

Assessment of the Impact of Effluents Discharge from Murang'a Town and Its Environs on the Water Quality of River Mathioya, Murang'a County, Kenya

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Abstract

Effect of effluents into rivers is of great economic, environmental and health concern. Chemical fertilizers are used extensively in modern agriculture, in order to improve yield and productivity of agricultural products. However, nutrients, leaching through the soil from agricultural activities, sewerage effluents and runoff from residential areas reaching river water resources are causing serious pollution. The purpose of this study was to determine the impact of effluent discharges on water quality of River Mathioya in Murang'a County, Kenya. Samples were collected upstream and downstream of Murang'a town along the Mathioya River. The pH, dissolved oxygen, electrical conductivity, total dissolved solid, total suspended solids and temperature were determined using the respective meters. Heavy metals were determined using flame atomic absorption spectrometry while sodium and potassium were determined using flame photometry. Nitrates and phosphates were determined using UV/Visible spectrophotometry. Fluoride ion selective electrode was used to determine fluoride. The study has shown that there was considerable amount of heavy metals in the water samples of Mathioya River, though the levels were below WHO maximum permissible levels for zinc 0.05 - 0.08, chromium 0.02 - 0.03, lead was below the limit of detection and copper 0.03 - 0.04 while iron 0.73 - 1.16 and manganese 0.88-2.24 mg/L exceeded this limit. The concentrations of the physicochemical parameters pH 6.94 - 7.76, TDS (37.84 - 54.59 mg/L), TSS (42.78 - 53.84 mg/L), DO (4.75 - 8.27 mg/L) and EC 63.89 - 80.17, nitrates (6.40 - 13.66 mg/L), phosphates (0.29 - 0.91 mg/L) and fluoride (0.68 - 0.88 mg/L).

Keywords: AAS, AES, UV/VIS, ISE, physico-chemical parameters, nutrients levels, heavy metals.

1. Introduction

Sewerage waste and runoff from residential and agricultural areas are reaching the rivers and causing serious pollution. Water quality depends on local geology, ecosystem, human uses, such as sewage dispersion, industrial pollution, and use of water bodies as heat sinks, (Asit and Cecilia, 2011). Water, the matrix of life is exposed to pollution and unhealthy environment, resulting in human affliction and diseases transmission due to rapid industrialization and population growth. Man-made activities are changing the morphology of the area of the river regimes and causing water pollution, (Simpi *et al.*, 2011). Water pollution affects both the fauna and the flora living in these water bodies, (Azizullah *et al.*, 2011). The WHO states that one sixth of the world's population; approximately 1.2 billion people do not have access to safe water and 2.4 billion people lack basic sanitation, (European Public Health Alliance, 2009).

Polluted water causes environmental health effects with the occurrence of water-borne diseases, for example, typhoid and cholera, and chemical poisoning in humans and animals; leading to loss of scenic beauty with water becoming unsuitable for recreational activities; and high cost of water supply as polluted water is expensive to treat. The common effects of trace metal toxicity to living organisms include cancer, brain disorder, kidney damage, renal damage and lethal to fish and other aquatic life. Deterioration of the quality of the aquatic environment leads to deoxygenation, eutrophication, siltation, habitat modification and toxicity of the water, (Ashraf *et al.*, 2010). The objectives of the study were to determine the physico chemical parameters such as pH, TDS, TSS, DO, temperature and electrical conductivity, to determine the levels of nitrates, fluorides and phosphates, to determine the levels of sodium, potassium and to determine the levels of Fe, Mn, Zn, Cu, Pb and Cr in the water of River Mathioya, Kenya.

1.1 Study area

Mathioya River under study originates from the Aberdares ranges. It joins Tana River at Sagana Bridge at the borders of Muranga and Kirinyaga County, Kenya.

2. Materials and methods

2.1 Sample collection and pretreatment

There were 20 sampling points along Mathioya River including both Murari and Karii streams. Triplicate samples were picked from each sampling point totaling 60 samples. The 20 sampling points were divided into 5 blocks; block 1(1 - 4), block 2 (5 - 8), block 3 (9 - 12), block 4 (13 - 16) and block 5 (17 - 20).

Samples for metal ions: Polyethylene sampling bottles were soaked with 5% nitric acid and rinsed thoroughly with distilled and de-ionized water. At each sampling site, the bottles were rinsed at least three times with river water before retaining a sample. Triplicate 500 mL of water samples were taken at each sampling site, immediately acidified with 5mL concentrated nitric acid to a pH of less than 2 and transported to the laboratory in an ice bath. Samples for phosphates and nitrates: At each sampling site, brown bottles were rinsed at least three times with river water before retaining a sample. The samples were then tightly capped and placed in a cooler box and immediately transported to the laboratory. They were filtered using whatman filter papers to avoid interference due to turbidity and color and then kept in a refrigerator at a temperature below 4°C, (Ozturk *et al.*, 2009).

2.2 Chemicals and reagents

Chemicals and reagents used were of analytical grade. They included; nitric acid (37%), hydrochloric acid (70%), sulphuric acid (98%), distilled water, hydrogen peroxide, zinc nitrate, ammonium chloride, potassium dihydrogen orthophosphate, lead (II) nitrate, sodium fluoride, sodium chloride, potassium chloride, copper (II) sulphate, lead nitrate, Chromium (VI) oxide, potassium dichromate, Lead (II) nitrate, Manganese (II) Chloride and zinc chloride, sodium hydroxide pellets (purity 98%). The chemicals were from Sigma Laboratories in the United States of America and Reagent Chemical services (UK).

2.3 Instrumentation

HANNA pH, temperature, TDS and conductivity meter (model H1991000) Jenway, UK, and digital portable dissolved oxygen meter HACH DO175 were used. Win lab meter (Model WH200202) for the TSS. Fluoride meter an ion selective combination Electrode, model 96-09Thermo, manufactured by Orion Research of Beverly Mass Company, USA. Flame emission photometer model FP6410 from scientific products of Halstead, Essex, England, using air-acetylene fuel fitted with sodium, potassium and lithium filters. Beckman DU640UV/Vis Doublebeam spectrophotometer from Arthur H. Thomas Company. Flame atomic absorption spectrophotometer (AAS - Shimadzu AA 7000) model with an air/nitrous-acetylene burner.

2.4 Experimental Procedures

2.4.1 Determination of physico-chemical parameters

All the analyses were determined according to the American public health association standard methods (APHA) for examination of water and wastewater, (APHA, 2005). A pre-calibrated HANNA pH, temperature, TSS, DO, TDS and conductivity meter was used for pH, temperature, total dissolved solids, total suspended solids and electrical conductivity measurements. Temperature, total dissolved solids and conductivity readings were also taken at the same time as pH. Dissolved oxygen was measured using a digital portable dissolved oxygen meter and Win lab meter was used to determine the TSS.

2.4.2 Determination of phosphates, nitrates and fluoride

Phosphate: 50.0 mL of the sample were pipetted into a clean, 125 mL volumetric flask. 0.05 mL phenolphthalein indicator were added and 2.5 M H₂SO₄ solution added dropwise to just discharge the red color which developed. 8.0 mL combined reagent added and mix thoroughly. After at least 10 min but no more than 30 min, absorbance was measured for each sample at 880 nm, using reagent blank as the reference solution. Nitrate was determined using UV-Vis spectrophotometer. The procedure involved addition of 1 ml of concentrated hydrochloric acid into 50 mL of the samples to decompose the carbonates. Samples absorbance were read at 220 nm from the calibration curve.

Fluoride: 25.00 mL of 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 ppm fluoride standard solutions were pipetted into a 100 mL

volumetric flask and 50 mL of total ionic strength adjustment buffer solution reagent added and diluted to the mark with deionized water then stoppered and thoroughly mixed. Then 50 mL of the sample were pipetted into a 100 mL volumetric flask and topped to the mark with TISAB solution and stirred. The electrode was rinsed with deionized water and blot dried and lowered into the standard solutions, after 5 minutes stable readings were attained and recorded. After measuring all the standard solutions a calibration curve was prepared by plotting the relative mV versus the logarithms of the concentrations of the standards and a slope (s) obtained. Then the concentrations of the samples were read from the calibration curve and from the data obtained mg/L fluoride concentrations were calculated.

2.4.3 Determination of Sodium and Potassium

Sodium and potassium ions were determined by flame emission photometry. Standards of sodium and potassium were used to calibrate the flame photometer at wavelengths of 589 and 768 nm respectively. The samples concentrations were obtained from the standard calibration curve.

2.4.4 Determination of Heavy Metals

Water samples were digested in triplicates according to the method described by (APHA, 2005). 10 mL of the filtered water were digested with 5 mL of concentrated nitric acid at 100°C with the addition of 3 drops of hydrogen peroxide until there was no brown fumes. The mixture was filtered using whatman 0.45µm filter paper in a 100 mL volumetric flask and topped with distilled water for aspiration into the flame atomic absorption spectrophotometer. The sample solutions were then introduced into the flame and their absorbance values were used to calculate the concentration.

3. RESULTS AND DISCUSSION

3.1 Physico-chemical parameters

Their pH mean values ranged from 6.94 ± 0.22 in block 5 to 7.46 ± 0.26 in block 3 (Table 1). The pH levels were within the WHO optimum limits for drinking and potable water, which is 6.5 and 8.5, (WHO 2006). All the mean values of pH obtained for all the samples fell within the WHO range but were slightly above the natural background level of 7.0. This increase in pH of the water samples above the natural background levels may be due to the presence of dissolved carbonates, bicarbonates present in the water, organic pollution and the domestic waste discharge draining into the river system as it traverses the habited areas, (Araoye, P. A., 2009). Similar findings were also reported during study on the seasonal variation of pH and dissolved oxygen concentration in lake Ilorin, Nigeria, (Araoye, P. A., 2009).

The average temperature ranged from 20.53 ± 0.98 °C in block 3 to 24.60 ± 0.69 °C in block 5 (Table 1). There was noticeable slight variation in temperature of samples in block 4 and 5, this is due to the lower volumes of water in the Murari and Karii streams compared to the bigger Mathioya River, but not significantly different ($p > 0.05$). The electrical conductivity varied between a minimum mean of 63.89 ± 0.11 µScm in block 1 to 80.17 ± 0.31 µScm in block 5 (table 1). All samples were within this limit of 700 µScm. Conductivity showed a positive correlation with total dissolved solids. The fluctuations in EC are due to fluctuation in total dissolved solids and salinity, (Pandey G.C. 2002). The total suspended solids in the sampled water ranged from 42.78 ± 0.27 mg/L in block 1 to 53.84 ± 0.68 mg/L in block 3 (Table 1). This was higher than the WHO permissible limit of 30mg/L. Total suspended solid content of water depends on the amount of suspended particle, soil, silt and is directly related to turbidity of water. Disposal of sewage and industrial effluents contributes suspended matter to rivers, (Keramat A. A., (2008). Low level of total suspended solids were recorded for Kosi River at Utrakhand, Iran, and the average value of TSS varies from 3 to 174 mg/L, (Reddy and Venkateswar 2006), which are slightly higher than River Mathioya. The higher amount of total suspended solids in the collected samples were attributed to run off from Murang'a town solid garbage dumps wastes which results in the presence of several suspended particles. Total dissolved solids ranged from 37.84 ± 0.76 mg/L in block 1 to 54.59 ± 0.18 mg/L in block 5 (Table 1). Higher values of total dissolved solids are attributed to the presence of silt and clay particles in the river water. The level of TDS fell within tolerable limits for drinking water as it did not exceed 500 mg/L, (Singh and Chandel, 2006). The TDS values followed the same trend as electrical conductivity. It is seen that a linear relationship existed between TDS and EC. A similar trend of TDS was also observed during study on analytical study of heavy metals of industrial effluents at Jaipur, Rajasthan (India), (Singh and Chandel, 2006). The study also concluded that electrical conductivity would increase with increase in TDS values, (Singh and Chandel, 2006).

Dissolved oxygen mean concentration ranged from 4.75 ± 0.32 mg/L in block 5 to 8.27 ± 0.58 mg/L in block 1 (Table 1). The dissolved oxygen for sustaining aquatic life is 4 mg/L, while for drinking purposes it

is 6 mg/L. The decrease in dissolved oxygen between block 1 and blocks 2 to 5 could be attributed to waste being discharged into the river from people living along the river. This indicates that most of the discharges are organic in nature and hence required oxygen for decomposition. Mostly these wastes are in the form of organic soaps and other detergents used for washing purposes along the riverside. Lower dissolved oxygen might also be due to higher turbidity and increased suspended materials which affected dissolution of oxygen, (Janjua *et al.*, (2009). The range of dissolved oxygen recorded 4.75 mg/L to 8.27mg/L, shows that the water is of good quality and will promote the growth and survival of fish. Similar observation was recorded during a study on limnology and trophic status of shahpur dam reservoir, Pakistan, (Janjua *et al.*, (2009).

Table 1: Mean concentration of some Physico-chemical parameters

Sampling block	pH	Temp.	EC	TSS	TDS	DO
1	7.44±0.09	22.46±0.74	63.89±0.11	42.78±0.27	37.84±0.76	8.27±0.58
2	7.76±0.16	20.90±0.06	64.75±0.13	49.70±0.46	41.13±0.52	5.31±0.60
3	7.46±0.26	20.53±0.98	76.94±0.11	53.84±0.68	50.14±0.46	5.46±0.39
4	7.09±0.17	24.60±0.69	65.58±0.12	48.22±0.04	43.48±0.93	4.92±0.82
5	6.94±0.22	23.70±0.76	80.17±0.31	47.11±0.57	54.59±0.18	4.75±0.32

3.2 Phosphate, nitrate and fluoride

Phosphates mean levels ranged from 0.29 ± 0.05 mg/L in block 1 to 0.91 ± 0.04 mg/L in block 4 (Table 2) against the maximum allowed limit of 45 mg/L. Phosphate contamination comes from disposal of commercial detergents, body wastes, food additives fertilizers and pesticides used in farming activities, (Goldman and Horne, 2009). Excess phosphate in water promotes an algal bloom. The rapid growth of algae and phytoplankton can decrease the amount of dissolved oxygen in a body of water. Algae reproduce and die rapidly, and the decomposition of algae depletes dissolved oxygen in the water. Thus, the organism population can be seriously minimized. The levels of phosphates in the River Mathioya waters could be attributed to increasing loading of human wastes, animal wastes, agricultural activities on land and detergents used along the river, (Kamal *et al.*, 2007). The same observation were made during a study on the physico-chemical properties of water of Mouri River, Khulna, Bangladesh (Kamal *et al.*, 2007).

Nitrate mean concentration levels ranged from 6.40 ± 0.20 mg/L in block 1 to 13.66 ± 0.50 mg/L in block 4 (Table 2). The values recorded for nitrate were all below the WHO permissible limits of 50mg/l. Lower findings were obtained during a study on the levels of nitrate ions in water from selected wells and points along Kimondi River, Nandi County, Kenya, (Magut and Terer, 2012). They found the level to range from 0.18 mg/l to 0.66mg/l. The increasing use of artificial fertilizers, the disposal of wastes (particularly from animal farming), (Akinsola, 2005). The nitrates found in the water samples could have come from leaching and run-off from human activities such as agriculture where nitro-phosphate fertilizers are used in the farmlands along the river. Other sources include domestic effluents and emissions from combustion engines which also reach the river. Raw waste effluents from factories and sewage treatment usually have high levels of ammonia and nitrogenous wastes which can lead to rapid multiplication of bacterial population. These can elevate the levels of nitrates in the adjacent water bodies through aerobic and anaerobic bacteria activities, (Nolan and Hitt, 2006). There was significant difference between the levels of nitrates across all the sampling block but there was no significant difference between blocks 4 and 5 ($p < 0.05$). The minimum mean level of fluoride ranged from 0.68 ± 0.02 mg/L to 0.88 ± 0.02 mg/L. (Table 2) against the maximum allowed limit of 1.5mg/L. There was significant difference between the levels of fluoride between sampling block 1 upstream before receiving the town effluents and all the other sampling blocks, ($p < 0.05$). The fluoride found in the water samples could be attributed to weathering and leaching of bedrock with high fluoride concentrations. Same results were reported during a study on evaluation of ground water and tap water quality in the villages surrounding Chuka town, Kenya, (Ombaka O. *et al.*, 2013).

Table 2: Means concentration of nitrate, phosphate and fluoride in (mg/l)

Sampling blocks	NO ₃ ⁻	PO ₄ ³⁻	F ⁻
1	6.40±0.20	0.29±0.05	0.68±0.02
2	8.37±0.47	0.75±0.17	0.77±0.13
3	12.37±0.37	0.65±0.05	0.88±0.02
4	13.66±0.50	0.91±0.04	0.83±0.05
5	12.40±0.81	0.85±0.03	0.71±0.02

3.3 Sodium and potassium

The minimum mean level of sodium ranged from 73.93 ± 0.72 mg/L to 106.18 ± 0.45 mg/L (Table 3) against the maximum allowed limit of 200mg/L. The presence of sodium in the samples might be due to high rate of mineralization in the sediments, increasing sodium into the nutrient pool thereby making more sodium to solubilize. Similar findings in the study on physico-chemical analysis of surface and ground water of Bargarh district, Orissa, India were observed, Mahananda H. B. *et al.*, (2005). There was significant difference between the levels of sodium in sampling block 1 upstream before the river receive the town effluents in blocks 2 to 5 at p<0.05 downstream. The minimum mean level of potassium ranged from 3.35 ± 0.10 mg/L to 17.63 ± 0.56 mg/L (Table 3). The presence of potassium in the samples might be due to the geochemical strata along the river, Mahananda H. B. *et al.*, (2005). Similar findings on physico-chemical analysis of surface and ground water of Bargarh district, Orissa, India were observed, (Mahananda H. B. *et al.*, 2005). There was significant difference between the levels of potassium in blocks 1, 2, 3 and 5 (p < 0.05).

Table 3: Mean concentration of Sodium and Potassium (mg/L)

Sampling blocks	Na ⁺	K ⁺
1	73.93 ± 0.72	3.35 ± 0.10
2	93.89 ± 0.88	6.70 ± 0.93
3	88.74 ± 0.87	9.60 ± 0.49
4	98.17 ± 0.74	8.29 ± 0.69
5	106.18 ± 0.45	17.63 ± 0.56

3.4 Heavy metals

The minimum mean level of iron ranged from 0.73 ± 0.03 mg/L to 1.16 ± 0.26 mg/L (Table 4) against the maximum allowed limit of 0.5 mg/L Fe²⁺. The presence of iron in water samples analyzed is attributed to inflows from garages metal works and commercial establishments in the upstream, sewage waste discharge into Karii stream, car wash sheds and natural deposits. Physicochemical and bacteriological characteristics of water samples from Irigu river, Meru County, Kenya, were investigated and the results showed that the iron were higher than the WHO acceptable limits in drinking water (Ombaka and Gichumbi, 2012). There was significant difference between the levels of iron in block 1 and sampling block 4 and 5 (p < 0.05).

The minimum mean level of manganese ranged from 0.88 ± 0.05 mg/L to 2.24 ± 0.10 mg/L (Table 4) against the maximum allowed limit of 0.1mg/L. The presence of manganese in water samples is attributed to vehicular emission and inflows from garages metal works and commercial establishments in the town, sewage waste, wastewater from town effluents, petrol stations, carwash sheds and paints and plastics. On a study on heavy metals in surface water of Warri River, Delta state, recorded values of manganese in river water ranging from 0.020-0.680 mg/L, (Wogu and Okaka 2011). Similar study from Athi-Galana-Sabaki tributaries, Kenya, showed that the concentrations of lead, manganese and chromium in water were more

than the WHO recommended limit thus posing immediate fears of bioaccumulation in human, (Muiruri *et al.*, 2013). There was significant difference between the levels of manganese between sampling block 3 and 5 ($p < 0.05$).

The minimum mean level of zinc ranged from 0.05 ± 0.05 mg/L to 0.08 ± 0.01 mg/L (table 4) against the maximum allowed limit of 3.00 mg/L. The presence of concentration of zinc in Mathioya River water samples might be due to agricultural run-off on sediments in the river, carrying various zinc based pesticides used in agricultural practices. This largely agrees with findings recorded during a study on heavy metals (Cu and Zn) in sediments of Ilangrose Lake, Wales, (Wales J. *et al.*, 1991). There was significant difference between the levels of zinc between sampling block 1 and 3, 4 and 5 ($p < 0.05$).

The minimum level of copper ranged from 0.03 ± 0.01 mg/L to 0.04 ± 0.02 mg/L (table 4) against the maximum allowed limit of 1 mg/L. Presence of copper in the water samples is attributed to corrosion of copper containing alloys in the pipe fittings in Murang'a town. Copper may occur in natural waters, waste waters and industrial waters as soluble salts and precipitated copper compounds, (Callatay and Francois, 2005). During a study in Cairo, Egypt, to determine heavy metals (copper, lead, and chromium) in drinking water and their environmental impact on human health, the results showed that there is a relationship between chronic diseases and the geological environment, (Hanaa *et al.*, 2000). There was no significant difference between the mean levels of copper in all the sampling blocks, ($p < 0.05$).

The levels of lead in all the five sampling blocks were below the limit of detection (LOD) (Table 4). The world health organization (WHO) allowable limit in drinking water is 0.05 mg/L. The sources of lead into Mathioya River could include; sewage, paints from garages and buildings, old automobiles and fertilizers. Lead is the most significant of all the heavy metals because it is toxic, very common and harmful even in small amounts, (Mebrahtu and Zerabruk, 2011). High concentration of lead in the body can cause death or permanent damage to the central nervous system, the brain, and kidneys, (Mebrahtu and Zerabruk, 2011). The minimum mean level of chromium ranged from 0.02 ± 0.01 mg/L to 0.03 ± 0.01 mg/L (Table 4) against the maximum allowed limit of 0.050 mg/L. Similar results were obtained in a study on surface water of Warri River, Nigeria, where levels of chromium ranging from 0.02 mg/L to 0.06 mg/L were recorded. The presence of chromium in the water samples could be attributed to sources like; cement, dyes, paints, printing ink, detergents, wood preservatives among others, (Hilgenkamp, 2006), which are common in Murang'a town and its environs. Uses of large amounts of phosphate fertilizers in agriculture and many types of pesticides may also led to the relatively high concentrations of chromium in water, (Mandour and Azab, 2011). There was no significant difference between the levels of chromium in the five sampling blocks, ($p < 0.05$).

Table 4: Mean concentrations of heavy metals (mg/L)

Sampling block	Fe	Mn	Zn	Cu	Pb	Cr
1	0.73 ± 0.03	0.88 ± 0.05	0.05 ± 0.02	0.03 ± 0.01	LOD	0.02 ± 0.01
2	0.81 ± 0.07	0.92 ± 0.04	0.06 ± 0.02	0.03 ± 0.01	LOD	0.03 ± 0.01
3	0.84 ± 0.05	2.24 ± 0.10	0.08 ± 0.01	0.03 ± 0.01	LOD	0.02 ± 0.01
4	1.54 ± 0.30	1.23 ± 0.32	0.07 ± 0.02	0.04 ± 0.02	LOD	0.03 ± 0.01
5	1.16 ± 0.26	2.19 ± 1.23	0.08 ± 0.01	0.03 ± 0.01	LOD	0.03 ± 0.01

CONCLUSION

The physico-chemical parameters, nitrates, phosphates and fluorides were all within the acceptable guidelines on drinking water by the WHO. The level of sodium, potassium and heavy metals (Zn, Cu, Cr, and Pb) mean concentration were all within the acceptable guidelines, while iron and manganese exceeded the guideline. Iron could be attributed to natural deposits while manganese could be from Murang'a town effluents. During water

treatment iron and manganese should be removed to acceptable limits for drinking water. The water samples from blocks 4 and 5 were more polluted with almost all the studied parameters than blocks 1(upstream). Blocks 2 and 3 also had higher mean concentrations than block 1, but their concentrations were lower than blocks 4 and 5 because of dilution by Mathioya River water. Results obtained shows that Murang'a town and its environs are capable of polluting river.

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