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NUTRIENT POLLUTANT LOADS AND THEIR EFFECTS ON WATER QUALITY OF PERKERRA RIVER, BARINGO COUNTY, KENYA

K. S. Fred*[1], J. C. Faith[1], L. K. John[1], K. Providence [2] and M. Justin [1]

1-Department of Chemistry & Biochemistry, Chepkoilel University College, P.O. Box 1125-Eldoret;

2- School of Public Health, Moi University, P.O. Box 3900, Eldoret.

ABSTRACT

In order to sustain productivity in crop yield, soil nutrients should be replenished using inorganic fertilizers. Appropriate use of fertilizers based on recommendation is generally expected to cause little adverse impact on the environment and health. However, trace amounts of nitrates and phosphates have been detected in soil and water. This has led to increased concerns regarding the potential effects of these inputs on non-target organisms. The objective of this paper was to investigate and quantify nutrient residues in water, sediments and soil in river Perkerra, Baringo county. The samples were collected from five sampling sites. Phosphate and nitrate content were determined using Olsen and calorimetric methods respectively. The highest nitrate in water, sediments and soil recorded were 4.98, 8.24 and 8.13ppm respectively. The highest phosphate concentration was 0.016ppm in water and 33.34ppm in soil compared to WHO value of 10ppm. The dissolved oxygen ranges between 2.15 and 4.42 ppm. The chemical oxygen demand ranges between 13.20 and 53.75ppm. The highest value of 53.75ppm in this study was above the Kenya Bureau of Standards (KEBS) value of 50ppm. The river water studied is therefore polluted with nutrient residues and is not recommended for direct domestic use since some parameters studied are far above the KEBS standards.

Key words: nitrates, phosphates, chemical oxygen demand, biochemical oxygen demand, dissolved oxygen.

†Corresponding author's E-mail address: **<fksegor@yahoo.com>**

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INTRODUCTION

At present, more food is produced from a smaller area of cultivated land with less labour than ever before due to improved agricultural productivity. Part of this development can be attributed to the use or application of sophisticated agricultural techniques, advanced agricultural practices and the selection of more appropriate plant varieties. Fertilizers, organic or inorganic materials containing one or more of the nutrients mainly nitrogen, phosphorous, potassium and other essential elements required for plant growth, provide plant nutrients that are naturally lacking.

Heavy nutrients in river, lake or estuary may cause water bodies to become eutrophic with an increase in phytoplankton growth or algal bloom and the development of hypoxic or anoxic conditions thus threatening the life of fish and other aquatic species. Heavy phytoplankton growth results in undesirable aesthetic effects, manifested in unpleasant colour and odour problems. Low phytoplankton growth on the other hand is an indication that a water body is oligotrophic or poorly nourished with respect to nutrients. There is need therefore to have optimum content of nutrients for sustainability. Over application of chemical fertilizers on water logged ground or on sites where the crop is unable to use the chemical leads to surface run-offs or leaching. The residual nitrogen nitrate is liable to pollute ground surface waters, causing eutrophication (Bandara *et al*, 2005; Sharpley, 1999).

High concentration of nitrates in drinking water is a health hazard and is thought to cause miscarriages in pregnant women and blood poisoning in young children, which can result in death (Syers *et al*, 1986; Weselek *et al*, 2007). It is also known to cause "oxygen debt" in the blood, a fatal condition known as methemoglobinemia or the blue baby syndrome (Nolan, 2002; Muller *et al*, 1995). The nitrite from ingested nitrate reacts with amines and amides in the stomach to produce highly carcinogenic N-nitroso compounds in the body (Jennings and Sneed, 1986). Over many years the amount of living matter increases leading to slow accumulation of dead organic matter on the bottom of the lake thereby raising the biochemical oxygen demand (BOD) level of the lake water (Syers *et al*, 1986; Horita *et al*, 1997). The primary pollutant associated with depletion of dissolved oxygen is carbonaceous BOD (Greenberg *et al.*, 1992).

In order to put in place strategies that can remedy pollution arising from the use of fertilizers, reliable data on residue levels in food, water and working environment is crucial (EMC, 1999 and 2006). Therefore, there is need to investigate and quantify the amount of nitrites, phosphates and BOD in drinking water, soil and sediments and advise the relevant authorities accordingly. Chemical oxygen demand (COD) measures amount of oxygen required to oxidize the organic matter in a waste water sample under specific conditions of oxidizing agent, temperature and time. The organic matter is converted to CO_2 and water, nitrogen is converted to ammonia while organic nitrogen in higher oxidation states is converted to nitrates regardless of the biological degradability of the substances (Greenberg *et al.*, 1992; Chardon, 2000). It is necessary to monitor their concentration to ensure that chronic doses do not have poisoning cumulative effects in plants, animals and man (WHO, 1992; USEPA, 2002). The findings from this study may be used as an integral part of risk assessment or

injury to human health and to the environment.

MATERIALS AND METHODS

Study area and Sampling points

The study area is along the Perkerra River. The samples were collected from Chemasusu forest to Lake Baringo (area 1207km^2), a distance of 95 kilometers. The river covers Baringo county and is situated in an arid and semi-arid lands (ASAL) of Kenya. The river drains into Lake Baringo, a semi arid area of Kenya. The source of this river is Chemasusu forest. Figure 1 shows the study area and location of the five sampling sites. The residents living along the river depend on its waters for domestic use. There are many commercial flower farms around Eldama Ravine town-ship, from where there is a possibility of surface water being contaminated by fertilizer residues from the flower farms.

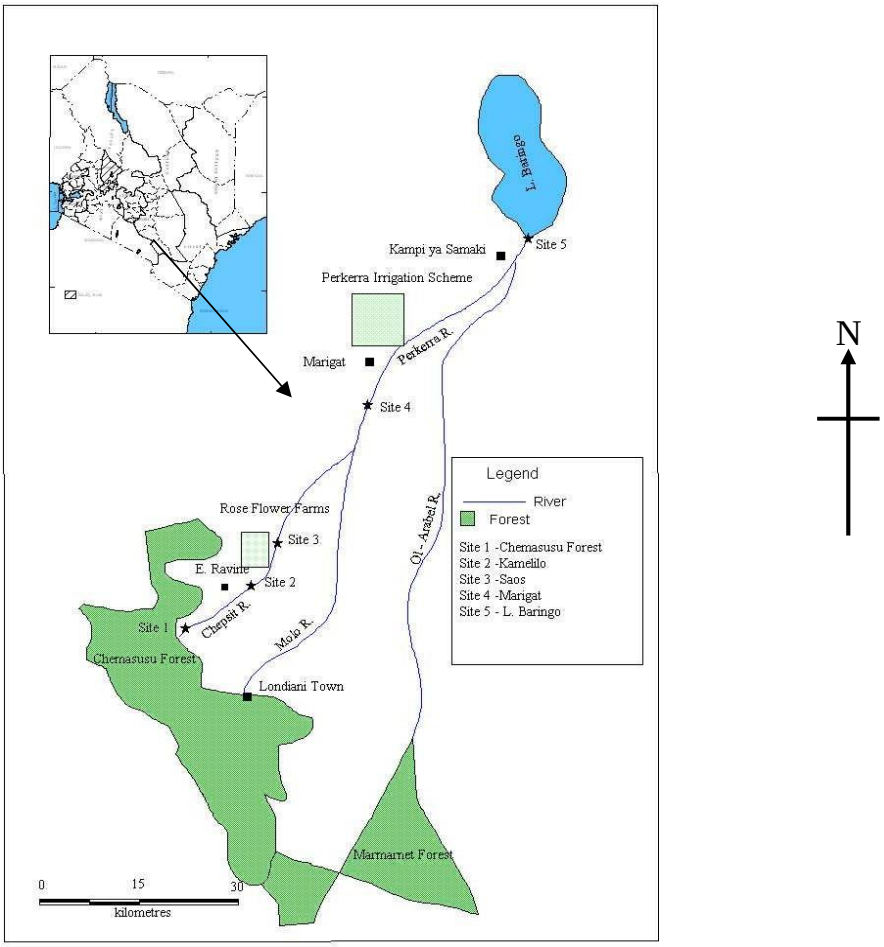

Figure 1: Map of the study area

Chemical reagents

In all cases, analytical grade reagents were used unless stated otherwise. These included; anhydrous sodium sulphate

(Na_2SO_4), florisil**,** ammonium chloride (NH_4Cl), buffer solutions pH 4.00 and pH 7.00, sodium hydroxide, salicylic acid, nitrate free water, stock nitrate solution, intermediate nitrate solution, hydrochloric acid (HCl), sulphuric acid (H_2SO_4), potassium antimonyl tartrate ($KSbC_4H_4O_6$), ammonium molybdate ($(NH_4)_6Mo_7O_{24}.H_2O$), ascorbic acid, ferrous ammonium sulphate ($Fe(NH_4)_2(SO_4).6H_2O$), potassium dichromate ($K_2Cr_2O_7$), potassium dihydrogen orthophosphate, sodium bicarbonate ($NaHCO_3$), potassium chloride (KCl). The purities of all the reagents used in preparation of all the stock solutions (1000 ppm) were above 99%. The reagents were obtained from Fischer Scientific chemical Suppliers, Nairobi.

Sampling

The sampling sites are shown in Figure 1. Sampling was done in triplicates for water, soil and sediments from each of the five stations studied during both the dry and wet seasons.

Water samples from the river were in one litre amber bottles, which had previously been rinsed with hexane and the sample. The samples were transported to the laboratory in ice boxes containing ice and were analysed within 48 hours of sampling.

Subsurface sediments were scooped from the river bed using soil augre in triplicates and stored in aluminium foil and were transported to the laboratory in ice boxes with ice. Extraction was done within 48 hours of sampling.

Soil samples were collected randomly in triplicates along the river using soil auger. The soil was stored in aluminium foil and transported in ice boxes. Extraction was done within 48 hours of sampling.

Determination of pH

The pH meter was measured using digital pH meter model HANNA 211. Calibration of the electrode with 2 buffer solutions of pH 4 and pH 7 prior to its use was done.

Dissolved oxygen meter

The dissolved oxygen meter used was a HI 9143 Microprocessor HANNA model. The instrument was calibrated using KCl.

Colorimetric determination of nitrates

Concentrations of nitrate in the samples were determined using standard method (Okalebo *et al*, 2002). Approximately 10 g KNO_3 was dried at 105 ^oC for 2 hrs then cooled in a dessicator. 1000 ppm NO_3^- -N stock solution was prepared and from this stock solution, the following standards were prepared: 0, 2, 4, 6, 8, and 10 ppm NO_3^- -N.

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 pipetted to each test tube, mixed well immediately the acid was added and left to stand for 30 minutes. 10.0 ml of NaOH solution was added to each test tube, mixed well and left to stand for one hour for full colour development. The absorbance of both the standard and sample were read at 410 nm, using a UV/Visible spectrophotometer (model spectroscan 30).

Determination of phosphates (Olsen method)

The Olsen method was adopted for the calorimetric determination of total phosphate (Olsen *et al*, 1954; Okalebo *et al*, 2002).

Extracting solution

42 g of $NaHCO_3$ was weighed in a 1 litre

beaker. About 500 ml of distilled water was added and dissolved by heating then, allowed to cool and the pH of the solution adjusted to 8.5 by adding 1M NaOH. The contents were filled up to the 1 litre mark with distilled water.

4% ammonium molybdate, $(NH_4)_6Mo_7O_{24}.H_2O$)

20 g of ammonium molybdate was dissolved in about 300 mL distilled water and diluted to 500 ml with distilled water.

0.1 M ascorbic acid

1.78 g of ascorbic acid was dissolved in 100 mL of distilled water.

0.06M Potassium antimonyl tartrate ($KSbC_4H_4O_6$)0.274 g was dissolved in 100 mL of distilled water.

Determination of chemical oxygen demand (COD)

The COD in the samples was determined using standard method (Clair *et al*, 2003). 2.5 mL sample was measured and transferred into borosilicate culture tubes then 1.5 ml of potassium dichromate digestion solution added. 3.7 mL H_2SO_4 was carefully run down inside the vessel so that an acid layer formed under the sample digestion solution layer. Contents were mixed thoroughly before applying heat to prevent local heating of vessel bottom and possible explosive reaction. The borosilicate culture tubes were then placed in block digester and refluxed for 2hrs, cooled to room temperature. The contents were then transferred into an Erlenmeyer flask and 1-2 drops ferroin indicator added and placed on a magnetic stirrer and stirred while titrating with 0.01M FAS. The end point was marked by a sharp colour change from blue-green to reddish brown. Distilled water blank was made and treated in the same manner.

Determination of biochemical oxygen demand (BOD)

The BOD in the samples was determined using standard method (Norton, 1946). 20 ml of sample was measured in-situ and transferred into the BOD bottle. Distilled water was added until it was filled to overflow. The initial oxygen reading was read using the DO meter HI 9143 Microprocessor HANNA model. The solution was stoppered carefully not to trap in any air bubbles and then incubated in the water bath in an inverted manner. The temperature was maintained at 20 ^oC. The solution was incubated for 5 days. At the end of the five days, the final oxygen reading was recorded. The BOD is given by the difference between the initial and the final readings (HACH, 1999).

Data Analysis

The results were corrected according to recovery rates. Data was subjected to linear analysis using Microsoft Excel, EuraChem and SAS software packages. The 0.05 significance level for probability was used as a criterion of statistical significance. Quality assurance and quality control procedures for the laboratory included analysis of triplicates, EPA standards, blanks and spikes.

RESULTS AND DISCUSSION

Nitrates in water

Nitrates mean values in water for the dry and wet seasons and their standard deviations (SD) are shown in Table 1.

Table 1: Nitrates concentration in water at the five sampling sites.

Site	Season	Concentration(ppm) ±SD
1	Dry	2.03 ± 0.0100
	Wet	2.94 ± 0.0058
2	Dry	4.53 ± 0.0208
	Wet	4.46 ± 0.0200
3	Dry	4.98 ± 0.0208
	Wet	4.02 ± 0.0200
4	Dry	3.51 ± 0.0208
	Wet	4.09 ± 0.0100
5	Dry	3.45 ± 0.0300
	Wet	3.58 ± 0.0200

The concentration of nitrates in the five sampling sites were significantly different at sites 1, 4 and 5 (LSD = 0.0236, CV = 0.51987). During the dry season, nitrates at sampling stations 1, 2, 3, 4 and 5 varied between 2.03 and 4.98ppm with the mean values of 2.03 ± 0.0100, 4.53 ± 0.0208, 4.98 ± 0.0208, 3.51 ± 0.0208 and 3.45 ± 0.0300ppm, respectively. During the wet season, nitrates at all the sampling stations varied between 2.94 and 4.46ppm with the mean values of 2.94 ± 0.0058, 4.46 ± 0.0200, 4.02 ± 0.0200, 4.09 ± 0.0100 and 3.58 ± 0.0200ppm, respectively. As is expected, Site 1 (source of the river) showed low levels of nitrates both during the dry and wet season since there are no farming activities at site 1.

An increase in nitrates values observed at sites 2 and 3 could be attributed to the runoff from the resident's farms at site 2. The increase at site 3 could be attributed to the runoff from the rose flower greenhouses situated near Chepsit River. The decline in nitrate levels at sites 4 and 5 is attributed to the conversion of nitrates to nitrites (Rao *et al*, 2007) by the high temperatures along Marigat and Lake Baringo and also due to dilution effects as Chepsit River joins with other rivers like Molo. The nitrate levels for all the sites sampled during both the dry and wet seasons were below the water quality standards (10 ppm) set by WHO.

Nitrates in sediments

Nitrates concentrations at sites 3 and 4 were significantly different ($p < 0.05$) while nitrate concentrations were not significantly different at sites 1, 2 and 5 ($p = 0.1441$, CV = 3.5315). Nitrates mean values at all sampling sites during the dry season varied between 2.61 and 8.24 ppm as presented in Figure 2.

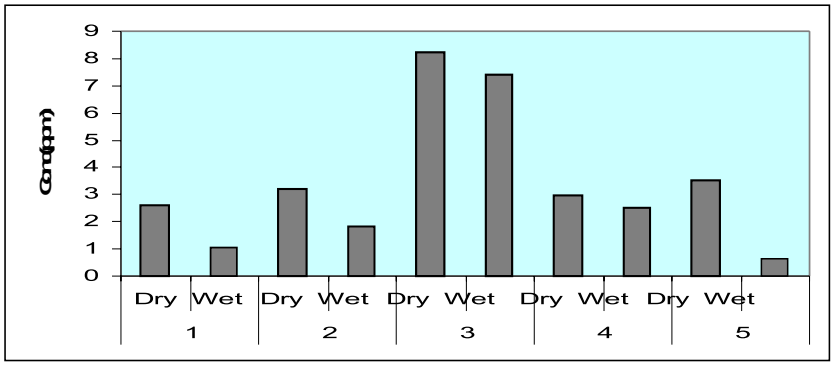

Fig 2:Variation in nitrates concentration in sediments during the dry and wet season.

The drastic increase in nitrates levels during both the dry and wet seasons at site 3 shows that there was high level of concentration of nitrates in the flower farms effluents (8.24 ± 0.0200ppm for the dry season and 7.39 ± 0.0152ppm for the wet season) due to high use of fertilizers containing nitrates. The level of nitrates at site 5 increased more than site 4 during the dry season as a result runoff from the Perkerra irrigation, scheme which uses nitrates containing fertilizers coupled with the accumulation of nitrates downstream (Bandara *et al*, 2006; USEPA, 2002).

Nitrates in soil

Nitrates mean value of 3.456 ± 0.014ppm was recorded in the five sites during the dry and wet seasons. The mean nitrates levels for the dry season varied between 2.29 and 8.13 ppm while during the wet season, the mean values were 1.54 ± 0.0058, 3.34 ± 0.0100, 6.19 ± 0.1000, 1.65 ± 0.0100 and 1.07 ± 0.0200ppm respectively (Table 2).

Table 2: Nitrates concentrations in soils during the dry and wet seasons.

Site	Season	Concentration(ppm) ±SD
1	Dry	2.29 ± 0.0100
	Wet	1.54 ± 0.0058
2	Dry	3.47 ± 0.0200
	Wet	3.34 ± 0.0100
3	Dry	8.13 ± 0.0208
	Wet	6.19 ± 0.1000
4	Dry	4.89 ± 0.0000
	Wet	1.65 ± 0.0100
5	Dry	5.00 ± 0.0200
	Wet	1.07 ± 0.0200

The highest values were recorded at site 3 during both seasons (Table 2). This is attributed to the containing fertilizers in the rose flower farms around the area.extensive use of nitrate

Phosphates in water.

The mean phosphate concentration in water samples at the five sites is shown in Fig 3.

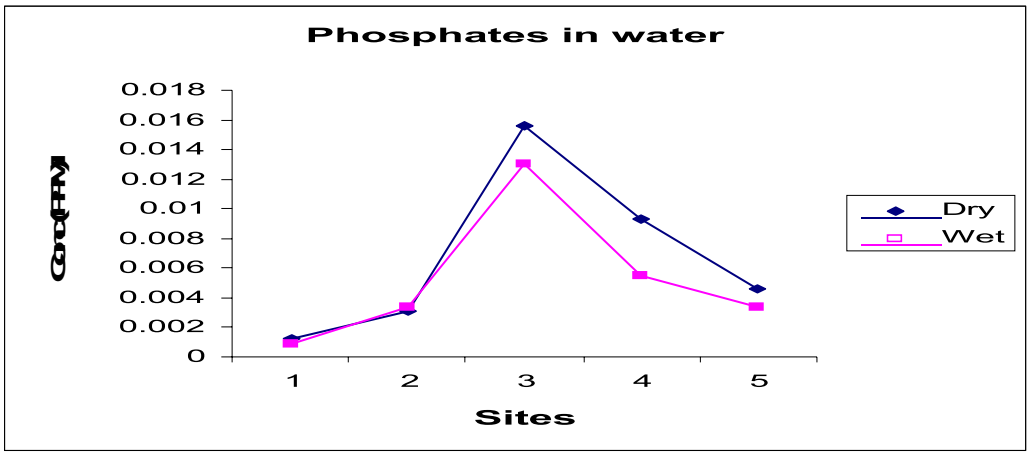

Fig 3: Variation in phosphates concentration in water during the dry and wet season.

The phosphates levels at site 3 were higher during dry season (0.0156ppm) than during wet season (0.0130ppm). Sites 4 and 5 showed a gradual decrease in phosphate concentration during both seasons. The phosphate levels in water samples in all cases were below the KEBS limits (10.0ppm) thus, safe for domestic use.

Phosphates in soil.

Mean phosphate concentrate levels at all the five sampling sites were significantly different ($p = 0.0168$). Figure 4 illustrates the variation of PO_4^{3-} levels in the 5 sampling sites along Perkerra River. The slight increase observed at site 2 could be attributed to the runoff (Sharpley, 1992) emanating from agricultural farms and Eldama Ravine municipal wastes.

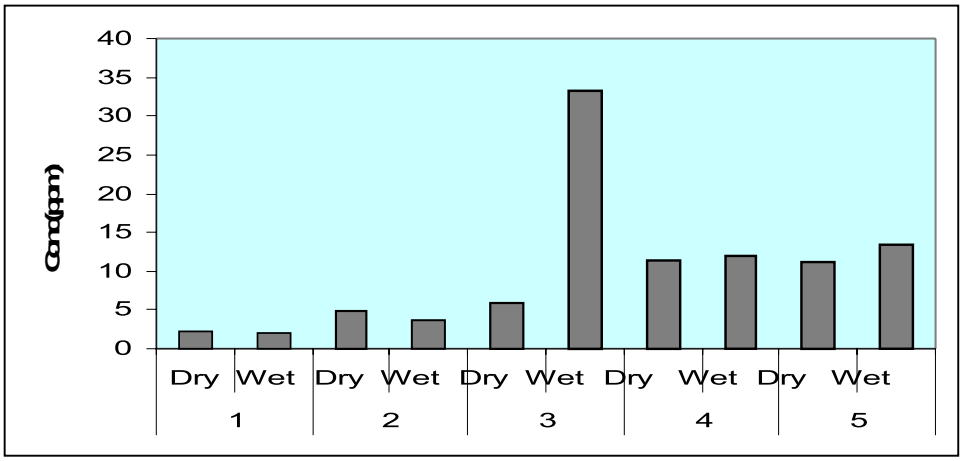

Fig 4: Variation in phosphates concentration in soil during the dry and wet season.

The sharp increase in phosphates at site 3 (33.34 ± 0.0058ppm) during wet season may be attributed to the rains during wet season washing phosphates from the flower green houses situated just a few meters away from site 3. The slight increase in phosphate concentration during wet season at site 5 could also be associated to phosphates usage in Perkerra irrigation scheme being washed towards the lake by flood waters.

Dissolved oxygen (DO)

Figures 5 and 6 show variation of DO, BOD and COD with sampling sites and seasons. The mean values of DO during the dry and wet seasons were in the range 2.15 – 4.42ppm and 2.97 – 4.38ppm respectively. From the data, it was observed that there was slight decrease in DO level in sites 2, 3 and 4 during the dry and wet seasons compared to site 1. This is probably due to the fact that there could be less pollution at site 1. Sites 2, 3 and 4 showed, however, marked decrease in DO during both seasons probably due to the increase in temperature and escape of DO from the surface of the water. The decrease in DO levels may also be due to the high microbial activities in the municipal runoffs at site 2 and also agricultural runoffs at site 3. The high microbial activities could be due to high level of organic matter, hence, increased utilization of DO for decomposition process. The data reveals that increase in temperatures leads to decrease in DO and vice versa. There was a slight increase in DO at site 5 compared to site 4 probably due to the decrease in temperatures.

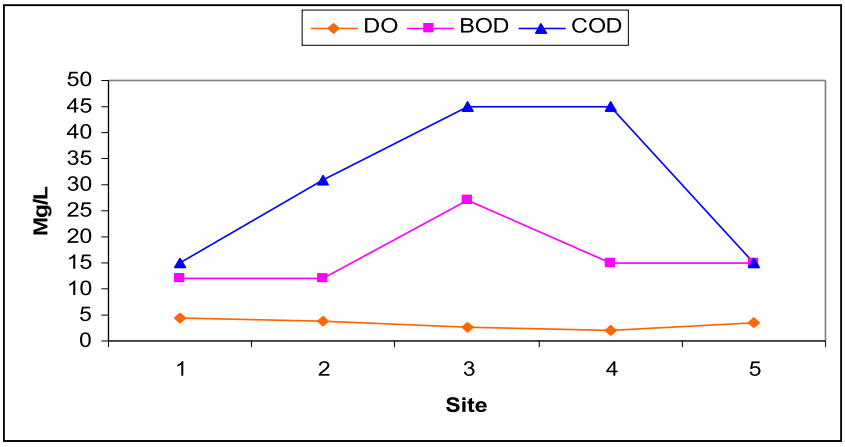

Fig 5: Variation in DO, BOD and COD during the dry season.

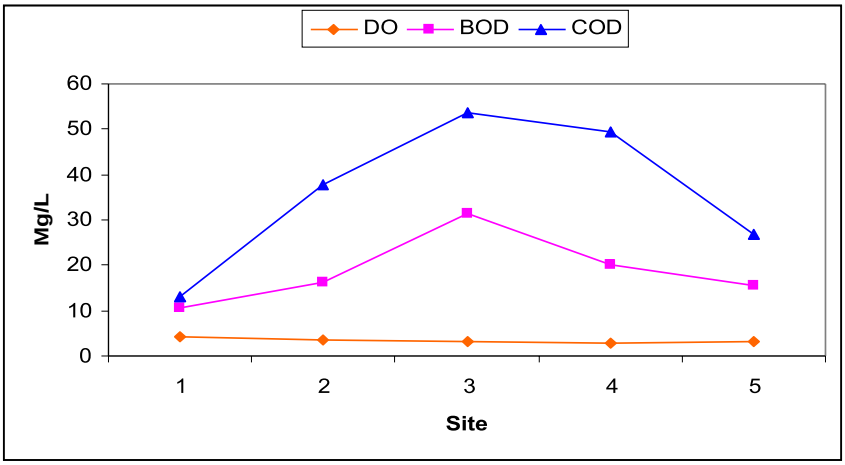

Fig 6: Variation in DO, BOD, and COD during the wet season.

Biochemical oxygen demand

The mean values of BOD during the dry and wet seasons ranged between 12.01 to 27.2ppm and 10.45 to 31.46ppm respectively. From the data, it was observed that BOD levels were highest at site 3 during both seasons. This could probably be due to the high level of organic matter in the agricultural effluents from the flower farms coupled with high temperatures, which increase the rate of microbial decomposition, which requires high oxygen demand, hence, increasing BOD levels. The presence of algae also would increase the BOD levels at this site. The results show that as the temperature increases, BOD also increases and vice versa. Downstream, from sites 4 and 5, there was a significant decrease in BOD values pointing towards the self-purification processes, which could be due to the efficiency of natural cleaning capacity of the river and also dilution of the river by Molo River that joins the Perkerra River. The values of BOD in this study were, however, below the KEBS recommended standards of 50ppm, thus the water is safe as far as BOD is concerned.

Chemical oxygen demand

The levels of COD at different sampling stations are shown in Figures 5 and 6. From the data, it is evident that COD levels are highest at site 3 during both seasons. This is probably due to the high level of chemical species present in the agricultural effluents from the flower farms, which demands high level of oxygen for oxidation of organic matter by a strong chemical, hence, increasing COD levels. Downstream, from sites 4 and 5, there is a significant decrease in COD values pointing towards the self- purification processes, which could be due to the efficiency of natural cleaning capacity of the river and also dilution of the river by Molo River which joins the Perkerra River. The values of COD at site 3 (53.75ppm) during the wet season in this study are above the KEBS recommended standards of 50ppm, thus the water is not safe at site 3 as far as COD is concerned. The water is used by the residents at site 3 for domestic use.

CONCLUSION

The results obtained indicate that the most important pollutants found in River Perkerra are nitrates and phosphates residues from the

commercial flower farms and Perkerra irrigation scheme. Nitrate levels in water during the dry and wet seasons range between 2.03ppm and 4.98ppm, below the standards set by KEBS (10ppm). Phosphates were found to be below the WHO standards (10ppm) in water samples. Phosphates were found to be highest in soil at site 3 (33.34ppm). The high nitrate and phosphate concentrations were attributed to the organic matter entering the drainage from the leaching of agricultural runoff from the flower farms using lots of fertilizers

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