catchment area, Mwea Irrigation Scheme, Kirinyaga County, Kenya. The samples were collected from six selected sampling sites in February and May 2021 representing dry and wet seasons respectively, by the meteorological department and based on the human activities and crops grown. The physicochemical parameters determined were pH, total dissolved solids (TDS), total suspended solids (TSS) and electrical conductivity (EC) in water samples and pH and total organic carbon content in the sediment samples. The pH of water samples ranged from 6.12 ± 0.12- 6.91± 0.17, as Total dissolved solids were at 10.03 ± 2.04 mg/L - 100.04 ± 1.10 mg/L while Total Suspendeed Solid values were 103.01 ±3.51mg/L -316.01 ± 6.81 mg/L, and Eelectrical Conductivity was in the range of 30.01± 1.21 µscm^{-1}-200.13 ± 2.01 µscm^{-1}. In the sediment samples, the pH ranged from 5.42 ± 0.12 - 7.52 ± 0.11 and the organic matter content ranged from 27.72± 0.62 - 49.07± 0.78. The farmers applied 12 different pesticides, under different trade names and active ingredient. Chlorpyrifos was the highest used pesticide by 72 % of the farmers followed by Lambda-cyhalothrin at 64 %. The pesticides obtained from the samples were Metalaxyl, chlorpyrifos, and lambda cyhalothrin. In the water samples, chlorpyrifos residue levels ranged from 3.60±0.92 µg/L - 88.24 ±65.97 µg/L, with Metalaxyl from < 0.05 µg/L - 4.24 ± 1.75 µg/L, while Lambda cyhalothrin were in the range of < 0.005 - 3.75±0.72 µg/l in both the dry and wet seasons. Generally, the Chlorpyrifos residue levels were higher in wet season than the dry season while Metalaxyl and Lambda-cyhalothrin values were higher in the dry than wet season. Metalaxyl residue levels in sediment samples in the dry ranged from < 0.05 µg/kg - 1.27±0.90 µg/kg for wet seasons, while Chlorpyrifos ranged from 4.77±17 µg/kg - 47.78±7.12 µg/kg and Lambda-cyhalothrin values were from < 0.005-0.67±0.18 µg/kg in both the dry and wet seasons respectively. Chlorpyrifos pesticide residue levels were the highest in the sample matrices, due to its widespread use to control ticks and fleas from the livestock in the study area. For the chlorpyrifos pesticide levels, all the sites in the dry season were within the acceptable limits of 30 µg/L except site 2. However, the levels were higher than the limit except in sites 1 and 3. For the Metalaxyl and lambda-cyhalothrin pesticides, all the sites had levels that were below the set limits for drinking water by WHO of 10 µg/L.

Keywords: Chlorpyrifos, lambda-cyhalothrin, metalaxyl, Mwea Irrigation Scheme, Kirinyaga County, Pesticide residue

INTRODUCTION

Pesticides are the substances or a mixture of substances, used for the prevention, killing, repelling, or reduction of any forms of harm to plants or animal life caused by any pest [1]. Agricultural pesticides have been used by farmers to increase yields, leading to an increase in agricultural production. Application of insecticides and fungicides has increased production yields in arable farming while significantly reducing fatalities caused by crop storage [2]. However, some agricultural pesticides are not easily biodegradable hence the chemical components of the pesticides remain in the farms, or are vaporized into the atmosphere, dissolved, and buried into the soil through infiltration and carried into water bodies by water runoff [3].

The most prevalent way to classify pesticides is according to their chemical composition and active ingredient, which refers to the element attached to the hydrocarbon structure [4].This classification method assists in establishing application rates, necessary precautions during usage, and the means of application [5].

There have been growing concerns about the harmful side effects of pesticides on humans and the environment [4]. Both the immediate and long-term effects resulting from bioaccumulation in the food chain pose a threat to the health of plants, animals, and humans [6]. Pesticide poisoning mainly happen when the pesticides intended for controlling pests and diseases affect the non-target organisms such as humans and other animals [7].

Surface and ground water samples along River Pampanga in Philippines have revealed presence of organochlorine pesticide residues in the water. These included endrin, dieldrin, BHC, chlordane, and endosulfan [8]. Studies on organochlorine pesticide (OCP) levels in water, air, sediment, fish, and marine mammals along the South American coasts and in open waters has shown that OCP concentrations were greater in semi-enclosed areas, such as estuaries and bays near major cities [9]. The excessive use of pesticides in aquatic ecosystems has been documented to pose significant risks to fish species, including salmon. These pesticides impact both primary producers and macroinvertebrates within these ecosystems [10]. A study conducted at the Nyando River catchment, Lake Victoria, showed that the banned organochlorine pesticides are still detected in the catchment area [11]. Water and sediment samples from the Nyando/Sondu-Miriu Basin were tested for specific pesticide residues, and the results revealed that banned organochlorine pesticides continue to be used in the area [12]. The pesticide residue levels have also been found to be varying depending on the season of the year with sediments containing the highest residue limits [13]. The Coastal region of Kenya has been reported to contain pesticides residues levels in sediments [14]. Studies have also shown varying pesticide contamination levels in the Lake Victoria basin. Organochlorines and organophosphates were found in different levels and frequencies in fish, water, sediments, and weeds from the Nzoia River [15]. Higher levels of lindane, α-BHC, and β-BHC have also been found in soil sugar belt zone of Lake Victoria [16].

MATERIALS AND METHODS

Study Area and Design

Mwea Irrigation Scheme is located in Kirinyaga County which is about 100 kilometers north-east of Nairobi city, as given by the National Irrigation Board [17]. It is situated in the Mwea East and Mwea West sub-Counties, located between latitude 37°13′ E and 37°30′ E, and longitude 0°32′ S and 0°46′ S (Figure 1). The sources of water for irrigation in Mwea Scheme are Thiba and Nyamindi Rivers [18]. The types of irrigation practiced are; Distribution system (earthen canals), Conveyance system (partially lined canals), and Application system (basin/flood irrigation) [17].

The study area covered Thiba River, including the banks of the river and the stretch of the river along the Mwea Irrigation Scheme. Six sampling sites were selected along the river from where water and sediment samples were collected. Sites 5 and 6 were in the upstream while 1 and 2 downstream sections (Figure 1). Water and sediment samples were collected in February and May 2021 representing the dry and wet seasons respectively. The coordinates and altitude of each sampling site were taken and recorded, the observed agricultural activities around the sampling sites were taken and recorded as shown in Table 1.

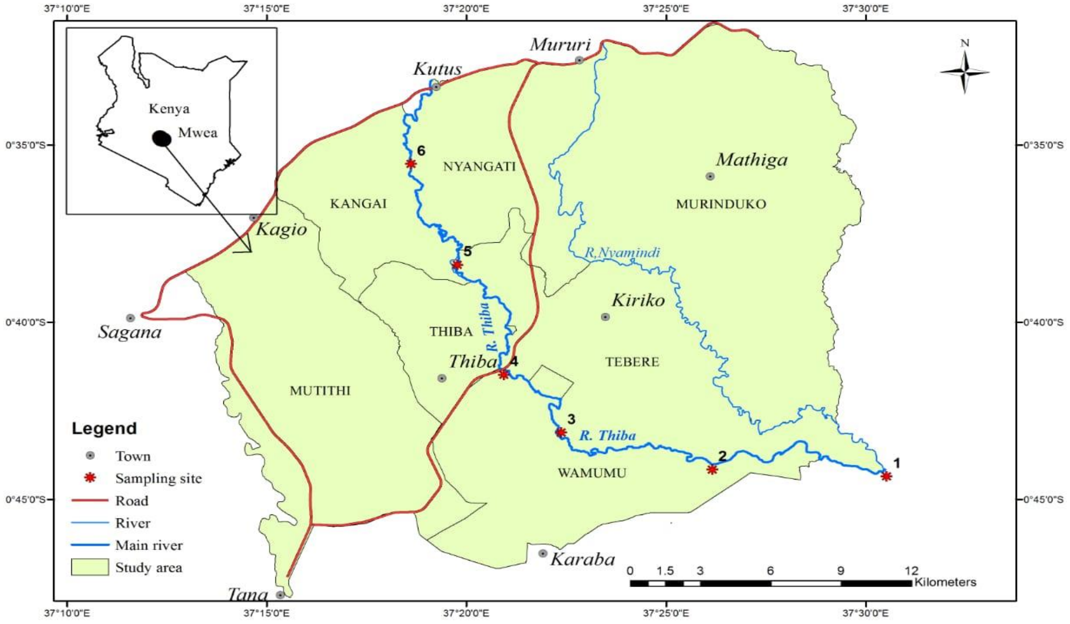

Figure 1: Map of Mwea irrigation scheme showing the sampling sites along Thiba River [19]

Table 1: Description of the sampling sites in Mwea Irrigation Scheme.

Site	Local Name	GIS coordinates	Altitude (M)	Anthropogenic Activities
1	Kiumbu	37°29′ S, 0°44′ W	1088	Crops: maize, sorghum, Bananas, miraa, sugarcane. Livestock: Cows, sheep, goats, donkeys
2	Ndindiruku	37°25′ S, 0°43′ W	1141	Crops grown: maize, sorghum, tomatoes, French beans Livestock: Cows, sheep, goats
3	Kiamanyeki	37°22′ S, 0°42′ W	1159	Crops: Rice, Tomatoes, French beans Livestock: Cows, sheep, goats, donkeys
4	Wang'uru (Mwea)	37°21′ S, 0°41′ W	1175	Crops: Rice, Tomatoes, French beans, Onions Livestock: Cows, sheep, goats, donkeys
5	Kutus	37°19′ S, 0°34′ W	1320	Crops: maize, bananas, cabbages, coffee and cattle farming.
6	Yakimoni	37°20′ S, 0°32′ W	1388	Crops: maize, bananas, cabbages, coffee, tea and cattle farming

Chemicals and Reagents Used

HPLC grade isooctane, acetone, hexane, sodium sulphate, alumina, and dichloromethane were purchased from Sigma-Aldrich, USA, through the local agent Kobian Kenya LTD. Analytical grade Sodium chloride and anhydrous sodium sulphate were purchased from Kobian Kenya Limited.

Equipment and Instruments Used

Soxhlet set up was used in the extraction of sediment and soil samples. Water samples were extracted using 2 L volume separatory funnel. A glass column of 150 mm length and 20 mm internal diameter was used in the clean-up of the samples, while the samples volumes were reduced using a LABCONCO rotary evaporator. All masses were measured with analytical Shimadzu AUW220D analytical weighing balance. The extracted samples were stored in a lab-line blast resistant fridge and a deep freezer was used for storing sediment samples awaiting extraction. Agilent technologies gas chromatograph (Agilent 6890N, Palo Alto, USA) coupled to mass spectrometry (Agilent 5973, USA) was used for analysis of the pesticide residues. Model IQ 150 pH meter was used to measure the pH and TDS while scientific Martin instruments model Mi 306 was used to measure the electrical conductivity of water samples.

Determination of Physicochemical Parameters

The physiochemical parameters analyzed in water samples were pH, total dissolved solids (TDS), electrical conductivity (EC) and total suspended solids (TSS). The physicochemical parameters analyzed for the sediment samples were sediment pH and the organic matter content. Scientific pH meter (model IQ 150) was used to measure the pH and TDS of the water samples. The EC was determined by using scientific Martin instrument model Mi 306 while the total suspended solids (TSS) in water were calculated by determining the mass of the suspended solids in a given volume of the Thiba River Water. The organic matter was determined using the standard reference method ASTM D 2972.

Water Samples Collection, Extraction and Clean-up.

Water samples were taken from six sampling sites along the river. The sites were selected systematically along the entire stretch of the river passing through the scheme. Two sites were selected upstream, two midstream, and two in the downstream section of Thiba River (Figure 1 and Table 1). The water samples were collected in triplicate in February and May 2021 representing the dry and wet seasons respectively from six sampling sites in the study area. The water samples were collected in 2.5 L clean and dry amber bottles. The water samples were labeled according to site of collection, stored temporarily in polyurethane cool-boxes before being transportation to the pesticide analytical laboratory for extraction and analysis.

Extraction of the water samples was done following the solvent-solvent extraction method, using dichloromethane (DCM) as the extraction solvent, using the EPA method 3510C. Two liters of water were placed in a beaker, and the pH was measured. Subsequently, 50 ml of phosphate buffer at pH 7 was added, along with a few drops of 0.1 M sodium hydroxide or 0.1 M hydrochloric acid to adjust the pH to 7. The sample was then transferred to a 2 L separatory funnel, where 100 g of analytical grade sodium chloride was added to extract the pesticides from the aqueous layer. The mixture was shaken vigorously to dissolve the salt. Then, 70 ml of DCM was added to the separatory funnel, and the solution was shaken for two minutes, with intermittent venting to relieve pressure, before being allowed to settle for 10 minutes for layer separation. The lower organic layer was decanted into a 250 ml round-bottomed flask, which was then covered with aluminum foil. The remaining aqueous layer was subjected to two additional extractions with 70 ml of DCM, and the resulting extracts were combined in the round-bottomed flask. To preserve the extract, 2 ml of isooctane was added, and the mixture was concentrated to 10 ml using a LABCONCO rotary evaporator in a 40 °C water bath. The concentrated sample was then transferred to a glass vial, the flask was rinsed with DCM, and the rinse was added to the extract. Finally, the sample was stored in a refrigerator at -4 °C until clean-up.

A chromatographic column measuring 25 cm in length and 1.5 cm in diameter was prepared by filling it with a 1 cm layer of blacked-out sodium sulfate, followed by 15 g of deactivated alumina, and an additional 1 cm layer of blacked-out sodium sulfate. The column was then conditioned with 15 ml of triple-distilled hexane. The extracted samples were subsequently loaded into the column and eluted with 165 ml of hexane into a 250 ml round-bottom flask. After elution, 2 ml of isooctane was added to the cleaned sample as a preservative, and the sample was concentrated to 2 ml using a LABCONCO rotary evaporator. Finally, the concentrated sample was transferred to a clean vial and refrigerated awaiting analysis.

Sediment Samples Collection, Extraction and Clean-up

Sediment samples were collected in February and May, 2021 representing the dry and wet seasons respectively. The sediment samples were scopped from six sites from where water samples were collected (Figure 1 and Table 1) systematically on the banks along the river. 200 g of cores of sediment from a depth of 0-30 cm were scopped using a shovel from five selected sites within a river banks from each sampling site and then the samples were mixed to form a composite sample. Four replicates of 100 g of sediment samples from each site were picked in sterilized aluminum foil. Two of sediment samples from each site were spiked with 4 ml of 100 mg/kg of the pesticide's standard mixture for field recoveries studies. The spiked samples were labeled Batch "A" while the un-spiked "B" and then transported to the pesticides analytical laboratory at Department of Chemistry, University of Nairobi for analysis.

The samples were extracted using the Soxhlet method using dichloromethane (DCM) as the extraction solvent. A 20 g sample of sediment sample was mixed with 60 g of analytical-grade anhydrous sodium sulfate and left to dry overnight. The mixture was then ground into a powder using a mortar and pestle. The dried sample was placed into a Soxhlet thimble. Next, 200 ml of dichloromethane was added into a 250 ml round-bottom flask, and placed on a heating mantle. The thimble containing the sample was inserted into the Soxhlet extractor, which was connected to the flask containing dichloromethane. A Soxhlet condenser was attached to the top of the extractor, and the extraction was carried out for 16 hours. Once the extraction was completed, 2 ml of isooctane was added to the extract as a preservative before it was concentrated to 10 ml using a rotary evaporator. The concentrated extract was then transferred to a 20 ml glass vial, and the round-bottom flask was rinsed three times with 1 ml portions of dichloromethane.

For the clean-up, a chromatographic column measuring 25 cm in length and 1.5 cm in diameter was prepared by filling it with a 1 cm layer of blacked-out sodium sulfate, followed by 15 g of deactivated alumina, and an additional 1 cm layer of blacked-out sodium sulfate. The column was then conditioned with 15 ml of triple-distilled hexane. The extracted samples were subsequently loaded into the column and eluted twice with 165 ml of hexane into a round-bottom 250 ml flask. After elution, 2 ml of isooctane was added to the purified sample as a preservative, and the sample was concentrated to 2 ml using a LABCONCO rotary evaporator. Finally, the concentrated sample was transferred to a 5 ml clean vial and refrigerated awaiting analysis.

Analysis of Pesticide Residue Levels in Water and Sediment Samples

Agilent technologies gas chromatograph (Agilent 6890N, Palo Alto, USA) coupled to mass spectrometry (Agilent 5973, USA) was used for analysis of the pesticide residues levels in water and sediment samples. The data was processed using Microsoft Excel 2021. For data analysis, the Statistical Package for the Social Sciences (SPSS) version 20 for Windows was utilized. Pearson Correlation (two-tailed) was used to estimate the level of correlation between the pesticide residues and the physicochemical parameters.

RESULTS AND DISCUSSION

Water Physicochemical Parameters

The values of water physiochemical parameters are shown in Table 2.

Table 2 Water Samples Physiochemical parameter levels in the dry and wet seasons.

Dry Season				
Site	**pH**	**TDS (mg/l)**	**TSS (mg/l)**	**EC (µscm^{-1})**
1	6.51 ±0.21	100.04 ±1.10	290.11 ±5.81	200.13± 2.01
2	6.53 ±0.20	80.02 ±1.01	248.10 ± 3.62	150.04 ±1.50
3	6.50 ±0.16	60.01 ± 2.11	219.02 ±8.51	130.06 ±2.01
4	6.52 ±0.15	60.11 ±1.05	183.01 ±7.80	100.02 ±1.04
5	6.43 ±0.11	40.05 ±2.01	154.03 ±76.01	80.02 ±1.07
6	6.41 ±0.12	20.01 ±1.03	103.01 ±35.11	50.03 ±1.02
Wet season				
1	6.53 ±0.15	60.03 ±1.11	316.01 ± 6.81	130.01 ±1.51
2	6.82 ±0.13	60.06 ± 2.01	296.02 ± 4.32	120.10 ±1.22
3	6.91 ±0.17	40.10 ± 1.10	278.01 ± 9.33	100.02 ±1.20
4	6.81 ±0.11	40.03 ±2.12	237.11± 5.21	90.04 ±1.03
5	6.12 ±0.12	20.10 ± 2.02	196.13 ± 8.60	40.05 ±1.06
6	6.33 ±0.14	10.03 ± 2.04	155.01 ± 56.11	30.01±1.21
Recommended values in drinking water				
WHO	6.5 - 8.9	1000	500	500
KEBS	6.5 - 8.5	1200	500	1000

Source:[19], [20]

pH of Water Samples

The biological productivity of an aquatic system is related to water pH therefore its measurement is of significance [15]. The pH of the water samples ranged between 6.1 ± 0.12 - 6.9 ± 0.17 (Figure 2). All the pH levels fell within the recommended ranges of 6.5-8.9 by the World Health Organization [19] and 6.5 - 8.5 by Kenya Bureau of Standards [20] for natural water bodies except the levels at sites 5 (Kutus) and 6 (Yakimoni) in the dry season with pH of 6.43 ±0.11 and 6.41 ± 0.12 respectively, while for wet seasons were 6.12 ± 0.12 and 6.33 ± 0.14 (Table 2) respectively. Consequently, there were no significant fluctuations in water pH across various sites or seasons. This consistency is likely due to the river's natural buffering capacity, which effectively neutralizes any basic or acidic discharges from the nearby town and runoff. Moreover, pH levels are known to be influenced by both temperature and water runoff. The acidic pH in the Thiba River water samples could be due to the soils in the catchment being acidic hence the water getting acidic as it flows along the surface [21].

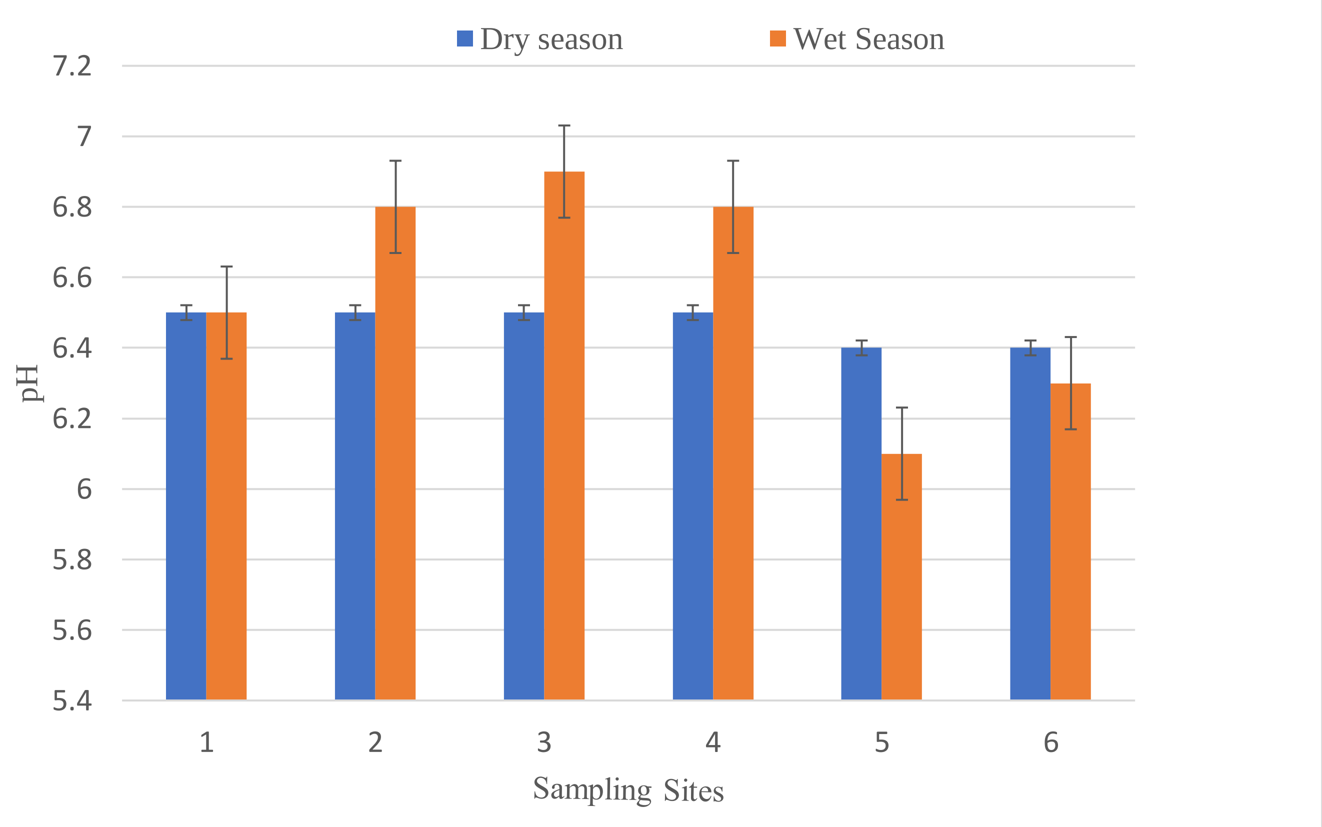

Figure 2: pH of Water Samples in the dry and wet seasons

Total Dissolved Solids in Water Samples

Total dissolved solids (TDS) encompass the inorganic salts and organic materials dissolved in water, typically including cations like sodium, calcium, potassium, and magnesium, along with anions such as carbonate, chloride, fluoride, sulfate, and nitrate. The analytical quality of drinking water is evaluated based on its TDS content, with levels below 300 mg/L considered excellent, while those falling between 900 mg/L and 1200 mg/L are deemed poor [20]. The World Health Organization categorizes water exceeding 1200 mg/L in TDS as unsuitable for drinking purposes [19]. In the Mwea catchment area of the Thiba River, high TDS levels likely stem from urban and agricultural runoff. The lowest TDS value of 10.03 ± 2.04 mg/L was recorded at site 6 in the rainy season, while the highest value of 100 ± 1.10 mg/L was from site 1 in the dry season, as indicated in Table 2. The TDS values were higher in the dry season than wet in Thiba River catchment area (Figure 3). All measured values fell below the WHO's permissible for drinking water limit of 1000 mg/L [19] and KEBS' limit of 1200 mg/L [20], applicable to both irrigation and domestic water. The US Environmental Protection Agency (EPA) has established a recommended TDS standard of 500 mg/L for drinking water. Elevated TDS concentrations can induce laxative effects and impart an unpleasant mineral taste to drinking water [21].

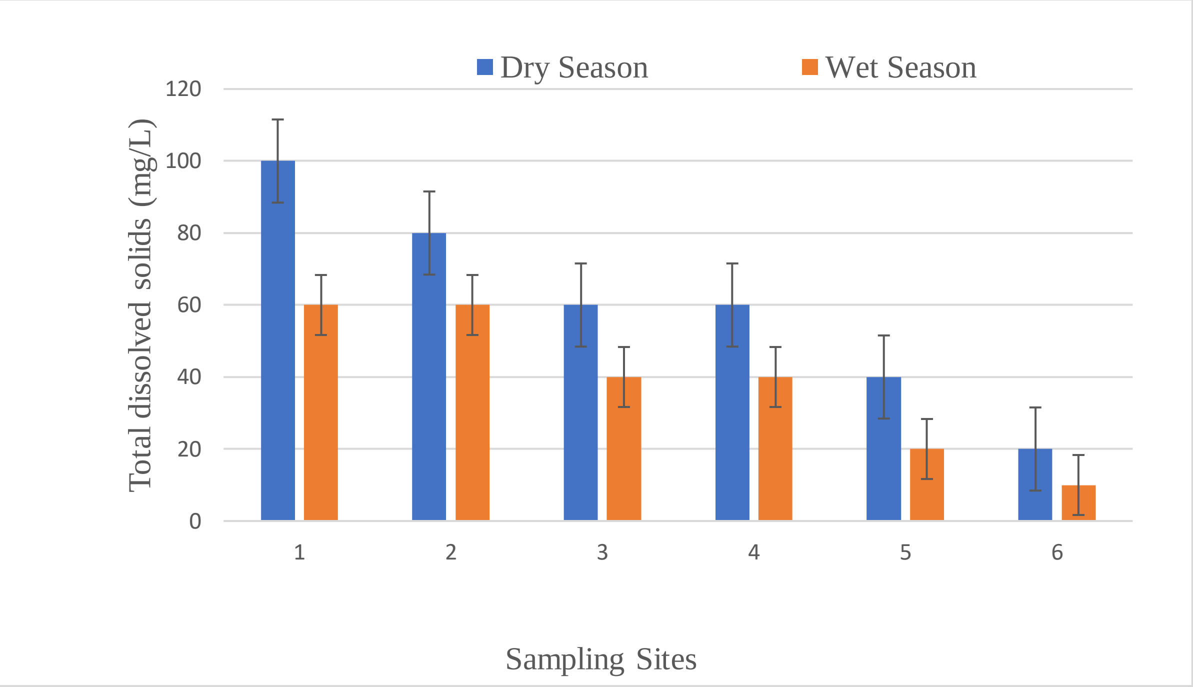

Figure 3: Total Dissolved Solids in Water Samples in the Dry and Wet Seasons

Total Suspended solids (TSS) in Water Samples

The total suspended solids (TSS) levels in the Thiba River catchment area differed from each other and generally increased as the river flows downstream. The TSS levels ranged from 103.01 ± 35.11 mg/L - 290.11±5.81 mg/L and 155.01 ± 56.11 - 316.01± 6.81 mg/L in the dry and wet seasons respectively (Table 2). The increase in levels (Figure 4) could be attributed to water run-off, irrigation channels erosion, and the anthropogenic activities in the area.

The seasonal distribution of TSS were similar in its trend as the river flows downstream in both the sampling seasons (Table 2). However, the TSS levels were higher per site in the wet season than dry as shown in Figure 4. It was also noted that the TSS in both the dry and wet seasons were well related to the particle size. The difference was larger as the particle size increased downstream. The TSS for the water samples in the dry and wet seasons as summarized in Table 2 and Figure 4.

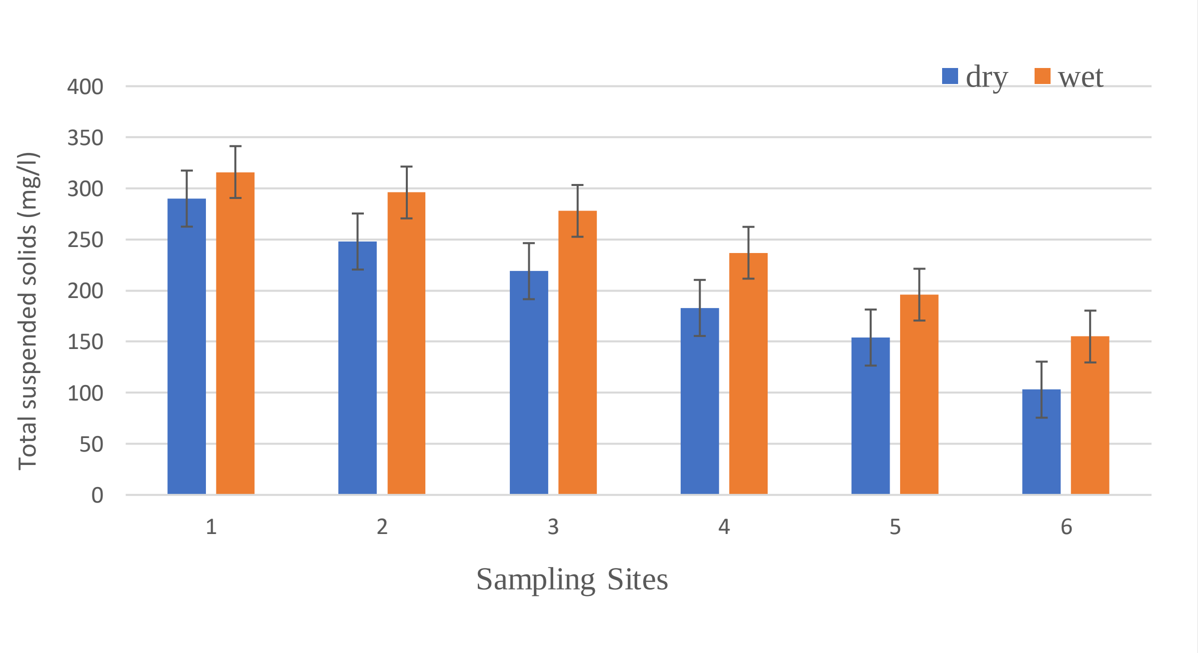

Figure 4: Total Suspended Solid in Water Samples during the dry and wet seasons

Electrical Conductivity of Water Samples

Electrical conductivity indicates a solution's capacity to conduct electricity. It is commonly utilized in industrial and environmental contexts as a cost-effective and rapid method for gauging the ionic concentration in a liquid. The conductivity of water is directly correlated with temperature, meaning it rises as temperature increases and declines as temperature decreases. Additionally, it is closely associated with Total Dissolved Solids (TDS). In the case of Thiba River water, conductivity generally increased downstream, with site 6 in the upstream registering a conductivity of 50.03 ±1.02μscm^{-1} in the rainy season and 30.01±1.21μscm^{-1} in the dry season, while site 1 in the downstream had a conductivity of 200.13± 2.01μscm^{-1} in the rainy season and 130.01 ±1.51μscm^{-1} in the wet season (Table 2). The upstream section exhibited lower dissolved solids due to minimal anthropogenic activities in that area (Table 1). Notably, all electrical conductivity levels from the water samples were lower than values for drinking water quality standards set by WHO [19] and KEBS [20] of 500 µs/cm and at 1000 µs/cm respectively (Figure 5).

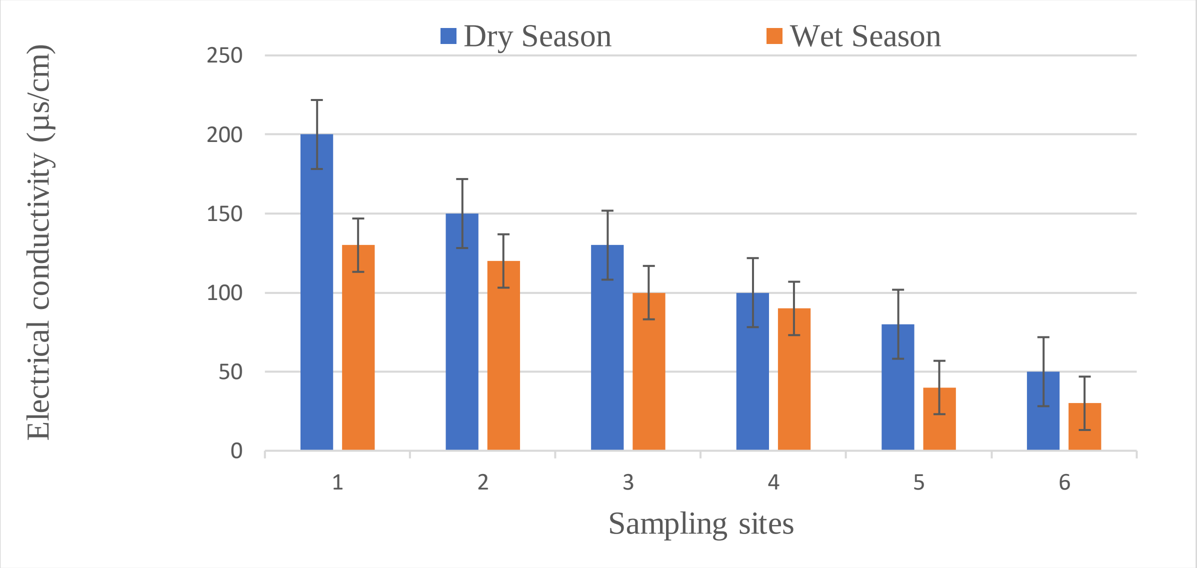

Figure 5: Electrical Conductivity of water samples in the dry and wet seasons

Sediment Samples Physicochemical Parameters

The physicochemical parameters determined for the sediment samples included sediment pH and sediment organic matter content (Table 3).

Table 3: Sediment pH and percentage organic matter content in the dry and wet seasons

site	pH	Organic Matter Content (%)
Dry season		
1	7.52± 0.11	31.04± 0.42
2	7.41± 0.12	30.61± 0.19
3	6.93± 0.14	34.54± 0.67
4	6.51± 0.13	27.72± 0.62
5	5.42± 0.12	41.06± 0.51
6	6.62± 0.14	37.34± 0.96
Wet season		
1	7.42± 0.12	36.54± 0.93
2	7.23± 0.13	38.59± 1.02
3	7.01± 0.15	37.10± 0.22
4	7.14± 0.12	33.65± 0.94
5	6.32± 0.11	48.30± 0.28
6	6.53± 0.12	49.07± 0.78

Sediment Samples pH

The highest pH of 7.52 ± 0.11 was at site 1 while lowest of 5.42 ± 0.12 in site 5 in the dry season (Table 3). Most of the pH ranged between 6.51 ± 0.13 and 7.52 ± 0.11. There was a consistent trend of increase in sediments pH levels downstream. The sediment pH levels per site were higher in the dry season than the wet season (Figure 6) and as compared to the water samples (Figure 2), the sediment pH was higher per site across the sampling seasons (Figure 6).

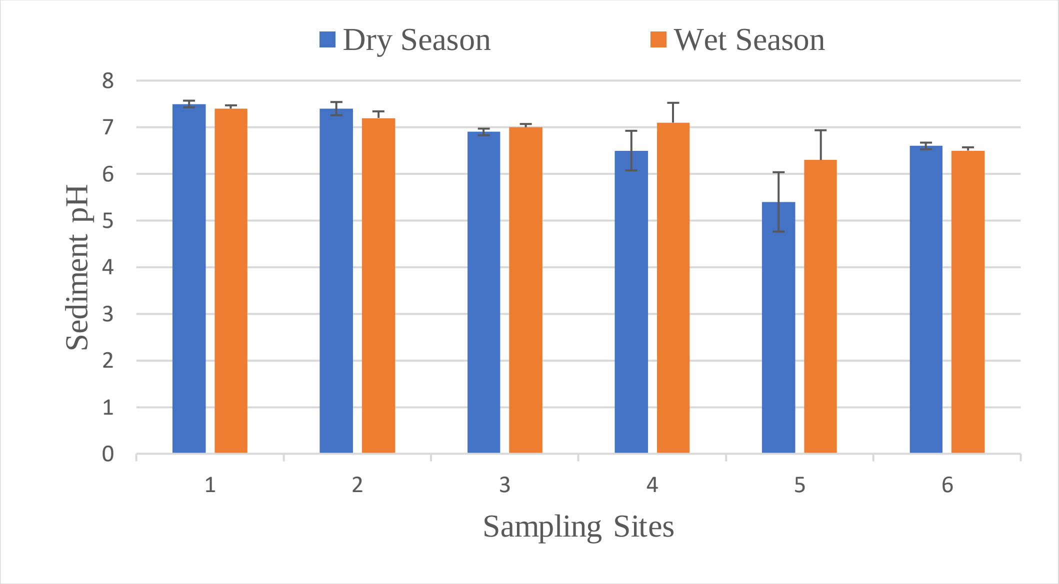

Figure 6: Sediment samples pH in the dry and wet seasons

Sediment Samples Organic Matter Content

The organic content levels in sediment is the ratio of the mass of the organic matter in a given mass of sediment to the mass of the dry sediment solids and it is expressed as a percentage. Site 5 had the highest sediments organic matter content levels in both the dry and wet seasons of 41.06 ± 0.51 and 48.30 ± 0.28 respectively (Table 3). This could be due to the influence of the nearby Kutus Town and Kirinyaga University having its organic wastes deposited in the soils and into the river (Table 1). The organic matter in the sediment samples across the sampling sites were higher in wet season than the dry season (Figure 7).

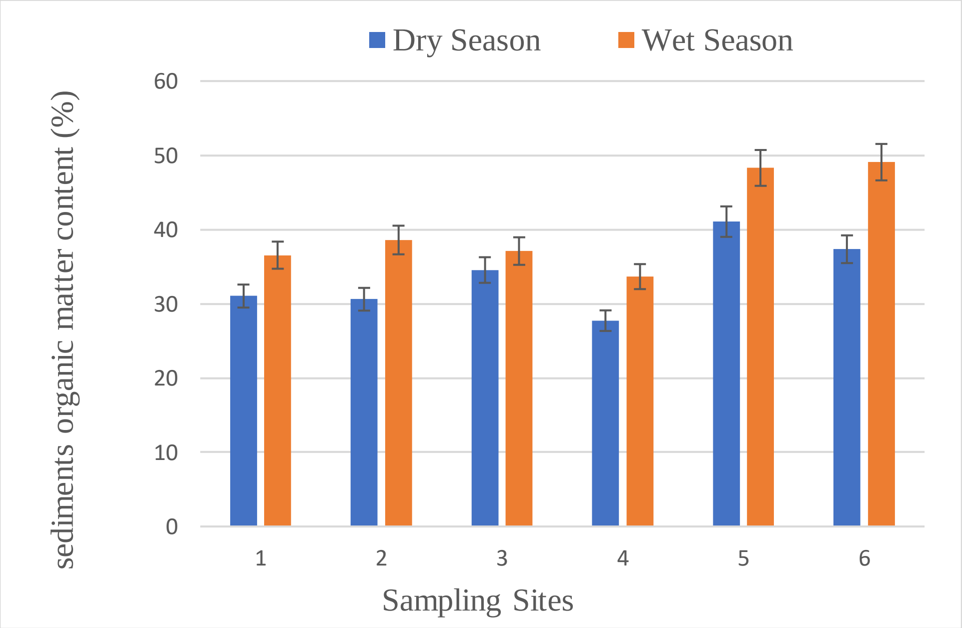

Figure 7: Percentage Sediment organic matter contents in the dry and wet seasons

Pesticides Residue Levels in Water and sediment Samples in the dry and wet seasons

Pesticides Standards Limits of Detection and Average Percentage Recovery Levels

The gas chromatograph - mass spectrometry (GC-MS) was used to analyze the three pesticides reference standards that were among the most prevalently used by the farmers in the catchment area to prepare the calibration curves, to obtain the limits of detection (LOD) and percentage recovery levels for each pesticide standards. For the pesticides analyzed, the LODs were found to be 0.05 µg/L for metalaxyl, 0.05 µg/L for chlorpyrifos, and 0.005 µg/L for lambda-cyhalothrin (Table 4) in the water samples.

The mean percentage recoveries of the pesticides' residue levels were between 89.35± 5.12 % for lambda-cyhalothrin to 105.06± 9.58 % for chlorpyrifos. Table 4 shows mean ± standard deviation (S.D) recoveries of the pesticides in water and sediment samples. Matrix effects were not adjusted in the detected pesticide residue levels in the samples, as all recovery values fell within the acceptable range of between 70-120 % [22].

Table 4: Pesticides Standards Limits of Detection and Average Percentage Recovery Levels

Pesticide	Limit of Detections (µg/L)	water recovery (% ± S. D)	sediment recovery (%±S. D)
Metalaxyl	0.05	102.86 ± 4.06	102.84 ± 6.09
Chlorpyrifos	0.05	105.01± 9.58	96.71 ± 6.09
Lambda-cyhalothrin	0.005	89.35 ± 5.12	89.96 ± 11.32

Mean ± S.D n= 3

Pesticides Residue Levels in Water Samples in the dry and wet seasons

The pesticide residue levels ranged from <0.05 µg/L - 4.24 ± 1.75 µg/L for metalaxyl, 7.12 ±1.16 µg/L - 39.42 ± 5.89 µg/L for chlorpyrifos and <0.005 µg/L - 3.74625 ± 0.72296 µg/L for lambda-cyhalothrin in the dry season (Table 5). The highest levels were at Site 2 in the downstream section of the study area. This could be due to the increased livestock and crop farming activities in the area leading to washing off and water run-off into the river. The lowest chlorpyrifos levels were at Site 3, in the midstream section. This could be attributed to the limited livestock farming in the area. Chlorpyrifos is mainly used by the farmers in the study area for the control of ticks in cattle dips and flies on the fields. With reduced usage on cattle farming, there is the probable reduced presence of residues washed off to the rivers. The moderately higher residue levels from site 4 in the midstream and site 5 in the upstream could be attributed to the waste discharges from the nearby towns, industrial activities and learning institutions.

Table 5: The pesticide residue levels in water samples in dry and wet seasons

Site	Metalaxyl (µg/L)	Chlorpyrifos (µg/L)	Lambda- cyhalothrin (µg/L)
Dry Season			
1	1.66 ± 0.05	14.18 ± 3.49	< 0.005
2	4.24±1.75	39.42 ± 5.89	< 0.005
3	<0.05	7.12 ± 1.16	3.75 ± 0.72
4	1.69 ± 0.09	10.24 ± 2.25	1.32 ± 0.08
5	<0.05	22.46 ± 3.84	< 0.005
6	<0.05	12.76 ± 2.53	< 0.005
LOD	0.05	0.05	0.005
Wet Season			
1	<0.05	23.60 ± 0.92	< 0.005
2	<0.05	49.36 ± 20.76	< 0.005
3	1.22 ± 0.06	8.94 ± 1.94	< 0.005

4	1.46 ± 0.09	37.32 ± 9.54	< 0.005
5	1.23 ± 0.11	88.24 ± 5.97	0.18±0.01
6	<0.05	43.10 ± 5.87	< 0.005
Recommended levels			
WHO	10	30	10

[23], n=3, mean ± standard deviation

Spatial and seasonal variation of pesticide residue levels in river water samples

The chlorpyrifos residue levels were higher in the wet than dry season. This can be explained by the fact that chlorpyrifos has a photolysis half-life of approximately three to four weeks in water [15], which leads to its degradation. Consequently, residues are likely to be present only from recent applications. It is expected that these residues will be higher during the rainy season due to runoff from cattle dips and barns, as well as from residues lingering from past contamination. Moreover, seasonal variations were found to impact pesticide residue levels, with samples showing a trend of higher levels in the wet season than dry season. This indicates that more pesticides are washed into the river during the rainy season due to rainfall and splashing [11]. Surveys revealed that farmers primarily apply the pesticide for tick control in cattle dips and for managing flies on their farms. This could explain the elevated residue levels in downstream areas where cattle farming is common. The high residue concentrations observed at Kutus Bridge and Wanguru Bridge are linked to discharges from nearby towns and rainwater runoff into the river.

In contrast, the levels of metalaxyl and lambda-cyhalothrin pesticides were higher in the dry season compared to the wet season. This difference can likely be attributed to the dilution of pesticides in the river caused by flooding, runoff, and the washing away of pesticides from agricultural areas during the rainy season [12]. Additionally, the reduced usage of these pesticides during the wet season may contribute to this trend, as pests are typically more abundant in the dry season, resulting in increased application by farmers. Rainwater tends to eliminate more pests and insects in their larval stages, leading to a decrease in their numbers during the rainy season.

Comparison of pesticides residue levels in river water with levels in other areas

A study conducted on clofenvinphos, an organophosphate pesticide used for tick control, in western Kenya, showed that the concentration of clofenvinphos in milk samples ranged from 0.52 to 3.90 mg/L during the dry season and from 1.58 to 10.69 mg/L in the wet season [24]. This indicates that residue levels were higher in cattle dips during the dry season compared to the wet season. This observation aligns with the current research, which also indicated that residue levels of lambda-cyhalothrin and metalaxyl were greater in the dry season than in the wet season, while chlorpyrifos showed higher levels during the wet season. Another study reported a maximum concentration of chlorpyrifos of 5.42 µg/L along the Tana River [25]. In comparison, the current study recorded the highest levels of chlorpyrifos at 88.24 ± 5.97 µg/L in the wet season and 39.42 ± 5.89 µg/L in the dry season, both surpassing the WHO's drinking water limit of 30 µg/L [26]. Water samples collected from Ondiri swamp and the Nairobi River also showed elevated pesticide residue levels during the wet season compared to the dry season, which was attributed to significant runoff from adjacent agricultural activities in the rainy season [27]. In this study, most of the water samples, residue levels for chlorpyrifos were below the recommended drinking water limit during the dry season but exceeded the 30 µg/L threshold established by WHO in the wet season [26].

Pesticides Residue Levels in Sediment During the Dry and Wet Seasons

Sediments were chosen as matrices of concern for analysis because they function as sink for majority of hydrophobic organic contaminants. They strongly attach to the sediments particulate matter due to their hydrophobic active sites and good octanol-water partition coefficient (K_{ow}) [28]. The mean pesticide residue levels in sediment samples in the dry season ranged from <0.05 µg/kg - 1.55±0.99 µg/kg for metalaxyl, 4.77±17 µg/kg - 47.78±7.122 µg/kg for chlorpyrifos, and <0.005 µg/kg for lambda-cyhalothrin as shown in Table 6. The chlorpyrifos residue levels were highest in Site 2 at 47.78 ± 7.12 µg/kg and this could be attributed to the broadening of the river at the site hence more accumulation of the pesticide on the river banks.

The mean pesticide residue levels in sediment samples in the wet season ranged from <0.05 µg/kg - 1.27±0.90 µg/kg for metalaxyl, 7.68 ± 1.87 µg/kg - 48.68 ± 1.87µg/kg by chlorpyrifos, and <0.005 µg/kg for lambda-cyhalothrin except for Site 1 that had 0.67 ± 0.058 µg/kg residue levels. The metalaxyl residue levels in the sediment samples were generally higher in the mid and downstream sections of the study area and this could be attributed to pesticides accumulating downstream as they get washed by run off rain water into the river from farms and flooding from the upstream sections [12]. This can be backed up with the pesticide residue levels in water and soil samples in the wet seasons. Lambda-cyhalothrin residue levels were very low and value of 0.67 ± 0.058 µg/kg was analyzed in Site 1 in the downstream section in the wet season (Table 6). This could also imply that the pesticide residue levels accumulated downstream of the study area. The levels were relatively higher at site 4 and site 5 and this is attributed to water run-off and wash off from the Kirinyaga university and the Kutus towns' discharges, and the contaminants from the farms into the river during the rainy season.

Table 6: Pesticide residue levels in sediment samples in the dry and wet seasons

Site	Metalaxyl (µg/kg)	Chlorpyrifos (µg/kg)	Lambda-Cyhalothrin (µg/kg)
Dry Season			
1	< 0.05	4.77 ± 0.17	< 0.005
2	< 0.05	47.78 ± 7.12	< 0.005
3	1.54±0.46	9.50 ± 3.03	< 0.005
4	< 0.05	9.32 ± 2.33	< 0.005
5	< 0.05	13.17±2.86	< 0.005
6	1.55±0.99	20.49±3.34	< 0.005
Wet Season			
1	1.25 ± 0.55	11.35 ± 1.90	0.67± 0.058
2	1.27 ± 0.90	48.68 ± 1.87	< 0.005
3	< 0.05	9.57±2.49	< 0.005
4	1.26 ±0.10	10.66 ± 3.78	< 0.005
5	< 0.05	28.64 ± 7.90	< 0.005
6	< 0.05	29.24 ± 1.57	< 0.005

N=3

Spatial and seasonal variation of pesticides residue levels in sediment

Sediment samples in the wet season exhibited higher pesticide residue levels than in the dry season. This was primarily due to runoff from agricultural fields and water from cattle dips and cow sheds flowing into the river shortly after pesticide application. Moreover, pesticide residue concentrations were greater in sediments than in water samples. The strong sorption interactions in sediment environments are because of their physical and chemical properties [25]. The substituents in pesticides alter the physical attributes of organic compounds, making them denser than water because of the high atomic weights of the substituents bonded to carbon atoms (like chlorine in organochlorines and phosphate in organophosphates). These carbon-substituent bonds are very stable and resist breakdown. Sorption is influenced by the substituent concentration, surface area, and organic matter in the sorbent [25]. However, the average levels of chlorpyrifos were generally higher in water samples compared to sediment samples, as this pesticide degrades easily, leading to lower absorption into sediment and thus lower residue levels found in the sediment.

Comparison of pesticide levels in sediment samples with levels in other areas

Research conducted in Lake Naivasha found that chlorpyrifos residue levels in sediment samples were higher in the wet season (11.2-30.0 ng/g) than dry season (4.7-17.4 ng/g) [29]. These results are consistent with those of the present study, which also noted reduced chlorpyrifos residue levels in sediment samples taken in the dry season relative to those collected in the wet season (Table 6). In the Nyando/Sondu-Miriu Basin, water samples showed organophosphates (OPs) below detectable limits, whereas sediment samples exhibited higher concentrations of malathion and diazinon [12]. Furthermore, a study in the Nyando River catchment area of

Lake Victoria indicated that OCPs were still present in the sediments [11]. Sediment samples in the Lake Victoria basin displayed higher residue levels than those in the water [13], and the coastal region of Kenya has also been documented to have pesticide residues in sediment [14].

Correlation of Pesticide Residue Levels in Water and Sediment

The Statistical Package for the Social Sciences (SPSS) was employed to calculate Pearson's correlation coefficients, quantified by the value (r) which ranges from -1.000 to +1.000. A positive r value indicates a direct relationship between variables, while a negative r value signifies an inverse relationship [30].

This study examined the residue levels of chlorpyrifos in water and sediment, focusing on their relationship with the physicochemical parameters of total dissolved solids (TDS) and organic matter content. Pearson correlations were calculated to investigate the connections between chlorpyrifos and TDS in water samples during both dry and wet seasons. Furthermore, correlations were determined between chlorpyrifos levels and organic matter content in sediment. In the dry season, TDS in water showed a positive correlation with chlorpyrifos levels ($r = 0.082$, $p > 0.05$), while in the wet season, a negative correlation was observed ($r = -0.372$, $p > 0.05$) across the six sampling sites. For sediment samples, chlorpyrifos residue levels followed a similar trend, showing a negative correlation with organic matter content in the dry season ($r = -0.100$, $p > 0.05$) and a positive correlation in the wet season ($r = 0.527$, $p > 0.05$) across all six sampling sites as shown in Table 7.

Table 7: Correlation of TDS and OM with chlorpyrifos levels in water and sediment in the dry and wet seasons.

Dry Season		TDS	OM Sediment
Water	Pearson Correlation	.082	-.018
	Sig. (2-tailed)		.973
	N	6	6
Sediment	Pearson Correlation	.029	-.100
	Sig. (2-tailed)	.957	.851
	N	6	6
Wet Season		TDS	OM Sediment
Water	Pearson Correlation	-.372	.583
	Sig. (2-tailed)	.468	.225
	N	6	6
Sediment	Pearson Correlation	-.426	.527
	Sig. (2-tailed)	.400	.283
	N	6	6

A comparative inter-matrix correlation of chlorpyrifos levels in water and sediment across the dry and wet seasons revealed a positive correlation for water samples ($r = 0.384$, $p > 0.05$), and a negative correlation for sediment samples ($r = -0.278$, $p > 0.05$). In the dry season, the relationship between chlorpyrifos levels in water and sediment samples was also strong positive correlation ($r = 0.874$, $p > 0.05$) and continuing this positive trend in the wet season ($r = 0.939$, $p > 0.05$) a shown in Table 8.

Table 8: Correlation of chlorpyrifos levels in water and sediments in the dry and wet seasons

Dry Season		Water	Sediment
Water	Pearson Correlation	1	.878
	Sig. (2-tailed)		.023
	N	6	6
Sediment	Pearson Correlation	.874	1
	Sig. (2-tailed)	.023	
	N	6	6
Wet Season		Water	Sediment
Water	Pearson Correlation	1	.939

	Sig. (2-tailed)		.005
	N	6	6
Sediment	Pearson Correlation	.939	1
	Sig. (2-tailed)	.005	
	N	6	6

CONCLUSION

All assessed physicochemical parameters in water and sediment from the study area conformed to the recommended levels set by WHO and KEBS. The water samples' pH across all sampling sites showed no significant variation based on location or season. The pH, TDS, and TSS levels of sediment samples were generally elevated in the dry season than wet. Electrical conductivity of water samples increased downstream in both the seasons. Organic matter content in sediment was higher in the wet season than dry in all the sampling sites, with Site 5 (Kutus) showing the highest organic matter levels in both the seasons, likely due to its proximity to Kutus town and Kirinyaga University, where organic waste is deposited into the soil and Thiba River.

Three pesticides, metalaxyl, chlorpyrifos, and lambda cyhalothrin, were detected at varying levels in water and sediment samples during both dry and wet seasons across six selected sampling sites. Variations in residue levels by season were noted, which may stem from the different chemical properties of each pesticide, as well as point and non-point sources of contamination and the diverse agricultural practices along the river. In the water samples, chlorpyrifos levels increased downstream, with Site 5 (Kutus) exhibiting the highest levels during the wet season, even though it is located in the upstream section of the river. This was due to the dense population in the area and higher number of cattle dips which flood in the wet seasons, run off water from the cowsheds. This too can be explained by the relatively higher solubility of chlorpyrifos in water. The metalaxyl pesticide levels showed similar trend increasing downstream with Site 2 (Ndindiruku) having the highest value of 4.24 ± 1.75 µg/L in the dry season. However, the lambda cyhalothrin pesticide residue levels were relatively lower than chlorpyrifos and metalaxyl and ranged from < 0.05 µg/L. - 3.75±0.72 µg/L. In the water samples range was chlorpyrifos > metalaxyl > lambda cyhalothrin pesticides residue levels.

The pesticides residue levels increased downstream in sediment samples. However, the chlorpyrifos pesticide quantities in sediment were relatively higher than in water samples in the dry season and relatively lower in wet. This could be attributed to the pesticides being diluted and washed off by rain water into the river in the wet season. The relatively higher chlorpyrifos pesticide residue levels in the wet season could also be attributed to farmers applying more pesticides to increase their farm produce and to curb pests and diseases that increase during the rainy season. There were higher recorded concentrations in the wet season than the dry season in water and the reverse in trend in sediments with higher concentration being in the dry than wet season. There were higher levels of the pesticide residues in the sediments than water samples. This was due to the fact that pesticides residues get attached to the sediment organic matter that were higher than those in water. Chlorpyrifos had the highest levels, this was due to the insecticide's widespread use in controlling ticks and fleas in the study area. Most of its levels were above the set limits for drinking water of 30 µg/L by WHO [26]. For the metalaxyl and lambda-cyhalothrin, their levels in water and sediments were generally below the set limits by WHO [26][31].

Disclosure Statement

The authors declare no conflict of interest.

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