British Journal of Applied Science & Technology
18(3): 1-16, 2016; Article no.BJAST.30209
ISSN: 2231-0843, NLM ID: 101664541

SCIENCEDOMAIN *international*
www.sciencedomain.org

Spatial and Seasonal Variation of Selected Water Quality Parameters in Chania River Catchment, Kenya

P. K. Kimani[1*], G. T. Thiong'o[1] and J. K. Mwangi[2]

[1]*Department of Chemistry, Jomo Kenyatta University of Agriculture and Technology, Kenya.*
[2]*Department of Civil, Construction and Environmental Engineering, Jomo Kenyatta University of Agriculture and Technology, Kenya.*

Authors' contributions

This work was carried out in collaboration between all authors. Authors JKM and GTT designed and supervised the study. Author PKK performed the statistical analysis, wrote the protocol, wrote the first draft of the manuscript and managed literature searches for the MSc project. Author PKK managed the analyses of the study, literature searches and statistical analyses. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/BJAST/2016/30209
Editor(s):
(1) Manjinder Singh, Department of Biological and Agricultural Engineering, University of Georgia, Georgia, USA.
Reviewers:
(1) Suheyla Yerel Kandemir, Bilecik University, Turkey.
(2) Kies Fatima, University of Milan-Bicocca, Italy.
Complete Peer review History: http://www.sciencedomain.org/review-history/17265

Original Research Article

Received 25th October 2016
Accepted 2nd December 2016
Published 17th December 2016

ABSTRACT

River systems in Kenya have been under threat from anthropogenic based pollution for a long time. River Chania which originates from the Aberdare Ranges and flows through highly productive agricultural land towards Thika town is one of these rivers. It is the only source of water for Thika town and parts of Machakos County. Non-point pollution from agricultural lands and point pollution resulting from settlement have led to water quality degradation in the river. The aim of this study was to investigate water quality in River Chania, assess types of pollution from the catchment and propose mitigation measures. Water sampling and analysis was done in accordance with the standard methods of the American water works association and statistical packages used for statistical analysis. Sampling was done in both wet and dry seasons and on seven different locations along a selected stretch of the river. Physical parameters were determined onsite using

**Corresponding author: E-mail: paulkimani90.pk@gmail.com;*

portable meters while anions; SO_4^{2-}, NO_3^--N, NO_2^--N, PO_4^{3-} and Cl^- were determined using spectrophotometric methods. Metals analyzed were; Na, K, Ca, Mg, Mn, Fe, Zn, Cu, Pb and Cd using Atomic absorption spectrophotometer. Turbidity was the highest recorded parameter during the wet season with a mean of 169.4 NTU and its strong correlation with 75% of the parameters (Pearson's $r > 0.5$) meant that farming in the upper catchment had an effect on nitrate and phosphate among others leaching into the river during the wet season. In summary, 45% of the parameters showed significant seasonal variation ($p<0.5$) with mean concentration of 50% of the parameters being higher during the dry season. Turbidity, nitrate, nitrite, manganese, iron and lead exceeded WHO guidelines indicating poor water quality in the catchment. As domestic and industrial waste water contribute to point pollution downstream, unsustainable farming practices give rise to significant nonpoint pollution upstream of the river. The study recommends strict enforcement of environmental laws to curb point pollution and an incentive based approach to reduce non-point pollution with public enlightenment on how to control anthropogenic activities.

Keywords: Chania River; correlation; metals; sampling; significance; variation; water quality.

1. INTRODUCTION

What has man done to the environment is a question well reciprocated by what the environment is currently doing to man. Water pollution through anthropogenic sources such as agriculture and urbanization has been on an increase and as water quality degradation occurs so will water unavailability and water borne diseases become rampant [1]. Poor water quality arising from pollution causes ailments such as cholera, jaundice, gastro-enteritis, infectious hepatitis and many others which is why factual information about water quality status is necessary [2].

Water is a key resource that supports all living things in the biosphere and is core for sustainable growth of an economy [3]. Only 2.5% of the world's water is fresh and only 0.01% of this is present in lakes, rivers and soils [4]. Demand from these freshwater resources is generated by urbanization, population growth, increasing production and consumption along with industrialization [5]. Water pollution from anthropogenic sources reduces usability of these freshwater sources further. Good water quality, together with adequate quantity of water, are necessary for achieving Sustainable Development Goals for health, food and water security hence it is of concern that water pollution has worsened since the 1990s in the majority of Africa [5,6].

Kenya's growing and rapidly urbanizing population has put pressure on its river systems. In 1992, the country had 647 m^3 of renewable freshwater resource per capita per annum which has declined by more than 200 m^3 per capita per annum to date [7]. Past studies have focused more on the urbanization aspect of pollution such as sulfamethoxazole and other antibiotics in Nairobi River and high concentration of coliform bacteria in Sosiani River [8,9]. Rivers flowing in catchment areas are supposedly thought to be clean from effects of pollution as most of them flow in a rural settings free from the so called urban based pollution.

River catchments are ecosystems which are a source of water provisioning and regulating ecosystem services. There exists an ecosystem-food-water-energy nexus which makes regular assessments of catchment areas necessary to sustain food, water and energy production [10]. Chania River catchment is one of the rich agricultural hubs in Kenya and faces eminent threat from both point and non-point pollution. Limited literature is available on water quality along River Chania which is the main river flowing in this catchment. The river is important as it caters for the highly agricultural areas upstream and at the same time for water supply to the increasing population of Thika and Nairobi towns. Kenya's economy is dependent on agriculture and as population increase so does food productivity which results in putting a strain on land use to cater for food production and available water resources for irrigation [11]. Downstream land has been converted to cater for urbanization and as a result more farming mushroom upstream in this catchment. Land use changes coupled with poor farming practices increase water pollution in rivers originating from this catchment areas and impacts high cost for water treatment and poor health to downstream water users [12,13].

1.1 Water Pollution

There are two ways in which a river can get polluted. One is through natural pollution as a result of leaf falls, decaying animals, fresh erosion of banks, run-off of silt, accumulation of extraneous vegetable matter and acid discharge of pit bogs. The other way is through anthropogenic sources such as industrial waste water, domestic sewage, agriculture, etc. Anthropogenic sources can further be divided into point and non-point sources of pollution [14].

Any identifiable source from which pollutants are discharged e.g. a pipe, factory, industrial outlets or waste water treatment plants are regarded to as point sources of pollution. Nonpoint sources (NPS) are sources that can be harder to identify such as runoffs from agricultural land and mining sites termed as rural NPS. Urban NPS may include runoffs from roofs, streets and construction sites [15]. Strict guidelines are put in place by environmental control bodies such as the national environmental management agency (NEMA) in Kenya to protect rivers from point based pollution. However this type of command and control measure fails miserably in addressing non-point based pollution.

In this study seasonal and spatial variations of water quality parameters in River Chania and two of its main tributaries, Kimakia and Karimenu were studied. The study aimed to investigate the current state of water quality parameters, how changes in water quality occurs between the seasons and how land use changes affect water quality. The results also showed the type of water pollution in the catchment. This was necessary since point and non-point based pollution require different mitigation measures for effective action on water quality degradation.

2. MATERIALS AND METHODS

2.1 Study Area

River Chania originates from Aberdare water tower which is the second largest water tower in Kenya. Aberdare ranges are located in central province of Kenya which consists of 160 Km long mountain range of upland north of Kenya's capital Nairobi with an elevation of 3500 meters above sea level. It is a source of major rivers such as River Tana and Athi. River Chania is a tributary of River Tana. River Chania flows through highly productive agricultural land and a forested area. The catchment comprises of three distinct land use zones.

The upper most part consist of a protected forested zone bordered by a tea growing area. The second zone consists of coffee growing area and due to recent falling coffee prices, most of the farmers are converting land from coffee growing to mixed subsistence farming with the major shift being towards pineapple growing. The terrain is steep in this area and most of farming is done on this land. The third zone consists of settled areas near Thika town whereby farming is minimal. In this zone, increasing population and urbanization has led to conversion of previous agricultural land into that for housing development. There is no existing sewerage system provided by the municipality for this estate. Thika Town is part of this zone and depends on water abstracted from River Chania for its water supply. The town also acts as an industrial hub for the capital city, Nairobi. Demographic growth in the past years shows an increase from around 18,387 people in the year 1969 to approximately 136,917 people settled in the urban areas of the district as per the year 2009 [16]. This growth is projected to be greater than 200,000 people living in Thika town all who will be dependent on water supply from this river. Fig. 1 shows a map digitized through use of ArcGIS at the Jomo Kenyatta University of Agriculture and Technology GIS labs. The map shows places where water was sampled marked in a star shape and showing the three rivers marked in blue.

2.2 Sampling and Analytical Procedures

Sampling was done for wet and dry season in November, 2015 and March, 2016 respectively. Sampling point selection was based on non-probability judgment sampling to capture distinct land use changes which were known beforehand. Water samples were collected in accordance to EPA guidelines in order to obtain a representative sample [17]. Sample transport, preservation and maximum holding periods proposed by the EPA guidelines were adhered to. Seven sampling stations were selected and are described in the Table 1.

Physical and Chemical analysis of the samples was done as per standard procedures prescribed by American Public Health Association [18]. Global reference was recorded for each sampling point through global positioning system (GPS). Twenty water quality parameters were determined and the methods used for estimation are as described on Table 2. The reagents used were analar grade and double distilled water was used to avoid contamination. Potable meters were used to measure physical parameters, an ultraviolet/ visible (UV/VIS) spectrophotometer (Shimadzu 1800) was used for the analysis of anions while total metals were analyzed by a Shimadzu 6200 Atomic Absorption Spectrophotometer (AAS) while Sodium and potassium were analyzed by a Flame Photometer AFP 100. Table 2 shows the parameters that were analyzed and the analytical method used for the analysis.

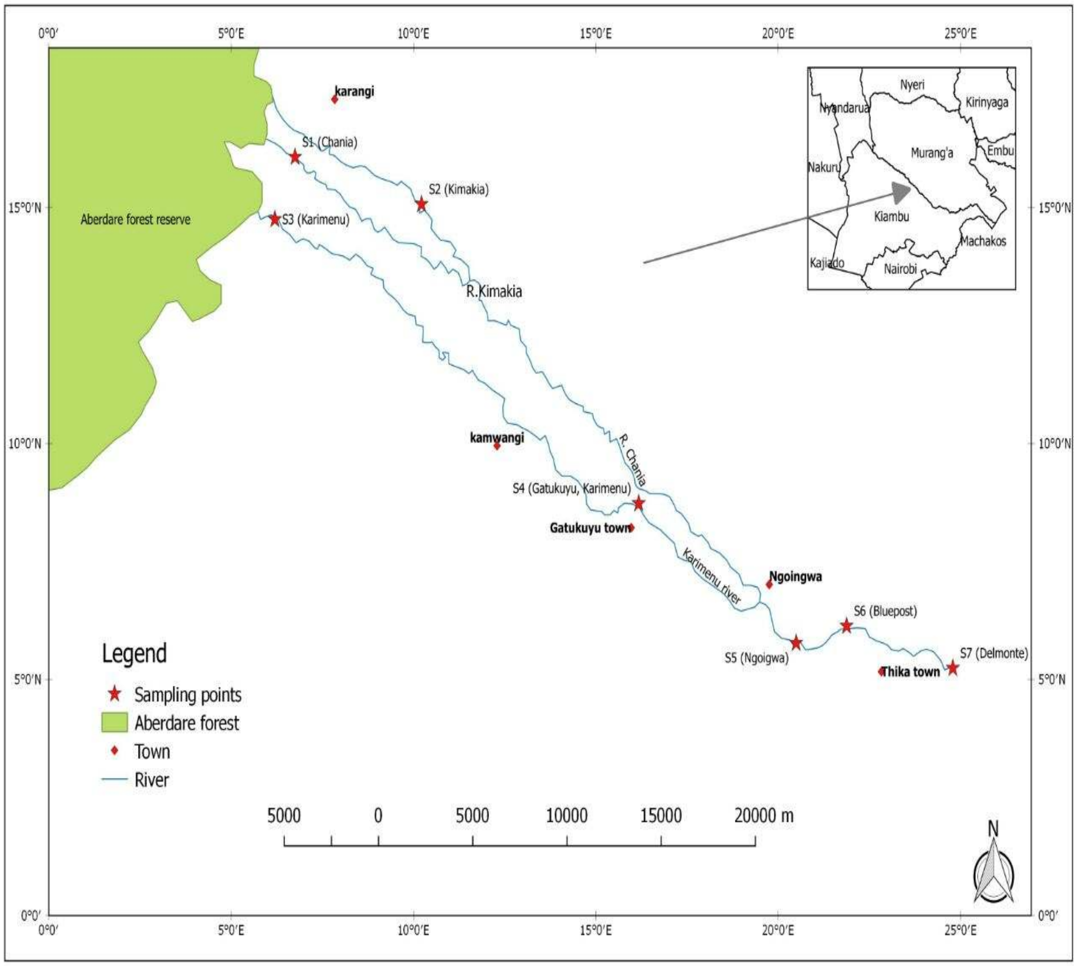

Fig. 1. Map showing sampling points and the area of study [19]

Table 1. Description of the study sites and their codes

Stations	Description
S1	River Chania at Matara bridge, upstream just after the forested area in the tea zone
S2	River Kimakia at Gatura Bridge, located upstream just below Gatura town.
S3	River Karimenu at Matara Bridge, upstream just after the forested area in the tea zone
S4	River Karimenu at Gatukuyu Bridge, downstream and after the coffee zone.
S5	River Chania at Ngoigwa Bridge, on the onset of Ngoigwa estate.
S6	River Chania at Blue post Bridge, After Ngoigwa estate just before confluence with Thika River and before intake weir of Thika water treatment.
S7	River Chania at Delmonte Bridge, a few kilometers after Thika town.

**S = Station*

Table 2. Water quality parameters, units and analytical methods of estimation

Parameter	Abbreviation	Units	Analytical method
Temperature[a]	T	ºC	Thermometer
Conductivity[a]	E.C	µS/cm	Conductivity Meter
Total dissolved solids[a]	TDS	Mg/l	TDS meter
Turbidity[a]	Turbidity	NTU	Turbidity Meter
H^+ ion concentration	pH	-	pH meter
Nitrate[b]	NO_3^-	mg/l	Screening method
Nitrite[b]	NO_2^-	mg/l	Sulphanilic acid method
Total Phosphate[b]	PO_4^{3-}	mg/l	Ascorbic acid method
Sulphate[b]	SO_4^{2-}	mg/l	Turbidimetric method
Chloride[b]	Cl^-	mg/l	Mercuric Thiocyanate method
Total Metals[c]	Na and K	mg/l	Atomic emission spectroscopy
Total Metals[c]	Mg, Ca, Mn, Fe, Zn, Cu, Pb, Cd	mg/l	Atomic absorption Spectroscopy

**S = Siemens,* NTU=Nephlo Turbidimetric Units, *a=physical parameters, *b=anions, *c=cations*

2.3 Statistical Method

Analysis for each parameter was performed in triplicate and the observations for each sampling station were expressed as *mean ± S.D* (Standard Deviation) to show precision and calculated via IBM Statistical Package for Social Sciences (SPSS, v.23). A two tail paired t-test was done to test for seasonal variation that was significant at a 95% confidence interval ($p=0.05$). Spatial variations for each season were tested by use of one way analysis of variance (ANOVA) at 95% confidence level. A probability level of $p<0.05$ was considered statistically significant. Karl Pearson's correlation coefficient, r, for wet season data was calculated to show parameters that were strongly correlated ($r>0.5$) *to each other*. Standard error of the mean difference was calculated to inference data to the whole population.

3. RESULTS AND DISCUSSION

A summary of the raw data for physical parameters and anions is presented on Table 3 for both seasons and representing each sampling station. Table 4 consists of raw data for the metal ion concentration in the river water for each sampling station and for both seasons. The data is represented as mean ± SD (n=3).

3.1 Temperature and pH

As per the results on table, the range for pH was between 7.00±0.08 to 7.63±0.05 and 6.83±0.01 to 7.63±0.03 (Table 3) during the wet and dry season respectively. All sampling points were within the range of 6.5 to 8.5 provided by the WHO. Seasonal variations for pH was statistically insignificant while spatial variations were significant showing slightly alkaline water in the agricultural area (S1, S2) and in the town area (S7) (Table 5 and Table 6). Inputs from fertilizer use, domestic and industrial waste water is cause for this during wet season [20]. pH was strongly correlated to nitrate concentration ($r=0.82$) for the wet season and hence higher pH can be associated to surface run offs carrying nitrogenous fertilizer. Temperature ranged between 16.83±0.26℃ to 20.30±0.22℃ and 18.87±0.05℃ to 23.63±0.05℃ during the wet and dry season respectively. Seasonal variations for temperature were statistically significant and this can be associated to the mean daily temperatures for the dry season being higher. Spatial variations for temperature were significant as a result of altitude at which the sample was taken, time of day and weather condition played part on temperature variation.

Table 5 and Table 6 show the results of a two-tail paired t-test and a one-way ANOVA to test for significance seasonal and spatial variations respectively. A probability level of less than 0.05 was considered to be significant for both tests and also whereby the $F_{calculated}$ and $T_{calculated}$ were greater than the $F_{critical}$ and $T_{critical}$ respectively. The mean difference (MD) shows variation between the two seasons for each sampling point. The greater it is the larger the difference for each sampling station between the two seasons. Standard deviation of the difference (SDD) shows the variation between the sampling station and the mean difference. Greater SDD means higher spatial variation of each pair of sample. The standard error of the mean difference in this case inferences the results to the whole population whereby, if multiple samples were to be taken again for both seasons, they would have the same standard deviation as the SEMD indicating that they would vary between the two seasons in a way described by the SEMD value.

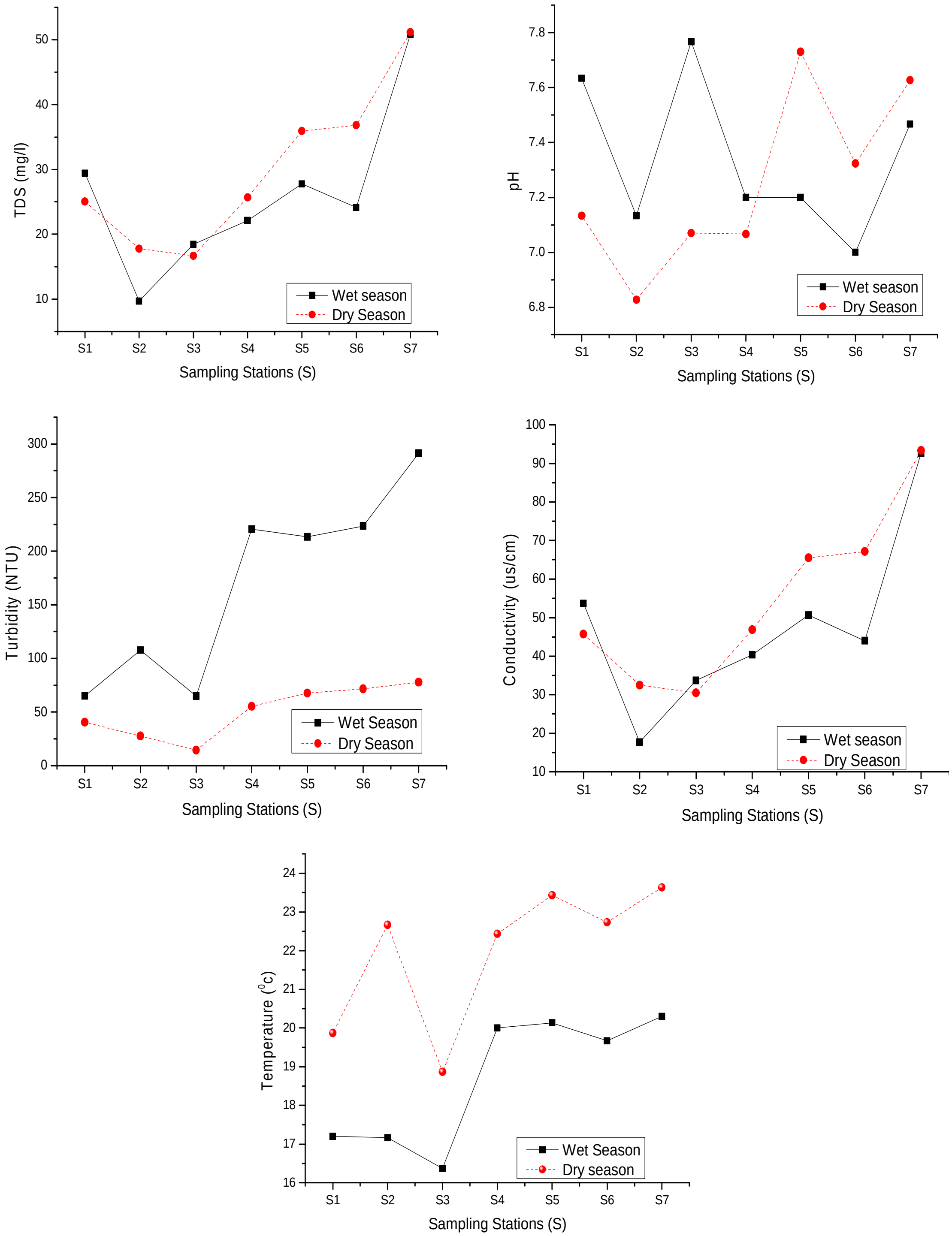

Fig. 2. Line graphs showing trends in spatial and seasonal variations for physical parameters and pH

Table 3. Showing physical and chemical anion parameters concentration

Parameter		S1	S2	S3	S4	S5	S6	S7	WHO	KEBS
Temperature (℃)	WET	17.20 ±0.36	17.20 ±0.12	16.36 ±0.26	20.00 ± 0.16	20.13 ± 0.05	19.67 ± 0.25	20.30 ± 0.22	-	-
	DRY	19.87 ±0.05	22.67 ±0.12	18.87 ± 0.05	22.43 ± 0.09	23.43 ± 0.05	22.73 ± 0.05	23.63 ± 0.05		
Conductivity (µS/cm)	WET	53.67 ±0.94	17.67 ±0.47	33.67 ±1.25	40.33 ±0.47	50.67 ± 1.7	44.00 ± 1.63	92.67 ± 3.09	*500-5000*	*1000*
	DRY	45.70 ±0.37	32.47 ±0.26	30.43 ±0.12	46.83 ±0.21	65.50 ± 0.22	67.13 ± 0.25	93.33 ± 0.12		
TDS (mg/l)	WET	29.42 ±0.52	9.68 ±0.26	18.45 ±0.68	22.11 ±0.26	27.77 ± 0.93	24.12 ± 0.90	50.80 ± 1.70	*1000*	*1500*
	DRY	25.05 ±0.21	17.79 ±0.14	16.68 ±0.07	25.67 ±0.11	35.90 ± 0.12	36.8 ± 0.14	51.17 ± 0.07		
Turbidity (NTU)	WET	**65.07 ±1.97**	**107.7 ±1.06**	**64.83 ±2.30**	**220.57 ±0.78**	**213.33 ±2.95**	**223.43 ±3.31**	**291.33 ±2.62**	*5*	*5*
	DRY	**40.43 ± 3.4**	**27.7 ±0.33**	**14.5 ±1.47**	**55.27 ±1.20**	**67.67 ±3.68**	**71.57 ±1.48**	**77.73 ±1.44**		
pH	WET	7.63 ± 0.05	7.13 ±0.05	7.77 ±0.05	7.20 ±0.08	7.20 ±0.08	7.00 ±0.08	7.47 ±0.09	*6.5 – 8.5*	*6.5 – 8.5*
	DRY	7.13 ± 0.03	6.83 ±0.01	7.07 ±0.01	7.07 ±0.01	7.73±0.06	7.32±0.02	7.63±0.03		
Nitrite (NO_2^-) mg/l	WET	0.17 ± 0.00	0.15 ± 0.00	**0.22±0.00**	**0.28±0.00**	**0.24±0.00**	**0.22±0.00**	**0.27±0.01**	*0.2 - 3*	*0.2 - 3*
	DRY	**0.28 ± 0.00**	**0.23 ± 0.00**	**0.26±0.00**	**0.30±0.00**	**0.29±0.00**	**0.24±0.00**	**0.49±0.00**		
Nitrate (NO_3^-) mg/l	WET	2.57 ± 0.01	1.45 ± 0.00	2.01±0.01	1.3±0.00	1.14±0.00	1.12±0.00	1.43±0.00	*50*	*10*
	DRY	0.72 ± 0.00	0.64 ± 0.00	0.70 ± 0.00	0.77±0.01	0.77±0.00	1.02±0.00	1.23±0.00		
Phosphate (PO_4^{3-}) mg/l	WET	0.04 ± 0.00	0.23 ± 0.00	0.33 ± 0.00	1.68 ±0.00	2.27 ±0.00	1.38 ±0.00	2.45 ±0.01	*5*	*5*
	DRY	0.33 ± 0.02	0.18 ± 0.00	0.01 ± 0.00	0.08 ±0.00	0.23 ±0.00	2.29 ±0.01	0.73 ±0.02		
Sulphate (SO_4^{2-}) mg/l	WET	46.33 ± 0.18	23.20 ± 0.18	38.80 ± 0.17	38.50±0.35	49.70±0.16	44.22±0.30	63.87±0.35	*250*	*400*
	DRY	63.08 ± 0.68	27.22 ± 0.62	35.25 ± 0.54	72.32±0.41	40.31±0.87	49.55±0.95	82.22±0.87		
Chloride (Cl^-) mg/l	WET	4.84 ± 0.00	2.41 ± 0.00	4.13 ± 0.00	5.16±0.00	4.6±0.00	4.39±0.00	6.12±0.00	*250*	*250*
	DRY	3.25 ± 0.03	2.45 ± 0.06	1.89 ± 0.01	2.06±0.01	4.27±0.01	4.72±0.09	5.41±0.01		

**Bolded values are values that were above the recommended limit by WHO. *KEBS = Kenya Bureau of Standards*

Table 4. Showing metal ion concentration for the two seasons

Parameter	Season	S1	S2	S3	S4	S5	S6	S7	WHO	KEBS
Na^{+} mg/l	WET	3.78 ±0.01	1.08 ±0.02	3.29 ±0.01	4.02 ±0.01	5.00 ±0.01	4.27 ±0.01	5.24±0.02	*200*	*200*
	DRY	4.41 ±0.01	1.71 ±0.15	3.11 ±0.01	4.41 ±0.01	5.05 ±0.01	6.35 ±0.01	6.46 ±0.15		
K^{+} mg/l	WET	1.57 ±0.09	0.33 ±0.01	1.24 ±0.01	1.57 ±0.09	1.57 ±0.65	1.83 ±0.09	2.09 ±0.13	*30*	-
	DRY	2.08 ±0.05	0.85 ±0.05	1.64 ±0.01	1.60 ±0.05	1.64 ±0.01	2.53 ±0.05	1.33 ±0.01		
Ca^{2+} mg/l	WET	1.04 ±0.21	0.82 ±0.15	1.82 ±0.50	2.99 ±0.24	4.59 ±0.46	5.05 ±0.54	6.91 ±0.21	*250*	*250*
	DRY	1.35 ±0.43	2.02 ±0.4	2.54 ±0.24	3.84 ±0.08	4.61 ±0.21	4.53 ±0.12	6.57 ±0.18		
Mg^{2+} mg/l	WET	0.89 ±0.01	0.52 ±0.01	0.43 ±0.05	0.73 ±0.01	0.96 ±0.02	1.17 ±0.03	2.02 ±0.02	*50*	*100*
	DRY	0.65 ±0.10	0.80 ±0.01	0.51 ±0.05	1.06 ±0.01	1.41 ±0.01	1.32 ±0.01	1.72 ±0.01		
Mn^{2+} mg/l	WET	0.19 ±0.01	0.29 ±0.01	0.31 ±0.02	**0.64 ±0.03**	**0.97 ±0.01**	**0.86 ±0.02**	**1.94 ±0.02**	*0.4*	*0.1*
	DRY	0.11 ±0.01	0.20 ±0.01	0.11 ±0.02	0.20 ±0.05	0.09 ±0.01	0.09 ±0.03	0.21 ±0.01		
Fe^{3+} mg/l	WET	**5.79 ±0.15**	**9.40 ±0.15**	**6.12 ±0.33**	**12.59 ±0.39**	**16.57 ±0.44**	**36.54 ±1.62**	**49.99 ±0.61**	*0.3*	*0.3*
	DRY	**2.71 ±0.18**	**1.45 ±0.35**	**1.67 ±0.11**	**3.40 ±0.23**	**1.24 ±0 .17**	**1.31 ±0.12**	**1.95 ±0.33**		
Zn^{2+} mg/l	WET	0.33 ±0.00	0.24 ±0.00	0.28 ±0.00	0.25 ±0. 00	0.26 ±0.00	0.31 ±0.00	0.33 ±0.00	*3*	*5*
	DRY	0.09 ±0.00	0.09 ±0.00	0.08 ±0.00	0.09 ±0.00	0.10 ±0.00	0.10 ±0.00	0.09 ±0.00		
Cu^{2+} mg/l	WET	0.16 ±0.02	0.16 ±0.02	0.17 ±0.02	0.16 ±0. 01	0.20 ±0.18	0.18 ±0.21	0.21 ±0.01	*1-2*	*0.1*
	DRY	0.03 ±0.00	0.05 ±0.02	0.02 ±0.02	0.13 ±0.01	0.14 ±0.02	0.12 ±0.01	0.11 ±0.03		
Pb^{2+} mg/l	WET	<DL	<DL	<DL	<DL	**0.34 ±0.02**	<DL	**0.47 ±0.03**	*0.01*	*0.05*
	DRY	<DL	<DL	<DL	<DL	**0.40 ±0.02**	**0.49 ±0.04**	**0.59 ±0.02**		
Cd^{2+} mg/l	WET	<DL	<DL	<DL	<DL	<DL	<DL	<DL	*0.003*	*0.005*
	DRY	<DL	<DL	<DL	<DL	<DL	<DL	<DL		

Bolded values are values that were above the recommended limit by WHO
<DL = below detection limit, KEBS = Kenya Bureau of Standards

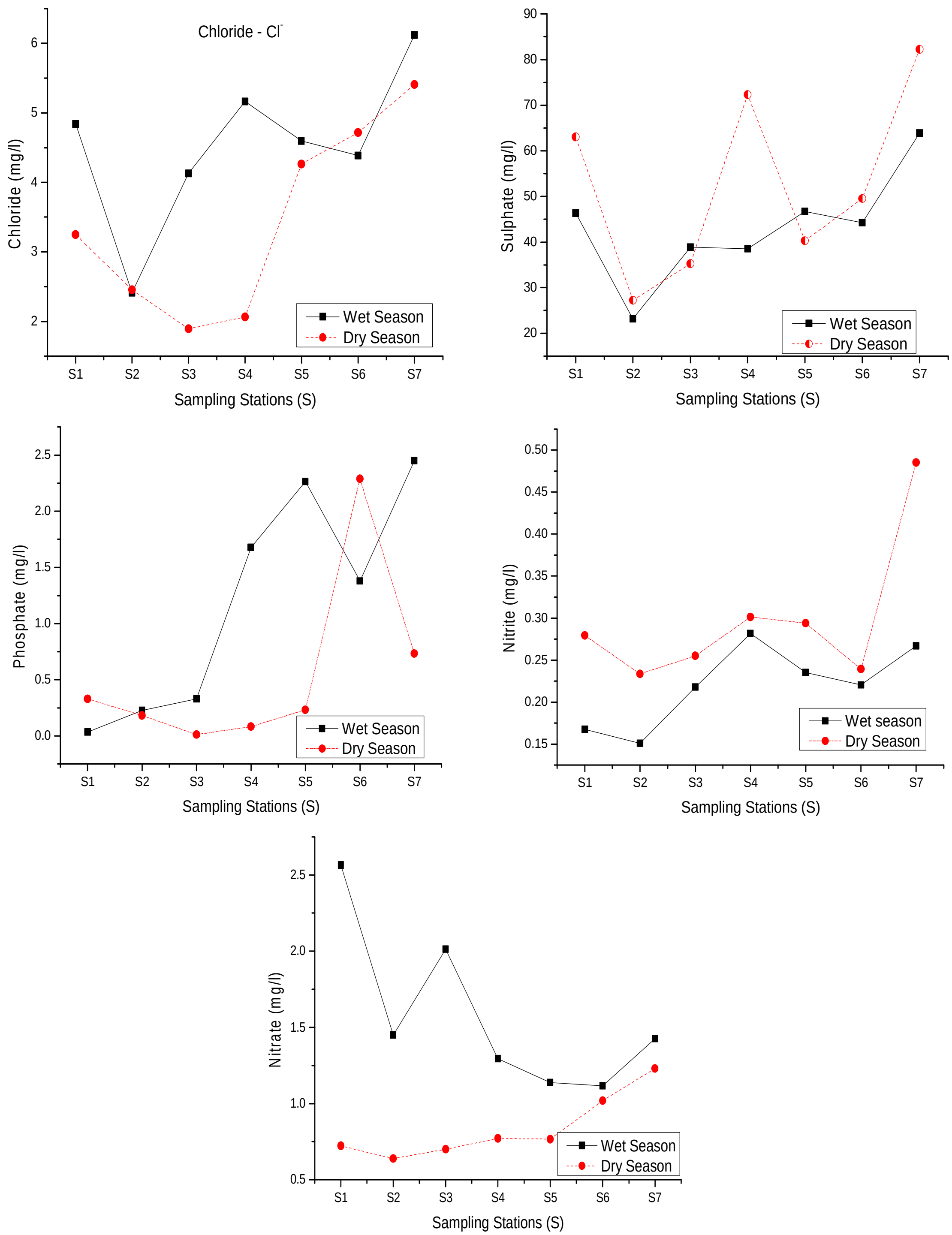

Fig. 3. Line graphs showing trends in spatial and seasonal variations for anions

3.2 Turbidity

Turbidity ranged from 64.83±2.30 NTU to 291.33±2.62 NTU during the dry wet season and from 14.5±1.47 NTU to 77.73±1.44 NTU during the dry season. Mean turbidity values should be below 0.1 NTU for effective disinfection as high levels of turbidity mask micro-organisms from disinfection and stimulate growth of bacteria. Appearance of water with a turbidity of less than 5 NTU is usually acceptable for water used for drinking [21]. All the stations were above the 5 NTU limit with wet season turbidity being highest downstream at S7 with 291.33 NTU which poses great risk to the aquatic biota. Spatial Variation of turbidity were significant for both seasons. Increasing turbidity downstream indicate that anthropogenic activities and change of land use have a major effect on turbidity of the river water. Seasonal variation of turbidity was statistically

Table 5. Paired t-test showing seasonal variations at 95% confidence level *(P=0.05)*

Parameter	**Seasonal variation ($T_{critical}$=2.45, *P=0.05*, df=6)**				
	M.D	**SDD**	**SEMD**	**$T_{calculated}$**	**Significance**
Temperature	3.26	1.05	0.4	**8.17**	<0.001
EC	6.96	11.19	4.23	*1.65*	0.151
TDS	3.81	6.14	2.32	1.64	0.151
pH	3.81	6.14	2.32	*1.64*	0.618
Turbidity	118.77	68.34	25.83	**4.60**	**0.004**
Nitrate	0.74	0.64	0.24	**3.06**	**0.022**
Nitrite	0.08	0.07	0.03	**2.93**	**0.026**
Phosphate	0.64	1.14	0.43	*1.50*	0.185
Sulphate	9.75	14.10	5.33	*1.83*	0.117
Chloride	1.08	1.27	0.48	*2.27*	0.064
Sodium	0.69	0.76	0.29	2.39	0.054
Potassium	0.21	0.49	0.19	1.12	0.302
Calcium	0.32	0.64	0.24	1.32	0.233
Magnesium	0.12	0.29	0.11	1.07	0.324
Manganese	0.60	0.59	0.22	**1.07**	**0.037**
Iron	17.61	17.27	6.53	**2.68**	**0.036**
Zinc	0.19	0.03	0.01	**13.44**	**<0.001**
Copper	0.09	0.04	0.02	**5.63**	**0.002**
Lead	0.18	0.20	0.08	**4.38**	**0.005**

**Bolded values shows significant variation, *df =degrees of freedom*

Table 6. One-way ANOVA showing spatial variations at confidence level 95% *(P=0.05)*

Parameter	**Spatial variation (df=6, $F_{critical}$=*4.76, P=0.05*)**			
	Wet season		**Dry season**	
	Fcalculated	**Sig.**	**Fcalculated**	**Sig.**
Temperature	**120.19**	.000	**1328.38**	.000
EC	**419.10**	.000	**33.76**	.000
TDS	**420.36**	.000	**17835.19**	.000
pH	**31.60**	.000	**240.17**	.000
Turbidity	**2990.15**	.000	**241.14**	.000
Nitrate	**5294.23**	.000	**14080.17**	.000
Nitrite	**279.07**	.000	**1583.44**	.000
Phosphate	**266753.03**	.000	**14879.24**	.000
Sulphate	**4518.93**	.000	**1606.41**	.000
Chloride	**202312.50**	.000	**2036.36**	.000
Sodium	**7.35**	.001	**888.15**	.000
Potassium	**23.63**	.000	**444.29**	.000
Calcium	**72.86**	.000	**91.61**	.000
Magnesium	**246.39**	.000	**235.27**	.000
Manganese	**2080.16**	.000	**10.45**	.000
Iron	**1171.59**	.000	**24.46**	.000
Zinc	**8.06**	.001	**7.56**	.001
Copper	**13.03**	.000	**8.06**	.001
Lead	**16.44**	.000	1.00	0.463

**df =degrees of freedom, *Bolded values show spatial significance* significant (*P=0.004*) showing high influx of sediments in form of surface run-off during wet season as a result of poor agricultural practices upstream and failure to protect riparian zones in all the three zones. Standard error of the mean difference for turbidity, E.C and TDS were high which is as a result of both spatial, seasonal changes and also different anthropogenic activities surrounding the study area.

3.3 Total Dissolved Solids and Conductivity

TDS and conductivity were all within the WHO guideline limit. Solutes such as such as sodium, calcium, magnesium, and chloride contribute to the measure of TDS and conductivity. There exists proportionality between the extent of Conductivity and TDS with the degree of pollution [20]. The range for TDS was between 9.68±0.26 mg/l to 50.80±1.70 mg/l for the wet season and from 16.68±0.07 mg/l to 51.17±0.07 mg/l for the dry season. Conductivity varied between 17.67±0.47 µS/cm to 92.67±3.09 µS/cm and from 30.43±0.12 µS/cm to 93.33±0.12 µS/cm during the wet and dry season respectively. Seasonal variations for both conductivity and TDS were found to be statistically insignificant with the slight increase during the dry season being related to the fact that volume of the river is low and a high evaporation ratio over rainfall. Spatial variations for both were significant for each season indicating different human activities along the river. TDS and EC values are higher downstream for both seasons attributed to sewage mixing and increasing anthropogenic activities along the river such as quarrying, riparian zone cultivation, laundry among others.

3.4 Nitrite

Nitrite ranged was between 0.15±0.00 mg/l to 0.27±0.01 mg/l and between 0.23±0.00 mg/l to 0.49±0.00 mg/l. Nitrite was statistically found to vary significantly between the two seasons and spatial variations were also significant. The conversion of nitrate to nitrite is favored by high temperatures [22] and it being the reason as to why nitrite was higher during dry season than the wet season bringing about seasonal variation. S4 and S7 high nitrite concentration for both seasons can be attributed to landfills from old quarries at S4 and industrial including domestic waste water at S7. All samples apart from two during the wet season (S1 and S2) were above the WHO provisional guideline value of 0.2 mg/l posing a health hazard while all the points for both seasons were below the WHO guideline value of 3 mg/l. Nitrite reacts with Nitrosatable compounds primarily amines, in the body to form N-nitroso compounds which are considered carcinogenic to humans [21].

3.5 Nitrate

The range for nitrate was between 1.12±0.00 mg/l to 2.57±0.01 mg/l and 0.77±0.00 to 1.23±0.00 mg/l during the wet and dry season respectively. Spatial and seasonal variations for nitrate were found to be statistically significant indicating that there is more nitrate being carried to the river during the wet season than during the dry season. All sampling stations recorded nitrite concentration that was below the WHO guideline limit of 50 mg/l. High nitrate concentration upstream during the wet season was rather unexpected and can be explained by surface runoff carrying nitrogen based fertilizers into the river. Tea cultivation uses a large amount of fertilizers compared to other crops and that this usage is increasing gradually over the years [23]. Nitrate varied significantly between the seasons with higher nitrate during rainy season and this is because temperature is low and oxygen tension is also low due to saturation with water Conversion of nitrate to nitrite is favored by elevated temperatures which was not the case during wet season and hence nitrate accumulates during rainy season and explains the seasonal variations [22].

3.6 Phosphate

All the samples recorded phosphate concentrations that were below the WHO guideline value of 5 mg/l. The range for phosphate was from 0.04±0.00 mg/l to 2.45±0.01 mg/l and 0.01±0.00 to 2.29±0.01 mg/l during the wet and dry season respectively. Seasonal variation was statistically insignificant as spatial variations were significant. The slight seasonal difference observed is attributed to accumulation of phosphates from surface runoff of anthropogenic activities such as agriculture especially from coffee zone, washing and laundry, domestic and industrial waste discharges [24]. Spatially, the increasing trend downstream can be attributed to the change in land use as the farm areas contribute through use of phosphate based fertilizer while domestic sewage and industrial effluent increasing phosphate concentration downstream. There is a lot of leaching of phosphate into the river in form of surface run-off during the wet season. Lack of existing sewage lines at the estate on both sides of the river contributed to high level of phosphate leaching at station S6 during dry season.

3.7 Sulphate

Wet season sulphate was higher and ranged from 23.20±0.18 mg/l to 63.87±0.35 mg/l compared to dry season whose range was 27.22±0.62 mg/l to 82.22±0.87 mg/l. High concentration at S7 from both seasons is contributed by industrial, municipal and domestic waste water discharges. Tea and coffee zones concentration (S1-S4) is attributed to fertilizer use as ammonium sulphate which could be a source of sulphate is used as a fertilizer that lowers soil pH and also provides essential nitrogen [25]. Sulphate concentrations were below the guideline limit of 250mg/l for all the sampling points [21].

3.8 Chloride

Chloride ranged between 2.41±0.00 mg/l to 6.12±0.00 mg/l and 1.89±0.01 mg/l to 5.41±0.01 mg/l during the wet and dry season respectively. Seasonal variations were found to be statistically insignificant but spatial variations were significant indicating that land use changes and anthropogenic activities add amounts of chloride to the river water downstream. Chloride concentrations were however below the WHO guideline of 250 mg/l [26]. Anthropogenic sources of chloride include human sewage, livestock waste, synthetic fertilizers (primarily KCl), and chemical industries [27]. High Cl^- concentrations upstream, S1, S3 and S4 are as a result of fertilizer use owing it to chloride being strongly correlated to potassium (*r=0.93*). Domestic sewage at S6 and industrial effluents mixing with urban waste water at S7 give rise to high chloride in the river water.

3.9 Metals

High metal ion concentration present in surface water may create either acute or chronic poisoning in fish and other aquatic animals, not forgetting humans too. It is usually the ionic forms which produce the immediate fish kills whereas the complexed metal compounds tend to act by accumulation in the body tissue over a considerable longer period [14].

3.10 Sodium and Potassium

In dilute waters, sodium content is usually below 10 mg/l while potassium is commonly half or a tenth of that of sodium [28]. Sodium concentration ranged between 1.71±0.15 mg/l to 6.46±0.15 mg/l in the dry season and from 1.08±0.02 mg/l to 5.24±0.02 mg/l during the wet season. Potassium ranged from 0.33±0.01 mg/l to 2.09±0.13 mg/l during the wet season and from 0.85±0.05 mg/l to 2.53±0.05 mg/l during the dry season. The concentration of sodium and potassium were all below the WHO guideline limit. There was no significant seasonal variation for both while spatial variations were significant for each indicating land use changes occurring. Quarries, car washing and laundry activities add considerable amounts that accumulate downstream. Strong correlation of potassium to chloride ion (*r=0.93*) indicate fertilizer leaching from agricultural land contributing to potassium concentration [27].

3.11 Calcium and Magnesium

Calcium concentration during the wet season ranged from 0.82±0.15 mg/l to 6.91±0.21 mg/l while during the dry season, calcium ranged from 1.35±0.43 mg/l to 6.57±0.18 mg/l. Magnesium ranged from 0.43±0.05 mg/l to 2.02±0.02 mg/l during the wet season and from 0.51±0.05 mg/l to 1.72±0.01 mg/l during the dry season. The highest concentrations for both were recorded at S7 however, all the sampling points recorded values that were below the WHO guideline limits. Seasonal variations were statistically insignificant with the slight increase in calcium and magnesium concentration during dry season as a result of lower volume of river water. Spatial variation were significant for both and show gradual increase downstream attributed to effects of urbanization and change in anthropogenic activities [29].

3.12 Manganese

Manganese is an essential element for both humans and animals however over exposure has associated health risk. High levels of manganese are associated with industrial pollution as typical levels in freshwater are typically 0.01 – 0.2 mg/l [21]. During the wet season S4, S5, S6 and S7were the only stations downstream that had values above WHO recommended guideline value of 0.4 mg/l during the wet season. Manganese concentration varied significantly between the seasons and also spatially with wet season having higher concentration and can be attributed to surface run-off from land-fills and garbage disposal near the river at S4-S6, domestic and industrial waste water at S7 [30].

Table 7. Correlation coefficient matrix for water quality parameters during the wet season

	ºC	pH	EC	TDS	Turb.	NO_3^-	NO_2^-	PO_4^{3-}	SO_4^{2-}	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	Mn^{2+}	Fe^{2+}	Zn^{2+}	Cu^{2+}	Pb^{2+}
℃	1.00																		
pH	-0.56	1.00																	
EC.	0.56	0.24	1.00																
TDS	0.56	0.24	1.00**	1.00															
Turb	0.96**	-0.52	0.62	0.62	1.00														
NO_3^-	-0.74	0.82*	-0.01	-0.01	-0.76*	1.00													
NO_2^-	0.75	-0.09	0.52	0.52	0.76*	-0.49	1.00												
PO_4^{3-}	0.94**	-0.37	0.64	0.64	0.94**	-0.72	0.82*	1.00											
SO_4^{2-}	0.56	0.27	0.97**	0.97**	0.59	0.01	0.56	0.64	1.00										
Cl^-	0.61	0.26	0.88**	0.88**	0.59	0.01	0.75	0.64	0.91**	1.00									
Na^+	0.72	0.07	0.80*	0.80*	0.66	-0.21	0.73	0.77*	0.89**	0.90**	1.00								
K^+	0.65	0.10	0.82*	0.82*	0.63	-0.10	0.69	0.65	0.90**	0.93**	0.95**	1.00							
Ca^{2+}	0.84*	-0.27	0.77*	0.77*	0.91**	-0.60	0.71	0.90**	0.79*	0.68	0.80*	0.77*	1.00						
Mg^{2+}	0.67	-0.07	0.93	0.93	0.77*	-0.26	0.46	0.70	0.88**	0.73	0.69	0.74	0.86*	1.00					
Mn^{2+}	0.77*	-0.15	0.84*	0.84*	0.88**	-0.51	0.66	0.87*	0.80*	0.68	0.70	0.66	0.95**	0.92**	1.00				
Fe^{2+}	0.69	-0.28	0.74	0.74	0.83*	-0.50	0.49	0.70	0.71	0.55	0.58	0.65	0.92**	0.92**	0.91**	1.00			
Zn^{2+}	0.07	0.40	0.72	0.72	0.13	0.42	0.03	0.06	0.76*	0.61	0.52	0.69	0.39	0.67	0.38	0.52	1.00		
Cu^{2+}	0.64	-0.06	0.76*	0.76*	0.71	-0.45	0.50	0.81*	0.77*	0.55	0.72	0.60	0.89**	0.79*	0.89**	0.76*	0.35	1.00	
Pb^{2+}	0.61	0.30	0.80*	0.80*	0.67	-0.34	0.47	0.79*	0.75	0.57	0.65	0.50	0.77*	0.78*	0.87*	0.65	0.27	0.93**	1.00

**   shows significant correlation at 95% confidence level*
*** Shows significant correlation at a 99% confidence level*

3.13 Iron

Although Iron essential in the metabolism of both plants and animals, its presence in water in large amounts stains laundry and plumbing fixtures due to its oxyhydroxide precipitate as noticeable taste of iron occurs above 0.3 mg/l [21,31]. All samples recorded Iron concentration greater than the recommended guideline value of 0.3 mg/l by WHO. Concentration of Iron during the wet season ranged from 9.40±0.15 mg/l to 49.99±0.61 mg/l whereas during the dry season, iron ranged from 1.31±0.12 mg/l to 3.40±0.23 mg/l. Seasonal and spatial variation were statistically significant. Iron exist either as a true solution or as a colloid in the form of suspended particles and therefore high concentration observed during wet season was as a results of high suspended sediments in the water as during the dry season suspended sediments were minimal [32]. Iron increases downstream as turbidity increases and also industrial and domestic waste water add considerable amount of iron to the water for both seasons.

3.14 Zinc and Copper

Seasonal and spatial variations were statistically significant. All samples were below the recommended upper limit by WHO of 3 mg/l for zinc and 2.5 mg/l for copper. High values during wet season can be attributed to resurfacing sediments as Zinc and copper are readily absorbed onto sediments. Low turbidity during dry season was related to decrease in these sediments [33].

3.15 Lead and Cadmium

Only a few stations recorded lead concentration as the others were below the limit of detection. Lead occurs in river water downstream and it is attributed to increasing anthropogenic activity and industrial waste discharges from Thika town at S7. All samples were above the recommended upper limit by WHO of 0.01 mg/l posing a health risk to the aquatic biota and domestic users of the river water. Lead exposure leads to neurotoxic effects in the body and it now occurs at lower levels of exposure than previously anticipated [34]. Cadmium was not detected in the river water.

3.16 Correlation

Correlation analysis measures the closeness of the relationship between two variables at a time. Correlation coefficient will have values between +1 or –1 which show the probability of attaining a linear relationship between variables in x and in y [2]. This analysis attempts to establish the nature of the linear relationship between the variables and thereby provides a mechanism for prediction [35,36,37]. Table 7 shows the correlation coefficients (R) between physicochemical parameters for the wet season. Turbidity was strongly correlated to all the other parameters apart from pH, nitrate and zinc. However, pH was strongly correlated to nitrate with medium correlation to zinc. Temperature was correlated strongly to calcium phosphate and sulphate as electrical conductivity was strongly correlated to most metal cation concentration. Sulphate being strongly correlated to chloride, sodium, potassium, calcium, magnesium and zinc could mean that most of these metals occur in combination with the sulphate ion. Strong correlation between the parameters and turbidity is clear indication that as turbidity increases downstream from soil erosion and sediment loading which is as a result of land use change, most parameters are added at the same time due to such effects of surface run-off. Surface run-off is non-point based and hence some of these pollutants can be regarded to be from non-point sources. Nitrate does not follow this trend as higher concentration was observed upstream than downstream. Conductivity and TDS were strongly correlated to each other and with all other parameters besides pH and nitrate. This relates to increasing dissolved solids and consequently higher conductivity. Strong correlation of turbidity to other parameters therefore can form a basis of prediction of the water quality parameters.

4. CONCLUSION

Turbidity, nitrite, manganese, iron and lead were the only parameters above the WHO recommended guideline values. This poses a health threat to the aquatic life and downstream water users as well as imposing a high cost for water treatment. Land use changes in the catchment result to the varying concentration of the parameters as is evident from significant spatial variations. As these changes continue to occur, most of these parameters will record even higher concentrations over the coming years. Surface runoff leads to high concentration of turbidity, nitrate, phosphate, chloride, manganese and iron during the wet season. Sediment erosion enter into the river from failure to protect the riparian zones as poor farming practices lead to weak soils upstream and a source of non-point based pollutants. Domestic waste water and industries located along the river discharge their untreated waste water to the river resulting to point based pollutants downstream. On the upper areas of the catchment, non-point based pollution is a menace and contribute to poor water quality for the downstream water users. Poor farming practices and lack of better land management practices contribute to such pollution upstream. The study recommends that regulatory bodies constantly monitor water quality and use strong legislative environmental laws to implement control measures for proper effluent treatment to curb point based contaminants downstream of River Chania. Adoption of an incentive based approach with public enlightenment on controlled anthropogenic and better farming practices is recommended to reduce non-point based pollution upstream. Further studies should be done regularly to monitor pollution. Pesticide leaching and biological aspects of water quality should be studied for future work.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Yerel S. Water quality assessment of porsuk river, Turkey. Journal of Chemistry. 2010;7(2):593-599.
2. Verma S, Verma A. Correlation study to predict water quality for drinking purpose. 2014;4(5):823–830.
3. United Nations Environmental Program, (UNEP). A snapshot of the world's water Quality: Towards a global assessment. United Nations Environment Programme, Nairobi, Kenya. 2016;162.
4. Gray NF. Water technology: An introduction for environmental scientists and engineers (2nd Ed.). Oxford: Elsevier Butterworth-Heinemann; 2005.
5. WWAP (United Nations World Water Assessment Programme). The United Nations World Water Development Report 2015: Water for a Sustainable World. Paris, UNESCO; 2015.
6. United Nations Environmental Program, (UNEP). Annual Report; 2015.
7. Kenya Water Towers Agency (KWTA), Kenya water towers status report: Saving our future and heritage, A call to action. Onyango M, Ochugboju S, Karinga M, Owuor Y. Editors. Kenya; 2015.
8. Ngumba E, Gachanja A. Occurrence of selected antibiotics and antiretroviral drugs in Nairobi River Basin; 2015.
   Available:http://doi.org/10.1016/j.scitotenv.2015.08.139
9. Chepkemboi SR. Impact of Urban waste on Seasonal Water quality; 2014.
   Available:http://doi.org/10.13140/RG.2.1.4535.5122
10. Egoh BN, Lanzanova D, Grizzetti B, Bidoglio G, Pagliero L, Bouraoui F, Mubareka S. Mapping water provisioning services to support the ecosystem – water – food – energy nexus in the Danube river basin, Ecosystem Services. 2016;17(7): 278–292.
11. Kithiia S. Water quality degradation trends in Kenya over the last decade. Water Quality Monitoring and Assessment. 2011;23.
12. Mwangi JK, Thiong'o GT, Gathenya JM. Assessing the water quality status of Sasamua watershed, Kenya. Paper presented at the fifth JKUAT Scientific, Technological, and Industrialization Conference held at Juja main campus 17th -19th November; 2010.
13. Marshall S. The water crisis in Kenya : causes, effects and solutions. Global Majority E-journal. 2011;2(1):31–45.
14. Ellis KV, White G, Warn AE. Surface water pollution and its control, Macmillan press ltd, London; 1989.
15. Hill MK. Understanding environmental pollution. Cambridge University Press; 2010.
16. Kenya National Bureau of Statistics (KNBS). Statistical Abstract; 2013.
   ISBN: 9966-767-45-2
17. Environmental Protection Agency (EPA). EPA Guidelines: Regulatory monitoring and testing. Water and wastewater sampling. Environment protection authority. Duncan D, Harvey F, Walker M. Editors. South Australia; 2007.
18. American Public Health Association (APHA). Standard methods for the examination of water and waste water 21st edition. Washington DC; 1998.
19. River Chania catchment. [Computer map]. 1:5000: Digitized from Google Earth using ArcGIS [GIS software]. Version 8.3. Department of Geomantic Engineering & Geospatial Information Systems. JKUAT; 2016.

20. Rizvi N, Katyla D, Joshi V. Seasonal and spatial variation in the water quality of River Hindon at NCR. International Journal of Current Research. 2016;8(4):31282–31289.
21. World Health Organization, (WHO). Guidelines for drinking-water quality; Third edition incorporating the first and second Agenda. Gordon B, Callan P, Vickers C. Editors, Recommendations WHO Chronicle Geneva. 2008;1(38):564.
22. Nwankwoala HO, Pabon D, Amadi PA. Seasonal distribution of nitrate and nitrite levels in eleme abattoir environment, River state Nigeria. Journal of applied science environmental management. 2009;13(4): 35-38.
23. Mathenge MK. Fertilizer types, availability and consumption in Kenya. Paper presented at the 6th National Fertilizer Conference in Kenya, on Towards Increased Use of Fertilizer and Improved Seed for Food Security and Economic Growth, KARI headquarters, Nairobi Kenya; 2009.
24. Massoud M, El-Fadel M, Scrimshaw M, Lester J. Land use impact on the spatial and seasonal variations of contaminant loads to Abou Ali River and its coastal zone in North Lebanon. Agricultural Engineering International. 2004;4(1).
25. World Health Organization, (WHO). Sulfate in drinking-water background document for development of WHO guidelines for drinking-water quality. Guidelines for Drinking Water Quality; 2004.
26. World Health Organization, (WHO). Chloride in drinking-water; background document for development WHO Guidelines for drinking-water quality, health criteria and other supporting information. Geneva. 1996;2(2).
27. Kelly WR, Panno SV, Hackley K, Kelly WR. The sources, distribution, and trends of chloride in the waters of Illinois State. Geological Survey, (March); 2012.
28. Pitter P. Hydrochemistry. (In Czech). 3rd ed. Vydavatelství VŠCHT, Praha; 1999.
29. World Health Organization, (WHO). Calcium and magnesium in drinking-water: Public health significance, Geneva; 2009.
30. Papafilippaki AK, Kotti ME, Stavroulakis GG. Seasonal variations in dissolved heavy metals in the Keritis River, Chania, Greece. Global Nest Journal. 2008;10(3):320–325.
31. Dojlido J, Gerald AB. Chemistry of water and water pollution. Ellis Horwood, London; 1993.
32. Hiraide M, Ishii M, Mizuike A. Speciation of iron in river water. Analytical sciences. 1988;4(6):605-609.
33. Sholkovitz ER, Copland D. The coagulation, solubility and adsorption properties of Fe, Mn, Cu, Ni, Cd, Co and humic acids in a river water. Geochimica et Cosmochimica Acta. 1981;45(2):181-189.
34. Järup L. Hazards of heavy metal contamination. British medical bulletin. 2003; 68(1):167-182.
35. Mulla JG, Farooqui M, Zaheer A. A correlation and regression equations among water quality parameters. International Journal of Chemical Science. 2007;5(2):943-952.
36. Kumar J, Jana AK, Bansal A, Garg R. Development of correlation between BOD and COD for refinery waste. Indian Journal of Environmental Protection. 2005; 25(5):405-409.
37. Lilly Florence, Paulraj A, Ramachandramoorthy T, Water quality index and correlation study for the assessment of water quality and its parameters of Yercaud Taluk, Salem District, Tamil Nadu, India Chemical Sciences Transactions. 2012;1(1):139-149.

Peer-review history:
The peer review history for this paper can be accessed here:
http://sciencedomain.org/review-history/17265