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International Journal of Current Research
Vol. 8, Issue, 10, pp.40300-40306, October, 2016

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

SEASONAL CHANGES IN NUTRIENT CONCENTRATION IN RIVER ISIUKHU WATERSHED, WESTERN KENYA, EAST AFRICA

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ARTICLE INFO

Article History:
Received 16th July, 2016
Received in revised form
05th August, 2016
Accepted 20th September, 2016
Published online 30th October, 2016

Key words:
Agriculture,
Eutrophication,
Kakamega Municipality,
Land use,
Nitrates,
Peri-urban.

ABSTRACT

Rivers are vulnerable to eutrophication as a result of increased deposition of nutrients from human activities taking place within watersheds. Uncontrolled release of nutrients into these important freshwater ecosystems can compromise water quality status for domestic consumption and create unfavourable habitat conditions for aquatic biota. This study investigated the seasonal fluctuations in the levels of nitrate-nitrogen and phosphate-phosphorus at various land uses in River Isiukhu, Kenya from January to June 2013. Land use significantly impacted on phosphate-phosphorus ($F=11.1$, $p<0.05$) and nitrate-nitrogen concentrations ($F=13.7$, $p<0.05$). The forest land use recorded the lowest concentration of nitrate-nitrogen (2.24 Mg L^{-1}) and phosphate-phosphorus (0.07 Mg L^{-1}) while the mixed agricultural land use recorded the highest level of the two nutrients i.e. (5.7 Mg L^{-1}) and (0.2 Mg L^{-1}) respectively. Nutrient concentrations increased in river sections with high intensity of human activities and increased destruction of the riparian vegetation. The concentrations of the two nutrients studied varied with the changes in the amount of rainfall received in the watershed. The lowest concentrations of the two nutrients were observed in February 2013 when only 32.5 mm of rainfall was received while the highest concentrations occurred in April at the peak of the rainy season. Spearman rank order correlation revealed positive correlations between the amount of rainfall and the concentrations of nitrate-nitrogen and phosphate-phosphorus. From this study, it is recommended that there is need to regulate the nature of human activities taking place in the riparian areas due to the potential impact of these activities on nutrient levels.

Citation: *Zedekiah Odira Onyando, William A. Shivoga, Charles K. Kigen and Henry O. Lung'ayia, 2016*. "Seasonal changes in nutrient concentration in River Isiukhu watershed, Western Kenya, East Africa", *International Journal of Current Research*, 8, (10), 40300-40306.

INTRODUCTION

Human civilization and development of the world's major cities, in the past and present, have depended on water supply from rivers making these water resources major destinations for wastewaters from domestic, industrial and agricultural activities (Milovanovic, 2007). This is exacerbated by the fact that currently, human population is on the increase and will continue to rise in the future with some estimates projecting a total global population of 9 billion by 2050, with a larger proportion of this growth expected in the third world (United Nations, 1997). The growing human population is already exerting increased pressure on freshwater resources making the diminishing of the quality and quantity freshwater one of the major issues facing the humans particularly in developing countries (Vialle *et al.,* 2011).

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With the increase in population in the developing world, many societies are looking for extra space for agricultural land leading to encroachment of riparian areas and unregulated expansion of urban centres in most watersheds. Such anthropogenic activities have the capacity to alter surface characteristics hence greatly influencing the quality and quantity of run-offs leading to pollution (Jun and Zong-Guo, 2006).

Besides anthropogenic activities, natural phenomena are also believed to be contributing to contraction of water resources worldwide. For example, increasingly unpredictable seasonal discharge of storm-waters into lotic ecosystems due to climate variabilities synergistically compounds river discharges and the water quality (Fan, 2010). Exhaustion of the natural soil nutrients has forced farmers to use organic and inorganic fertilizers in agro-ecosystems leading to high influx of run-off waters, rich in nutrients in rivers and streams. This has, in many occasions resulted into eutrophication which has both health and ecological repercussions in aquatic ecosystems.

Eutrophication hence remains one of the challenges facing tropical water resources. This necessitates the need for water quality and pollution studies which generate information that is pertinent in designing and implementation of sustainable water resource management strategies to mitigate eutrophication (Zhou, 2007).

The presence of such pollutants in water has potential harmful effect on both aquatic biota due to the alteration of the physical habitat conditions and humans who use such waters for various purposes. This is due to the fact that despite the potential pollution of river and stream water by anthropogenic activities at catchment and sub-catchment scales, stream waters still remains an important source of domestic water supply to many rural communities and the urban-poor, particularly in the developing world, making the consumption of contaminated drinking water to remain one of the most significant causes of ill health worldwide (Ford, 1999). In order to combat water quality degradation due to increased nutrient release, there is need to conduct spatial and temporal studies in water quality (Raburu and Okeyo, 2010 and Bu, 2010). Hence, scientists have always and continue to be prompted to investigate the relationships between water quality and land use changes on spatio-temporal basis world-wide.Many studies perquisite to the development of sustainable river management strategies have been conducted (e.g. Tong and Chen, 2002; Ngoye and Machiwa, 2004 and Shivoga, 2007 among others). Most of such studies have always concluded that agricultural land use has a strong influence on stream water nitrogen (Johnson *et al.,* 1997; Smart *et al.,* 1998; Raburu *et al.,* 2009 and Shivoga 2005) while urban land use greatly influences phosphorus concentrations (Hill, 1981). These important nutrients and other associated sediments are believed to be washed away from the landscape by storm waters (Ahearn, 2005) or surface run-offs. Therefore, in order to understand the nutrient dynamics in watershed, water analyses should be done during rainy seasons for it is during these periods that the landscape is directly connected to the waterways (Basnyat *et al.,* 1999).

Most of the strategies for managing rivers in the tropics have been borrowed from spatio-temporal water quality studies conducted in temperate regions (Wantzen *et al.,* 2006). Though the findings obtained from such studies are comparable in trend, they cannot be generalized to all tropical watersheds because each watershed has unique biophysical and socioeconomic processes leading to land use change (Tu and Xia, 2006) hence variant extents and characteristics of impacts. This challenge has made the long-term seasonal dynamics of nutrient level in rivers and development of watershed-specific conservation plan to remain poorly understood (Moulton and Wantzen, 2006) particularly in developing countries. River Isiukhu drains a region with diverse land use practices (ranging from agriculture mainly upper and lower courses, undisturbed forested area within the Kakamega Forest and peri-urban surroundings within the Kakamega Municipality) with currently highly variable patterns of precipitation. Despite the diverse land uses, seasonal rainfall patterns and the potential vulnerability of this ecosystem to pollution, no temporal water quality study has been done in this watershed except Onyando *et al.* (2013) which only observed spatial dynamics in water quality. The current study postulated that the seasonal rainfall patterns within the watershed have different levels of impact on the nutrient concentration within the river. The objective of this study was therefore to compare variations in phosphate-phosphorus and nitrate-nitrogen levels between forest, peri-urban and agricultural land uses alongside changes in precipitation within watershed.

MATERIALS AND METHODS

Study area

This study was conducted in River Isiukhu lying between 00 21 N, 34° 47’ and 34° 58’ Eat 1573 M above sea level in Kakamega County, Western Kenya in East Africa (Figure 1). It is a tributary of River Nzoia, one of the major inlets of Lake Victoria, the second largest freshwater lake in the world. The river’s catchment has human population density of about 241 people per km^2. It drains an area with four distinctland use gradient of ranging from agriculture (mainly sugar-cane farming along the upper course and mixed farming along the lower course), undisturbed forested area within the Kakamega Forest and peri-urban surroundings within the Kakamega Municipality.

The catchment receives high rainfall (2000 mm per annum), that is well distributed and thunderstorms due to its position near the equator and proximity to Lake Victoria. The rainfall is bimodal with long rains experienced between March and May and short rains from August to October. From the end of December to February is usually a dry season. Mean annual temperatures range from 26°C-32°C and average 25.6° while the mean maximum and minimum temperatures are 27°C and 15°C respectively (KWS, 1994).

Sample collection

Stratified randomized design was used whereeach land use type was considered as a stratum. For each stratum, four sampling stations (Figure 1) were randomly selected. At each sampling station, 3 replicate samples were collected once per week from January to June 2013. The samples were collected using 1L plastic bottles (previously washed with dilute hydrochloric acid and rinsed three times with distilled water) for the laboratory analysis of nitrate-nitrogen and phosphate-phosphorus. 1 milliliter of phenyl mercuric solution (molarity of 50 MgL^{-1}) was added to each water sample to stop biological activity. The sample bottles were labeled to show the sampling station, date, and time of collection and stored on ice in a cool box and transported to the laboratory, where they were stored at $4^{\circ}C$ in the refrigerator. Laboratory analysis was done within 24 hours in Zoology laboratory at Masinde Muliro University of Science and Technology and Water Resources Management authority (WRMA) laboratory in Kakamega. Secondary data on the mean Monthly rainfall (mm) during the study period was obtained from the Meteorological Department, Kenya.

Laboratory analysis of samples

Phosphate-phosphorus PO_4^{3-}-P was determined through ascorbic acid method as described in APHA (2005). Five intermediate phosphate standard solutions of concentration range of 0.01-0.5 mgL^{-1} were prepared from a potassium dihydrogen phosphate stock solution. To each standard solution, 1 drop of phenolphthalein indicator was added followed by 5 N hydrochloric acid until the red colour disappeared.

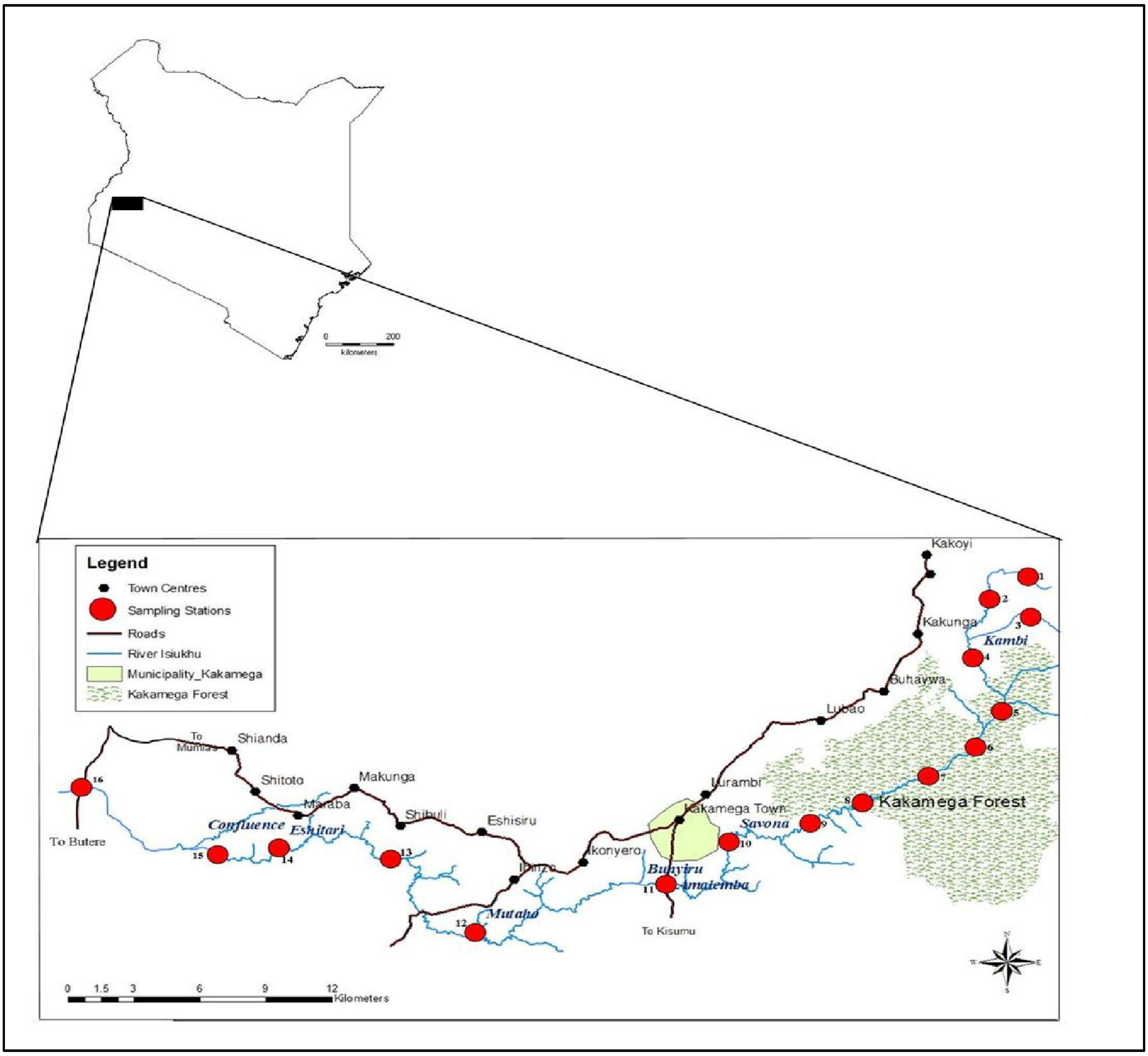

Figure 1. Map of River Isiukhu watershed showing the sampling stations

They were further treated by adding 8.0 ml of a combined reagent made by mixing 50 ml of 5N H_2SO_4, 5 ml of potassium antimonyltertrate solution, 15 ml of ammonium molybdate and 30 ml of ascorbic acid solutions. After 15 minutes, the absorbance of each standard was measured at 880 nm using a T170 UV/VIS Spectrophotometer after zeroing using a reagent blank.

A calibration curve was drawn by plotting absorbance against the concentration of $PO4^{3-}$-P. 50 ml of water sample from each sampling site was treated with phenolphthalein indicator, 5N sulphuric acid and 8 ml of combined reagent as was done for the standard solutions. The absorbance was then measured after 15 minutes using a T170 UV/VIS Spectrophotometer at 880 nm wavelength. The spectrophotometer was zeroed using a reagent blank. The concentration of PO_4^{3-}-P in mgL^{-1} per sample was then determined from the standard curve. Nitrate-nitrogen (NO_3^--N) was determined using ultra-violet screening spectrophotometric method according to APHA (2005). This involved the preparation of six intermediate nitrate standard olutions of concentration range 0.1-3.0 mgL^{-1} diluted to 50 ml from a stock solution. Each standard solution was treated using 1 ml of 1N HCL and absorbance immediately read from T170 UV/VIS Spectrophotometer at 220 nm wavelength. A standard curve was constructed by plotting absorbance against concentration. From each water sample, 50 ml was measured, treated with 1 ml of 1 N HCL and absorbance read immediately from the T170 UV/VIS Spectrophotometer at 220 nm. The spectrophotometer was zeroed using reagent blank. Concentration of NO_3^--N per sample in mgL^{-1} was then determined from the standard curve.

Data analysis

Statistical data analyses were done using Statistical Analysis System (SAS) Version 9.1. The mean concentration of each nutrient per land use in every month was calculated. Least Significant Difference (LSD) analysis was used as a *post hoc* test to identify significant differences in the means of the two nutrients in different months. The mean concentration of each nutrient per month was correlated (Pearson Correlation) with the mean rainfall to check the nature of the relationship between nutrient concentration and mean monthly rainfall.

RESULTS

Mean monthly rainfall

The amount of rainfall received in the study area decreased from January to February then increased from March to June. The lowest amount of rainfall was recorded in February during the peak of dry season while the highest amount was recorded in June 2013 (Figure 2).

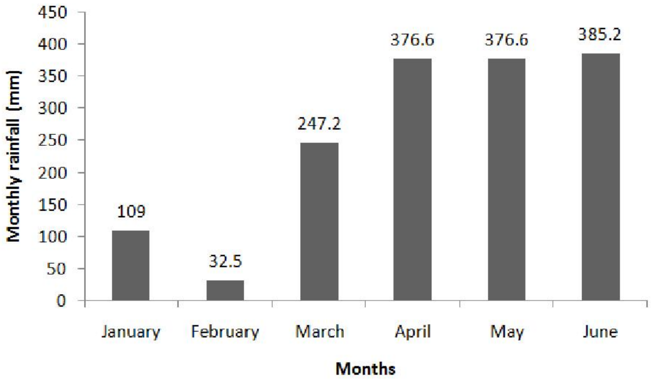

Figure 2. The variation of mean monthly rainfall within River Isiukhu watershed from January to June 2013.

means at the four land uses being statistically different from one another (Figure 3). At each land use, the concentration of nitrate-nitrogen was lower than that of phosphate-phosphorus (Figure 3).

Concentrations of nitrate-nitrogen and phosphate-phosphorus in different seasons

The concentration of the nutrients changed with the changes in the amount of rainfall received (Table 2 and Figure 3), showing seasonal variation. The highest concentrations (Mg L^{-1}) of both nitrate-nitrogen and phosphate-phosphorus were recorded in April while the lowest means of these two nutrients occurred in February (Figure 4). The concentrations of these two nutrients within the river decreased from January to February then increased from March to June 2013.

Relationship between nutrient concentration and mean monthly rainfall

Spearman rank order correlation between the concentrations of phosphate-phosphorus and nitrate-nitrogen. There was a linear relationship between nitrate-nitrogen concentration and mean monthly rainfall received (p=0.001) with equation y = 0.002x +1.589 (R^2=0.371).

Table 1. Changes in nitrate-nitrogen and phosphate-phosphorus concentrations (±SD) along land use gradients in River Isiukhu from January to June 2013 (Means bearing the different letters of alphabet are significantly different)

	Land use			
Nutrient	Sugar cane	Forest	Peri-urban	Mixed agriculture
Phosphate (Mg L^{-1})	0.09±0.05c	0.07±0.06d	0.16±0.1b	0.2±0.18a
Nitrate (Mg L^{-1})	2.71±1.66c	2.24±1.1d	5.01±0.99b	5.7±1.88a

Table 2. Seasonal changes in nitrate-nitrogen and phosphate-phosphorus concentrations (±SD) along land use gradients in River Isiukhu from January to June 2013

Months	Nutrients analysed	January	February	March	April	May	June
Monthly rainfall (mm)		109.00	32.50	247.20	376.60	376.60	385.20
Sugar cane	NO_3^--N (Mg L^{-1})	1.36±0.99	1.99±1.09	2.50±1.30	3.45±1.79	2.19±1.16	2.22±1.16
	PO_4^{3-}-P (Mg L^{-1})	0.04±0.02	0.05±0.03	0.06±0.03	0.12±0.02	0.05±0.01	0.06±0.03
Forest	NO_3^--N (Mg L^{-1})	1.86±0.39	0.54±0.03	2.15±0.84	2.72±1.14	1.79±0.75	1.84±0.73
	PO_4^{3-}-P (Mg L^{-1})	0.29±0.01	0.08±0.03	0.07±0.03	0.11±0.01	0.02±0.13	0.05±0.11
Peri-urban	NO_3^--N (Mg L^{-1})	2.99±0.33	3.84±0.44	4.94±0.51	5.42±0.89	4.61±0.68	4.82±0.73
	PO_4^{3-}-P (Mg L^{-1})	0.04±0.03	0.04±0.02	0.09±0.04	0.23±0.08	0.10±0.03	0.13±0.07
Mixed agriculture	NO_3^--N (Mg L^{-1})	2.34±1.09	1.86±0.07	5.59±1.61	6.1±1.89	5.24±1.80	5.39±1.81
	PO_4^{3-}-P (Mg L^{-1})	0.08±0.03	0.01±0.00	0.17±0.05	0.27±0.22	0.16±0.06	0.16±0.01

Concentrationsof nitrate-nitrogenandphosphate-phosphorus at various land uses

Concentrations of the two nutrients varied with land use change. The lowest concentrations of both nitrate-nitrogen and phosphate-phosphorus were recorded within the forest land use while the highest concentrations of the two nutrients were observed within the mixed agricultural land use (Table1). Land use had a significant impact on PO_4^{3-}-P concentration (F=11.1, p<0.05). The mean concentrations of PO_4^{3-}-P in forest and sugar-cane land uses were significantly different (t=4.91, p<0.05). The mean concentrations of these two nutrients in per-urban and mixed agricultural land uses were also statistically different (t=20.33, p<0.05).Land use had a significant impact on nitrate-nitrogen concentration (F=13.7, p<0.05) with the

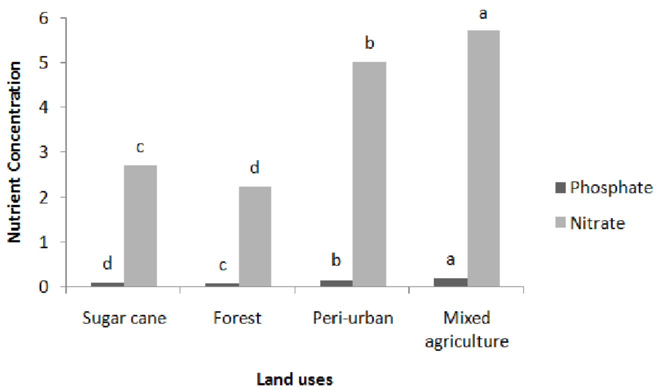

Figure 3. Mean nitrate-nitrogen and phosphate-phosphorus concentrations (±SD) in River Isiukhu from January to June 2013. Means bearing the different letters of alphabet are significantly different

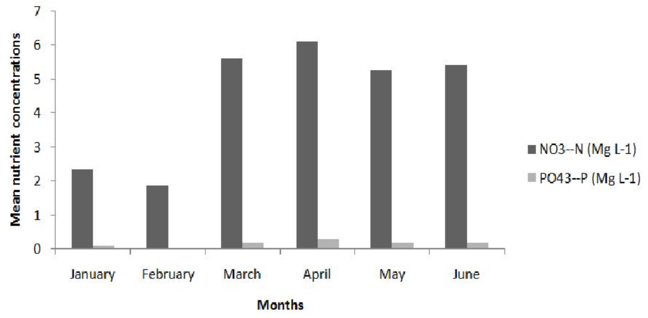

Figure 4: The variation in the mean nutrient concentration within mixed agricultural land use within River Isiukhu watershed from January to June 2013.

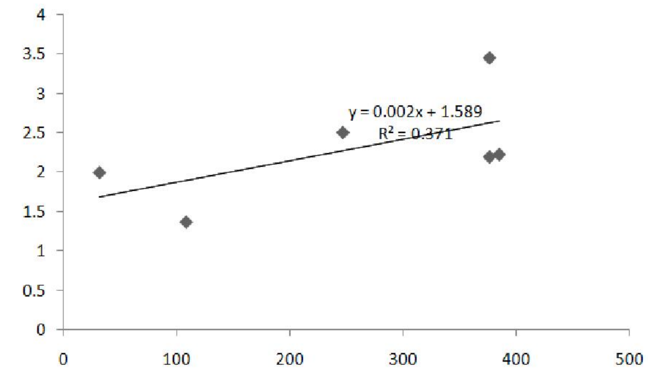

Figure 5: The relationship between nitrate-nitrogen concentration and mean monthly rainfall within mixed agricultural land use within River Isiukhu watershed from January to June 2013.

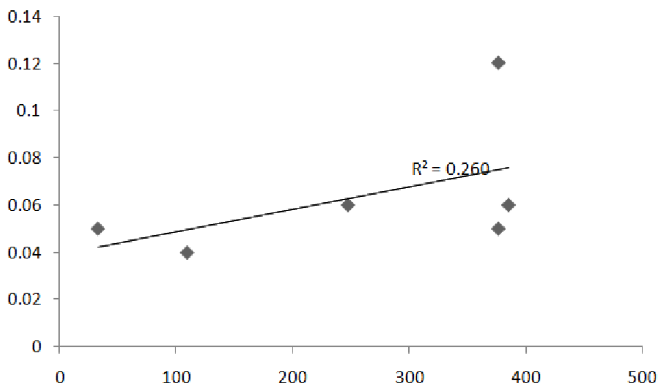

Figure 6: The relationship between phosphate-phosphorus concentration and mean monthly rainfall within mixed agricultural land use within River Isiukhu watershed from January to June 2013.

The concentration of nitrate-nitrogen within the river increased with increase in the amount of rainfall in the watershed (Figure 5). Phosphate-phosphorus concentration was positively with mean annual rainfall received within the watershed (p=0.001) with (R^2 = 0.2601) as shown in Figure 6.

DISCUSSION

Concentrations of nitrate-nitrogen and phosphate-phosphorus at various land uses

The high concentration of phosphate-phosphorus (PO_4^{3-}-P) in peri-urban and mixed agricultural areas is likely due to the increases in paved surfaces in Kakamega municipality and peri-urban areas that allow large numbers of storm drains could shunt P-rich runoff contributing additional P to the river. In River Nile Shehata and Badr (2010) observed increased nutrient concentration in settlement areas while Shivoga *et al.* (2007) reported that in River Njoro, phosphate levels rose in densely settled areas around Egerton University. Sonoda *et al.* (2001), while investigating thenear-stream land use effects on stream-water nutrient distribution in an urbanizing watershed, also reported increased phosphorus load with increasing peri-urban and agricultural activities. Similarly, the high concentration of NO_3^--N observed within the mixed agricultural area (Figure 3) also indicates that NO_3^-N increased with increasing agricultural activities in River Isiukhu watershed. Mixed agricultural land use involves application of both organic and inorganic fertilizers which promote crop yields (Shivoga *et al.,* 2007). USGS (1992) and Shivoga *et al.* (2007) all reported increase in nutrient load in streams with increased human activities in a watershed.

Shineni and O'Reilly (2007) also observed that in tropical streams on the northeast of Lake Tanganyika, loading of phosphorus into streams results from accelerated use of the watershed by humans, poor recovery of the nutrient from agricultural applications and detergent use that high nitrate levels in river sections where most of the riparian vegetation has been removed, absorption of nutrients for plant growth and production is greatly reduced making more nitrogen to be easily leached from the soil after erosionand deposited in the river channel.

Forest land use within the Kakamega Tropical Rainforest recorded lower mean concentrations of both NO_3^--N and PO_4^{3-}-P because of reduced human activities. This forested area is protected by the Kenya Forest Service hence reducing human interferences. The dense riparian vegetation slows down the speed of storm water, effectively buffers the neighbouring soil against erosion hence providing more time for filtering out most of the nutrients contained in the overland run-off (Shivoga *et al.* 2007). The low nutrient concentration recorded in this section concurs with the general observation that the concentration of phosphorus in streams which are less impacted is usually between 0.01 - 0.05 MgL^{-1} (Wetzel, 2001). The increasingly high nitrate-nitrogen concentration downstream in River Isiukhu is therefore attributed to high levels of disturbances within the watershed.Increased agricultural activities, involving uncontrolled use of fertilizer and urbanization within the watershed increase nutrient load in the river, which can potentially which can initiate eutrophication.

Concentrations of nitrate-nitrogen and phosphate-phosphorus in different seasons

Nutrient concentrations in the river varied with the amount of rainfall received (Table 2) showing that rainfall impacts on nutrient loads leading to seasonal fluctuations. Rainfall results in to the formation of storm waters whenever the rate of infiltration into the soil is lower than the amount of rainfall received. According to Allan (1995), rates of erosion and transportation of nitrates into a river system is determined by the slope of the watershed. Such storm waters have the tendency to drain from upland areas within the watershed into the river channel. Previous studies have also reported seasonal changes in nutrient levels. For example, Raburu and Okeyo (2010) reported that the water chemistry of the Nyando River Basin varied temporally even in cases where no significant variation was observed on s sub-catchment scale. Sunblad et al. (1994), Probst *et al.* (1995), and Moreau *et al.* (1998) all reported that there are seasonal changes in the concentration of nutrients particularly in agricultural areas and that higher changes are recorded during high flow periods.

Depending on the quantity and velocity, such waters have the capacity to transport large amounts of materials eroded from the land, some of which dissolve in water, releasing nutrients. Nitrate-nitrogen and phosphate-phosphorus, besides being eroded from agricultural farms, are also derived from municipal wastes washed into the river by surface run-off. Their concentrations rose within municipality probably as a result of inputs from municipal wastes in the peri-urban environment.However, these findings contrast other previous findings that have stated that seasonal changes in water quality are not a universal phenomenon. For example, Topalian *et al.* (1999) attributed such seasonal variation to regular intermittent pollution pulses.

Relationship between nutrient concentration and mean monthly rainfall

Increased rainfall during rainy seasons often results in accelerated runoff and erosion from the watershed contributing to elevation of the levels of nitrate-nitrogen and phosphate-phosphorus. This explains the linear relationships between nitrate-nitrogen and phosphate-phosphorus concentration and mean monthly rainfall in the watershed (Figure 5 and 6). Some of the materials or sediments deposited into the water channel contain sediments rich in nitrates and phosphates compounds which dissolve in water to release the two nutrients. This concurs with Kibichi *et al.* (2007) who also reported a positive correlation between total phosphorus and Total Suspended Solids (TSS). This could also indicate that nitrate-nitrogen and phosphate-phosphorus are of the same origin within the watershed.

Conclusions

There are spatial variations in the concentrations of phosphate-phosphorus and nitrate-nitrogen in River Isiukhu that correspond with changes in riparian land uses within the watershed. Forest land use zones shows lower mean values of these two nutrients while peri-urban and mixed agricultural land use zones show higher mean values. Nutrient concentrations in River Isiukhu fluctuate with changes in the amount of rainfall received in the watershed. High nutrient levels occur during rainy seasons while low nutrient levels occur during dry season. There is a positive relationship between phosphate-phosphorus and nitrate-nitrogen concentrations. The concentration of one of these two nutrients can be used in predicting the concentration of the other.

Recommendations

More studies, that take relatively longer periods of time, are required to confirm the observed spatio-temporal trends in nutrient levels in the River Isiukhu. Studies are recommended to confirm this.

There is need for more studies to be conducted on the different tributaries of this river in order to understand their possible impacts on the water quality of this river basin. The major tributary i.e. River Lusumu needs to be studied because no water quality study has ever been done within its watershed. Finally, there is need to for the development of effective watershed management strategies within the River Isiukhu Watershed by different stakeholders to control the utilization of the riparian land. Soil erosion and land-sliding need to be mitigated in areas where the banks are less protected and very unstable should be prioritized as this can control sedimentation.

Acknowledgements

We are grateful to several people and organizations who contributed during the research and the development of this manuscript. We would like to thank The National Council for Science and Technology (NCST) and German Academic Exchange Service-Africa (DAAD) for funding our project. Finally, we thank the Department of Biological Sciences at Masinde Muliro University of Science and Technology and Water Resources Management Authority (WRMA) for giving us laboratory space where the analyses of samples were done.

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