Assessment of Available Phosphates and Nitrates Levels in Water and Sediments of River Isiukhu, Kenya

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Abstract Surface water contamination has become one of the main environmental issues of concern and a challenge to the world population, especially in the developing world, that face potable or usable water security. In this study concentrations of available nutrients (PO_4^{3-} and NO_3^-) in sediments and water along River Isiukhu, within Lake Victoria catchment area in Kenya are presented. Sediments and water samples were collected from 11 sampling sites along River Isiukhu. Available phosphorus was determined by a Spectrophotometric method in which the ammonium phosphomolybdate complex, was reduced by ascorbic acid in the presence of antimony to give a distinct blue color complex. Available nitrate was measured spectrophotometrically at 420nm using UVI609PC UV/VIS Spectrophotometer. Physicochemical parameters such as temperature, pH, dissolved oxygen, turbidity, salinity, conductivity, were measured on-site using mobile Hydrolab Quanta. Phosphates concentrations ranged from 1.18 ± 0.09 to 3.28 ± 0.5 in water (mg/l) and 2.30 ± 0.03 to 4.51 ± 0.31 in sediment (mg/kg) and nitrates concentrations ranged from 0.15 ± 0.04 to 0.75 ± 0.03 in water (mg/l) and 0.75 ± 0.02 to 1.93 ± 0.05 in sediment (mg/kg). The coefficient of variation (CV) depicted that all the physical-chemical parameters measured varied widely except pH and temperature. Pearson's correlation matrix was used to show the relationship between nutrients concentrations in sediments and water and also for the physical-chemical parameters at significant differences accepted at $P \leq 0.05$. There was variation in Pearson correlation coefficient analysis for all the parameters tested.

Keywords: phosphates, nitrates, sediments, correlations, River Isiukhu

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1. Introduction

Pollution of the aquatic ecosystem is a worldwide issue and the possibility of it in influencing human health is of great concern [1]. Today, nutrients, particularly phosphate and nitrate, are amongst the most pervasive pollutants of freshwater across the globe [2], if the maximum contaminant level (MCL) for nitrate in public drinking water supplies in the United States (U.S.) is 10 mg/L as nitrate-nitrogen (NO_3-N). This concentration is approximately equivalent to the World Health Organization (WHO) guideline of 50 mg/L as NO_3 or 11.3 mg/L NO_3-N (multiply NO_3 mg/L by 0.2258). To avoid eutrophication in rivers the Western Canadian Guidelines of 0.05 mg/L for soluble phosphate in freshwater was established. This is because nitrogen and phosphorus are very useful soil elements that are used to control yields of crops and its fertility with nitrogen being the most important for crop plants and its availability is closely associated with plant productivity [3]. Nitrates can enter the aquatic ecosystem as a result of farming activities (as well as excessive use of inorganic nitrogenous composts and fertilizers), from wastewater discharge and nitrogenous waste products [4,5,6] situated in the vicinity of the ecosystem. Phosphorus is a key component in most fertilizers and is crucial for higher agricultural output to sustain our food supplies [7]. Therefore, a huge quantity of phosphorus used as fertilizer in the form of superphosphate, Nitrogen, phosphorus and potassium (NPK) goes into the aquatic ecosystem through a precipitation reaction with highly reactive aluminum (Al^{3+}) and iron (Fe^{3+}) in acidic, and calcium (Ca^{2+}) in calcareous or normal soils [8]. Also, wastewaters from laundering agents contain phosphates. This is because most laundry detergents contain approximately 35% to 75% sodium triphosphate ($Na_5P_3O_{10}$).

High concentrations of available nutrients in the aquatic ecosystem result in unjustifiable growth of aquatic plants, including algae, which suppresses other less tolerant species [2]. Surplus nutrients can affect the quality of water when water and soil containing nitrogen and phosphorus are washed down into water bodies through surface runoff [9]. Polluted water can contain excess nutrients and pathogens which can affect human health, destroy marine species and disturb the ecological cycle [10]. Elevated levels of phosphates and nitrates in water bodies are the most common cause of eutrophication [11,12]. Phosphorus is a major limiting nutrient in water bodies it is interesting to research its concentrations in water bodies and their effects on both the aquatic ecosystem and living organisms. Therefore, eutrophication and water quality is maintained by controlling the entry of the phosphorous [13]. Also, excessive nitrates are known to cause diverse health effects to the human being, such as "Blue Baby Syndrome" or "methemoglobinemia" [14]. Currently, there has been a concern overexposure of nitrate and its increased risk of negative risks impact on human and aquatic organisms' health [15].

River Isiukhu is a tributary of River Nzoia which subsequently drains into Lake Victoria, the second largest lake in the world. Therefore, the pollution of the River Isiukhu affects Lake Victoria. Water from River Isiukhu is important because this ecosystem provides water for human beings' consumption, a source of livelihood for residents within the basin and also forms habitats for aquatic animals. River Isiukhu passes through several urban towns such as Kakamega and Mumias town, informal sector (where several cottage industries exist)

and agricultural zones (of maize, beans, and sugarcane plantations) which mainly rely on the use of agrochemical products. As the water passes through these areas, it collects domestic, agricultural and industrial wastes that may contain nutrients. This is discharged into the river through run-offs and can bioconcentrate in aquatic animals and eventually settling at the bottom sediment. There is only one study by [16] that has reported on pollution of Isiukhu River, but with Heavy metals. However, water quality in such rivers may be impacted by unacceptable levels of pollutants such as nutrients [17]. There is no comprehensive study that has been carried out on the levels of physico-chemical parameters including the bioavailable nitrate and phosphate of River Isiukhu. It is this among other reasons that this study was focused to fill this gap by investigating the levels of the key physico-chemical parameters and available nutrients within this important basin. Nitrates and phosphates pollution monitoring is needed to provide baseline data that can be used by decision and policy makers for sustainable environmental management of river basins and aquatic ecosystems.

2. Material and Methodology

2.1. Study Area

The present study was carried out along River Isiukhu in Kakamega County, Kenya. River Isiukhu originates from the Nandi Escarpment and flows through the Kakamega Forest before reaching Kakamega Town, Figure 1 shows the map of Isiukhu River.
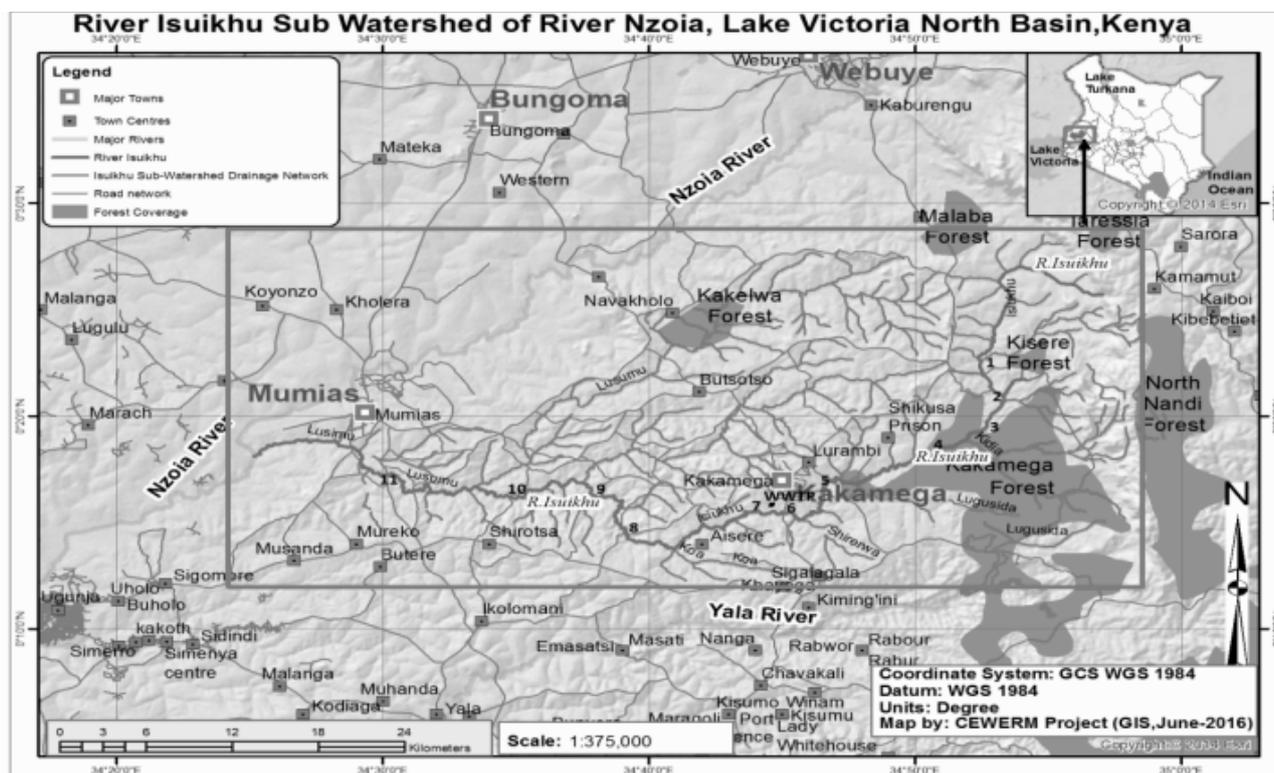

Figure 1. A map of Isiukhu River (Kenya) within the Lake Victoria Basin, showing various sites where sampling was carried out.

The sampling sites were designated as follows: 1. Ichina, 2. Ivakale, 3. Kimangeti, 4. Senyende, 5. Savona, 6. Shirere, 7. Rosterman, 8. Mwimbatsiro, 9. Shibeye, 10. Mutono, 11. Ekero.

The river transverse among three zones; upstream, midstream and downstream catchment areas. The main activities taking place include agriculture (upstream), urbanization and industrialization i.e. cottage industries (midstream) and agriculture (downstream). The selection of these points was based upon human activities taking place near the river banks such as sand harvesting, livestock keeping, and farming, urban effluent discharge in the river and accessibility.

2.2. Chemicals, Reagents and Equipment

Analytical reagents such as H_2SO_4 (sulphuric acid), HNO_3 (nitric acid), $(NH_4)_6Mo_7O_{24}$ (ammonium molybdate), $C_8H_{10}K_2O_{15}Sb_2$ (potassium antimonyl tartrate), $C_6H_8O_6$ (ascorbic acid), NaOH (sodium hydroxide), $NaHCO_3$ (sodium hydrogen carbonate), H_3BO_3 (boric acid), KH_2PO_4 (potassium dihydrogen phosphate), $C_7H_5NaO_3$ (sodium salicylate), K_2SO_4 (potassium sulfate), $C_7H_6O_3$ (salicylic acid) and KNO_3 (potassium nitrate) were purchased from Kobian Kenya Limited. At all times, fresh reagents were used and greater care was taken to avoid chemical contamination. Shimadzu UVI609PC UV/VIS Spectrophotometer (country), Ambassador Laboratory Electric Oven, analytical balance 526 from India and Hydrolab quanta.

2.3. Sample Collection and Pretreatment

Physico-chemical parameters (pH, conductivity, temperature, salinity and dissolved oxygen) were determined on-site along River Isiukhu using Hydrolab quanta.

At each sampling site, the bottles were rinsed at least three times before sampling using River Isiukhu water. A sample of about 500 ml of water was taken in a clean acid-washed polyethylene bottle. The samples were correctly labeled using appropriate codes and then transported to Masinde Muliro University laboratory in a cool box, filtered using nylon 0.45 µm membrane filters and stored in the refrigerator at 4°C before analysis.

The sediment sample was collected using Ekman Grabber, placed in clean plastic containers, labeled using appropriate codes, stored in a cool box and transported to Masinde Muliro University laboratory. Upon reaching the laboratory, sediment samples were air-dried for several days and later oven-dried at 105 °C for 24 hours using Ambassador Laboratory Electric Oven 526 (India) to obtain a constant weight. The sediment samples were then crushed and sieved using 2 mm.

2.4. Preparation of Standards and Samples for Nutrients Analysis

2.4.1. Preparation of Phosphate Standards

250 ppm of standard phosphate solution was prepared by weighing 1.0984 g of oven-dried KH2PO4 (AR) and transferring to a clean 1-liter volumetric flask and dissolve in distilled water to a 1000 ml mark. 0,1,2,5,10,15,20 and 25 ml of the above 250 ppm P stock solution were pipetted into a clean 500 ml volumetric flask and 100 ml of the Olsen's extracting solution added and filled to the 500 ml mark with distilled water. These solutions contained 0, 0.5, 1.0, 2.5, 5.0, 7.5, 10.0 and 12.5 ppm P respectively.

2.4.2. Preparation of Combined Reagent

When making the combined reagent all reagents were allowed to reach room temperature before they were mixed. Sulphuric acid 2.5M (50 ml) were transferred on a plastic bottle, 15 ml of ammonium molybdate solution were added in the bottle and mixed, 30 ml of ascorbic acid solution was then added in the bottle and mixed and then 5 ml of potassium antimonyl tartrate solution added and mixed thoroughly. The reagent was stored in an opaque bottle. The combined reagent is stable for less than 8 hours so it was freshly prepared for each experiment.

2.5. Phosphate Extraction in Water Samples

A measured 25 ml of the water sample were transferred into the conical flask and 1ml of concentrated H_2SO_4 and 5 ml of concentrated HNO_3 added. The sample was digested until the solution becomes colorless (to remove the HNO_3). The flask was cooled and 20 ml of distilled water and 1 drop of phenolphthalein indicator was added and mixed. A drop of 1M NaOH was added to the sample solution acquired a faint pink tinge. The neutralized solution was filtered using a 0.45µm membrane filter to remove the turbidity of the particles. The filtered samples were transferred into a 100 ml volumetric flask and topped to the mark using distilled water. The P content of the digested sample was determined by using the molybdate colorimetric test (a combined reagent was prepared and 8 ml of it taken and added to 25 ml of the sample). Samples were analyzed using Uv-Visible spectroscopy at wavelength 880nm.

Preparation of extracting solution (0.5 M sodium bicarbonate, $NaHCO_3$) for phosphate in sediment

42 g of $NaHCO_3$ (AR) were dissolved in 1litre of distilled water and the pH adjusted to 8.5 using 1M NaOH (40 g of AR NaOH dissolved in 1litre of distilled water).

2.6. Phosphate Extraction from Sediment Samples

Oven-dried sieved sediment samples (2 mm) were accurately weighed (2.5 g) into shaking bottles and 50 ml of the extracting solution added to each bottle. The bottles were covered with aluminum foil and shaken on a mechanical shaker for 30 min. The contents were filtered through a Whatman No.42 filter paper. Activated charcoal was used to get a clear solution. After filtration, 20 ml of each sample filtrate were pipetted into a 50 ml volumetric flask and 5 ml 0.8 M boric acid added to each flask, 10 ml of the prepared ascorbic acid solution was added and topped up to the mark with distilled water and covered with aluminum foil and left for 1hr. The absorbance was read on the UV machine at a wavelength of 880nm. Phosphate concentration in water and sediment concentrations was calculated as shown.

$$P\left(mg\ Kg^{-1}\right)=\frac{\left(\left(a-b\right)/g\right)\times v\times f\times1000}{1000\times w}$$

Where a = absorbance of P in the sample, b = absorbance of P in the blank, g = gradient of the calibration curve, v = volume of the extracting solution, f = dilution factor and w = weight of the sample.

Stock solution: 1000 mg/L NO_3 - Place 7.223 g potassium nitrate (KNO_3) that had been oven-dried at 105ºC and cooled in a desiccator into 1000 ml volumetric flask and filled to the 1000ml mark with distilled water. Working standards were prepared by transferring 0, 2.0, 4.0, 6.0, 8.0, 10.0 ml of the standard solution (50µg ml^{-1}) into a clean labeled set of 100ml volumetric flasks. Each volumetric flask was filled to the mark with 0.5M K_2SO_4 extracting solution.

2.8. Nitrates Extraction from Water Samples

A water sample was filtered using a nylon 45 micro filter and 20 ml of the sample were placed in the conical flask and to this 1 ml of sodium salicylate solution which was freshly prepared was added. The bottles were then put in the oven and samples dried at a temperature of 95ºC. The resulting residues were dissolved quantitatively by adding 1 ml of concentrated sulphuric acid and the bottles swirled carefully while still warm. Next, 40 ml of distilled water was added and mixed. Finally, 7 ml of potassium - sodium hydroxide tartrate solution was added, mixed and the absorbance determined at a wavelength of 420nm.

2.9. Nitrate Extraction from Soil Samples

Oven-dried sieved sediment samples (2 mm) were accurately weighed (5.0 g) into plastic shaking bottles and to each of the sample 50 ml of 0.5 M Potassium Sulphate (K_2SO_4) extracting solution added. Aluminum foil was placed on each bottle and the contents are shaken for one hour. The contents were then filtered through the No.42 Whatman filter paper. 0.5 ml of the sample extract, blanks, and the standard series were transferred into suitably marked test tubes and 1.0 ml of salicylic acid added to each tube, mixed well and left to stand for 30 minutes. 10 ml of 4 M Sodium hydroxide was then added to each test tube mixed well and left for 1hour for full yellow color development. The absorbance was measured at wavelength 420 nm. A calibration curve was plotted. The values of the sample and the blank were read. The concentration of nitrates in water and sediment samples were calculated as shown

Calculation

$$NO_3\left(\mu g\ kg^{-1}\right)=\frac{\left(\left(a-b/g\right)\right)\times f\times1000}{w}$$

Where a = absorbance of NO_3 in the solution, b = absorbance of NO_3 in the blank, g = gradient of the calibration curve, v = volume of the extract, w = weight of fresh soil.

2.10. Quality Control and Assurance

Calibration curves were used to quantify the concentration and to show the regression analysis of nutrients. The standard calibration curves bracketed all quantified concentrations in sample digests and displayed r^2 values of > 0.99. Control samples (water and sediment) were obtained from a spring approximately 1 km inside Kakamega Forest, where there was no likely contamination. The control sample of water had concentrations below detection limits, and the sediment control sample gave background concentration of nitrates (0.6 mg/kg) and phosphates (0.1 mg/kg). Results from the repeatability experiment for phosphates and nitrates were done every fortnight on sediment samples from Savona sampling sites gave the following concentrations presented in Table 1:

Table 1. Repeatability tests results on phosphates and nitrates on Savona sample 2 mm sediment particles

Nutrients	PO_4^{3-}(mg/Kg)	NO_3^- (mgKg)
Week one	3.28 ± 0.16	1.43 ± 0.08
Week three	3.66 ± 0.21	1.56 ± 0.15
Week five	2.96 ± 0.36	1.58 ± 0.19
Week seven	3.37 ± 0.27	1.47 ± 0.12
Week nine	3.56 ± 0.24	1.51 ± 0.14

2.11. Data Analysis

The data derived from various determinations were subjected to statistical analysis using SPSS V20 at a 95% confidence level. The data obtained were analyzed using a one-way analysis of variance and significant differences accepted at P≤0.05. Post Hoc Turkey's test was used to separate means. The data obtained were also subjected to Pearson correlation analysis to test if the correlation was significant between phosphates and nitrates in water and sediment samples. The coefficient of variation was used to show how the concentrations varied within the sampling sites.

3. Results and Discussion

3.1. Physico-Chemical Parameters

The Physico-chemical parameters in all the eleven sampling sites in River Isiukhu are summarized in Table 3. Temperature is a factor of great importance for the aquatic ecosystem, as it affects the organisms, as well as the physical and chemical characteristics of water. The minimum temperature was 19.13 ± 071 ºC at Ichina and the maximum was 22.54 ± 0.53 ºC at Ekero (see Table 2). All the sampling sites had temperature levels within the permissible limits of 28 - 32 ºC set for drinking [18]. The coefficient of variation showed slightly significance difference among the studied sites. The temperature of river water may be influenced by vegetation cover around the sampling sites.

Dissolved oxygen is an indication of the physical, chemical and biological processes that are taking place in an aquatic system [19]. The minimum DO observe for the studied sites was 5.15 ± 0.08 mg/L Shirere sampling sites respectively and the maximum DO observe was 7.43 ± 0.22 mg/L at Ivakale sampling sites (see Table 2). The levels were slightly higher in some sampling

sites when compared to the permissible limits for drinking water [18]. The coefficient of variation showed a significant difference among the studied sites. The lower concentrations of DO obtained at Shirere were due to the addition of high organic contents from slaughterhouse around the sampling site resulting in oxygen depletion. Lower oxygen level in water indicates corrosion of chemical substances which raise the temperature level [20]. Increase dumping of waste especially domestic wastes have been found to increase concentration of nitrates and phosphates in water bodies resulting to increase in algae and plant growth in the aquatic ecosystem which subsequently depletes the oxygen level.

pH is usually monitored for assessments of aquatic ecosystem health, irrigation and drinking water sources, industrial discharges and surface water runoff. The lowest pH concentration was recorded at 7.05 ± 0.13 at Kimangeti and the highest concentration of 7.64 ± 0.06 at Rosterman (see Table 2). These values were within the permissible 6.5 - 8.5 set limits of drinking water [18]. The coefficient of variation showed a slight significant difference among the studied sites.

Salinity concentration was constant throughout the sampling sites recorded, 0.04 ± 0.01 pss and 0.05 ± 0.01 pss (see Table 2). It was observed that salinity concentration was constant from upstream to the downstream.

The range of conductivity obtained from River Isiukhu was 0.06 ± 0.01 μScm^{-1} 0.10 ± 0.01 μScm^{-1} at Ivakale and Mutono respectively. The coefficient of variation showed a statistically significant variation for electrical conductivity between the upstream, midstream and downstream. The highest level of electrical conductivity was observed at Ekero sampling sites. This indicates high levels of dissolved solids and subsequently the corresponding impurities in the water.

Turbidity, in most cases, is due to colloidal and extremely fine dispersions. In many aquatic systems, water clarity is determined by the abundance of suspended algae. Eutrophic systems (containing high nutrient concentrations) support large algal populations, which reduce the clarity of the water and increase its color. When the color of the water is affected it promotes microbial proliferation hence negatively affecting the water quality [20]. The lowest turbidity concentration recorded was 80.60 ± 2.97 NTU and 86.97 ± 9.42 NTU at Ichina and Kimangeti sampling sites and the highest concentration was 323.67 ± 213.82 NTU (see Table 2). The values obtained for River Isiukhu were above the permissible limits 5 NTU of drinking water [18]. The coefficient of variation showed a significant difference among the studied sites. The high concentration of turbidity might be due to the proximity of the studied sites to the towns and intensive agricultural areas, that receives agricultural runoff and domestic and municipal wastes. Higher concentrations of turbidity are usually as a result of the discharge of water as a result of floating sediments carried by the river from catchment areas and also from surface runoff. Thus, the entire river was generally polluted posing a great danger to aquatic lives and the people using it for domestic and irrigation purposes.

Table 2. physic-chemical parameters of different sampling site along River Isiukhu, Kenya

Sampling site	Temperature °C	CV (%)	Conductivity μScm^{-1}	CV (%)	DO mg/L	CV (%)	PH	CV (%)	Salinity pss	CV (%)	Turbidity NTU	CV (%)
Ichina	19.13 ± 0.71^e	3.69	$0.08 \pm 0.01^{a, b,c}$	13.04	$6.38 \pm 0.16^{a, b,c}$	2.55	$7.23 \pm 0.11^{b, c,d}$	1.57	0.04 ± 0.01^a	13.33	80.60 ± 2.97^b	3.69
Kimangeti	$19.98 \pm 0.49^{d, e}$	2.44	0.07 ± 0.01^c	8.31	$6.67 \pm 0.24^{a, b,c}$	3.53	7.05 ± 0.13^d	1.89	0.04 ± 0.01^a	15.72	86.97 ± 9.42^b	10.83
Ivakale	$20.56 \pm 0.39^{b, c,d}$	1.91	0.06 ± 0.01^c	22.16	7.43 ± 0.22^a	2.90	$7.40 \pm 0.02^{a, b,c,d}$	0.27	0.04 ± 0.01^a	15.72	116.00 ± 7.00^b	6.03
Senyende	$21.13 \pm 0.04^{b, c}$	0.19	$0.09 \pm 0.00^{a, b,c}$	4.10	$6.53 \pm 0.57^{a, b,c}$	8.68	$7.41 \pm 0.09^{a, b,c,d}$	1.22	0.04 ± 0.01^a	13.33	$147.00 \pm 12.00^{a, b}$	8.16
Savona	$21.29 \pm 0.05^{b, c}$	0.25	$0.07 \pm 0.00^{b, c}$	6.19	$5.72 \pm 0.39^{b, c}$	6.88	$7.51 \pm 0.10^{a, b,c}$	1.33	0.04 ± 0.01^a	13.33	$154.33 \pm 7.64^{a, b}$	4.95
Shirere	$19.98 \pm 0.53^{d, e}$	2.64	$0.09 \pm 0.01^{a, b,c}$	8.57	5.15 ± 0.08^c	1.62	$7.57 \pm 0.06^{a, b}$	0.77	0.04 ± 0.01^a	13.33	$154.33 \pm 8.50^{a, b}$	5.51
Rosterman	$20.38 \pm 0.29^{c, d}$	1.44	$0.09 \pm 0.01^{a, b,c}$	10.34	$6.62 \pm 0.48^{a, b,c}$	7.29	7.64 ± 0.06^a	0.80	0.04 ± 0.01^a	13.33	$143.00 \pm 5.00^{a, b}$	3.50
Mwimbatsiro	$20.73 \pm 0.04^{b, c,d}$	0.19	$0.08 \pm 0.00^{a, b,c}$	4.55	$7.29 \pm 0.85^{a, b}$	11.62	$7.42 \pm 0.24^{a, b,c,d}$	3.20	0.04 ± 0.01^a	13.33	$161.67 \pm 6.03^{a, b}$	3.73
Shibeye	$20.94 \pm 0.14^{b, c,d}$	0.68	$0.08 \pm 0.01^{a, b,c}$	18.09	$7.06 \pm 0.53^{ab, c}$	7.52	$7.45 \pm 0.13^{a, b,c}$	1.81	0.05 ± 0.01^a	12.36	$175.67 \pm 17.47^{a, b}$	9.95
Mutono	21.50 ± 0.04^b	0.19	0.10 ± 0.01^a	12.98	$6.73 \pm 0.64^{a, b}$	9.44	$7.14 \pm 0.21^{c, d}$	2.99	0.05 ± 0.01^a	12.36	$231.00 \pm 60.65^{a, b}$	26.26
Ekero	22.54 ± 0.53^a	2.35	$0.10 \pm 0.01^{b, c}$	13.98	$5.95 \pm 1.08^{a, b,c}$	18.11	$7.23 \pm 0.14^{b, c,d}$	1.88	0.04 ± 0.01^a	13.33	323.67 ± 213.82^a	66.06
(WHO, 2008)	<40		750		5.0 - 7.0		6.5 - 8.5				5	

Mean ± Standard error values followed by same letters within the same column are not significantly different ($p < 0.05$), CV = Coefficient of variation. The Physico-chemical concentrations having the same superscripts in the same column indicates that the concentrations are not significantly different.

Table 3. Pearson correlation coefficient (r) between physic-chemical parameters in all sampling stations in River Isiukhu, Kenya

	Temperature	Conductivity	DO	pH	Salinity	Turbidity
Temperature	1	0.405	0.895*	-0.064	0.319	0.885*
Conductivity	0.405	1	0.164	-0.007	0.707*	0.662*
DO	.895*	0.164	1	0.364	0.137	0.056
pH	-0.064	-0.007	0.364	1	0.234	0.096
Salinity	0.319	0.707*	0.137	0.234	1	0.485
Turbidity	.885*	.662*	0.056	0.096	0.485	1

* Correlation is significant at the 0.05 level (2 tailed).

Table 4. Concentration of phosphates and nitrates in water and sediment of River Isiukhu, Kenya

Sampling sites	PO_4^{3-}				NO_3^-			
	Water	CV (%)	Sediment	CV (%)	Water	CV (%)	Sediment	CV (%)
Ichina	1.18 ± 0.09^f	7.45	2.30 ± 0.03^e	1.30	0.15 ± 0.04^f	23.68	0.75 ± 0.02^g	3.06
Ivakale	$1.49 \pm 0.05^{e, f}$	3.41	2.50 ± 0.20^e	7.92	$0.23 \pm 0.04^{e, f}$	18.21	0.85 ± 0.03^g	3.15
Kimangeti	$2.22 \pm 0.08^{c, d}$	3.40	$2.95 \pm 0.22^{b, c, d, e}$	7.61	$0.21 \pm 0.04^{e, f}$	17.34	$1.33 \pm 0.06^{e, f}$	4.17
Senyende	$1.90 \pm 0.18^{d, e}$	9.53	$2.73 \pm 0.31^{c, d, e}$	11.44	0.30 ± 0.05^e	15.51	1.16 ± 0.05^f	4.57
Savona	$2.74 \pm 0.40^{a, b, c}$	14.57	$3.44 \pm 0.22^{b, c}$	6.26	$0.57 \pm 0.10^{b, c, d}$	17.39	$1.50 \pm 0.11^{c, d, e}$	7.16
Shirere	$3.12 \pm 0.07^{a, b}$	2.38	4.51 ± 0.30^a	6.65	$0.68 \pm 0.05^{a, b}$	7.25	1.93 ± 0.01^a	0.55
Rosterman	$2.75 \pm 0.01^{a, b}$	0.40	3.52 ± 0.33^b	9.35	$0.53 \pm 0.04^{c, d}$	7.42	$1.80 \pm 0.04^{a, b}$	2.17
Mwimbatsiro	$2.55 \pm 0.44^{b, c}$	17.19	$2.63 \pm 0.35^{d, e}$	13.37	0.50 ± 0.03^d	6.71	$1.42 \pm 0.14^{d, e}$	9.71
Shibeye	$2.66 \pm 0.41^{a, b, c}$	15.41	$2.95 \pm 0.25^{b, c, d, e}$	8.53	$0.61 \pm 0.04^{a, b, c, d}$	6.98	$1.54 \pm 0.10^{c, d}$	6.29
Mutono	$3.02 \pm 0.02^{a, b}$	0.76	$3.36 \pm 0.30^{b, c, d}$	8.96	$0.66 \pm 0.04^{a, b, c}$	5.64	$1.66 \pm 0.04^{b, c}$	2.48
Ekero	3.28 ± 0.05^a	1.51	4.18 ± 0.19^a	4.64	0.75 ± 0.03^a	3.69	1.93 ± 0.05^a	2.69

Mean ± Standard error values followed by same letters within the same column are not significantly different (p< 0.05). Nutrients concentration ha ving the same superscripts in the same column indicates that the concentrations are not significantly different.

3.1.1. Relationship between Physico-Chemical Parameters

Pearson correlation coefficient (r) revealed physic-chemical parameters showed some significant relationship with each other at p < 0.05 as shown in Table 3.

The results showed a positive significance relationship between temperature and DO (r = .895*), temperature and turbidity (r = .885*), salinity and conductivity (r = .707*) and turbidity and conductivity (r = .662*). A negative correlation was observed between temperature and pH (r = -0.064) and also between pH and conductivity (r = -0.007). A positive correlation was observed between temperature and conductivity (r = 0.405), temperature and salinity (r = 0.319), conductivity and DO (0.164), DO and pH (r = 0.364), DO and salinity (r = 0.137), DO and turbidity (r = 0.056), pH and salinity (r = 0.234), pH and turbidity (r = 0.096) and salinity and turbidity (r = 0.485) (see Table 4).

3.2. The Concentration of Phosphates and Nitrates in Water and Sediments

The results of phosphates and nitrates levels in sediments and surface water of the Isiukhu River at different sampling sites are presented in Table 4. Phosphates concentrations in river water samples were between 1.18 ± 0.09 mg/L to 3.28 ± 0.05 mg/ L at Ichina and Ekero sampling sites respectively as shown in Table 4 below. The results of the coefficient of variation showed that phosphate concentration varied significantly (0.40% - 17.19%) within all the sampling sites studied (see Table 4). The study found out that phosphate concentration s in River Isiukhu water was above 0.5 mg/l which is the permissible limit by [6] for drinking water in all the sampling sites studied. Phosphates concentration in river sediments was between 2.30 ± 0.03 mg/kg to 4.51 ± 0.31 mg/kg at Ichina and Shirere sampling sites respectively as shown in Table 4. The coefficient of variation result indicated that phosphate concentration in sediments varied significantly (1.30% - 13.37%) within all the sampling sites studied in River Isiukhu (see Table 4).

High phosphate concentration at Ekero water may be as a result of wastes coming from homes, animal wastes, car-washing activities because of the kind of soaps used along the river and agricultural activities from farms around River Isiukhu where fertilizers like NPK are extensively applied. Some sampling sites; Savona (2.74 ± 0.40 mg/L), Shirere (3.12 ± 0.07 mg/L), Rosterman (2.75 ± 0.01 mg/L), Mwimbatsiro (2.55 ± 0.44 mg/L), Shibeye (2.66 ± 0.41 mg/L), Mutono (3.02 ± 0.02 mg/L) and Ekero (3.28 ± 0.05 mg/L) (see Table 4) had phosphates concentration in water slightly above 2.2 mg/L which is the accepted limits [21]. These high phosphate levels observed at these sampling sites maybe because of surface runoffs from agricultural activities which involve heavy use of phosphates-based fertilizers and livestock waste in the surrounding areas along River Isiukhu. It can also be coming from laundry activities being performed by residents around those sampling sites using phosphate-containing detergents. If phosphate levels continue increasing in River Isiukhu with time, there is likely to be eutrophication which results in problems like excessive growth of water hyacinth. Also, these eutrophications result to DO depletion. The amount of phosphates found in an aquatic ecosystem depends on both the external phosphates load and its release and retention in the sediments. This is because sediments act as a sink where phosphates can be stored, and as a source of phosphates in the overlying aquatic ecosystem.

Nitrates concentrations in river water were between 0.15 ± 0.04 mg/l to 0.75 ± 0.03 mg/l at Ichina and Ekero sampling sites respectively as shown in Table 4. The coefficient of variation result showed that nitrate concentration in water varied significantly (3.69% - 23.68%) within all the sampling sites studied. From the study, it was observed that nitrate concentrations in River Isiukhu were below the permissible limits by [6]. Nitrates concentrations in sediment were between 0.75 ± 0.02 mg/kg to 1.93 ± 0.05 mg/kg at Ichina and Ekero sampling sites respectively as shown in Table 4. From the coefficient of variation obtained for nitrate concentration in sediment, it showed that the concentration varied significantly (0.55% - 9.71%) within all the sampling sites studied along River Isiukhu. In this study nitrates concentration in River, Isiukhu water was below the acceptable limits of 10 mg/L [22].

Progressive increase in nitrates levels in an aquatic ecosystem is a result of extensive use of man-made fertilizers and the discharge of wastes especially those from animal farming into the aquatic ecosystem [23]. The

nitrates found in the water samples from River Isiukhu could have come from anthropogenic activities like agricultural farming where nitro-phosphate fertilizers are used in the farmlands along the River Isiukhu, domestic effluents discharges and emissions from combustion engines which are discharged into the aquatic ecosystem through surface runoff. This is supported by the study by [24] found out that raw waste effluent from sewage treatment plants usually has high concentrations of nitrogenous wastes which can result in the rapid growth and increase of bacterial populations. During sampling periods domestic waste like excreta and urine were observed to be abundant along with River Isiukhu sampling sites. The farming activities around the sampled areas could also have contributed to the nitrate levels in sediments. In pregnant women and infants elevated levels of nitrates result in methemoglobinemia or 'blue-baby-syndrome' [25]. This is a very bad known health condition that can result in death.

Lower levels of nitrates were obtained by [11] during their study on the levels of nitrate ions in water from selected wells and points along Kimondi River, Nandi County, Kenya, which they found to range from 0.18 mg/L to 0.66 mg/L.

Elevated levels of both phosphates and nitrates were observed at the midstream and downstream while the lower concentrations were observed at the upstream. The lower levels of nutrients at the upstream can be attributed to the fact that the human population density at the upstream is low therefore the amount of domestic waste discharge into the river is low. Nitrates and phosphates which are responsible for eutrophication are usually produced in an aquatic ecosystem through organic matter decomposition [26,27]. Figure 2 and Figure 3 below show the trend in which phosphates and nitrates were accumulating in water and sediment as one moves from the upstream, midstream and downstream along River Isiukhu.
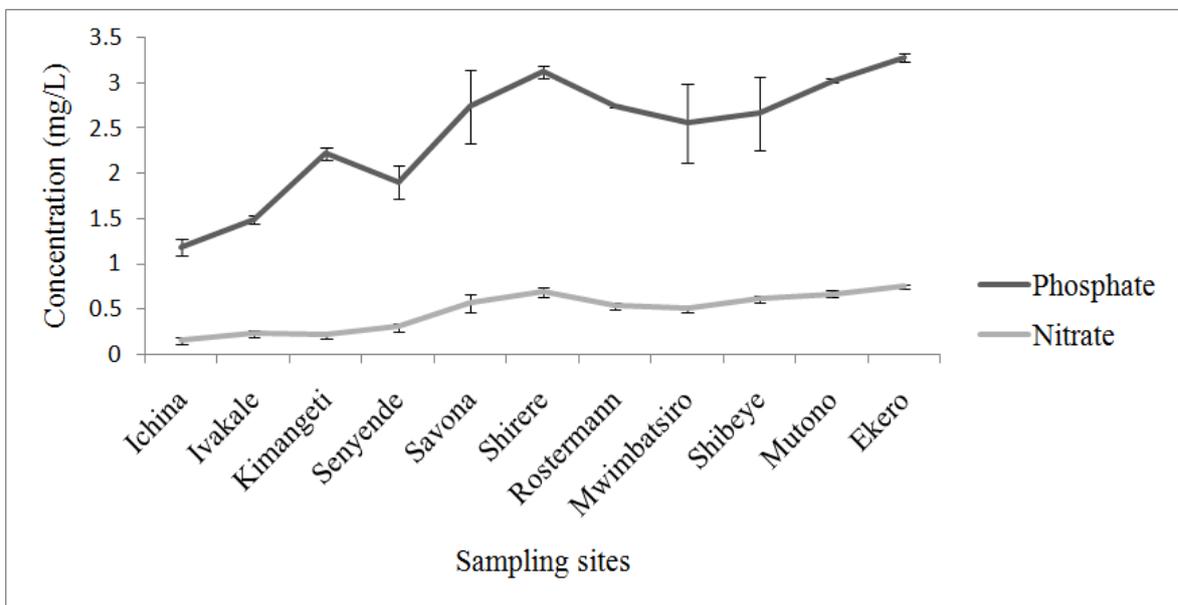

Figure 2. Phosphates and nitrates concentration in River Isiukhu water
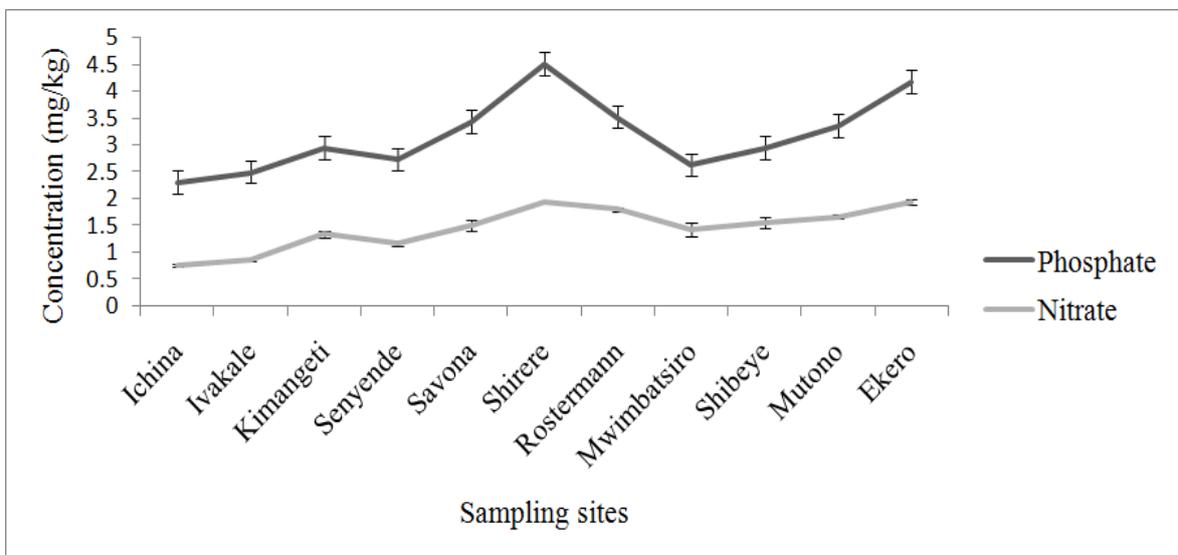

Figure 3. Phosphates and nitrates concentration in River Isiukhu sediment

Phosphates and nitrates showed similar trends in their concentration along River Isiukhu (in sediment and water) as observed in Figure 2 and 3. The phosphates and nitrates concentration increased along the river with the midstream showing higher concentrations compared to the upstream

3.2.1. Correlation Studies of Phosphates and Nitrates in Water and Sediment of River Isiukhu

The relationship between phosphates and nitrates in both water and sediment were analyzed and found to have a strong positive correlation r = 0.942, p = 0.000 and r = 0.891, p = 0.000 respectively, indicating that both originate from similar sources or are influenced by the same factors such as agriculture. This indicated that P and N have similar factors affecting their concentrations in a River. Phosphorus and nitrogen originate mostly from agricultural activities. The Isiukhu catchment is characterized by agricultural activities with the growth of sugarcane, maize, and beans dominating the upper stream, midstream and downstream. These crops require the intensive application of fertilizers such as Diammonium phosphate (DAP), Calcium Ammonium Nitrate (CAN), and Urea therefore, agriculture is the main source of nitrogen and phosphorus [28].

4. Conclusion and Recommendation

Levels of physico-chemical parameters pH, temperature, electrical conductivity, dissolved oxygen and salinity were all within the accepted guidelines for drinking water by [18] except for turbidity which was slightly higher. Generally, the physicochemical parameters increased down the river, midstream showing elevated levels.

Levels of nitrates from water samples within all sampling sites from River Isiukhu were below the acceptable limits for drinking water by [6] but phosphate concentrations were above the permissible limits by [6] for drinking water. Therefore, sustainable farming methods should be encouraged to avoid an influx of phosphates into the aquatic ecosystem and impact the quality of the domestic water system. Research should be done in the aquatic plants that are found along the River Isiukhu to determine whether similar concentrations of nitrates and phosphates are present. More research work needs to be undertaken during different seasons of the year to ascertain phosphates and nitrates in the aquatic ecosystem and the variations in the concentration during different times of the year. There is an urgent need to properly manage wastes from the Kakamega town, and other upcoming urban centers. In addition, regulation of activities such as use of fertilizers, which can cause emission nitrates and phosphates within the study area should be done.

Acknowledgments

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