SITE AND SEASONAL VARIATION OF SELECTED PHYSICOCHEMICAL

PARAMETERS AND LEVELS OF HEAVY METALS WITHIN THE AQUATIC

ECOSYSTEM IN SOUTH NYANZA SUGARCANE ZONE

BY

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ABSTRACT

Sugarcane farming has been the main anthropogenic activity done on a large scale in South Nyanza region of Western Kenya since 1979. Use of high rate of nitrogenous fertilizers has been in practice since the establishment of the sugar factory in this area. Studies have shown that use of fertilizers has had adverse impact on the quality of aquatic ecosystems. However, it remains unknown if the aquatic ecosystem within South Nyanza sugarcane zone has been similarly affected. It was therefore important to carry out a monitoring study to establish the sustainability of aquatic systems within this zone. Physicochemical parameters such as temperature, pH, turbidity, conductivity, biological oxygen demand, and organic carbon content, Fe, Zn, Cu, Cr, Pb and Cd were determined in two days of different seasons using standard procedures. The experiment was laid down in a two factor completely randomized design format with site as the main treatment and season as a sub factor. Analysis of variance and student t-tests were used to determine the differences between trends within seasons and among sites at 95% significant levels. The results indicated a significant reduction in pH of soils and aquatic systems within South Nyanza sugarcane fields as compared to different control sites. Other physicochemical parameters recorded a significant ($P \leq 0.05$) increase in their levels with some of them such as biological oxygen demand, turbidity and electrical conductivity being above recommended international aquatic systems levels. Reduction in soil pH levels has been documented to have direct effect on the increase of other physicochemical parameters such as heavy metals mobility in aquatic ecosystems. It was therefore concluded that sugarcane farming is affecting the quality of aquatic ecosystem within South Nyanza sugarcane zone and urgent measures such as correction of soil pH was needed to avoid the problem escalating beyond manageable levels.

CHAPTER ONE

1.0. Introduction

Sugarcane farming activities in South Nyanza Sugarcane zone started in 1979. This cash crop is extensively grown in this region by private small and large scale farmers led by the South Nyanza Sugar Factory that manufactures mill white sugar. Most of the small scale farmers rent out their land to the company and to private large scale farmers; hence most of the small scale farms also adopt usage of nitrogenous fertilizers used in the company nucleus estates and other large scale farms for better cane yields (Oliver, 2004). The fertilizers are used repeatedly in this zone with increasing magnitude every year as more farms are set aside for sugarcane plantation (Oliver, 2004).

Soil is one of the repositories for anthropogenic wastes and biochemical processes can mobilize them to pollute water supplies and impact food chains (Lark *et al.*, 2002). Trace heavy metals contamination in the soils is a major cause of concern because of their toxicity and threat to human life and the environment (Lark *et al.*, 2002). Heavy metals such as Cu, Cr, Cd and Pb are potential soil and water pollutants (Carvalho *et al.*, 1999). Heavy metal studies are necessary to evaluate both soil/sediment and groundwater contamination. The toxic heavy metals entering the ecosystem may lead to bioaccumulation (Lark *et al.*, 2002). Heavy metals like Fe, Cu, Zn and other trace elements are important for proper functioning of biological systems and their deficiency or excess could lead to a number of disorders (Carvalho *et al.*, 1999). Food chain contamination by heavy metals has become a burning issue in recent years because of their potential accumulation in biosystems through contaminated water and soil (Lark *et al.*, 2002).

Motdvet (1995) and Alloway (1995) have documented adverse effects of continued use of fertilizers on the soil chemistry that include but not limited to reduced soil pH, increased heavy metal loads, increased electrical conductivity and biochemical oxygen demand. Specifically, the adverse effects of increased fertilizer application have been documented to be triggered by reduced soil pH (Alloway, 1995). For instance, reduction of soil pH makes heavy metals in the soil to become more soluble, bioavailable and mobile (Alloway 1995) hence processes such as surface runoffs, leaching and soil erosions that are more evident in wet seasons aid in mobility of these heavy metals into aquatic ecosystems. In the mobility of heavy metals, it all starts with ionization of metals increasing at low pH thereby increasing their water solubility and mobility after which the hydronium (H^+) ions displace most other cations on negative surface charges.

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This reduces metal adsorption by cation exchange and organic complexation (Ford *et al.,* 2001). Besides, Duinker *et al* (1982) noted that use of commercial fertilizers affects soil chemistry and specifically lowers soil pH thereby increasing heavy metal solubility.

The accumulation of heavy metals in agricultural soils is of increasing concern due to the food safety issues and potential health risks as well as its detrimental effects on soil ecosystems (McLaughlin *et al.,* 1999). These metals have peculiar characteristics including that: they do not decay with time, they can be necessary or beneficial to plants at certain levels but can be toxic when exceeding specific thresholds and often occur as cations which strongly interact with soil matrix, consequently, heavy metals in soils can become mobile as a result of changing environmental conditions (Nyamangara *et al.,* 1999). Apart from the source of heavy metals, physicochemical properties of soil also affect the concentration of the heavy metals in soils. Organic matter and pH are the most important parameters controlling the accumulation and the availability of heavy metals in soil environment (Nyamangara *et al.,* 1999).

In the sugar industry, it has been realized that discharges from the factories have been reported to result in adverse ecological effects. The deterioration of surface and groundwater quality is perceived by farmers to be a consequence of changing or dynamic farm management strategies (Lark *et al.,* 2002). Most studies have shown that soil acidification takes place under sugarcane principally due to the use of N fertilizers containing or producing NH_4^+ (Sumner, 1997). All ammoniacal N fertilizers release protons when NH_4^+ is oxidized to NO_3^- by nitrifying micro-organisms. Also mineralization of organic matter can contribute to soil acidity by the oxidation of N and S to HNO_3 and H_2SO_4 (Sumner, 1997). Soil pH also decreases due to crop uptake of K, Ca and Mg. hydrogen will replace these cations on the soil exchange surface (Sumner, 1997). Industrial processing of sugarcane for production of sugar is a source of pollution for aquatic ecosystems, as large amounts of by-products and wastes are generated in the mills. The most important being wastewater generated in the factories (Ballester *et al.,* 1999). This wastewater is rich in organic matter and therefore increases BOD (biochemical oxygen demand) of waters receiving these. Elevated BOD promotes depletion of dissolved oxygen in the water and often causes anoxia (Ballester *et al.,* 1999). High nutrient concentration in this kind of effluent also contributes to the problem by enhancing algal blooms and promoting eutrophication of surface waters (Matsumura *et al.,* 2005).

Deposition and subsequent increase in aquatic systems physicochemical parameters have been documented to cause adverse effects on aquatic ecosystems. For instance, bioaccumulation and bio concentration of toxic heavy metal residues in aquatic environments can result in their transfer into food chains putting terrestrial consumers including humans and birds at risk (Wang, 1987; Gough and

Herring, 1993; Driscoll *et al.*, 1994; Ongley, 1996). Contaminated food webs can also cause health and economic disadvantages to people as contaminated commercial foods like fish become restricted or banned due to high heavy metal loads (Wang, 1987; Gough and Herring, 1993; Driscoll *et al.*, 1994; Ongley, 1996). It therefore becomes important to monitor and suggest possible mitigation measures that can help in controlling deposition and increase of these physicochemical parameters into aquatic ecosystems for apart from affecting the aquatic life, they indirectly affect human life as well (Wang, 1987; Gough and Herring, 1993; Driscoll *et al.*, 1994; Ongley, 1996). Some of the set interntional standards for physicochemical parameters above which aquatic systems become stressed and/or affect other organisms are shown in Table 1, 2.

Some International and national aquatic systems physicochemical parameters standard levels beyond which the systems become stressed have been shown in Table 1 while Table 2 shows permissible limits for international agricultural soil. A report on fertilizer usage on selected plots in South Nyanza sugarcane farms over the last 5 years indicates intensive application has been given in Table 3.

Table 1: International and national aquatic systems physicochemical water parameters

Parameter	Domestic water standard	Aquatic life standard
Temperature ^{o}C	< 30	< 40
pH	6.5 – 8.5	5 – 9
Conductivity $\mu S/cm$	< 50	< 1000
Biochemical oxygen demand		
Turbidity (NTU)	< 5	-
Chlorine (mg/l)	250	600
Fluorine (mg/l)	1.5	5
Iron	-	-
Zinc (mg/l)	2.0	45
Cupper (mg/l)	0.2	50
Chromium (mg/l)	0.1	50
Lead (mg/l)	0.1	< 10
Cadmium (mg/l)	0.01	< 10

Sources: KEBS, 1996; WHO, 1989.

Table 2: International agricultural soil standards

Parameter	Units	Permissible limits
Organic Matter	%w/w	>0.86
pH	-	4.0 – 8.5
E.Conductivity	µS/cm	< 4000
Cu	mg/kg	100
Cd	mg/kg	1.0
Cr	mg/kg	100
Zn	mg/kg	250
Pb	mg/kg	500
Fe	mg/kg	-

Source: Alloway, 1995

Table 3. History of repeated nitrogenous fertilizer application (in bags of 50 kg each) in some plots from South Nyanza Sugar Nucleus Estate farms in Western Kenya.

	Plots												
	102A		201A		306C		415B		508A		627B		524B	
Size	6.56(ha)		5.02 (ha)		3.67 (ha)		1.70 (ha)		7.41 (ha)		3.69 (ha)		2.43 (ha)	
Year	DAP	Urea	DAP	Urea	DAP	Urea	DAP	Urea	DAP	Urea	DAP	Urea	DAP	Urea
2005/06	50	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	40	NA	NA
2006/07	50	NA	40	45	35	50	15	NA	52	40	12	NA	10	NA
2007/08	50	55	NA	NA	NA	NA	NA	NA	NA	50	8	15	12	15
2008/09	NA	NA	30	NA	15	NA	NA	NA	NA	NA	NA	10	18	NA
2009/10	NA	25	NA	NA	NA	NA	NA	10	33	NA	NA	15	NA	5
Sum	150	80	70	45	50	50	15	10	85	90	20	80	40	20

NA: Not Applied

Source: Agronomy Section, South Nyanza Sugar Company.

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1.1. Statement of the Problem

South Nyanza sugarcane zone uses fertilizers in farming. The use of fertilizer is documented to affect the levels of physicochemical parameters and heavy metal loads in soils and aquatic systems hence deteriorates the quality of water. It is therefore not known the extent to which the use of fertilizers has affected the quality of water. It also remains unknown if there will be any seasonal variations in these parameters that determine the water quality.

1.2. Objectives of the study

1.2.1. Main objective

To determine site and seasonal variation of selected physicochemical parameters and levels of heavy metals within the aquatic ecosystem in South Nyanza sugarcane zone.

1.2.2. Specific objectives

i. To determine the variations in pH, turbidity, electrical conductivity, chlorine, fluorine, Fe, Zn, Cu, Cr, Pb, Cd in water and the levels of the heavy metals in sediments within Sare River in South Nyanza sugarcane zone.

ii. To compare the pH, total organic carbon and the heavy metals in the soils along Sare River in South Nyanza sugarcane zone.

iii. To determine the seasonal variation of the selected physicochemical parameters and heavy metals in Sare River in South Nyanza sugarcane zone.

iv. To compare the water quality parameters from different sites and seasons within aquatic ecosystems from Sare River against national and international aquatic ecosystems standards.

1.3. Hypotheses (H_0)

i. There is no variation in the pH, turbidity in water and heavy metal loads in sediments from aquatic ecosystems within South Nyanza sugarcane zone.

ii. There is no significant difference in the pH, TOC and heavy metals from the soils along Sare River compared to the levels in the control site.

iii. There is no seasonal variation of the selected physicochemical parameters and heavy metals in Sare River in South Nyanza sugarcane zone.

iv. The water quality parameters within aquatic ecosystem from Sare River are similar to national and international aquatic ecosystem standards.

If the null hypotheses shall not be accepted then the alternative shall be adopted.

1.4: Research Justification

Human beings and animals use water from Sare River and the quality is unknown. It is necessary to urgently assess the quality of the water to avoid further adverse effects on aquatic dependants. Little has been published concerning heavy metal pollution in Kenyan rivers and in particular on heavy metal levels in Sare River and canals within South Nyanza sugarcane Zone.

1.5: Significance of the study

This research intended to generate important information that stakeholders in sugarcane farming not only in South Nyanza sugarcane zone but other zones too are alerted of the consequences of their activities and possible mitigation measures that can be taken to avoid any future environmental disaster emanating from their farming activities.

CHAPTER TWO

2.0: Literature Review

2.1: Physicochemical parameters of water

Physicochemical parameters are key indicators used in evaluating the environmental fate specifically; used to determine the phase equilibrium distribution of a substance in a closed system (Domènech *et al.*, 2006). They are also indicators of water quality and mobility of heavy metals. The pH of safe drinking water is in the range 6.5–8.5 (WHO, 2004) while wastewater flowing from most sugar factories often has a pH of around 5 (Sumner, 1997). This is due to the effluent consisting of mainly sugar and its derivatives. These organic materials demand oxygen for their decomposition thereby depriving marine systems of the same hence lowering their pH (Sumner, 1997). When a marine system has slight excess of H_2CO_3, some of H dissociates into more H^+, HCO_3^-, CO_3^{2-} and due to the extra H^+, the pH will be lowered (Alloway, 1995). It is not known to what extent sugarcane growing has impacted on the pH of the soils in South Nyanza sugarcane growing belt. This study would assist in trying to ascertain the impact of sugarcane growing in this zone.

Floride occurs up to a maximum of 1.0 mg/l in some natural waters and a level of up to 0.8 mg/l has not been found physiologically harmful (WHO, 2004). When F levels in drinking water reach 1.5 mg/l it causes dental florosis (USEPA, 1980).The guideline value of 1.5 mg/l in drinking water has been proposed by World Health Organization (WHO, 2004). The local application of this value must take into account the climatic conditions and levels of water consumption (WHO, 2004). The F levels in the study area remain largely unknown making it necessary to conduct an assessment to find out the prevailing concentrations in the aquatic ecosystem in this sugarcane belt.

Chloride is present in all portable water supplies and sewage, usually as metallic salts. This 'essential' element in the diet passes through the digestive system unchanged and become one of the major components of raw sewage and eutrophication in water (Farr, 2004). A salty taste produced by Cl depends on the chemical composition of the water. A concentration of 250 mg/l may be detectable in some waters containing sodium ions. On the other hand, the typical salty taste may be absent in waters containing 1000 mg/l when calcium and magnesium ions are predominant (Farr, 2004). The Cl levels in this zone have not been clearly documented.

2.1.1: Biochemical Oxygen Demand (BOD)

BOD is the standardized measurement of quantity of oxygen required for the decomposition of certain organic and inorganic matter after 5 days, hence BOD_5. This parameter measures any substance that

microorganisms can consume using oxygen (SMRI, 2005).The maximum allowed level of BOD is 30 ppm (EMCA, 2006).

Industrial processing of sugarcane for production of sugar is a source of pollution for aquatic systems, as large amounts of by-products and wastes are generated in the mills. The most important being wastewater generated in the factories (Ballester *et al.*, 1999). This wastewater is rich in organic matter and therefore increases BOD of waters receiving these. Elevated BOD promotes depletion of dissolved oxygen in the water and often causes anoxia (Ballester *et al.*, 1999). High nutrient concentration in this kind of effluent also contributes to the problem by enhancing algal blooms and promoting eutrophication of surface waters (Matsumura *et al.*, 2005). It will be necessary to ascertain the BOD levels in the aquatic ecosystem within South Nyanza sugarcane zone so as to advise the users appropriately.

2.1.2: Turbidity

Turbidity is caused by the presence of suspended matter in a liquid (Willard *et al.*, 1992). Turbidity measurement is done in Nephelometric Turbidity Units (NTU) in drinking water. Turbidity is a concern for both health and aesthetic reasons. Particulate matter that creates turbidity can contain toxins, harbour microorganisms and interfere with disinfection (Matsumura *et al.*, 2005). In addition, organic matter in the water can react with disinfectants such as chlorine to create by-products. These by-products may cause adverse health effects (NAS, 1977). While turbidity may be measured in secure groundwater supplies (i.e., not under the direct influence of surface water), it is not a concern in treated water from these sources provided it does not hinder disinfection (WHO, 1998). It is good practice to ensure that water entering the distribution system from a secure groundwater supply has a low turbidity level around 1.0 NTU (USEPA, 1981). Both WHO (1998) and KEBS (1996) recommend turbidity of not more than 5 NTU in drinking water. Most people in South Nyanza sugarcane zone use Sare River water without subjecting it to further treatment but the turbidity levels of the water remain largely unknown hence posing a health risk to the users.

2.1.3: Electrical Conductivity

Electrical conductivity provides a rapid and convenient means of estimating the concentration of electrolytes (WHO, 1989). In waters containing mostly mineral salts the concentration is not very different from that of the dissolved solid matter (WHO, 1989). Electrical conductivity depends on the ionic strength of water. Conversely, the dissociation of most organic compounds is very small in comparison with that of inorganic ones, or they do not dissociate and they therefore conduct an electrical current very poorly, if at all (WHO, 2004). Freshly distilled water has a conductivity of about 1 to 2

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μS/cm or even less, but this increases, owing to the absorption of atmospheric carbon dioxide, to a value about twice as high (WHO, 2004). The electrical conductivity of most fresh and finished waters is in the range of about 50 to 500 μS/cm (WHO, 1989). The values for highly mineralized waters go up to 100 and even higher, and for some industrial wastes, they may be in excess of 10,000 μS/cm (WHO, 2004).

Sugarcane cultivated soils have lower electrical conductivity values as compared to uncultivated soils (Carvalho et al., 1999). Excess leaching of salts in sugarcane cultivated soils result in lower electrical conductivity (Carvalho et al., 1999). However, the levels of electrical conductivity of waters within South Nyanza sugarcane zone remain unknown. This is despite the fact that these waters are used for drinking besides animal usage.

2.2: Heavy Metals in Aquatic Ecosystem

Heavy metals like Cu, Zn and Pb are pollutants of great concern in aquatic ecosystems because of their environmental persistence, toxicity and ability to be incorporated into food chains and at high levels can have adverse effects on biota (El Nabawi et al., 1987). Sediment analysis provides a stable base for monitoring the pollution of an aquatic environment by heavy metals which are easily accumulated in suspended and bed sediments (NIH, 1999). Studies have also demonstrated that the determination of metal concentrations in sediments is more sensitive than dissolved concentrations as indicators of contamination in hydrologic systems (NIH, 1999).

2.2.1: Cadmium (Cd)

Cd is an element that occurs naturally in the earth's crust. Pure Cd is a soft, silver-white metal. However, Cd is not usually found in the environment as a metal. It is usually found as a mineral combined with other elements such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulfur (cadmium sulfate, cadmium sulfide) (USEPA, 1989). These compounds are solids that may dissolve in water but do not evaporate or disappear from the environment (Farr, 2004). All soils and rocks, including coal and mineral fertilizers, have some Cd in them (WHO, 1989). It can enter water from disposal of waste water from households or industries. Fertilizers often have some Cd in them and fertilizer use causes Cd to enter the soil (Farr, 2004). Spills and leaks from hazardous waste sites can also cause Cd to enter soil or water. Cd does not break down in the environment but can change into different forms. Most Cd stays where it enters the environment for a long time (Farr, 2004). Some of the Cd that enters water will bind to soil but some will remain in the water (Farr, 2004). Cd in soil can enter water or be taken up by plants. Fish, plants, and animals take up Cd from the environment (Farr, 2004). Eating food or drinking

water with very high Cd levels severely irritates the stomach, leading to vomiting and diarrhea. Studies have determined that Cd is probably carcinogenic to humans (USEPA, 1989). Small quantities of Cd cause adverse changes in the arteries of human kidneys (WHO, 2004). At concentrations above 200 ppb it is toxic to certain fish (Farr, 2004). In potable waters, the normal level of Cd is from 0.4 to 60 ppb (WHO, 2004). In most river waters the level gets to even higher than 200 ppb (USEPA, 1989). Studies in Australia have shown a sevenfold increase in Cd in the top soils under sugarcane compared with uncultivated sites (El Nabawi *et al.*, 1987), probably caused by Cd contamination in P fertilizers, which is common (Oliver, 2004). It is suspected that pre-harvest burning could dissipate Cd while trash blankets may concentrate Cd at the soil surface (El Nabawi *et al.*, 1987). The water from Sare River and the canals feeding into it is extensively used for both industrial and domestic purposes and knowing the level of Cd in it would help provide appropriate remedial advice.

2.2.2: Lead (Pb)

The toxicity of Pb is widely acknowledged. The Kenya Bureau of Standards (KEBS, 1996) reported that Pb content in drinking water should not exceed 0.05 ppm. In the United States of America, the national primary drinking water standard for maximum content of Pb is put at 0.05 ppm (USEPA, 1979; NRC, 1979). A safe guideline value of 0.01 ppm of Pb in drinking water has been given by WHO (1998). Allowable maximum limits for Pb in drinking water in the UK, EU and USA are 0.05 ppm, 0.01 ppm and 0.05 ppm respectively (Neubauer and Wolf, 2004). Most inorganic salts of Pb have poor to negligible solubility in water except for the acetate, nitrate, and chloride. Therefore water-borne Pb is minimal, because it forms essentially insoluble sulphates and carbonates (Stokinger, 1981). An exception is Pb-lined tanks and pipes in water distribution systems, which produce toxic concentration, both in acid and soft waters (Tsuchiya, 1977, USEPA 1980). A study of 969 U.S. water systems found an average Pb concentration at the tap of 0.0131 ppm with 1.4% of the samples exceeding the drinking water standard of 0.05 ppm (NAS, 1977). Pb levels at the tap may be higher than in the finished water at the treatment plant and a study of cities in USA with wide usage of Pb pipes have reported mean tap concentration of Pb to be 0.03 ppm with 26.7% exceeding 0.05 ppm standard (NAS, 1977).

Pb is a known neurotoxin (kills brain cells), and excessive blood lead levels in children have been linked to learning disabilities, attention deficit disorder, hyperactivity syndromes, and reduced intelligence and school achievement scores (Farr, 2004). Pb is the best-known example of problems associated with chronic low-level toxic element exposure. Studies show that Pb toxicity is associated with deficits in central nervous system functioning that can persist into young adulthood. Hair Pb is correlated with both reduced intelligence scores and lowered school achievement scores (Farr, 2004).

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World Health Organization (WHO) has recommended a provisional tolerable intake for Pb by adults and should not exceed 5 µg/kg (body weight)[-1] (WHO, 2004). They also recommend that no more than 50% of a population's blood Pb values should exceed 0.2 ppm. According to Snyder et al. (1975), the Pb balance for a 70 kg reference man requires an intake of 0.44 mg/day from food and fluids and 0.01 mg/day from air and loses 0.045 mg/day through urine, 0.3 mg/day through faeces and 0.1 mg/day through other routes for instance sweating. The total body burden has been estimated to range between 100 to 400 mg and thus increases with age (Tsuchiya, 1977). Snyder et al., (1975) reported a value of 120 mg to be the total burden with 11 mg in soft tissues. Pb is reputed to be a serious body poison (WHO, 1989). Natural waters generally contain up to 20 ppb of Pb, although in some cases 400 ppb of Pb have been reported (WHO, 2004).Pb has been reported to have gradual accumulation in the aquatic ecosystem in areas where sugarcane is grown (Carvalho et al., 1999). The levels of Pb in the aquatic ecosystem of South Nyanza sugarcane plantations remain largely unpublished and this research would help bring out some needed information so as to come up with remedial measures.

2.2.3: Copper (Cu)

The Kenya Bureau of Standards (KEBS, 1996) reported that safe drinking water should not contain more than 0.1 ppm of Cu. The World Health Organization (WHO, 1998) requires that Cu in drinking water should not exceed 1 ppm. Consumers might complain of stained laundry and sanitary ware if they use safe drinking water containing at least 1ppm of Cu (WHO, 1998). Allowable maximum limits for Cu in drinking water in the United Kingdom (UK), European Union (EU) and United States of America (USA) are 3 ppm, 1 ppm and 1 ppm respectively (Neubauer and Wolf, 2004).

Cu in water has been noted to be exceedingly toxic to aquatic biota in contrast to low toxicity to mammalian consumers of water (USEPA, 1980). Whereas concentrations as low as 0.005 to 0.025 ppm are lethal to some invertebrate and fish species within 4 days, the recommended standard for public water supplies based on palatability is 1 ppm (WHO, 1998). Undesirable taste and odour might be perceived with aqueous concentrations greater than 1 ppm (USEPA, 1980). The greater sensitivity of most aquatic biota could be as a result of high surface to volume ratios of algae and, highly permeable gill surface area in various fish species that facilitates rapid uptake of large amounts of Cu (WHO, 1998). Consequently, sensitivity of aquatic biota to water borne metals is analogous to mammalian sensitivity to air borne metals as a result of rapid respiratory uptake. Although Cu is an essential element for all life, at high concentrations, it is potentially toxic to soil microorganism, soil fauna, and higher plants (Vulkan et al., 2000). Studies have reported adverse effects of Cu on soil microbial biomass, populations of individual species, microbial biodiversity and microbial mediated process (Vulkan et al.,

2000). In most studies involving soil microorganisms or plants in soils, toxicity has been expressed in terms of total soil concentrations or some operationally defined extractable (Vulkan *et al*, 2000). Existing legislation or guidelines in the United Kingdom (UK) on Cu in soils are also based on total concentrations (WHO, 1998).

Studies have established that total Cu concentrations in soils do not reflect bioavailability, and the relationships between bioavailability and operationally defined fractions of the metal are often influenced by other soil properties (Parker *et al.*, 1995). Free metal activity is the main factor controlling metal toxicity into aquatic organisms and the same free metal ion activity in soil and water is one of the key factors controlling metal bioavailability to soil microorganisms and plants (Parker *et al.*, 1995). Also, soil microorganisms or microbial processes appear to be more sensitive to Cu toxicity than higher plants (WHO, 2004). Cu is a micronutrient required in very small amounts and its common range in plant tissues, has been observed to be 3 to 50 ppm (Farr, 2004). Cu plays a significant role both as a micronutrient and as a constituent of Cu protein enzyme essential in plant red-ox processes. However, higher values can easily interfere with the growth of aquatic plants and hence the Lake Victoria basin ecosystem. Baker (1974) also reported toxicity of Cu to various types of plants when the amount added over a period of time exceeds 150 to 400 ppm in soil. Cu is generally known to be an essential trace element to man and in fact to all vertebrates. The human adult Recommended Daily Allowable (RDA) Cu intake is 2 to 3 mg though some studies indicate that levels between 1 and 2 mg could maintain a positive Cu balance (NAS, 1980). It is a component of most vital enzymes; including tyrosinase, cytochrome oxidase, and amine oxidases (Piscator, 1977; USEPA, 1980). Cu is largely combined with serum albumin and alpha-globulin ceruloplasmin, which serve to transport and regulate it in the body (Stokinger, 1981). The metabolism of Cu involves a turnover of the Cu-containing enzymes. Menke's disease, a Cu deficiency disease, is a disorder in the metabolism whereby there exists an inability to absorb Cu (USEPA, 1980). Cu is especially essential in the electron transfer processes which also involve iron in haemoglobin, photosynthesis in plants and the terminal step of mitochondrial respiration and hence Cu influences life support functions like production of red blood cells and carbohydrate synthesis (Malmstrom, 1979). Cu, together with Fe, is the dominating prosthetic metal ion in the electron-carrier proteins participating in the biological oxidation of organic substrates by dioxygen. As a transition element, Cu has a particular chemical suitability of having a functional role in electron transfer and oxygen transport proteins as it has two common valence states; Cu (I) and Cu (II). Furthermore, the oxidation-reduction potential governing the relative predominance of these two valence states is sensitive to the nature and steric arrangement of the surrounding ligand potentials (Reinhammar, 1979).

In addition, it has been found that Cu^+, like the low valence forms of many other transition metals, in certain complexes can bind O_2 and CO reversibly (Prasad and oberleas, 1976) despite the fact that O_2 is a neutral symmetric molecule. However, at high doses, Cu is one of the common metallic elements toxic to humans found in polluted environments (Purves, 1977). A condition known as Wilson's disease is due to inability to utilize Cu and is a hereditary metabolic disorder whereby there is accumulation of Cu in some organs of the body, the most sensitive being the brain and liver (USEPA, 1980; Prasad and Oberleas (1976). Acute Cu poisoning also causes hemolytic anaemia (Finelli *et al.,* 1981). Cu is actively absorbed in the stomach and duodenum. Typically about half of the ingested dose is absorbed, but this can be decreased by competition with Zn and binding by ascorbic acid and other organic compounds. However, except for a few occupational exposures, daily intakes of airborne Cu, even near smelters are negligible compared to oral ingestion. Similarly, dermal absorption is negligible through intact skin. However, Cu can also be excreted and the major excretion route for the absorbed Cu is the bile. Minor routes of Cu excretion include sweat, urine, and saliva (USEPA, 1980; Stokinger, 1981). High loadings of Cu in arable land are attributed to excess use of organic fertilizers (McLaughlin *et al.,* 1999). Cu has been reported as a contaminant in water samples and stream bed sediments collected in rivers draining regions that have extensive sugarcane farming (Carvalho *et al.,* 1999). It is important to know the level of Cu in the water from Sare River and the tributaries since quite a large population in this depend on the water for their daily use.

2.2.4: Iron (Fe)

Fe is an essential mineral. It is a component of haemoglobin and cytochromes. The recommended daily allowance is 10 mg for men and 18 mg for women (NAS, 1980; Stokinger, 1981). Fe is a major metabolic factor and enzymes require Fe for their activity and in some cases it is weakly bound, for example, with aconitase (Beinert and Kennedy, 1989). Fe is a major control element in many enzymes involved in secondary metabolism and the body requires Fe for their activity (Da Silva and Williams 1991). Since some of these are enzymes, including hormones, Da Silva and Williams (1991) concluded that, at least in prokaryotes, there is a relationship between the levels of free Fe^{2+} and the whole of the cell activity up to the point of initiation of cell division. Fe may cause conjunctivitis, choroiditis, retinitis if it conacts and remains in the tissues. Chronic inhalation of excessive concentrations of Fe oxide fumes or dusts may result in developing pneumoconiosis, called siderosis, which is observable as an x–ray change. No physical impairement of lung function has been associated with siderosis. Inhalation of excessive concentrations of Fe oxide may enhance the risk of lung cancer development in workers exposed to pulmonary carcinogens (USEPA, 1989).The Kenya Bureau of Standards (KEBS) (1996)

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reported that safe drinking water should not exceed 0.3 ppm of Fe. It was reported by WHO (1998) that in drinking water, levels of at least 0.3 ppm stain laundry and sanitary ware. Allowable limits for Fe in drinking water in the UK, EU and USA are 0.2 ppm, 0.2 ppm and 0.3 ppm respectively (Neubauer and Wolf, 2004).Fe (III)-O-arsenite, pentahydrate may be hazardous to the environment; special attention should be given to plants, air and water. It is strongly advised not to let the Fe enter into the environment because it persists in the environment (NAS, 1977).

Fe is found in virtually every food, with higher concentrations in animal tissues than in plant tissues (Hammond and Beliles, 1980). In the United States (U.S) and Europe, men consume 16 mg/day and women, 12 mg/day. Some drinking water is high in Fe concentration. About 140 µg Fe/day comes from average United States drinking waters (Snyder et al., 1975). The total body burden is estimated to range from 4.2 to 4.5 g (Stokinger, 1981; Snyder et al., 1975). According to Snyder et al. (1975), the Fe balance for a 70 kg reference man, is intake from foods and fluids 16 mg/day and airborne intake of 0.03 mg/day. Losses of Fe occur through urine 0.25 mg/day, faeces 15 mg/day, and through other routes 0.51 mg/day. For a 50-kg reference woman, the values are 12 mg/day and 0.03 mg/day, respectively, for intake and 0.20 mg/day, 11 mg/day and 1.2 mg/day for losses through urine, faeces and other routes respectively, including (0.6 mg/day as menstrual loss).Intestinal absorption of Fe, especially Fe (II), is a complicated process. The rate of uptake is inversely related to the state of the body's Fe stores (Hammond and Beliles, 1980). In adults Fe absorption has been found to be 30% (Snyder et al., 1975). Toxic signs are caused by free Fe in human body. The signs appear after the carrier has been saturated with Fe (Stokinger, 1981). The normal Fe intake for children is 10 – 20 mg/kg body weight. It had also been reported that workers with Fe pneumoconiosis had an average 160 µgFe/100 g serum compared to 127 µgFe/100 g in unexposed workers (Stokinger, 1981). Level of Fe in aquatic ecosystems has been reported to be high irrespective of the type of land use (Carvalho et al., 1999). Not much has been published regarding Fe levels in the South Nyanza sugar belt and it would be necessary to carry out an assessment of its level hence the study.

2.2.5: Zinc (Zn)

Zn is ubiquitous in mammalian tissues and is involved in the activity of many enzymes. Thus, Zn participates in metabolic processes (USEPA, 1980). Zn is essential in enzymes and enzymatic functions, such as DNA, RNA, and protein synthesis; carbohydrate metabolism; utilization of nitrogen and sulphur; and cell division and growth. It is important for spermatogenesis, ova formation, and foetal nutrition. It is also involved in pituitary and adrenal gland metabolism. Absolute amounts required range from 1.1 mg/day in infancy, 2.2 mg/day in childhood and adulthood, 2.8 mg/day at puberty, 2.55 to 3.0

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mg/day in pregnancy and 5.45 mg/kg body weight during lactation (Taylor *et al.*, 1982). Zn is present in erythrocytes as the Zn metallo-enzyme carbonic anhydrase; in the leucocytes, in several metallo-enzymes; in the plasma, bound mainly to albumin and in the serum, bound to α-macroglobulin and to amino acids. Zn is also essential for the activity of the following enzymes: alcohol dehydrogenase, carboxypeptidose, leucine aminopeptidase, alkaline phosphatase, carbonic anhydrase, RNA-polymerase, and DNA-polymerase. Thymidinekinase is also Zn dependent (USEPA, 1980).

The Kenya Bureau of Standards (KEBS, 1996) reported that safe drinking water should not exceed 5 ppm of Zn. A safe level of 3 ppm of Zn in drinking water might make consumers complain about its appearance and taste (WHO, 1998). The U.S. Environmental Protection Agency (1980) and WHO (1998) standard for Zn in drinking water is 5 ppm based on the bitter taste Zn imparts to water at that level. Allowable maximum limits for Zn in drinking water in the UK and USA is 5 ppm (Neubauer and Wolf, 2004). Zn is present in drinking water usually at concentrations much less than 5 ppm although soft waters could have such concentrations from materials used in the distribution systems and household plumbing (USEPA, 1980). A study of Boston tap water in the US, levels of Zn were found to be up to 1.6 ppm with a mean of 0.2 ppm (USEPA, 1980). There was an increase in Zn levels at the tap over finished water levels indicating Zn pick up from the pipe; this was attributed to the soft acid nature of Boston's water. In the more acidic water of Seattle, Zn levels in tap water were higher than in the finished water 95% of the time 10% exceeding the 5 ppm drinking water standard. The highest reported level was 5.5 ppm (NAS, 1977).

The taste threshold for Zn in water is 15 ppm. Level as high as 675 to 2280 ppm in water are emetic (Stockinger, 1981). In the United States of America, National Academy of Sciences (NAS, 1974) published Recommended Daily Allowances (RDAs) of 15, 20, and 25 mg Zn/day for adults, pregnant women and lactating women accordingly. Surveys of adults of different ages and physiological states including pregnancy and lactating found that normal daily Zn intakes range between 8.6 to 11.4 mg/day or 46 to 67% of the RDAs (Solomons, 1982). A daily intake via food for the U.S adult population was noted to be 10 to 20 mg Zn/day (USEPA, 1980). A mean value of 0.6 mg Zn/L in United States drinking water would contribute 0.5 to 1 mg Zn/day (Snyder *et al*, 1975). Zn bioavailability from food ranges from 10 to 40% (Solomons, 1982) while Snyder *et al* (1975) considered 35% Zn absorption from food to be the optimum value. However, excessive Zn intake has been associated with Cu deficiency anaemia. Apparently, Zn interferes with Cu and Fe metabolism (USEPA, 1980).

A study involving assessment of the level of this heavy metal would help in planning remedial action to avoid potential future environmental catastrophe.

2.2.6: Chromium (Cr)

Cr in soils strongly attaches to soil particles and as a result it does not move towards groundwater (Dennis et al., 2003). In water Cr adsorbs to sediment and become immobile. Only a small part of the Cr that ends up in water eventually dissolves (Dennis et al., 2003). Crops contain systems that arrange the Cr uptake to be low enough not to cause any harm. But when the amount of Cr in the soil rises, this can still lead to higher concentrations in crops. Acidification of soil can also influence Cr uptake by crops. Plants usually absorb only Cr (III). Cr is not known to accumulate in the bodies of fish, but high concentrations, due to the disposal of metal products in surface waters, can damage the gills of fish that swim near the point of disposal. In animals Cr can cause respiratory problems, a lower ability to fight disease, birth defects, infertility and tumor formation (Dennis et al., 2003).

People can be exposed to Cr through breathing, eating or drinking and through skin contact with Cr or its compounds (WHO, 1989). The level of Cr in water is generally low. In drinking water the level of Cr is usually low as well, but contaminated well water may contain the dangerous Cr(IV); hexavalent Cr (USEPA, 1980). For most people eating food that contains Cr (III) is the main route of Cr uptake, as Cr (III) occurs naturally in many vegetables, fruits, meats, yeasts and grains. Various ways of food preparation and storage may alter the Cr contents of food. When food is stored in steel tanks or cans Cr concentrations may increase (Farr, 2004). Cr (III) is an essential nutrient for humans and shortages may cause heart problems, disruptions of metabolisms and diabetes. But the uptake of too much Cr (III) can cause health effects as well, for instance skin rashes (Farr, 2004). Cr (VI) is a danger to human health, mainly for people who work in the steel and textile industry (Cheryl et al, 2000). Cr (VI) is mainly toxic to organisms. It can alter genetic materials and cause cancer (Cheryl et al, 2000). Cr salts are used in industrial processes and enter water bodies through discharges of waters (WHO, 1989). The normal level of Cr (VI) in drinking water is 3 to 40 ppb (WHO, 1989). Cr has been reported as a major contaminant of organic fertilizers in the sugarcane growing plantations of Brazil (Carvalho et al., 1999). Since the water from Sare River and canals is used by the surrounding community without any significant treatment, it was necessary to carry out a study to assess the prevailing levels.

CHAPTER THREE

3.0. Methodology

3.1. Area of Study

The study area was South Nyanza Sugarcane Zone lying between $0°55'S$, $34°33'E$ and $0°47'S$, $34°25'E$ with an elevation of between 1260 m and 1477 m. The factory draws its water from Sare River which has a number of tributaries. The factory effluent is discharged back to the same river downstream. The area generally experiences an equatorial type of climate. The annual temperatures range from a minimum of $18°C$ to a maximum of $30°C$. Most of the rain is received during the long rain season which is from March to May while the short rains season is from October to November. During the rains the canals may carry with them residues of fertilizers applied on the agricultural lands into Sare River.

The choice of study area was based on the level of fertilizer application as well as on the location of the tributaries that feed Sare River whose water is used in Awendo Township and by the South Nyanza Sugar factory. The Company Nucleus Estates use fertilizers in virtually every plot as opposed to the individual farmer owned plots (Outgrowers) where fertilizer usage is insignificant as a number of farmers may not be able to afford the high cost of fertilizers.

3.2. Experimental Design and Sampling

The experiment was laid down in a two factor completely randomized design with site as the main factor and season as sub factor. Sampling was done in October 2008 during the wet season and in January 2009 in dry season. The sampling was done over 12 sites along and within Sare River. These included Mulo: $0°58'00.78''S$, $34°35'16.30''E$, Elev. 1464 m; Ng'ur Nyoyo: $0°57'54.82''S$, $34°35'05.20''E$, Elev.1461 m ; Marienga: $0°56'30.04''S$, $34°34'08.40''E$, Elev. 1443 m; Sony/Rinya Bridge: $0°54'07.44''S$, $34°32'23.48''E$, Elev.1418 m; Adega: $0°54'18.26''S$, $34°32'06.41''E$, Elev. 1418 m; Awendo: $0°54'17.16''S$, $34°31'57.57''E$, Elev. 1414 m; Sony/Ranjira Bridge: $0°53'55.16''S$, $34°31'23.18''E$, Elev.1411 m; Kombogo: $0°53'00.66''S$, $34°31'27.50''E$, Elev. 1404 m; Adel: $0°53'00.68''S$, $34°32'04.56''E$, Elev. 1420 m; Ogada: $0°50'34.38''S$, $34°29'42.61''E$, Elev.1361 m; Kodhia: $0°49'20.50''S$, $34°30'01.41''E$, Elev. 1312 m; Riat: $0°49'31.16''S$, $34°23'25.05''E$, 1258 m. Ranen Hill ($0°51'00.03''S$, $34°33'59.97''E$) at an elevation of 1482 m was chosen for control site for soil.

Four 500 ml of surface water samples were taken from each sampling site in glass bottles, four 100 g samples of surface sediments, four 15cm deep top soil samples in black plastic bags using a big spoon

and PVC pipes (1.5cm in diameter), respectively, in each of the sampling sites per trip. The sampling was done in replicates for water, sediment and soil. For water and sediment sampling, a shallow point (approximately 2 m into the river and in the middle of the canal), river bank left and river bank right were pooled and treated as one sampling site whereby three samples were collected and taken as replicates with a fourth as back up. In each case the samples were taken at an interval of 10 m apart during each sampling trip that was also done at an interval of 3 hours.

3.3. Sample preparation before extraction

Once collected, the surface water samples were transported in an icebox at $0^{\circ}C$ to the laboratory for storage and processing while surface sediments and top soils were kept in black plastic bags and transported to the laboratory for analysis. Water samples were acidified using 1 ml of concentrated nitric acid and stored at $4^{\circ}C$ to preserve them as processing continued (Nichole and Mason, 2001). Surface sediment and top soil samples were dried at room temperature then ground by a pestle and mortar in order to normalize for variations in grain size distribution. The samples were then sieved through a 45 μm mesh sieve and kept in clean plastic containers ready for processing.

Four water samples measuring 500 ml each were collected from each sampling site in the rivers using amber plastic bottles. In each case, 3 samples were analyzed while the fourth one was kept for back up. There were 12 sites and from each site three replicates were subjected to treatment (analyzed) for six heavy metals namely; Fe, Zn, Cu, Cr, Cd and Pb; Cl and F levels in water and certain physicochemical parameters in water including temperature, pH, turbidity, conductivity and BOD.

3.4. Determination of heavy metals in surface soils and sediments

Total surface sediment extractions were carried out according to the procedure of Tack and Verloo (1999) with slight modifications. A mass of one gram of sediment was dried in an oven at $104^{\circ}C$, cooled in a desiccator and weight measurement taken before being put in a 50 ml Pyrex digestion tube and 10 ml mixture of concentrated nitric acid and concentrated hydrochloric acid (4:1, aqua ragia digestion) added. Following digestion for 3 hours in a Gerhardt digester at $100^{\circ}C$, the contents were filtered through 0.45 μm polyethersulfoon filter membrane into a 50 ml volumetric flask and made up to volume with double-distilled water after addition of 1.5 mg/ml of strontium chloride (analytical grade, $SrCl_2.6H_2O$). The purpose of strontium chloride was to remove interference in absorption of the specific metal by other metals at the same wavelength by acting as a buffer and to minimize ionization of the

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metal atoms (Ikuo *et al.*, 1965). The same procedure and that of Alloway (1995a) were adopted for both fertilizer and top soil samples with slight modifications.

The extract was analyzed for Pb, Cu, Cr, Zn, and Fe using Shimadzu AA-6200 Atomic Absorption Spectrophotometer with their respective Hamatsu hollow cathode lamps. Wavelengths of 283.3 nm, 324.8 nm, 357.9 nm, 213.8 nm, and 243.3 nm were used to measure absorbances of Pb, Cu, Cr, Zn and Fe, respectively (Berman, 1986; Ongeri, 2008). Before analysis was done, the AAS machine was calibrated.

3.5. Determination of Heavy Metals in Water

The procedure adopted by Mzimela *et al.* (2003) for total metal extraction was followed. A water sample measuring 200 ml was filtered through a 1 μm cellulose acetate filter with mill pores into an acid-washed 500 ml Erlenmeyer flask. The samples were acidified to 1% (2 ml) with conc. nitric acid (AR), placed on a hot plate at $60^{\circ}C$ and allowed to evaporate to approximately 30 ml. The evaporated sample was transferred to a 50 ml volumetric flask and made up to volume with double distilled water after addition of 1.5 mg/ml of strontium chloride. The extract was analyzed for Pb, Cu, Cr, Zn, and Fe using Shimadzu AA-6200 Atomic Absorption Spectrophotometer with their respective Hamatsu hollow cathode lamps. Wavelengths of 283.3 nm, 324.8 nm, 357.9 nm, 213.8 nm, and 243.3 nm were used to measure absorbances of Pb, Cu, Cr, Zn and Fe, respectively (Berman, 1986; Ongeri, 2008). Before analysis was done, the AAS machine was calibrated.

3.6. Measurement of pH, Temperature, Turbidity and Electrical conductivity

Water pH and temperature were measured directly in the field using a pH meter (3071 Jenway) and a mercury thermometer, respectively. For soil pH a method adopted from Rhodes (1982) was used; whereby 50 ml of deionized water was added to 20 g of crushed soil, stirred well for ten minutes and allowed to stand for 30 minutes before stirring again for two minutes; then the pH measured using a pH meter (3071 Jenway). Turbidity and Electrical conductivity were measured insitu using a turbidity meter (Hanna instruments Hi 93703 microprocessor turbidity meter) and electrical conductivity meter (Konduktometer, CG 857) respectively.

3.7. Biochemical Oxygen Demand Analysis

The method by Mzimela *et al.* (2008) was used where ten milliliters of 0.1N $KMnO_4$ (potassium permanganate), 50 ml of distilled water and 10 ml of (1:3) concentrated sulphuric acid were added to

each of two 250 ml conical flasks. 10 ml of the water sample was added to one of the flasks while to the second flask 10 ml of distilled water was added, this forming the blank. The contents of each of the flasks were mixed well and allowed to stand for one hour after which 10 ml of 10% potassium iodide (KI) was added to each of the two flasks. The liberated Iodine was titrated against 0.1N sodium thiosulphate with starch indicator.

3.8. Determination of Total Organic Carbon

A method, as described by Okalebo *et al.* (2002), was used to determine total organic carbon. In this method 10 g of well mixed air dried sample was heated in an oven for 3 hours at 105°C in a crucible and the difference in weights noted as the moisture content. The sample was then placed in a Vulcan A-550 muffle furnace in a crucible and the temperature increased gradually from 100, 200, to 550°C then maintained at 550°C for eight hours. The grayish white ash sample was then removed and cooled in a desiccator, then weighed. The difference in weight between the moisture free sample and the ash represented the total organic carbon of the sample.

3.9. Statistical Analysis

The means and ranges of the data collected were determined in this study. Ms Excel was used for data manipulation while a two factor completely randomized design in the MSTAT-C was used to separate the means of the sites and seasons and generate the least significance differences at 95% Confidence level.

CHAPTER FOUR

4.0: Results and Discussion

4.1: Site variations in physicochemical parameters; heavy metals in water and the levels of the heavy metals in sediments

4.1.1: Site variations in physicochemical parameters of water from Sare River and tributaries

The results of the physicochemical parameters of water from the different sites are shown in Table 4. The temperature profile of the water samples varies significantly ($P \leq 0.05$) and ranged from mean values of 23.77^0C to 25.53^0C. The temperature ranges were below 30^0C, which is the recommended limit for no risk according to the World Health Organization water quality guidelines for domestic use (WHO, 1989). Based on these guidelines, the temperature of the water from Sare River and tributaries does not appear to pose any threat to the homeostatic balance of the receiving water bodies, in conformity with the findings of Jaji *et al.* (2007). The pH regimes vary significantly ($P \leq 0.05$) in the sample points throughout the study period and ranged from 6.47 (Ogada) to 6.98 (Adel). Generally, the obtained pH values fall within the World Health Organization standard of 6.5 to 8.5 for full contact recreation water (WHO, 1989). The EU has set pH protection limits of 6.0 to 9.0 for fisheries and aquatic life (Chapman, 1996). The results indicate that pH levels are generally less than the neutral value of 7, indicating slight acidity. The results show variations in pH with sites and the sites within the area with heavy sugar plantations (Adega, Awendo, Ogada) had the lowest pH suggesting potential impact of intensive fertilizer use and this is in agreement with previous studies on conditions that fertilizer application impacts on the pH of the aquatic ecosystem (Carvalho *et al.*, 1999). Increasing rates of nitrogeneous fertilizers generally increase soil acidity (Owuor *et al.*, 1990). The nitrogeneous fertilizers are known to produce H^+ by the following reaction (1), which is induced by soil bacteria (Ishibashi *et al.*, 2004):

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + H^+ \dots\dots\dots\dots\dots\dots\dots\dots\text{Reaction (1)}$$

Thus, during the application of these fertilizers to the soil, the rate of nitrification is reported to be higher and inorganic nitrogen may be rapidly converted to nitrate producing H^+, which acidifies the soil.

The turbidity profile varies significantly ($P \leq 0.05$) amongst the sample points throughout the study and ranged from 69.18 NTU in Mulo to 108.89 NTU in Kombogo. The latter is located just after the factory raising the possibility of increased contaminants from the factory effluent and storm drains. The turbidity values obtained from the stations in the two seasons were higher than World Health Organization standard of 5 NTU (WHO, 2004). The excessive turbidity in water can cause problems with water purification processes such as flocculation and filtration, which may increase treatment costs (WHO, 2004). High turbid waters are often associated with the possibility of microbiological

contamination as high turbidity makes it difficult to disinfect water properly (WHO, 2004). However, the turbidity values were generally higher in the sites downstream. The increase in these values could be attributed to surface runoff and erosion carrying soil even under very low rainfall conditions (Chapman, 1996).

Table 4: Levels of physicochemical parameters of water from Sare River and tributaries

	Mulo	N/Nyoyo	Marienga	S/Rinya	Adega	Awendo	S/R Bridge	Kombogo	Adel	Ogada	Kodhia	Riat	Mea seas
Sites													
Wet season	22.57	22.9	23.07	23.13	23.23	23.13	23.63	23.8	23.87	23.77	24.1	24.1	23.
Dry season	24.97	25.53	26.03	26.03	26.13	26.5	26.37	26.8	26.97	26.97	26.9	26.97	26.
Mean Sites	23.77	24.22	24.55	24.58	24.68	24.82	25	25.3	25.42	25.37	25.5	25.53	
LSD (P≤0.05)										0.35			0.
S.D										1.58			
CV%										1.1			
Interaction										0.49			
Wet season	6.37	6.15	6.42	6.47	5.9	6.24	6.23	6.2	6.66	5.83	5.83	6.27	6.
Dry season	7.51	7.14	7.44	7.48	7.1	7.37	7.67	7.59	7.3	7.11	7.79	7.72	7.
Mean Sites	6.94	6.65	6.93	6.98	6.5	6.81	6.95	6.89	6.98	6.47	6.81	7	
LSD (P≤0.05)										0.41			0.
S.D										0.71			
CV%										4.76			
Interaction										0.58			
Wet season	98.46	132.06	130.25	113.67	120.31	241.4	125.22	151.31	113.54	121.3	117.47	159	135.
Dry season	39.89	39.13	41.78	38.57	35.93	53.93	83.25	66.47	36.44	40.83	41.42	95.39	51.
Mean Sites	69.18	85.59	86.01	76.13	78.12	147.67	104.24	108.89	74.99	81.07	79.44	127.2	
LSD (P≤0.05)										5.72			13.
S.D										51.41			
CV%										4.83			
Interaction										8.09			
Wet season	100.6	224.33	120.3	81.87	85.65	451.67	129.27	143.11	120	177.4	133.83	91.37	154.
Dry season	91.07	101.37	103.4	73.6	77.87	258.33	84.2	68.63	101.8	139.4	96.47	74.73	105.
Mean Sites	95.83	162.85	111.85	77.73	81.76	355	106.73	105.87	110.9	158.4	115.15	83.05	
LSD (P≤0.05)										8.83			20.
S.D										81.93			
CV%										5.33			
Interaction										12.49			
Wet season	64.17	69.18	66.37	63.26	66.69	73.13	69.74	85.67	58.57	65.96	55.27	35.9	64.
Dry season	42.8	45.32	45.09	39.44	40.7	49.41	48.28	66.78	42.28	43.74	43.21	34.35	45.
Mean Sites	53.49	57.25	55.73	51.35	53.7	61.27	59.01	76.22	50.42	54.85	49.24	35.12	
LSD (P≤0.05)										5.85			13
S.D										14.28			
CV%										8.41			
Interaction										8.28			

Key: LSD –Least Significant Difference; SD – Standard Deviation; CV – Coefficient of Variation

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The electrical conductivities of the water samples varied significantly (P≤0.05) and ranged from 77.73 μS/cm at Sony-Rinya Bridge to 355.00 μS/cm at Awendo. Generally, higher conductivities were observed in the waters from the areas with heavy cane plantations where there is high use of fertilizers. The national limit for electrical conductivity in domestic water supply is a maximum of 50 μS/cm (KEBS, 1996). In all the sample points, this limit was exceeded. Thus, the parameter does give concern and it could make the waters unsuitable for direct domestic use. The BOD of the water samples generally varied from 35 mg/l in Riat to 76 mg/l in Kombogo that is just after the factory suggesting possibility of the impact of the factory effluent that is discharged upstream of this point. The values obtained were higher than the Kenyan guideline for BOD in domestic water (EMCA, 2006). There was significant (P≤0.05) interaction effect for all the physicochemical parameters.

While rainfall may dilute and weaken the effects of point source pollution, it also increases the contribution of the non-point sources or diffuse pollution through land runoff from agricultural fields (Jaji et al., 2007). The results of the analyses for most of the parameters did not show uniformity in the expected trends in water quality from upstream to downstream stations on the receiving water. It is expected that the concentration of most downstream points should be higher than that of upstream points (Jaji et al., 2007). This did not hold for a number of stations in this study. The highest BOD level was recorded just after the South Nyanza Sugar factory treated wastewater discharge point at Kombogo suggesting increased organic load from the factory discharge. Water from canals and River Sare South Nyanza Sugarcane farms is within the permissible limits of 6.5–8.5 (WHO, 1993; KEBS, 1996; EMCA, 2006; USEPA, 1979).

4.1.2: Halide and heavy metals levels in water from Sare River and tributaries

Halide and heavy metals levels in water from Sare River and canals were determined and the results shown in Tables 5, 6. The F regimes vary significantly (P≤0.05) in the sample points throughout the study and ranged from 36.67 ppb at Ng'ur Nyoyo to 118.08 ppb at Awendo. The Cl profile of the water samples varied significantly (P≤0.05) and recorded the lowest concentration at Mulo (175 ppb) while the sample from Awendo exhibited the highest concentration at 575 ppb. The levels for both halides fall within the World Health Organization guideline limit for domestic water of 250 ppm and 1.50 ppm for Cl and F respectively (WHO, 1989).

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Table 5: Levels (ppb) of Cl and F in water from Sare River and tributaries

		Mulo	N/Nyoyo	Marienga	S/Rinya	Adega	Awendo	S/R Bridge	Kombogo	Adel	Ogada	Kodhi a	Riat	Mean Season
Cl	Wet Season	216.67	366.67	400	300	350	750	283.33	300	266.67	300	400	316.67	354.17
	Dry Season	133.33	116.67	150	150	133.33	400	216.67	150	183.33	83.33	150	150	168.06
	Mean Sites	175	241.67	275	225	241.67	575	250	225	225	191.67	275	233.33	
	LSD (P≤0.05)										69.19			163.07
	S.D										149.23			
	CV%										20.85			
	Interaction										97.85			
F	Wet Season	101.67	55	68.33	66.67	71.67	211.67	113.33	100	75	163.33	103.33	71.67	100.14
	Dry Season	14.67	18.33	13.67	13.67	19	24.5	27.67	21	20	23.5	22.33	17.33	19.64
	Mean Sites	58.17	36.67	41	40.17	45.33	118.08	70.5	60.5	47.5	93.42	62.83	44.5	
	LSD (P≤0.05)										19.82			46.71
	S.D										52.79			
	CV%										26.04			
	Interaction										28.03			

Key: LSD –Least Significant Difference; SD – Standard Deviation; CV – Coefficient of Variation

The concentration profile of the heavy metals (Fe, Zn, Cu) in the water samples varied significantly (P ≤ 0.05) in all the locations as depicted in Table 8. The concentrations of Cr, Cd and Pb were below detection limit. The concentration of Fe varied from 2.71 to 9.61 µg/l; Zn from 2.36 to 4.91 µg/l and Cu ranged from 2.02 to 4.27 µg/l. The obtained levels are within the World Health Organization limits for Cr, Cd, Pb, Cu and Zn (WHO, 2004). According to the study there is no detrimental effect on the aquatic ecosystem caused by these heavy metals (WHO, 2004). The levels for the detected heavy metals varied significantly (P ≤ 0.05) due to locational variations and generally increased downstream of Sare River with the water samples from within the areas of heavy cane plantations (Adega, Awendo, Adel, Ogada and S/Ranjira bridge) being higher than most of the other areas in line with a study by Carvalho *et al* (1999).

Table 6: Heavy metals levels ((µg/L) in water from Sare River and tributaries

							Sites							
		Mulo	N/Nyoyo	Marienga	S/Rinya	Adega	Awendo	S/R Bridge	Kombogo	Adel	Ogada	Kodhia	Riat	Mean Season
Fe	Wet Season	6.64	3.31	7.23	4.24	13.28	15.41	17.06	14.91	15.59	15.5	13.62	13.95	11.73
	Dry Season	0.65	1.21	1.18	1.18	1.67	1.98	2.15	2.31	2.46	2.34	2.18	2.18	1.79
	Mean Sites	3.64	2.26	4.2	2.71	7.48	8.7	9.61	8.61	9.03	8.92	7.9	8.06	
	LSD ($P \leq 0.05$)										0.86			2.03
	S.D										6.06			
	CV%										10.04			
	Interaction										1.22			
Zn	Wet Season	4.37	5.47	6.3	6.89	7.43	7.32	6.62	6.07	7.85	8.3	7.23	7.25	6.76
	Dry Season	0.36	0.57	0.67	0.67	0.86	1.05	1.13	1.45	0.88	1.51	1.33	1.22	0.97
	Mean Sites	2.36	3.02	3.49	3.78	4.14	4.18	3.88	3.76	4.36	4.91	4.28	4.23	
	LSD ($P \leq 0.05$)										0.34			0.81
	S.D										3.02			
	CV%										6.99			
	Interaction										0.49			
Cu	Wet Season	3.84	4.45	3.72	5.58	5.85	5.27	6.19	6.38	6.56	6.67	5.86	6.89	5.6
	Dry Season	0.21	0.66	0.44	0.44	0.73	0.95	0.95	1.15	1.09	1.49	1.17	1.64	0.91
	Mean Sites	2.02	2.55	2.08	3.01	3.29	3.11	3.57	3.76	3.82	4.08	3.51	4.27	
	LSD ($P \leq 0.05$)										0.4			0.94
	S.D										2.51			
	CV%										9.65			
	Interaction										0.56			

Key: LSD –Least Significant Difference; SD – Standard Deviation; CV – Coefficient of Variation
NB: Pb, Cr and Cd were not detected in all the water samples

High levels of Fe in the samples from Sony-Ranjira Bridge (9.61 µg/L) and Adel (9.03 µg/L) could be attributed to their close `proximity to the factory and Awendo Town where there are intense human and industrial activities. The high level of Cu in Riat located furthest downstream is consistent with expected increase in contamination as you move downstream (Jaji et al., 2007). The low levels of heavy metals at Mulo and Ngur Nyoyo could be due to their location outside the nucleus estate where fertilizer application in farming is less intensive.

4.1.3: Levels of heavy metals in sediments within Sare River and tributaries

The results of the heavy metal levels of sediment samples from the different sites are shown in Table 7. The Fe profile of the sediment samples varies significantly ($P \leq 0.05$) and ranged from 23.28 µg/g (Mulo) to 27.43 µg/g (Sony-Rinya Bridge).

Table 7: Levels (µg/g) of heavy metals in sediments from Sare River and tributaries

	Mulo	N/Nyoyo	Marienga	S/Rinya	Adega	Awendo	S/R Bridge	Kombogo	Adel	Ogada	Kodhia	Riat	Mean season
									Sites				
Dry Season	25.6	26.22	28.383	29.98	30.55	30.23	29.8	31.17	31.33	30.75	30.67	29.97	29.55
Wet Season	20.97	20.75	24.6	24.88	20.4	23.15	24.8	23.4	22.22	22	20.55	21.72	22.45
Mean Sites	23.28	23.48	26.49	27.43	25.48	26.69	27.3	27.28	26.78	26.38	25.61	25.84	
LSD (P≤0.05)									1.2				2.83
S.D									4.04				
CV%									3.64				
Interaction									1.7				
Dry Season	4.05	4.55	4.38	4.85	5.13	5.02	4.93	5.03	5.07	4.8	4.72	4.93	4.79
Wet Season	3.32	3.5	3.85	3.62	3.8	3.63	3.63	3.38	3.55	3.22	3.7	3.38	3.55
Mean Sites	3.68	4.03	4.12	4.23	4.47	4.33	4.28	4.21	4.31	4.01	4.21	4.16	
LSD (P≤0.05)									0.32				0.76
S.D									0.72				
CV%									6.09				
Interaction									0.46				
Dry Season	3.12	3.03	3.22	3.42	3.48	3.55	3.52	3.53	3.55	3.57	3.57	3.55	3.43
Wet Season	2.6	2.62	2.9	3.2	2.8	3	3.22	2.82	3.02	3.3	2.97	3.17	2.97
Mean Sites	2.86	2.83	3.06	3.31	3.14	3.28	3.37	3.18	3.28	3.43	3.27	3.37	
LSD (P≤0.05)									0.25				0.6
S.D									0.35				
CV%									6.23				
Interaction									0.36				
Dry Season	1.62	2.07	1.97	2.02	2.18	2.17	2.18	2.08	2.1	2.12	2.27	2.25	2.09
Wet Season	1.1	1.22	1.5	1.22	1.28	1.6	1.78	1.47	1.58	1.5	1.6	1.7	1.46
Mean Sites	1.36	1.64	1.73	1.62	1.73	1.88	1.98	1.78	1.84	1.81	1.93	1.98	
LSD (P≤0.05)									0.16				0.38
S.D									0.38				
CV%									7.19				
Interaction									0.23				

Key: LSD –Least Significant Difference; SD – Standard Deviation; CV – Coefficient of Variation
NB: Cr and Cd levels were below detection limits for all sites in the two seasons

The Zn regimes vary significantly (P≤0.05) in the sample points throughout the study and ranged from 3.68 µg/g (Mulo) to 4.47 µg/g (Adega) while the Cu profile varies from 2.86 µg/g (Mulo) to 3.37 µg/g (Riat). The Pb profile recorded the lowest levels among the four trace metals detected varying significantly (P≤0.05) from 1.36 µg/g at Mulo to 1.98 µg/g at Sony-Ranjira Bridge. The levels generally increased downstream indicating more contamination as you get into the heavy plantation area. Sony-Rinya Bridge, Adega, Awendo, Sony-Ranjira Bridge, Adel, Marienga and Kombogo located within the

nucleus estate and are associated with intensive cane farming recorded the highest levels of heavy metals in sediment samples while Mulo, Ngur Nyoyo, Ogada, Kodhia and Riat that are outside the nucleus estate with low human activity registered the least concentrations levels. Sediments represent one of the ultimate sinks for heavy metal discharge into the environment (Luoma *et al.*, 1989). A correlation matrix constructed (Table 8) for the elements analysed in the sediment show positive correlation between Fe and Zn (0.637), Fe and Cu (0.785), Fe and Pb (0.578), Zn and Cu (0.519), Zn and Pb (0.642) and Cu and Pb (0.743). This is an indication that they were likely contributed simultaneously from their source (Chapman, 1996). Chapman (1996) had observed that concentration of heavy metals in sediments usually exceed those in the overlying water by 2-3 order of magnitude. The current study has shown an order of magnitude of sediment/water ratio of about 2 for Fe and much higher for Pb which was below the detection limit.

Table 8: Correlations of heavy metals in sediments from Sare River

	Fe	Zn	Cu	Pb
Fe	1.000			
Zn	0.637	1.000		
Cu	0.785	0.519	1.000	
Pb	0.578	0.642	0.743	1.000

4.2: Selected physicochemical parameters and heavy metals in the soils along Sare River and tributaries

4.2.1: Variation of pH and TOC in soils along Sare River and tributaries

The results of pH and TOC levels in soil samples from different sites are shown in Table 9. The pH regimes vary significantly ($P \leq 0.05$) in the sample points throughout the study period and ranged from mean values of 4.6 at S/R Bridge to 5.14 at Kodhia showing that the soils are acidic.Intensive use of fertilizers is an effort meant to enhance cane yields and makes use of sources that contain heavy metals thereby raising the levels of heavy metals in the soils used to grow sugarcane (Yadav *et al.*, 2010). These heavy metals are absorbed by the growing sugarcane, where they can reach phytotoxic levels (Yadav *et al.*, 2010). Reduction of soil pH in sugarcane plantation has been found to be due to use of nitrogenous fertilizers which reduce soil pH during the ammonification and nitrification processes (Woods *et al.*, 2003; Oliver, 2004).The TOC profile of the soil samples varies significantly ($P \leq 0.05$) and ranged from mean values of 3.68 at Kodhia to 5.82 at Adega. The TOC levels were well within the permissible limit of more than 1% (WHO, 1989).

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Table 9: Levels of pH and TOC (%) in soils along Sare River and tributaries

Item		Control	Mulo	N/Nyoyo	Murienga	S/Rinya	Adega	Awendo	S/R Bridge	Kombogo	Adel	Ogada	Kodhia	Riat	Mean Season
									Sites						
pH	Wet Season	5.70	4.62	4.42	4.58	4.21	4.35	4.29	4.16	4.68	4.17	4.26	4.24	4.33	4.36
	Dry Season	6.42	5.32	5.24	5.55	5.21	5.52	5.21	5.04	5.18	5.32	5.06	6.05	5.26	5.33
	Mean Sites	6.06	4.97	4.83	5.07	4.71	4.93	4.75	4.6	4.93	4.75	4.66	5.14	4.8	
	LSD(P≤0.05)									0.16		0.37			
	S.D									0.55					
	CV%									2.54					
	Interaction									0.22					
TOC	Wet Season	2.95	5.86	5.58	5.9	6.57	6.62	6.43	6.39	6.45	6.11	4.43	3.34	3.9	5.63
	Dry Season	2.38	3.39	3.62	4.42	4.42	5.02	4.69	4.33	4.07	4.04	3.74	4.01	3.95	4.14
	Mean Sites	2.66	4.63	4.6	5.16	5.5	5.82	5.56	5.36	5.26	5.08	4.09	3.68	3.92	
	LSD(P≤0.05)									0.46		1.09			
	S.D									1.16					
	CV%									7.44					
	Interaction									0.65					

Key: LSD –Least Significant Difference; SD – Standard Deviation; CV – Coefficient of Variation

## 4.2.2: Levels of heavy metals in the soils along Sare River and tributaries

The results of heavy metals levels in the soils along Sare River are presented in Table 10.

Fe levels vary significantly (P≤0.05) in the sample locations throughout the study period and ranged from mean values of 103.83 µg/g at Kodhia to 167.41 µg/g at Awendo. Zn concentration profile vary significantly (P≤0.05) in the sample locations throughout the study ranging from 84.07 µg/g at Kodhia to 137.68 µg/g at Awendo while Cu concentration regimes vary significantly (P≤0.05) from 20.59 µg/g at Mulo to 43.18 µg/g at Awendo. Cr concentration profile vary significantly (P≤0.05) and ranged from 2.72 µg/g at Kodhia to 6.18 µg/g at Sony-Rinya Bridge while Pb equally vary significantly (P≤0.05) in all the sites and ranged from 2.78 µg/g at Ng'ur Nyoyo to 4.88 µg/g at Awendo. Cd concentration was below detection limit while for the five heavy metals found; there was a general increase downstream as fertilizer application increased within the company owned nucleus estate farms. Despite Kodhia being a canal downstream, the concentration for all the heavy metals except Cu and Pb were least at this point possibly also due to less farming activity in the area. For all the soils covered in study, the levels were within the critical and normal range in soils (Alloway, 1995) suggesting that the soils are still suitable for normal farming. Studies have shown excessive concentration of heavy metals in agricultural soils (Alloway, 1995).

Table 10: Levels (µg/g) of heavy metals in Soils along River Sare and tributaries

	Control	Mulo	N/Nyoyo	Marienga	S/Rinya	Adega	Awendo	S/R Bridge	Kombogo	Adel	Ogada	Kodhia	Riat	Mean season
Wet Season	51.35	152.74	204.64	217.94	232.58	240.47	247.93	241.19	188.06	167.42	158.85	153.97	157.08	196.91
Dry Season	34.84	54.93	76.57	80.42	82.17	85.24	86.88	83.84	94.89	68.05	57.78	73.06	66.41	75.85
Mean Sites	43.10	103.83	140.61	149.18	157.37	162.86	167.41	162.51	141.47	117.73	108.32	113.52	111.75	
LSD(P≤0.05)									7.82		18.43			
S.D									66.97					
CV%									4.51					
Interaction									11.06					
Wet Season	17.65	121.17	152.12	153.95	184.38	197.43	206.7	187.27	141.95	152.88	134.85	126.9	129	157.38
Dry Season	14.35	40.93	38.33	55.97	60.87	68.53	68.67	64.55	46.367	46.88	42.78	41.25	45.42	51.71
Mean Sites	16.00	81.05	95.23	104.96	122.63	132.98	137.68	125.91	94.16	99.88	88.82	84.07	87.21	
LSD(P≤0.05)									12.68		29.89			
S.D									57.95					
CV%									9.55					
Interaction									17.94					
Wet Season	13.45	29.12	29.75	46.43	51.63	54.98	61.5	44.53	38.2	39.97	39.58	33.183	33.45	41.86
Dry Season	6.82	12.07	17.15	24.85	21.82	21.77	24.87	24.35	22.75	25.03	21.08	24.3	18.42	21.54
Mean Sites	10.13	20.59	23.45	35.64	36.73	38.38	43.18	34.44	30.48	32.5	30.33	28.74	25.93	
LSD(P≤0.05)									4.75		11.2			
S.D									13.05					
CV%									11.8					
Interaction									6.72					
Wet Season	1.08	4.82	5.85	6.533	6.8	6.98	7.55	6.65	5.05	6	5.2	4.92	5.3	5.97
Dry Season	0.88	0.62	4.4	5.45	5.55	4.75	3.72	3.35	2.25	2.33	2.1	3.52	1.93	3.33
Mean Sites	0.98	2.72	5.13	5.99	6.175	5.87	5.63	5	3.65	4.17	3.65	4.22	3.62	
LSD(P≤0.05)									0.55		1.3			
S.D									1.84					
CV%									9.35					
Interaction									0.78					
Wet Season	ND	4.6	5.57	5.08	6.05	5.32	6.65	5.82	5.1	4.13	5.52	5.15	5.05	5.34
Dry Season	ND	1.03	0	1.4	1.65	4.32	3.1	2.35	1.22	2.53	2.15	0.52	2.12	1.87
Mean Sites	-	2.82	2.78	3.24	3.85	4.82	4.88	4.08	3.16	3.33	3.83	2.83	3.58	
LSD(P≤0.05)									0.7		1.66			
S.D									2.02					
CV%									15.36					
Interaction									0.99					

Key: ND – Not detected
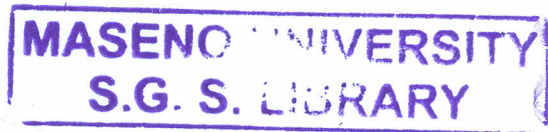
4.3: Seasonal variation of selected physicochemical parameters and heavy metals in Sare River

4.3.1: Seasonal variation of the physicochemical parameters of water and the heavy metals

The seasonal variation of the physicochemical parameters of the water samples are presented in Table 4. The temperature regimes of the water samples varied significantly ($P \leq 0.05$) and ranged from 22.57°C to 24.1°C during the wet season and 24.97°C to 26.97°C in dry season. The pH profile of the water samples did not vary significantly ($P \leq 0.05$) due to seasonal variations in all the sites and ranged from 5.83 at Ogada and Kodhia to 6.66 at Adel in wet season and 7.10 at Adega to 7.79 at Kodhia in dry season. The pH obtained were generally lower in wet season than in dry season. The lower pH could be attributed to enhanced ammonification and nitrification processes in wet season (Oliver, 2004).

The turbidity profile of the water samples varied significantly ($P \leq 0.05$) amongst the sample locations and ranged from 98.46 NTU at Mulo to 241.4 NTU at Awendo in wet season and 35.93 NTU at Adega to 95.39 NTU at Riat in dry season. The recorded turbidities were higher in wet season and increased downstream in line with a report by Sumner (Sumner, 1997) indicating that this was due to surface runoffs. Electrical conductivity regimes of the water samples varied significantly ($P \leq 0.05$) from 91.37 µS/cm at Riat to 451.67 µS/cm at Awendo during the wet season and 68.63 µS/cm at Kombogo to 258.33 µS/cm at Awendo in dry season. The conductivities recorded were much higher in wet season than the dry season. The increase in electrical conductivity in wet weather is in agreement with the observations made by (Alloway, 1995) that ionic mobility is enhanced in wet season.

The BOD of the water samples varied significantly ($P \leq 0.05$) from 35.9 mg/l in Riat to 85.67 mg/l in Kombogo during the wet season and 34.35 mg/l in Riat to 66.78 mg/l in Kombogo in dry season. The recorded BOD levels were higher in wet season possibly, due to surface runoffs (Willard et al., 1992). The seasonal variation of the Cl and F concentrations of the water samples are presented in Table 5. The Cl concentration of the water samples varied significantly ($P \leq 0.05$) from 216 ppb at Kodhia to 750 ppb at Awendo during the wet season and 83.33 ppb at Ogada to 400 ppb at Awendo in dry season showing a general decline during the dry season.The F concentration of the water samples varied significantly ($P \leq 0.05$) from 55 ppb at Ng'ur Nyoyo to 211.67 ppb at Awendo in wet season and 13.67 ppb at Sony-Rinya Bridge, Marienga to 27.67 ppb at Kombogo similarly indicating a decline during the dry season. In both seasons, water samples from Awendo registered the highest levels of Cl and F suggesting the location to be a major contamination point source. The Cl levels were much higher than the F concentrations in both seasons.

The seasonal variation of Fe, Zn and Cu concentrations of the water samples are presented in Table 6

Fe, Zn, Cu, varied significantly (P≤0.05) due to seasonal variations in all the locations. Fe levels varied from 3.31µg/l at Ng'ur Nyoyo to 17.06 µg/l at Sony-Ranjira Bridge during the wet season and from 0.65 µg/l at Mulo to 2.46 µg/l at Adel during the dry season. Levels of Zn in the water samples varied from 4.37 µg/l in Mulo to 8.3 µg/l in Ogada during the wet season and from 0.36 µg/l at Mulo to 1.51 µg/l at Ogada showing the two sites to be having the lowest and highest levels respectively. Cu levels in the water samples varied from 3.72 µg/l at Marienga to 6.89 at Riat in wet season and from 0.21 µg/l at Mulo to 1.49 µg/l at Ogada during the dry season. The reason for the trend could be due to high leaching caused by enhanced metal ionization during the wet season and decline in the heavy metal levels during the dry season due to limited leaching activity (Alloway, 1995). The leaching activity is largely influenced by the pH which is a major determinant of heavy metal mobility from the application points (Ford et al., 2001).

4.3.2: Seasonal variation of heavy metals in sediments within Sare River and tributaries

The seasonal variation of the heavy metal levels in sediments from Sare River and the tributaries are presented in Table 7.Fe, Zn, Cu, Pb varied significantly (P≤0.05) due to seasonal variations in all the locations with lower levels during the wet season. Fe varied from 20.4 µg/g at Adega to 24.8 µg/g at Sony-Ranjira Bridge during the wet season and 25.6 µg/g (Mulo) to 31.33 µg/g (Adel) in dry season while Zn had a variation of 3.22 µg/g (Ogada) to 3.85 µg/g (Marienga) in wet season and 4.05 µg/g (Mulo) to 5.13 µg/g (Adega) in dry season's varied from 2.60 µg/g (Mulo) to 3.30 µg/g (Ogada) in wet season and 3.03 µg/g (Ng'ur Nyoyo) to 3.57 µg/g (Ogada) while Pb varied from 1.10 µg/g (Mulo) to 1.78 µg/g (Sony-Ranjira Bridge) in wet season and 1.62 µg/g (Mulo) to 2.27 µg/g (Kodhia) during the dry season. The levels for sediments sampled from Mulo (outside the nucleus estate) were generally lower in than in reported in all other locations suggesting least pollution while the levels for the metals detected increased downstream confirming studies by Nyamangara et al (1999).

4.3.3: Seasonal variation of pH, TOC and heavy metals in soils along Sare River and tributaries

Seasonal variation of pH and TOC in the soils along Sare River is shown in Table 9. The pH profile vary significantly (P≤0.05) in the sample points throughout the study period and ranged from 4.16 (Sony-Ranjira Bridge) to 4.68 (Kombogo) during the wet season and 5.04 (Sony-Ranjira Bridge) to 6.05 (Kodhia). The mean pH for the samples from control site varied from 5.70 during the wet season to 6.42 in the dry season showing that they were significantly higher than those obtained from areas under heavy sugarcane plantations in line with a study by Alloway (1995). TOC regimes vary significantly (P≤0.05) and ranged from mean values of 3.34% (Riat) in wet season to 6.62% (Adega) and 3.39%

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(Mulo) to 5.02% (Adega) during the dry season indicating that the TOC of the soils were higher in areas under cultivation and that the levels were enhanced in wet seasons as reported by Chapman (1996). The seasonal variation of the selected heavy metals in the soils along Sare River is shown in Table 10. The mean Fe levels varied significantly ($P \leq 0.05$) and ranged from 152.74 µg/g (Mulo) to 247.93 µg/g (Awendo) during the wet season and 54.93 µg/g (Mulo) to 94.89 µg/g (Kombogo) in the dry season. The concentration profile of Zn in the soil from the sampled locations vary significantly ($P \leq 0.05$) and ranged from 12.17 µg/g (Mulo) to 206.70 µg/g (Awendo) in the wet season and 38.33 µg/g (Ng'ur Nyoyo) to 68,53 µg/g (Adega) during the dry season. The levels of Cu in the soils from the sampled sites vary significantly ($P \leq 0.05$) and ranged from 29.12 µg/g (Mulo) to 43.18 µg/g (Awendo) in the wet season and 12.07 µg/g (Mulo) to 25.03 µg/g (Adel) during the dry season while the levels of Cr in the soils from the sampled sites also varied significantly ($P \leq 0.05$) in a similar trend ranging from 4.82 µg/g (Mulo) to 7.55 µg/g (Awendo) in the wet season and 0.62 µg/g (Mulo) to 5.55 µg/g (Sony-Rinya Bridge) during the dry season. The Pb concentration profile similarly vary significantly ($P \leq 0.05$) in the soils from the sampled locations and ranged from 2.78 µg/g (Ng'ur Nyoyo) to 4.88 µg/g (Awendo) during the wet season and 0.00 µg/g (Ng'ur Nyoyo) to 4.32 µg/g (Adega). The seasonal variation of the heavy metal loads had similar trend in the two seasons, being higher in wet season and having a gradual increase downstream in tandem with a report by Alloway (1995).

4.4: Comparison of the water quality parameters from the different sites and seasons with the national and international standards

The water quality parameters in this study were compared with those from other studies and the results shown as depicted in Tables 11, 12. The mean pH values for the river Sare and canals during the wet season were below the values for other rivers like River Sio, Nyando, Nyamasaria and Sondu Miriu (Ongeri, 2008). For Lake Victoria and Winam Gulf the pH were comparable during the dry season to be slightly above neutral.

The electrical conductivity for water from the rivers Sare and its canals was lower than those reported for rivers Nyamasaria, Nyando and Sondu Miriu as well as for Lake Victoria and Winam Gulf that were higher than 140 µS/cm. Turbidity levels for both wet and dry seasons in rivers Sare and its canals were lower than those reported for Winam gulf, rivers Nyamasaria, Nyando and Sondu Miriu but higher than those for Lake Victoria and Sio River (Ongeri, 2008) according to KEBS standards these waters are not safe for human consumption because they are above the permissible limit of 5 NTU (KEBS, 1996).

BOD levels for both wet and dry seasons in rivers Sare and its canals were comparable to those reported for Winam gulf and Lake Victoria (Ongeri, 2008) and marginally above the USEPA, 1979 and EMCA,

2006 making these waters unsafe for human and domestic use. The contribution of the heavy sugarcane plantations around the factory to heavy metal burden into Sare River is significant making sugarcane farming a major contributor of heavy metals into the aquatic ecosystem. However, the levels of the heavy metals in Sare River are still much lower than most other rivers studied. There is therefore need to monitor soil pH which is a major factor in heavy metal mobility from the farms (Matsumura et al., 2005) so as to control their accumulation.

Table 11: Comparison between this study with some international standards on domestic water and reported levels for physicochemical parameters in other studies

	Temp ^{0}C	pH	Cond (μS/cm)	Turb (NTU)	BOD (mg/L)
This study[a] Dry season	26.35	7.44	105.9	51.1	45.12
This study[a] Wet season	23.44	6.22	155.0	135.3	64.50
KEBS[b] Standard	NG	6.5-8.5	NG	5.000	40
WHO[c] standard	NG	6.5-8.5	NG	NG	NG
USEPA[d] standard	NG	6.0-9.5	NG.	NG	30
EMCA(WQ)[g]2006 std	NG	6.5-8.5	NG	NG	25
Egyptian standard[f]	NG	6 – 9	NG	NG	NG
Winam Gulf[e]	NG	7.8	145.30	190.40	60
Lake Victoria[e]	NG	7.7	129.80	10- 37	45
Sio River[e]	28. 00	8.5	76.000	33.00	NG
Nyamasaria River[e]	28.00	7.3	143.00	202.00	NG
Nyando River[e]	26.00	7.5	230.00	980.00	NG
Sondu Miriu River[e]	28.00	7.6	170.00	410.00	NG

Key
NG – Not given in literature.
a – This study 2010 Kenya (number of examined samples:36), b – KEBS (1996) maximum permissible limits, c – WHO (1993) maximum permissible limits, d – USEPA (1979) permissible limits, e – Ongeri (2008) downstream for rivers, f – ECS (Egyptian chemical standards) (1994) permissible limits, g – Kenyan EMCA (WQ) (2006) Standards.

Table 12: Comparison of this study with other studies for heavy metals in domestic water

	Cr µg/L	Pb µg/L	Cu µg/L	Zn µg/L	Fe µg/L
This study[a] Dry season	ND	ND	0.91	0.97	1.79
This study[a] Wet season	ND	ND	5.60	6.76	11.73
KEBS[b] Standard	NG	50	100	5000	300
WHO[c] standard	NG	10	1000	5000	300
Water quality criteria[d] CMC	16	65	13	120	NG
CCC	11	25	9	120	NG
Turkish env. Guideline[e]:					
Class i	20	10	20	200	NG
Class ii	50	20	50	500	NG
Class iii	200	50	200	2000	NG
Class iv	>200	>50	>200	>2000	NG
Ol Deresi Stream[f]	16-110	11-370	11-94	150-4100	NG
Indian River Florida[g]	0.15	0.025	1.1	0.8	NG
Lambro River Italy[h]	2-66	2.2-138.8	1.1-134.4	NG	NG
Gediz River Turkry[i]	1-17	10-110	4.84	3-46	NG
USEPA[j]	NG	5	50	5000	300
UK[k]	NG	NG	50	5000	200
EU[k]	NG	5	10	100-5000	200
Canada[k]	NG	5	50	5000	300
USA[k]	NG	5	15	5000	300
Russia[k]	NG	3	100	5000	300
Winam gulf[m]	NG	14.2	53.60	237	2778
Rain water[m] (L. Victoria basin)	NG	NG	47.90	228.5	216.5
Well water[m] (L. Victoria basin)	NG	13.8	48.00	213.5	132.5
Municipal water[m] (L. Victoria basin)	NG	20.8	44.7	267.9	522.6
Nyamasaria river[m]	NG	4.6	52.40	253.1	3.049
Nyando river[m]	NG	14.4	57.50	232.3	2835
Sondu mirio river[m]	NG	18.4	47.00	225.2	2320
Dipsiz river[n]	0.092	0.405	0.365	1.051	NG
Background Conc. average[l]	NG	0.2	1.00	10	NG

Key

NG – Not given in literature. ND - Not Detected a – This study 2010 Kenya (number of examined samples: 18 for river and 8 for canals) b – KEBS (1996), c – WHO (1998), d – USEPA (1999), e – Turkish Environmental guidelines (1988), f Perkey et al. (2004), g – Trocine and Trefry (1996), h – Pettine et al. (1996), i – Bakaa and Kumru (2001), j – USEPA 1980), k – Neubauer and Wolf (2004), l – Klavins et al. (2000), m – Ongeri (2008), n – Ahmet et al. (2005), Class i – clean water for domestic use, Class ii – Fairly clean water for domestic use, Class iii – Polluted water, Class iv – Heavily polluted water.

CHAPTER FIVE

5.0: Conclusion, Recommendations and Suggestions for future studies

5.1: Conclusions

The study has established that the level of most physicochemical parameters of water from Sare River and its tributaries varied with sites and generally increased in dry season. The study also established that the level of some physicochemical parameters like turbidity, conductivity and BOD were above recommended guideline limits for natural waters. In addition, the presence of toxic heavy metals in sediment and water in the aquatic ecosystem of south Nyanza sugarcane zone was established. The information gathered suggest that the level of pollution of the aquatic ecosystem in South Nyanza sugarcane zone is still low but could rise with continued use of N fertilizers in the sugarcane plantations. The results of this study also show that direct domestic use of water from Sare River could pose health and environmental risk to the rural community who rely on these waters as their main source without subjecting them to treatment. This study further established that the heavy metals levels and physicochemical parameters in water varied with seasons. Heavy metals in soils also varied with seasons.

5.2: Recommendations

There is need to put in place mitigation measures to control acidification of the soil as this is enhanced by use of fertilizers and gradually polluting Sare River and its tributaries.

Residents around Sare River are advised to avoid using the river water for drinking as it is unsafe as indicated by the BOD and turbidity levels.

There is need to improve waste management facilities in Awendo town as the canal from the town appears most polluted in comparison to the other locations whose samples were studied.

5.3: Suggestions for future studies

There is need to determine the contribution of fertilizers to heavy metals loads in the aquatic ecosystem in South Nyanza sugarcane zone.

There is need to determine the contribution of the factory wastewater discharge to the pollution loads in the study area.

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