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Nutrient Loads and Heavy Metals assessment along Sosiani River, Kenya.

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Abstract
Pollution loads were investigated to obtain data on nature and level of contaminations. Soil, sediment and water were collected from five sites and analyzed. Nitrates were determined using UV spectrophotometric screening and colorimetric methods. Phosphates were determined using ascorbic acid and Olsen methods. Nitrates and Phosphates were below EMC and Kenya Bureau of Standards (KEBS) recommended values of 3.0 ppm and 10.0 ppm respectively. Heavy metals were analyzed using wet digestion method and values obtained were above the set limits. At site 3 values obtained were: for Iron (3.562±0.012, 3.033±0.131, 0.033±0.013 ppm), Lead (4.891±0.030, 1.39±0.030, 1.89±0.000 ppm), Cadmium (0.065±0.003, 0.103±0.002, 0.013±0.002 ppm), Zinc (2.372±0.031, 0.410±0.003, 0.310±0.033 ppm) and Copper (0.728±0.000, 0.113±0.000, 0.213±0.000 ppm) for soil, sediment and water, respectively. Concentrations exceeded KEBS permitted levels. Zinc values were above WHO standards of 0.50 ppm for drinking water. It can be concluded that river Sosiani water is not safe for domestic use.
Key words: Contamination, Heavy metals, Water, Soil, Sediment.

1.0 Introduction

Heavy metals are natural components of the earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements some heavy metals (e.g. selenium, zinc) are essential to maintain the metabolism of the human body. However at higher concentration they can lead to poisoning (Phillips, 1980). Heavy metals poisoning could result, for instance from drinking water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or enter via the food chain (Philips, 1980). Heavy metals are dangerous because they tend to bioaccumulate. Therefore, there is need to avoid their poisoning.

Phosphorous (P) is a essential nutrient for living organisms and exist in water bodies as both dissolved Journal of orthophosphate, polyphosphates and organically bound phosphate in particulates. It is generally the limiting nutrient for algae growth and therefore controls the primary productivity of a water body (Greenberg *et al.*, 1992). Artificial increases in concentrations due to human activities are principle causes of eutrophication. High concentrations of phosphate can indicate the presence of pollution and are largely responsible for eutrophic conditions. Phosphate concentrations are usually determined as orthophosphate, total inorganic phosphates or total P (Rhodes, 1982).

Nitrogen (N) is commonly found in combined form as nitrate in natural waters (Zetterstrom, 2005). Usually through the biological process of denitrification in anaerobic conditions nitrates may be reduced to nitrite (Zetterstrom, 2005). In rural and suburban areas the use of inorganic nitrate fertilizers can be a significant source of nitrates. A concentration exceeding 5mg/l NO_3^--N usually indicates pollution by human or animal waste or fertilizer runoff (Garry *et al.*, 1996). In lakes concentration of NO_3^--N in excess of 0.2 mg/l tend to stimulate algae growth and indicate possible eutrophic conditions (Zetterstrom, 2005). Drinking waters containing high nitrates can cause infant methaemoglobinaemia (blue babies). Methaemoglobinaemia is a condition where the ability of blood to absorb oxygen is impaired (Zetterstrom, 2005). It has been suggested that nitrate be reduced to less toxic forms through introduction of soluble, biodegradable organic matter into ground water sources (Zetterstrom, 2005).

2.0 Methods

2.1 Sampling and sample preservation

Sampling was done along river Sosiani. The sampling stations were; Site 1-Kaptagat (source of the river), Site 2-Islamic dam, Site 3-Sutan (next to the rose flower farm), Site 4-Kipkorgot Bridge and Site 5-Kapsaos. Three samples of water, soil and sediments were collected from each of the five stations and studied during both dry and wet seasons.

Soil and sediment samples were collected 1 meter away from the river using soil ogre from a depth of 5 centimeters from the surface. It was stored in small black polythene bags, labeled immediately and transported in ice boxes. Extraction was done within 48 hours of soil collection.
Water samples from the river were obtained using a water sampler and stored in one liter ampher bottles which had been rinsed with hexane and the sample. These were transported to the laboratory in ice boxes containing ice and were analyzed within 48 hours of collection.

2.2 Determination of nitrates
2.2.1 Colorimetric determination in soil and sediment samples

Working standards containing 0, 2, 4, 6, 8 and 10 µg/ml NO_3^-N was prepared, 0.5 ml of each standard and sample were micropippeted into suitably marked test tubes after which 1.0 ml of salicylic acid solution was pippeted to each test tube, mixed well and left for one hour for ull colour development. The absorbance of both the standard and sample was read at 410 nm. A graph of absorbance against standard concentration was plotted. The solution concentrations for each unknown and the blank were determined. The mean blank value was subtracted from the unknown; this gave a value for corrected concentration.

NO_3^-N (µg/g soil) = (C×V)/W

Where
C = Corrected concentration (µg/ml)
V = Extract volume (ml)
W = Weight of sample (g)

2.2.2 Ultra violet spectrophotometric screening method in water samples

50 ml of clear sample (filtered) was pippeted then added with 1 ml of 1N HCl. Standard curve was obtained by preparing standards in the range of 0 - 7 mg NO_3^-N/L by diluting to 50 ml the volumes of intermediate nitrate solution: 0, 1, 2, 3, 4, 5, 6, 7 ml standard treated by adding 1ml of 1M HCl. Transmittance was read for both the sample and the standards at 220 nm. A curve of transmittance versus concentration was constructed with which it was used to determine the concentrations of the samples.

2.3 Determination of phosphates

2.3.1 Determination of phosphates in water using ascorbic acid method
A sample 50 ml of the 5M H_2SO_4, 5 ml of potassium antimony tartrate, 15 ml of the ammonium molybdate and 30 ml ascorbic acid solution was measured and transferred into a 100 ml volumetric flask and filled to the mark with distilled water. A portion of the sample, 50 ml was pippeted and transferred into a clean beaker after which 0.005 ml (drop) phenolphthalein indicator was added. 8.0 ml combined reagent was then added and mixed thoroughly. After about 10 minutes but not more than 30 minutes, the absorbance of each sample was measured at 690 nm. Distilled water which was the blank was used to calibrate the spectrophotometer.

Calculation

P mg/L = mg P (in approx 58ml final volume) ×1000/volume (ml) of sample

2.3.2 Determination of phosphates in soil and sediments using Olsen method

2.3.2.1 Preparation of reagents and calculation

Extracting solution, 1M Sodium hydroxide (NaOH), 2.5M Sulphuric acid (H_2SO_4), 4% Ammonium Molybdate, $(NH_4)_6Mo_7O_{24}H_2O$), 0.1M Ascorbic acid, Potassium Antimonyl tartrate ($KSbC_4H_4O_6$), mixed reagent, extractant were prepared. About 0.4391 g of pre-dried potassium dihydrogen orthophosphate was dissolved in about 500 ml distilled water then filled up to the 1 liter mark with distilled water and mixed well. 20 ml of the standard stock solution was diluted to 100 ml with extracting solution to make 20 ppm Phosphorus. Standard series 0, 2, 4, 6, 8 and 10 ml of standard solution were pippeted into 100 ml volumetric flasks and filled up to the mark with extracting solution. These solutions had concentrations of 0, 0.4, 0.8, 1.2, 1.6, 2.0 ppm Phosphorus respectively.

Standard series sample extracts and blank was pippeted into 50 ml volumetric flasks and 1 ml of 2.5 M H_2SO_4 was added then swirled carefully to release CO_2 from the solution. About 8 ml of the mixed reagent was added,

mixed and filled up to the mark with distilled water and mixed again. After 15 minutes the concentration in ppm was read on the spectrophotometer at 882 nm.

Concentration of P in soil (ppm P) = (a-b) × 50/W

Where: a = Concentration of P measured in the sample (ppm)
b = Concentration of P measured in the blank (ppm)
W = Weight of the soil sample taken for analysis (g)

2.4 Wet digestion of samples for determination of heavy metals

Prior to acid digestion of samples, samples were dried and sieved through 0.2 mm sieve. About 1 g of the sample was weighed into a conical flask, 5 ml of concentrated nitric acid then added. The sample was then shaken for 2 minutes before 2 ml of concentrated HCl was added while shaking. The mixture was transferred into a hot plate and covered with a watch glass. The mixture was then heated for 2 hours until no more fumes evolved controlling temperatures at 70 $^{\circ}$C. The sample was then cooled, filtered and the filtrate diluted to 50 ml using distilled water. The solution was then ready for metal analysis. Stock and working solutions of Lead, Cadmium, Copper, Zinc and Iron were prepared then their concentrations determined using AAS.

2.5 Data Analysis

The data obtained was subjected to linear analysis using Microsoft Excel and SAS software packages. Quality assurance and quality control procedures for the laboratory included analysis in triplicates for the standards and blanks.

3.0 Results and Discussion

3.1 Nutrients

The mean values of nitrate and phosphate collected were analyzed within 48 hours and the results presented as follows.

3.1.1 Nitrate

The highest nitrate level was found to be below the recommended standards for drinking water (10 ppm) according to the European Community guideline values for drinking water (Shen *et al.*, 2007).

Table 1: Nitrate concentration in water, soil and sediment samples along river Sosiani (Mean±SD).

Site	Season	Concentration in water (% N) ± SD	Concentration in soil (% N) ± SD	Concentration in sediment (% N) ± SD
1	Dry	0.0038±0.0001	0.0002±0.0000	0.0001±0.0000
	Wet	0.0021±0.0002	0.0004±0.0002	0.0003±0.0002
2	Dry	0.0040±0.0020	0.0002±0.0001	0.0002±0.0001
	Wet	0.0042±0.0002	0.0003±0.0002	0.0007±0.0004
3	Dry	0.0047±0.0020	0.0005±0.0002	0.0005±0.0003
	Wet	0.0074±0.0058	0.0009±0.0004	0.0011±0.0002
4	Dry	0.0064±0.0020	0.0003±0.0002	0.0003±0.0000
	Wet	0.0082±0.0010	0.0011±0.0010	0.0014±0.0001
5	Dry	0.0070±0.0000	0.0005±0.0001	0.0005±0.0003
	Wet	0.0091±0.0001	0.0015±0.0001	0.0016±0.0001

Site 1 showed low level of nitrates during both dry and wet season this was due to no farming activities because this was the source of the river just a few metres from the forest. An increase in nitrates value at site 2 and 3 both in both dry and wet season was observed as shown in Table 1. This could be due to run off from the rose flower green houses. Nitrates level in water were high during wet season at site 3, 4 and 5 due to nitrates being washed

as surface runoff into the river by rain water. All the nitrates levels for all sites sampled were above the water quality standards set of 10 ppm (WHO, 1992). Nitrates concentration in sediment was high in wet season than dry season ranging between 0.0001±0.0000 to 0.0016±0.0001 as shown in Table 3. There was drastic increase in nitrates level both in dry and wet season at site 3, because of high level concentration of nitrates in the commercial flower farm effluents due to high use of fertilizers containing nitrates. Concentration in site 5 was higher than site 4 during dry season attributed to use nitrogenous fertilizers, industrial wastes and other pollutants from industries.

3.1.2 Phosphate

The total phosphate concentrations estimated as PO_4^- P at the sites were found to be in the range between 0.06±0.002 to 1.824±0.32 for water, soil and sediment samples in both dry and wet seasons as shown in Table 2. The higher values were observed during wet season. Highest values were at site 3, 4 and 5. For site 3, it could be due to some surface run-off of phosphate from the flower farm and discharging of untreated water to the river. Possibly for site 5 it can be attributed to the municipal wastes containing high concentrations of phosphate and therefore raised the value.

Table 2: Phosphate concentration in water, soil and sediment samples along river Sosiani (Mean±SD)

site	season	Concentration in water (ppm) ± SD	Concentration in soil (ppm) ± SD	Concentration in sediment (ppm) ± SD
1	Dry	0.0847±0.00006	0.06±0.02000	0.271±0.01528
	Wet	0.0902±0.00021	0.07±0.00546	0.290±0.03906
2	Dry	0.1632±0.00012	0.57±0.02421	0.590±0.02517
	Wet	0.1771±0.00025	0.74±0.03021	0.741±0.00035
3	Dry	0.1028±0.00400	1.50±0.05730	1.564±0.00000
	Wet	0.4013±0.00210	1.72±0.04213	1.824±0.32000
4	Dry	0.0174±0.00030	0.09±0.00542	0.145±0.06870
	Wet	0.0215±0.00025	0.63±0.06024	0.307±0.06530
5	Dry	0.0219±0.00006	0.27±0.06074	0.452±0.04320
	Wet	0.0286±0.00030	0.46±0.05741	0.551±0.08421

The phosphate concentration in water samples was significantly different as shown in Table 2. A double increase at site 2 could be due to run off from agricultural farms in the catchment area. A further increase in phosphate at site 3 during both dry and wet season was attributed to run off from rose flower green houses situated a few meters from the site. The farm uses phosphate fertilizers which are washed downstream. Phosphate level at site 3 was higher during wet season than during the dry season while site 4 and 5 also had increased values. The phosphate levels in water samples were below KEBS limits (10.0 ppm) thus safe for domestic use.

In sediments, sharp increase in phosphate at site 3 during both dry and wet seasons was due to runoff from flower farms which are washed downstream where samples were obtained. Site 4 showed a sharp decrease in phosphate concentration during both the dry and wet seasons as shown in Table 2. This decrease probably was due to dilution effect downstream. Level of phosphate was higher in sediments during wet season than the dry season due to the rain washing phosphates into the river which settled in sediments.

The phosphate concentration in soil samples at site 1 and 2 varied slightly during dry and wet season as shown on Table 2. The slight increase observed at site 2 could be attributed to runoff from agricultural farms which use phosphate fertilizers. A sharp increase in site 3 during wet season was attributed to heavy rains washing phosphates downstream. The slight increase at site 5 can be due to wastes from the town.

3.2 Toxic heavy metals

Mean values for heavy metals in water, soil and sediments samples are shown on Tables 3, 4 and 5 respectively.

Table 3: Mean Concentration levels of heavy metals in water in ppm ± SD for the dry and wet seasons

Site	Season	Cu	Zn	Pb	Cd	Fe
1	Dry	0.051±0.048	0.108±0.036	0.55±0.012	0.004±0.000	0.011± 0.050
	Wet	0.039±0.001	0.305±0.079	0.77±0.026	0.003±0.000	0.017±0.004
2	Dry	0.034±0.003	0.070±0.002	0.13±0.004	0.028±0.005	0.324±0.036
	Wet	0.021±0.000	0.571±0.098	1.09±0.037	0.007±0.000	0.562±0.024
3	Dry	0.275±0.003	0.129±0.067	0.02±0.000	0.012±0.000	2.897±0.082
	Wet	0.213±0.000	0.310±0.033	1.89±0.030	0013±0.002	0.033±0.131
4	Dry	0.036±0.003	0.118±0.044	0.18±0.006	0.041±0.008	1.655±0.046
	Wet	0.001±0.000	0.251±0.059	1.14±0.039	0.003±0.001	0.223±0.137
5	Dry	0.044±0.004	0.488±0.079	0.19±0.006	0.050±0.009	1.051±0.029
	Wet	0.077±0.002	0.548±0.076	0.74±0.025	0.007±0.001	3.789±0.129

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Table 4: Mean Concentration levels of heavy metals in soil in ppm ± SD for the dry and wet seasons

Site	Season	Cu	Zn	Pb	Cd	Fe
1	Dry	0.002±0.000	0.001±0.000	0.000±0.000	0.001±0.000	0.000± 0.000
	Wet	0.002±0.000	0.003±0.000	0.001±0.000	0.002±0.000	0.001±0.000
2	Dry	0.002±0.000	0.001±0.000	0.002±0.001	0.010±0.001	0.223±0.002
	Wet	0.003±0.000	0.005±0.098	1.092±0.037	0.007±0.000	0.053±0.001
3	Dry	0.573±0.003	1.760±0.066	1.021±0.000	0.012±0.000	3.107±0.002
	Wet	0.728±0.000	2.372±0.033	4.891±0.030	0.065±0.003	3.562±0.012
4	Dry	0.930±0.003	1.183±0.014	1.386±0.006	0.017±0.002	2.789±0.011
	Wet	0.837±0.000	1.451±0.059	3.147±0.039	0.056±0.003	3.342±0.010
5	Dry	0.320±0.004	1.882±0.061	1.095±0.006	0.020±0.001	2.921±0.006
	Wet	0.477±0.001	1.448±0.051	2.742±0.025	0.061±0.027	3.257±0.003

Table 5: Mean Concentration levels of heavy metals in sediments in ppm ± SD for the dry and wet seasons

Site	Season	Cu	Zn	Pb	Cd	Fe
1	Dry	0.041±0.048	0.008±0.036	0.05±0.012	0.002±0.000	0.011± 0.050
	Wet	0.049±0.001	0.015±0.079	0.07±0.026	0.003±0.000	0.017±0.004
2	Dry	0.024±0.003	0.070±0.002	0.03±0.004	0.028±0.005	0.324±0.003
	Wet	0.0311±0.000	0.021±0.098	0.09±0.037	0.007±0.000	0.562±0.002
3	Dry	0.173±0.003	0.129±0.067	0.12±0.000	0.012±0.000	1.897±0.082
	Wet	0.113±0.000	0.310±0.033	1.89±0.030	0013±0.002	3.033±0.131
4	Dry	0.026±0.003	0.118±0.044	0.18±0.006	0.041±0.008	0.117±0.004
	Wet	0.031±0.000	0.251±0.059	1.14±0.039	0.003±0.001	0.223±0.003
5	Dry	0.024±0.004	0.488±0.079	0.19±0.006	0.050±0.009	0.634±0.002
	Wet	0.037±0.002	0.548±0.076	0.74±0.025	0.007±0.001	0.893±0.001

Zinc concentrations were generally high during the dry season. Higher values could be due to zinc rich soils in the catchments area of the river. Site 3 showed elevated zinc values in water, soil and sediment samples. This implies that there was zinc input into the river through discharge from the flower farm. The mean concentration of zinc at site 1 and 2 probably was due to natural deposition in the area. There was a sharp increase in zinc concentration at site 5 this could probably be due to municipal and industrial effluents mainly the leachates from the waste dumpsite attributed to the heavy rains that generally washes the waste to the river. The concentration

both in wet and dry seasons were slightly (0.52 ppm) above the WHO standards recommended for drinking water (0.50 ppm). Hence the water is not safe for drinking as far as zinc levels are concerned.

Data analysis showed significant difference in copper concentrations among sites. However copper content of samples from upstream were significantly lower than those copper values observed in the downstream samples. Copper values in the samples range suggest that there could be copper input into the river from discharges from the flower farm. The drastic increase at site 3 ranging between 0.213 ppm to 0.275 ppm could be due to the use of copper based fungicides and fertilizers at the flower farm. The values decreased downstream due to the dilution effects. Copper levels were above KEBS limits 0.05 ppm at site 3 and 5 therefore the water is not safe for domestic use.

Iron concentration values in water were higher than both the WHO (0.3 ppm) and EC maximum allowable concentrations for fisheries and aquatic life. These could be attributed to the industries at the Eldoret municipality discharging its untreated waste water into the river. The high levels at site 2 represent background levels and could be due to the catchments area of the river. At site 3, values obtained were 3.562 ppm, 3.033 ppm, 0.033 ppm for soil, sediment and water respectively. Iron concentrations on the samples were very high both during the dry and wet season ranging between 0.011 ppm to 3.789 ppm. The highest concentration value was observed at site 5. This could be attributed to the runoff from the surrounding catchments areas. While increase observed at site 3 and 5 could be due to pollution from the town. Iron concentration was above KEBS limits of 0.01 ppm at site 3, 4 and 5 therefore not safe for domestic use.

A significant increase in lead values was observed at site 3 as 4.891, 1.39, 1.89 ppm for soil, sediment and water respectively, during the wet season due to runoff into the river from the discharges of the flower farm. The lead concentrations then decreased gradually due to efficiency of natural self cleaning capacity of the river. A further decrease at site 4 and 5 was attributed to self cleaning capacity of the river coupled with dilution. High levels of lead in sediments was attributed to the high rate of sedimentation since the water flows at a low velocity thus leading to accumulation of sediments loaded with lead concentration due to contamination of water with leaded gasoline. Drastic decrease in lead levels at site 4 attributed to dilution and a slight increase in lead value at site 5 shows that there was pollution from town effluents and vehicle emission.

Cadmium concentration in water samples showed very slight variations ranging from 0.003 to 0.028 ppm. The value of cadmium at site 1 was high which could be attributed to natural abundance in the area. There was an increase at site 4 with 0.041 ppm and 5 with 0.05 ppm due to run-offs from farms and pollution from town. Cadmium levels were far above the KEBS limits (0.01 ppm) in water (0.013), soil (0.065 ppm) and sediment (0.103 ppm) samples in site 3 during wet season. As evidenced from the results, nearly all the sites were above the set limits thus the water is not safe for domestic use.

4.0 Conclusion

The analysis of the data indicated that the quality of water in river Sosiani at site 1 and 2 was acceptable. However on moving downstream, the quality deteriorated due to the discharges from the flower farm and influx of municipal effluents. The water at site 3 was also enriched with substantial concentrations of phosphate and nitrates which facilitated the growth. The phosphate value at site 4 which was 0.0174 and 0.0215 ppm in water, 1.09 and 0.63 ppm in soil and 0.145 and 0.307 in sediments during dry and wet season, respectively, and the nitrate level at site 5 which was 0.0700 ppm and 0.0913 ppm in water, 0.0005 ppm and 0.0016 ppm in sediments, 0.0005 ppm and 0.0015 ppm in soil during dry and wet seasons, respectively, obtained were slightly lower. This could be a sign of recovery of the river through self cleaning. Site 5 was characterized by enhanced parameter levels of pesticide residues, heavy metals and even the nutrients analyzed. This could be due to pollution from the Eldoret municipal wastes.

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