

**THE EFFECTS OF NITROGENOUS FERTILIZERS ON SELECTED
PHYSICOCHEMICAL PARAMETERS AND HEAVY METALS LOADS
WITHIN NZOIA NUCLEUS SUGARCANE ESTATE FARMS IN WESTERN
KENYA**

BY

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Abstract

Continued use of nitrogenous fertilizers and biosolids in farming is known to affect the soil pH of the farms leading to acidic environment that promotes solubility, bioavailability and mobility of heavy metals. In addition, these fertilizers also contain residues of heavy metals that accumulate in soils and water bodies over time. Nzoia Sugar Company in western Kenya uses nitrogenous fertilizers in sugarcane farming and the effect of these agrochemicals on the environment were yet to be determined. Heavy metals and physicochemical parameters cause a great threat to the environment and human health if the levels go beyond allowable limits. The Presence of heavy metals in the aquatic environment also affects some physicochemical parameter like dissolved oxygen and chemical oxygen demand which become harmful to the aquatic animals and plants when they exceed certain limits. River Nzoia is already reported to be affected by heavy metals and physicochemical parameters like total phosphate, nitrate-nitrogen and dissolved oxygen beyond international levels. Therefore, there was need to determine point sources of the above parameters in order to suggest possible mitigation procedures. Nzoia sugarcane nucleus farms were used to represent sugarcane farming in the whole sugar belt region where Nzoia River transverses. Two factor completely randomized block design was used in sampling. Triplicates of surface water, surface sediments and top soil samples from the farms, canals and River Kuywa (a river that traverses the nucleus to join River Nzoia) were collected. Sampling was done twice in the year (dry season when there was no nitrogenous fertilizer application and wet season a week after nitrogenous fertilizer application). A pH meter, a mercury thermometer, a turbidity meter and an electrical conductivity meter were used to measure pH, temperature, turbidity and electrical conductivity respectively insitu. Ultraviolet spectrophotometric screening method, closed reflux colometric method, Wrinklers' method, Anils' method and Okalebos' method, were used in determining nitrate-nitrogen, chemical oxygen demand, dissolved oxygen, total phosphates and total organic carbon respectively, whereas AAS (AA-6200, Shimadzu) was used to analyze heavy metals. The data was analyzed using Analysis of variance (ANOVA) ($p \leq 0.05$) (two factor experiment) and students t-test ($P \leq 0.05$) used to check the variations. The research found out that lowering of soil pH by nitrogenous fertilizers affected the concentrations of heavy metals in the soils and the surrounding aquatic environments. The nitrogenous fertilizers used in the farms were also found to contain residues of heavy metals. Presence of heavy metals into the aquatic environment increased water conductivity levels and reduced dissolved oxygen in water due to bioavailability and reoxidation processes respectively. Surface runoffs and soil erosions in the sugar plantations were the major transport agents of the heavy metals in soils to aquatic environments as was determined from high water turbidity values during the long wet season. In addition the surface runoffs and soil erosions were also transporting the nitrate and phosphate residues from the fertilizers applied to the aquatic environment leading to pollution of the water.

Chapter 1

Introduction

Nzoia Sugar Company is located in Bungoma District, 20 km from Bungoma Town and five kilometers off the Bungoma - Webuye highway in Western province and within Kenya's sugar belt. It lies between $34^{\circ} 39' 03.90''\text{E}$ - $34^{\circ} 42' 15.89''\text{E}$ longitudes and $0^{\circ} 31' 34.17''\text{N}$ - $0^{\circ} 36' 14.24''\text{N}$ latitudes. The company occupies a total surface area of 4,629 ha. The factory serves over 30,000 farmers within Bungoma, Kakamega and Lugari Districts (Nzoia Sugar Company profile, 2009). The Nucleus Estate, whose total area is 4,000 ha, supplies 20% of sugarcane requirement for the company and the rest is by out-grower section with a total area of 16,500 ha. Currently, the area under cane is 3,500 ha. in the nucleus with an average plant crop yield of 124 TCH (Tones of Cane per Hectare) and Ratoon crop yield of 93 TCH (Nzoia Sugar Company profile, 2009). Major cane varieties cultivated include N14, CO421 and CO945 which are renowned for their high sucrose content (Nzoia Sugar Company profile, 2009). Nitrogenous fertilizers (Diammonium Phosphate (DAP) and Urea) are applied at the onset of the long rainy season that begins in March (Table 1.1 and 1.2, DDP, 1996). River Kuywa, which traverses the nucleus from Mt. Elgon, is highly depended upon by residents downstream for small scale fishing and other domestic uses (DDP, 1996).

Sugarcane farming is known to reduce soil pH (Oliver, 2004). In Papua New Guinea, the pH of top soils under sugarcane cultivation decreased from 6.5 to 5.8 between 1979 and 1996 (Oliver, 2004). In Fiji, a decline in soil pH from 5.5 to 4.6 was recorded over the first 6 years of cane cultivation and in Philippines; a decrease of 5.0 to 4.7 was recorded over 19 years of cane cultivation (Oliver, 2004). From existing literature, it has been found that the change in soil pH is mainly due to the use of acidifying nitrogenous fertilizers such as Urea and ammonium phosphates, coupled with nitrate leaching that occurs under the high rainfall conditions that often prevail in cane cultivation areas (Oliver, 2004).

Table 1.1. Monthly rainfall data during 1988 -1992 in Bungoma District western Kenya (Rainfall in mm).

Month	Long term mean monthly	1988	1989	1990	1991	1992
January	47.44	75.6	2.0	58.8	90.7	10.1
February	62.04	69.6	61.1	118.5	46.5	14.5
March	162.2	175.7	187.3	285.7	105.6	71.7
April	207.18	342.5	163.1	301.3	152.1	76.7
May	165.7	86.0	204.2	174.3	191.9	172.1
June	79.1	129.7	68.7	47.1	81.3	72.1
July	97.1	163.3	90.5	86.4	88.4	56.9
August	84.02	118.9	74.1	135.8	25.9	65.6
September	118.7	235.2	88.1	68.9	99.4	101.8
October	115.4	64.6	138.7	132.2	124.9	116.6
November	70.5	83.5	85.0	104.9	24.2	55.1
December	60.4	86.5	124.4	70.8	20.3	67.0
Mean Monthly Rainfall	105.9	135.9	107.3	132.1	87.6	73.4

Source: DDP, 1996.

Table 1.2. History of repeated nitrogenous fertilizer application (in bags of 50 kg each) in the studied plots from Nzoia nucleus estate sugarcane farms in Western Kenya.

	Plots													
	9053		8071		243		125		616		429		413	
	Size	20 (ha)	10 (ha)	4.48 (ha)	3.21 (ha)	2.43 (ha)	1.68 (ha)	3.11 (ha)						
Year	DAP	Urea	DAP	Urea	DAP	Urea	DAP	Urea	DAP	Urea	DAP	Urea	DAP	Urea
2005/06	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
2006/07	NA	NA	NA	NA	NA	18	20	NA	NA	10	7	NA	10	NA
2007/08	NA	NA	NA	NA	8	NA	NA	9	NA	10	5	7	9	NA
2008/09	NA	NA	NA	NA	10 b	NA	NA	NA	8	NA	NA	10	9	NA
2009/10	NA	NA	NA	NA	NA	NA	10	7	NA	10	NA	7	NA	5
Sum	0.0	0.0	0.0	0.0	18	18	30	16	8	30	12	24	38	5.00

Source: Agronomy section Nzoia Sugar Company. NA: Not Applied.

A Change in soil pH is usually accompanied with other chemical changes in both the soil and the receiving waters (Oliver, 2004). For instance, reduction of soil pH makes heavy metals in the soil to become more soluble, bioavailable and mobile (Alloway 1995a). Hence use of nitrogenous fertilizers affects the acidity of soils thus making heavy

metals readily available for transportation from soils to the aquatic environment especially during the long rainy season as compared to the long dry season due to surface runoffs, leaching and erosion of the soils. Furthermore, use of biosolids as fertilizers in sugarcane farming increases the total organic carbon of the soil hence influencing heavy metal transport (Xue, 2008).

In addition to the above problems associated with nitrogenous fertilizers, Mortvedt (1995) reports that nitrogenous fertilizers are contaminated with heavy metals that accumulate in soil with repeated application (Table 1.2). Lawrence and Brian (2002) also support the same arguments indicating that this has drawn the attention of farmers, environmental organizations, consumers, and public policymakers. Alloway (1995a) also has reported that inorganic fertilizers contain traces of heavy metals that accumulate in soils with repeated applications. However, of important concern is the fact that use of these fertilizers affects the soil pH and from Alloway's findings, chemical conditions in soil like soil pH are important secondary determinants of heavy metal transport and fate at the application sites (Alloway, 1995b). First, ionization of metals increases at low pH thereby increasing their water solubility and mobility (Alloway, 1995b). Second, hydroxonium ions (H_3O^+) displace most other cations on negative surface charges (Alloway, 1995b). This reduces metal adsorption by cation exchange and organic complexation (Ford *et al.*, 2001).

Once heavy metals find their way into the aquatic environments, a large amount gets deposited into the sediments due to other factors like dilution factor, sedimentation and precipitation (Odiete, 1999). It has been reported that heavy metal concentration in sediments can be several orders of magnitude greater than in water (Odiete, 1999). Sediment associated heavy metals pose a direct risk to detrital and deposit feeding benthic organisms, and may also represent a long-term source of contamination to higher trophic organisms (Odiete, 1999).

Bioaccumulation and bioconcentration 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 metal burdens (Wang, 1987; Gough and Herring, 1993; Driscoll *et al.*, 1994; Ongley, 1996).

Heavy metal solubility can be affected by several factors including temperature and pH changes (Carmen *et al.*, 2001). However, presence of the heavy metals in an aquatic environment can also affect its water electrical conductivity, chemical oxygen demand and dissolved oxygen (Duinker *et al.*, 1982). Soltanpour and Raley (1989) have reported several adverse effects that may arise if the above physicochemical parameters go beyond allowable limits. Such effects include death of aquatic animals due to lack of oxygen (Richard, 1991).

However, another major concern in the use of nitrogenous and phosphorous fertilizers in sugarcane farming is the fact that not all the applied fertilizers are utilized in the soils. Most of the inorganic nitrogen and phosphates applied find their way into aquatic environments due to surface runoffs, during the rainy seasons and leaching into ground water. Previous studies have shown that the addition of these nutrients to the water system would result in large proliferations of algae and water hyacinth, which have detrimental effects on the water quality (Fried *et al.* 2003; LVEMP, 2003). Algal blooms and water hyacinth deplete the oxygen supply in the water system and are harmful to other aquatic species (LVEMP, 2003). Additionally, nutrients cause taste and odor problems that result in reduced recreational use, and increased water treatment costs (Fried *et al.*, 2003). Cowi (2002) has indicated that annual loads of nitrogen and phosphorous in Lake Victoria from Nzoia River basin as 3,340 total N tonnes per year and 946 total P tonnes per year. These were the values partly responsible for growth of water hyacinth in Lake Victoria hence the need to determine their point sources.

This research therefore focused on finding the concentrations of heavy metal loads and some physicochemical parameters in water, sediments and soils in the long dry season and long rainy season in Nzoia nucleus estate farms from western Kenya. The heavy metal loads, pH and total organic carbon from the nucleus soil farms were compared to those from an adjacent control farm where fertilizers were not being used. In addition, the concentrations of heavy metals in the nitrogenous fertilizers (DAP and Urea) used for sugarcane farming were also tested.

1.1. Problem statements

According to Lalah *et al.*, (2008), River Nzoia is loaded with heavy metals and the main farming activity in the Nzoia River basin is sugarcane farming. Onyari and Wandiga, (1989) also reported the same problem at the mouth of River Nzoia in Lake Victoria. Sugarcane farming activities in Nzoia sugarcane zone that includes nitrogenous fertilizers application are believed to be the main source of these heavy metals.

Heavy metals have numerous effects on human health including: Wilson's disease (copper), Lead arthragia (lead), birth effects, infertility, tumor (chromium), carcinogenicity and trade regulations whereby certain foods like fish are banned in the global market due to high metal contamination levels (USEPA 1980, Snyder *et al.* 1975, NAS 1980, Dennis *et al.* 2003, Ongley, 1996).

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1.2. Research justification

Nitrogenous fertilizers including DAP and Urea used in sugarcane farming in the nucleus farms have been reported to lower soil pH (Oliver, 2004). Low soil pH has been reported to affect the solubility, bioavailability and mobility of heavy metals (Alloway, 1995a). The presence of heavy metals in the aquatic environment also affects other physicochemical parameters in the same environment. From the above statements therefore, it is concluded that sugarcane farming overtime affects heavy metal concentrations and other physicochemical parameters in the aquatic environment. Furthermore, the applied fertilizers will find their way into the aquatic environment through surface runoffs, soil erosion and leaching from their point of application. This in turn affects the concentrations of nutrients in the recipient aquatic environment (Lake Victoria Environmental Management Programme (LVEMP), 2003). Most of the research in sugar industry has been on the effects of nitrogenous fertilizers on soil pH with

reference to sugarcane productivity yet the effect of the reduced pH on Heavy metal mobility and water quality parameters have not been covered extensively.

1.3. Objectives

Main objective

This study aimed at determining the levels and the variations of heavy metal loads (Pb, Cu, Cr, Zn, Fe) and physicochemical parameters (temperature, pH, Total Organic Carbon (TOC), Chemical Oxygen Demand (COD), Dissolved Oxygen (DO), Electrical Conductivity (EC), Turbidity, NO₃-N and Total Phosphates) in top soils, surface sediments, and surface water in Nzoia sugarcane farms, canals, and River Kuywa during the long wet (April – June) season and the long dry season (January – March).

Specific objective

1. To determine the levels and the variations in pH, TOC and heavy metal (Pb, Cu, Cr, Zn and Fe) loads between the long wet and long dry seasons in the top soils from various sites within Nzoia Sugarcane nucleus estate farms and compare them with an adjacent farm that do not use nitrogenous fertilizers
2. To determine the concentrations of heavy metals in the fertilizers used (DAP and Urea) in farming activities within Nzoia nucleus estate farms.
3. To determine the levels and the variations in heavy metal (Pb, Cu, Cr, Zn, and Fe) loads in the surface sediments and surface water samples from canals within the nucleus estate farms and River Kuywa between the long wet and long dry seasons.
4. To determine the levels and the variations in water quality physicochemical parameters namely Temp, pH, TOC, COD, DO, EC, Turb, NO₃-N and TP in canals within the nucleus estate farms and River Kuywa between the long wet and long dry seasons.

1.4. Hypotheses

Null hypothesis H_0 :

That there were no changes in the means of heavy metal loads and physicochemical parameters within sites and between the long wet and long dry seasons; such that in case of any difference it was not associated with nitrogenous fertilizers applied during the wet season but other natural factors.

$$H_0: \mu_1 = \mu_2$$

Where: H_0 = the null hypothesis

μ_1 = the mean of population 1 (site n or long dry season)

μ_2 = the mean of population 2 (site n or long wet season)

n: 1, 2, 3....

Alternative hypothesis H_1 :

The changes in the means of heavy metal loads and physicochemical parameters respectively, and their variation between seasons and within sites were due to nitrogenous fertilizer application in the Nzoia nucleus estate farms during the long wet season.

$$H_1: \mu_1 \leq \mu_2$$

Where: H_1 = the alternative hypothesis

μ_1 = the mean of population 1 (site1 or long dry season)

μ_2 = the mean of population 2 (site n or long wet season)

n: 1, 2, 3...

Chapter 2

Literature review

2.1. Soil acidification

Soil acidification (declining soil pH due to net proton (H^+) accumulation) is a natural process that occurs during pedogenesis and is often associated with high rates of leaching. However, the rate of acidification can be accelerated through farming activities with the result that the soil resource may become significantly degraded. Under intensive agricultural production, continual acidification of these soils is likely to occur through the use of high inputs of ammonium-based nitrogen fertilizer inputs, the high level of base removal as a result of crop uptake and subsequent removal and the generally high rainfall environment of the region which facilitates the losses of basic cations through leaching (Moody and Aitken, 1995). Acidification of soils is usually accompanied with fertility loss and declining productivity (Ahern *et al.*, 1995). Degradation of the soil resource through the loss of fertility that accompanies acidification results in declining productivity and places the products of farming systems operating in acidifying environments subject to scrutiny under the recent ISO 14000 treaty (Moody and Aitken, 1995).

2.1.1. Processes of acidification

The nitrification of ammonium based fertilizers such as urea and organic N in crop residues (Organic Matter) is in itself an acidifying reaction. The reaction is carried out through the microbial conversion of NH_4^+ to NO_3^- with the consequent production of protons (H^+). The extent of acid generation by fertilizers is a function of the fertilizer type, environmental and edaphic factors (Wood *et al.*, 2003). Estimates of potential net acidity generated by frequently used fertilizer sources in the sugar industry are presented in Table 2.1, with Diammonium phosphate being the most acidifying and urea the least on the basis of N per kg fertilizer applied. In view of the potential acidity generated by nitrogenous fertilizers the equivalent amount of $CaCO_3$ required to neutralize this acidity is also shown in table 2.1. The theoretical amount of $CaCO_3$ required to neutralize the acidity generated from an application of $180 \text{ kg N ha}^{-1} \text{ y}^{-1}$, typical for the NO_3^- from ammonium-based fertilizer is a significant source of acidity generation in these production systems. In contrast, the addition of basic nitrate fertilizers such as $Ca(NO_3)_2$

causes little change in pH due to the lack of nitrification and may in some cases result in an increase in soil pH (Woods *et al.*, 2003). Although the production of NO_3^- through the nitrification process for nitrogenous fertilizers is a net proton accumulating reaction, the subsequent leaching of nitrate can result in a significant decline in exchangeable bases because Ca^{2+} and Mg^{2+} will move downwards as counter ions for the very mobile NO_3^- , resulting in an accumulation of protons at the point of nitrification (Haynes, 1983). Consequently, there is spatial disjunction between the production of NO_3^- and its subsequent uptake by the plant. The result is an accumulation of H^+ at point of production and net alkalization due to the uptake of NO_3^- by the plant at some other point in the profile. The uncoupling of these two processes results in net proton accumulation at one point in the profile and net alkalization at some other point. As long as nitrate is taken up at the point of production the outcome is neutral (Wood *et al.*, 2003).

Table 2.1. Estimated potential acidity produced through nitrogenous fertilizers in sugarcane plantations.

Source	Nitrification reaction	Net Potential acidity generated kmoles H^+ .kg N	Potential acidity generated from 180 kg N ha^{-1} kmoles H^+ ha^{-1}	^a Amount of CaCO_3 required to neutralize acidity generated by an application of 180 kg ha^{-1} (kg ha^{-1})
Urea	$(\text{NH}_4)_2\text{CO} + 4\text{O}_2 = 2\text{H}^+ + 2\text{NO}_3^- + \text{CO}_2 + \text{H}_2\text{O}$	0.072	13.0	650
Diammonium Phosphate	$(\text{NH}_4)_2\text{HPO}_4 + \text{O}_2 = 3\text{H}^+ + 2\text{NO}_3^- + \text{H}_2\text{PO}_4 + \text{H}_2\text{O}$	0.107	19.3	965

a: Assuming that 1 kmol requires 50 kg CaCO_3 to neutralize it.

Source: Wood *et al.*, 2003.

2.1.2. Evidence of accelerated acidification under sugarcane

Soil acidification rates can be measured in terms of absolute changes or relative to some control soil. In the former case, acid addition rates can be estimated from analyses of soils before and after a period of acidification as in long-term studies (Wood *et al.*, 2003). However, relative rates of acidification can also be derived from survey data (eg. fence line contrasts of developed and undeveloped sites). This approach has been used in

a number of studies in the sugar industry (Wood, 1985; Bramley *et al.*, 1996; Moody and Aitken, 1997). The use of fence line comparisons essentially results in a conservative estimation of the net acidification rate. As part of a wider study on the possible role of changes in soil properties over time on sugar yield decline (Garside *et al.*, 1997), differences in soil chemical properties between new land and land which had been under sugarcane monoculture for more than 20 years were examined in detail by Bramley *et al.* (1996). They found that there was no consistent effect of time under sugarcane monoculture on soil chemical properties across sites located in the Burdekin, Herbert and Tully Districts of North Queensland, Australia, either when the distribution of properties through the soil profile, or property values at specific depths were considered. However, marked effects were noted at some sites with respect to some soil properties and these were generally consistent with soil acidification. The changes included reduced topsoil pH in old land (0.5-1.5 pH units); increased exchange acidity and aluminium saturation in soils under old land, especially in the Herbert where percent Al saturation increased from approximately 5 to 20%. However, although little change was noted in the Tully soils where much higher Al % (45%) in both old and new land soils were measured, decreased cation exchange capacity (CEC) and increased anion exchange capacities (AEC) were found in old land soils at some sites in each region. Wood (1985) obtained similar results in a paired sites study in the Herbert River District, North Queensland, Australia, where he found that many of the differences in soil chemical properties between new cane land and land that had been under sugarcane for several years could be associated with soil acidification. Sugarcane soils were found to have a lower pH, lower cation exchange capacity and lower levels of exchangeable base cations (calcium, magnesium and potassium).

In addition, the analysis of soil samples from 1064 sites in the Herbert sugarcane area, taken as part of the CSR (Central Sugar Refinery, in Malaysia) Herbert River soil survey (Wood and Bramley, 1996), has shown that mean topsoil (0-20cm) pH_w (pH in 1:5 soil:water) is 4.97 and mean subsoil (40-60cm) pH_w is 5.28. Schroeder *et al.* (1996) have also reported marked acidification in a range of sugarcane soils in South Africa. The effects of soil acidification on sugarcane growth have received little attention from Australian researchers, presumably because Hetherington (1986) concluded that cane was tolerant of low pH-induced aluminium toxicity. However, Schroeder *et al.* (1996) reported marked differences between South African varieties in terms of their response to lime application suggesting that not only was cane affected by the effects of low soil pH,

but that these effects may be variety specific. In general, most crops perform best when the soil pH is approximately 5.6 to 6.0 (Tisdale *et al.*, 1985).

From the previous discussion it can clearly be seen that soil acidification is a continuing problem confronting the Australian sugar industry and that the largest potential acidifying component in a sugar production system is the contribution derived from the use of nitrogen fertilizers (Wood, 2003). The contribution to the total proton pool arising from the export of millable cane is relatively small compared to that derived from the nitrification of ammonium and urea based fertilizer sources, assuming that significant leaching occurs (Wood, 2003). The case would not differ in Kenyan sugar industry since the same agronomic practices for sugarcane are practiced.

Most research on acidification of sugarcane farms has been on sugarcane production with little being done on environmental effect. Alloway (1995a), points out that reduction in acidity of soil leads to naturally occurring heavy metals in the soils becoming more soluble, bioavailable and enhances their mobility. It is on the basis of this argument that the current research is mainly based upon.

2.2. Effects of Physicochemical parameters on heavy metals

Chemical conditions in soil are important secondary determinants of heavy metal transport and fate (Alloway, 1995b) including the naturally occurring heavy metals in soils. The importance of interactions between metals and solid phases of soils, soil water, and air within and above soil depends on a variety of chemical factors. Adsorption of metals from soil water to soil particles is the most important chemical determinant that limits mobility in soils (Alloway, 1995b). There are four general classes of these interactions: specific adsorption, co-precipitation, cation exchange, and organic ligand complexation (Alloway, 1995b). Specific adsorption involves partly covalent bonds between the heavy metal with lattice ions on soil particle surfaces. Co-precipitation involves formation of water insoluble precipitates of metal cations and anions such as carbonate, sulfide, or phosphate (Alloway, 1995b). Cation exchange is non-specific interaction of metals with negative surface charges on soil minerals, such as clay. Similarly, soil organic matter, for instance humus, adsorbs metals by forming chelate complexes with carboxyl groups of the humic substances playing a predominant role (Alloway, 1995b). The organic carbon fraction has a significant influence on heavy metal

transport. Specifically the anthropogenic heavy metals (Pb, Cu, Zn and Cr) are strongly correlated with soil organic carbon content (Xue, 2008).

Chemical conditions in soil like soil pH are important secondary determinants of heavy metal transport and fate at the application sites (Alloway, 1995b). First, ionization of metals increases at low pH thereby increasing water solubility and mobility. Second, hydroxonium ions displace most other cations on negative surface charges. This reduces metal adsorption by cation exchange and organic complexation (Ford *et al.*, 2001).

There exists a relationship between dissolved heavy metals and dissolved oxygen in water. This is due to reoxidation of the metals, which will make dissolved oxygen level to reduce with increase in dissolved metals. Thus an increase in dissolved oxygen also increases dissolved metals hence promoting their mobilization (Duinker *et al.*, 1982). Therefore any farming activity that increases heavy metal concentrations will automatically reduce dissolved oxygen.

When heavy metals are introduced into the aquatic systems, aquatic animals and plants may bioaccumulate these heavy metals into their system leading to a number of problems. Most of these problems manifest themselves in animals higher in their food chains hence international bodies have set limits of heavy metal burden and physicochemical parameters which aquatic environments should not exceed. Below, some of the problems associated with specific heavy metals and their international limits in domestic water are discussed.

2.2.1. Lead

Lead (Pb) is especially prone to accumulation in surface horizons of soil and this has been attributed to its low water solubility within an environmentally relevant pH range which results to very low mobility (Davies, 1995). Soil water contains only about 0.05-0.13% of the total soil lead concentration. Lead speciation is rather simple and Pb^{2+} is the dominant soluble form. It forms a number of highly insoluble precipitates like $Pb(OH)_2$, $Pb_3(PO_4)_2$, and $PbCO_3$ (Davies, 1995). Plant uptake factors for lead are low (0.01-0.10) due to very low water solubility (Davies, 1995).

Due to past uses of Pb in industrial processes and consumer products like paint and leaded gasoline, urban soils often contain high Pb concentrations, up to 1840 mg/kg of Pb (Lawrence and Brian, 2002). Neurological problems, especially in children, are the principal concern for chronic lead exposure (Goyer and Clarkson, 2001). Past uses of

food and beverage cans with Pb solder led to significant human exposures (Goyer and Clarkson, 2001). Dietary intakes of 400 to 500 $\mu\text{g}/\text{day}$ of Pb dropped to 120 $\mu\text{g}/\text{day}$ of Pb with elimination of this practice (Goyer and Clarkson, 2001). Consumption of Pb contaminated soil/food itself, rather than crop contamination, is a more likely exposure hazard (Goyer and Clarkson, 2001).

Lead is a contaminant in fertilizers (Mortvedt, 1995; Lawrence and Brian, 2002). Repeated application of these fertilizers leads to accumulation of Pb in the soils followed by leaching and transportation into water bodies (Stokinger, 1981). Once in water bodies Pb can enter the food chain hence affecting human life. Inorganic salts of Pb are almost insoluble in water except for the acetate, nitrate and chloride; meaning that water-borne Pb is minimal because it forms essentially insoluble sulfates and carbonates (Stokinger, 1981).

Lead is a dangerous metal once in the body system; for instance a study by Fairchild (1978) revealed that a single intra-cardiac injection of Pb acetate caused abnormal Deoxyribonucleic Acid (DNA) and Ribonucleic Acid (RNA) synthesis in mouse kidney. Similarly, Chakraborty *et al.* (1988) discovered that a high degree of abnormalities was found in tissue nucleic acids of rats treated with Pb. Other studies by Griggs (1964), and Vardhani (1986), show that there is tissue response in *Ancylostoma caninum* larvae and toxic effect of lead on immuno-physiology in mice, respectively. In 1996, Kenya Bureau of Standards reported that Pb levels in drinking water should not exceed 0.05 ppm (KEBS, 1996). Afterwards in 1998, the World Health Organization reported allowable maximum limits of Pb in drinking water as 0.01 ppm (WHO, 1998).

Under normal circumstances 300 μg of Pb are ingested daily by an adult while ingestion of at least 600 μg of Pb daily could result in intoxication (Kehoe, 1968). From works of Tsuchiya (1977) and Stokinger (1981), it is clear that other than deposition in bone and toxic reactions, Pb has minimal involvement with metabolism. A report from Snyder *et al.* (1975) indicates that 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 he loses 0.045 mg/day through urine, 0.3 mg/day through faeces and 0.1 mg/day through other routes like sweating. They gave a value of 120 mg as the total body burden with 11 mg in soft tissues. The total body burden has been estimated to range between 100 to 400 mg and this increases with age (Tsuchiya, 1977). Joint pains otherwise called "Lead arthralgia" are strongly associated with Pb induced gout caused by lead's interference with uric acid excretion through the kidney (Tsuchiya, 1977). Lead inhibition of guanine

aminohydrolase could also be involved in this (Cullen *et al.*, 1983). Nephrotoxicity is most commonly seen in childhood Pb toxicities (Cullen *et al.*, 1983). Lead causes tubular dysfunction, with ultrastructural changes in the mitochondria, which results in aminoaciduria, glysuria and phosphaturia, as well as gout (Cullen *et al.*, 1983). Lead is also associated with depression of endocrine functions, particularly the thyroid and adrenal (Tsuchiya, 1977; Cullen *et al.*, 1983). Cullen *et al.* (1983) also reported that, to some extent, Pb is associated with a high incidence of premature deliveries and spontaneous abortions in humans. In addition, they reckoned that Pb suppresses testicular functions and even causes sterility in men.

From the above discussions it is clear that Pb is a dangerous heavy metal whose consumption should be minimized. It was therefore necessary to determine point sources of this metal in this study for necessary mitigation measures.

2.2.2. Iron

The Kenya Bureau of Standards (KEBS, 1996) reported that safe drinking water should not exceed 0.3 ppm of iron. 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). According to Hammond and Beliles (1980), iron is found in almost every food with higher concentrations in animal tissues than plant tissues. Iron is an essential mineral hence a component of several cofactors including hemoglobin and cytochromes. Many enzymes require iron for their activity and, in some, it is weakly bound for example with aconitase (Beinert and Kennedy, 1989). Da Silva and Williams (1991) noted that iron is a major control element which enzymes involved in secondary metabolism require for their activity. They also reckoned that since some of these are enzymes, including hormones, 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.

NAS (1980) and Stokinger (1981) recommended a daily allowance of 10 mg for men and 18 mg for women. Snyder *et al.* (1975) wrote that the iron balance for a 70 kg reference man is from intake of foods and fluids at 16 mg/day and airborne intake of 0.03 mg/day, including losses via urine of 0.25 mg/day, faeces 15 mg/day, and through other routes at 0.51 mg/day. For a 50 kg reference woman, the values are 12 mg/day from

foods and fluids and 0.03 mg/day airborne intakes. Then 0.20 mg/day, 11 mg/day and 1.2 mg/day are lost through faeces, urine and other routes respectively and 0.6 mg/day as menstrual loss (Snyder et al., 1975).

Hammond and Beliles (1980), reported that intestinal absorption of iron especially Fe^{2+} , is a complicated active process and that the rate of intake is inversely proportional to the state of the body's iron stores. Snyder et al. (1975) reported adults iron adsorption to be 30% of total iron uptake. Intake of excess iron is also dangerous since signs appear after the carrier has been saturated with free iron in the blood (Stokinger, 1981). Forbes (1947) found that serious acute poisoning in children can occur following ingestion in excess of 1 g of iron. The normal iron intake for children is 10-20 mg/kg body weights. As discussed earlier, iron is found in virtually every food including water, plants and even aquatic animals and therefore it is necessary to monitor the accumulation of this iron in our natural waters to avoid toxicity of it in the higher animals through the food chains.

2.2.3. Copper

Copper is an essential trace element to man and to all vertebrates. Its allowable daily intake according to NAS (National Academy of Science, 1980), is 2 to 3 mg/day, although 1 to 2 mg/day could maintain a positive copper balance. According to reports by Piscator (1977) and USEPA (1980), copper is a component of most vital enzymes; including tyrosinase, cytochrome oxidase, and amine oxidase. It is largely combined with serum albumin and alpha-globulin ceruloplasmin, which serve to transport and regulate copper in the body (Stokinger, 1981). The metabolism of copper involves a turn over of the copper-containing enzymes.

Menke's disease which is a copper deficiency disease, is a disorder in the metabolism whereby there exists an inability to absorb copper (USEPA, 1980). Copper is especially essential in the electron transfer process which also involve iron in hemoglobin, photosynthesis in plants and the terminal step of mitochondrial respiration and hence Cu influences life support functions like production of red blood cell and carbohydrate synthesis (USEPA, 1980). Keevil and Mason (1978) observed that copper, together with iron, are the dominating prosthetic metal ions in the electron carrier proteins participating in the biological oxidation of organic substrates by dioxygen. Copper is a transition metal that has a particular chemical stability and 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 (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 (Lontie and Vanquickenborne, 1974) despite the fact that O_2 is a neutral symmetric molecule.

At high doses, however, copper is one of the common metallic elements toxic to humans found in polluted environments (Purves, 1977). Wilson's disease is due to inability to utilize copper and is a hereditary metabolic disorder whereby there is accumulation of copper in some organs of the body, the most sensitive being the brain and liver (USEPA, 1990; Prasad and Oberleas, 1976). Acute copper poisoning can also lead to hemolytic anemia (Finelli *et al.*, 1981) hence the need to monitor its presence in drinking water and soil. Copper is actively absorbed in the stomach and duodenum (Stokinger, 1981). Typically, about half of the ingested dose is absorbed, but this can be decreased by competition with zinc and binding to ascorbic acid and other compounds (Stokinger, 1981). However, copper can also be excreted and the major excretion route for the absorbed copper is the bile. Minor routes of excretion of Cu include sweat, urine, and saliva (USEPA, 1980; Stokinger, 1981). These are some of the problems that may arise if copper content is not checked in our domestic waters.

2.2.4. Zinc

Safe drinking water should not exceed 5 ppm of zinc (KEBS, 1996). A safe level of 3 ppm of zinc in drinking water might make consumers complain about its appearance and taste (WHO, 1998). The U.S. Environmental Protection Agency (1980) and World Health Organization (1998) standard for zinc in drinking water is 5 ppm based on the bitter taste zinc imparts to water at that level. Allowable maximum limits for zinc in drinking water in the UK and USA is 5 ppm (Neubauer and Wolf, 2004).

Zinc 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 house hold plumbing (USEPA, 1980). From a study of Boston tap water in the United States, levels of zinc were found at up to 1.6 ppm with a mean of 0.2 ppm (NAS, 1977). There was an increase in zinc levels at the tap over finished water

levels indicating zinc pickup from the pipe and this was attributed to the soft acid nature of Boston's water. In the more acidic water of Seattle, zinc levels in tap water were higher than in the finished water 95% of the time with 10% exceeding the 5 ppm drinking water standard. The highest reported level in Seattle was 5.5 ppm (NAS, 1977).

The taste threshold for zinc in water is 15 ppm. Levels as high as 675 to 2280 ppm in water are emetic (Stockinger, 1981). Zinc is ubiquitous in mammalian tissues and is involved in the activity of many enzymes. Thus zinc participates in many metabolic processes (USEPA, 1980). Zinc is essential in enzyme and enzymatic functions such as DNA, RNA and protein synthesis. It is also essential in carbohydrate metabolism, utilization of nitrogen and sulfur, cell division and growth. It is essential for spermatogenesis, ova formation, and foetal nutrition. It is also involved in pituitary and adrenal gland metabolism (USEPA, 1980).

Absolute amounts required range from 1.1 mg/day in infancy, 2.2 mg/day in childhood and adult hood, 2.8 mg/day at puberty, 2.55 to 3.0 mg/day in pregnancy, and 5.45 mg/kg body weights during lactation (Taylor *et al.*, 1982). Zinc is present in the erythrocytes as the zinc metalloenzyme carbonic anhydrase, in the leucocytes, in several zinc metalloenzymes in the plasma, bound mainly to albumin and in the serum, bound to a macroglobulin and to amino acids (Taylor *et al.*, 1982). Zinc is also essential for the activity of the following enzymes: alcohol dehydrogenase, carboxy peptidases, leucine aminopeptidase, alkaline phosphatase, carbonic anhydrase, RNA-polymerase, and DNA-polymerase (Taylor *et al.*, 1982). Thymidinekinase is also zinc dependent (USEPA, 1980). Excessive Zinc intake has been associated with copper deficiency anemia for it interferes with copper and iron metabolism (USEPA, 1980).

Zinc is a pollutant in most commercial fertilizers (Mortvedt, 1995) and hence its continued use may lead to accumulations at the application sites. The above discussed problems can therefore be minimized if proper mitigation measures are taken to control the source. It is therefore important to monitor zinc levels in drinking water so as to prevent problems that arise due to its toxicity.

2.2.5. Chromium

Chromium usually appears commonly in the environment as a trivalent salt Cr-III or Cr³⁺ (ATSDR, 2003). Found in air, water, soil and some foods, it is an essential trace

element, aiding in the metabolism of carbohydrates etc (ATSDR, 2003). It is found in foods such as cole crops, brewer's yeast and cereal grains ATSDR, (2003). Hexavalent Chromium (Cr VI) is the byproduct of industrial applications, including steel making, tanning, plating, and textiles (ATSDR, 2003). Considered by the USEPA to be a carcinogen, (Cr-VI or Cr⁶⁺) is readily absorbed by the body, and can lead to ulceration of the liver and nasal septum (ATSDR, 2003). Action of stomach digestion tends to change Cr⁶ to Cr³, but Cr⁶ is a strong oxidizer and can damage cell walls easily (ATSDR, 2003). Sources of Cr⁶⁺ in the Rivers and streams include steel manufacturing, tannery wastes, leather by-product, and sewage sludge (ATSDR, 2003).

Chromium attaches tightly to soil particles, and the usual exposure pathways are due to exposure to dusts and sediments (ATSDR, 2003). According to Dennis *et al.* (2003), only a small part of the chromium that ends up in water will eventually dissolve. Furthermore from his work, chromium causes respiratory problems, a lower ability to fight diseases, birth defects, infertility and tumor formation. Chromium (III) is an essential nutrient for humans and shortages may cause heart conditions, disruptions of metabolisms and diabetes (Cheryl and Susan, 2000). Excess chromium (III) causes negative health effects for instance skin rashes (Cheryl and Susan, 2000). Chromium (VI) is a danger to human health because it can alter genetic materials and cause cancer (Cheryl and Susan, 2000). It is therefore important to monitor it in the environment.

Chromium may exist in a number of oxidation states, but the most stable and common forms are Cr (III) and Cr (VI). These have sharply contrasting chemical properties: Cr (IV) exists as an anion; it is more readily extracted from soil and sediment particles and is considered the more toxic form (Alloway 1995). Chromate (CrO²⁻) is in pH dependent equilibrium with other forms of Cr (VI) such as HCrO₄⁻ and dichromate (Cr₂O₇²⁻) with CrO₄²⁻ the predominant form at pH > 6 (Alloway, 1995a). Chromium (III) on the other hand, is much less mobile and adsorbs to particulates more strongly. The solubility of Cr (III) decreases above pH 4 and above pH 5.5 complete precipitation occurs (Alloway, 1995a).

Chromium (VI) is the more stable form in equilibrium with atmospheric oxygen. However, Cr (VI), with its high positive reduction potential, is a strongly oxidizing species, and in the presence of soil organic matter Cr (VI) is reduced to Cr (III) (Alloway, 1995a). Reduction is more rapid in acid than alkaline soils (Cary *et al.*, 1977). Thus in the majority of soils, the relatively insoluble and less mobile Cr (III) form predominates and it generally occurs as insoluble hydroxides and oxides (Cary *et al.*, 1977). For example,

Cary *et al.* (1977) observed that additions of soluble Cr as either Cr (VI) or Cr (III) to soils reverted to forms which were insoluble and unavailable to plants. Following reduction of Cr (VI), it was concluded that insoluble Cr in the soils was present as hydrated oxides of Cr (III) complexing with soluble organic acids (e.g. citric acid, fulvic acids and soil extracts of water-soluble organic matter). The soil maintains small amounts of Cr (III) in solution above the pH at which uncomplexed Cr precipitates and is therefore a means of enhancing its mobility (Bartlett and James 1988). Bartlett and Kimble (1976) and Bartlett and James (1988) drew attention to the similarity of adsorption and solubility behavior between Cr(III) and Al(III) in response to changes in pH and phosphorus status of soils. Oxidation of a proportion of Cr (III) is considered a likely occurrence in soils with a pH greater than 5 and rich in oxidized Mn, although there are difficulties in detecting the transition because drying and storage seemingly destroy the capacity of soil to oxidise the element (Bartlett and James, 1988) In essence, the soil pH is lowered by drying (Bartlett and James, 1988). Bartlett and James (1979) found that the amount of Cr (III) oxidised to Cr(VI) was proportional to the Mn reduced and also to the amount reducible by hydroquinone. In situations where the Cr (VI) form remains in soil, Bartlett and Kimble (1976) contend that its adsorption capability is similar to that of orthophosphate and the anion will remain mobile only if its concentration exceeds both the adsorbing and the reducing capacities of the soil. In fact, adsorption of Cr(VI) in certain soils can offset its reduction (Bartlett and James, 1988)

2.3. Physicochemical parameters and their environmental impact

Phosphorus is essential to the growth of biological organisms, including both their metabolic and photosynthetic processes. Phosphorus occurs naturally in bodies of water mainly in the form of phosphates (Clark and John, 1991). Phosphates are classified as orthophosphates (PO_4^{3-} , HPO_4^{2-} and H_3PO_4); condensed phosphates or polyphosphates, which are molecules with two or more phosphorus atoms, oxygen atoms and in some cases hydrogen atoms combined in a complex molecule with organically-bound phosphates (Clark and John, 1991). Orthophosphates in an aqueous solution can be used for biological metabolism without further breakdown (Clark and John, 1991). Orthophosphates applied to agricultural or residential cultivated land as fertilizers may be carried into surface waters with storm runoff and melting snow (Franson, 1995).

Polyphosphates slowly undergo hydrolysis in aqueous solutions and are converted to the orthophosphate forms (Franson, 1995).

Primarily biological processes contribute to formation of organic phosphates (Clark and John, 1991). Polyphosphates enter sewage water through wastes and food residues (Alloway, 1995c). They may also be formed from orthophosphates in biological treatment processes and by receiving water organisms (Clark and John, 1991). Like polyphosphates, organic phosphates are biologically transformed back to orthophosphates. Phosphates are typically present in raw wastewaters at concentrations near 10 mg/L as P (Richard, 1991). During wastewater treatment, about 10-30% of the phosphates in raw wastewater is utilized during secondary biological treatment for microbial cell synthesis and energy transport (Richard, 1991). Additional removal is required to achieve low effluent concentration levels from the wastewater treatment process. Effluent limits usually range from 0.1-2 mg/L as P, with many established at 1.0 mg/L (Richard, 1991). Removal processes for phosphates from wastewaters involve incorporation into suspended solids and the subsequent removal of those solids (Richard, 1991) which form sludge and finally biosolids.

Rainfall can cause varying amounts of phosphates to wash off from farm soils into nearby waterways. Phosphate will stimulate the growth of plankton and aquatic plants which provide food for fish (LVEMP, 2003). This may cause an increase in the fish population and improve the overall water quality (LVEMP, 2003). However, if an excess of phosphate enters the waterway; algae and aquatic plants will grow wildly, choke up the waterway and use up large amounts of oxygen (LVEMP, 2003). This condition is known as eutrophication or over-fertilization of receiving waters. This rapid growth of aquatic vegetation eventually dies and as it decays it uses up oxygen. This process in turn causes the death of aquatic life because of the lowering of dissolved oxygen levels (LVEMP, 2003).

The addition of phosphates through the activities of humans can accelerate the eutrophication process of nutrient enrichment that results in accelerated ecological aging of lakes and streams (LVEMP, 2003). Phosphorus, especially in inland waters, is often the nutrient that limits growth of aquatic plants. Critical levels of phosphorus in water above which eutrophication is likely to be triggered are approximately 0.03 mg/L of dissolved phosphorus and 0.1 mg/L of total phosphorus (USEPA, 1980). The discharge of raw or treated wastewater, agricultural drainage, or certain industrial wastes that

contain phosphates to a surface water body may result in a highly eutrophic state, in which the growth of photosynthetic aquatic micro and macro organisms are stimulated to nuisance levels (Richard, 1991).

Aquatic plants like water hyacinth and mats of algal scum may cover surface water (LVEMP, 2003). As these algal mats and aquatic plants die, they sink to the bottom, where their decomposition by microorganisms uses most of the oxygen dissolved in the water. The decrease in oxygen severely inhibits the growth of many aquatic organisms, especially more desirable fish and in extreme cases may lead to massive fish kills (Richard, 1991). Excessive input of phosphorus can change clear, oxygen-rich, good-tasting water into cloudy, oxygen-poor, foul smelling, and possibly toxic water. Therefore, control of the amount of phosphates entering surface waters from domestic and industrial waste discharges, natural runoff, and erosion may be required to prevent eutrophication in water bodies and the nucleus estate farms of Nzoia have been suspected to be one of the point sources of phosphates from nitrogenous fertilizer application that needs to be known.

Nitrates and nitrites are families of chemical compounds containing atoms of nitrogen and oxygen. Occurring naturally, nitrates and nitrites are critical to the continuation of life on earth, since they are among the main sources from which plants obtain the element nitrogen. This element is required for the production of amino acids, which, in turn, are used in the manufacture of proteins in both plants and animals (Franson, 1995).

One of the great transformations of agriculture over the past century has been the expanded use of nitrogenous fertilizers and biosolids. Ammonium nitrate is one of the most important of these fertilizers (Alloway, 1995b). In recent years, this compound has ranked in the top fifteen among synthetic chemicals produced in the United States (Richard, 1991). The increased use of nitrates as fertilizer has led to some serious environmental problems. All nitrates are soluble, so whatever amount is not taken up by plants in a field is washed away into surface water and eventually into rivers, streams, ponds, and lakes. In these bodies of water, the nitrates become sources of food for algae, water hyacinth and other plant life, resulting in the formation of algal and hyacinth blooms as is the case of Lake Victoria (LVEMP, 2003). Such blooms are usually the first step in the eutrophication of a pond or lake (Fried *et al.*, 2003; LVEMP, 2003). Furthermore, some scientists believe that nitrates and nitrites may themselves be

carcinogens or may be converted in the body to a class of compounds known as nitrosamines, compounds that are known to be carcinogens (Richard, 1991). Total oxidized nitrogen is the sum of nitrate and nitrite nitrogen. Nitrate generally occurs in trace quantities in surface water but may attain high levels in some groundwater (Richard, 1991). In excessive amounts, it contributes to the illness known as methemoglobinemia in infants hence the limit of 10 mg nitrate-nitrogen/L being imposed on drinking water to prevent this disorder (USEPA, 1980).

The contamination of the water systems with inorganic nitrogen and phosphorus from nitrogenous fertilizer runoff is a pressing concern given their prevalence in agricultural application in the Nzoia Sugar Company nucleus estate farms. To maintain a healthy hydrologic network, it is necessary to understand the effects of these increased chemical concentrations on water quality. Previous studies have shown that the addition of these nutrients to the water system would result in large proliferations of algae and water hyacinth, which have detrimental effects on the water quality (Fried *et al.* 2003; LVEMP, 2003). Algal blooms and water hyacinth deplete the oxygen supply in the water system and are harmful to other aquatic species (LVEMP, 2003). Additionally, these nutrients cause taste and odor problems that result in reduced recreational use, and increased water treatment costs (Fried *et al.*, 2003). In an effort to maintain a healthy water system and to minimize algal growth, USEPA (1980) recommends that phosphate levels be kept below 0.1 mg/L and nitrate levels be kept below 10 mg/L. Furthermore Zwolsman *et al.* (1997) reported that dissolved metal behavior is influenced by redox chemistry and nitrate is a fair measure of redox condition in water. Also his reckoning that there is interplay between favorable redox conditions indicated by NO_3^- and low pH values which all lead to high concentrations of dissolved metal is well noted. Dobermann and Fairhurst (2000) reported that the ammonium form of nitrogen is rapidly converted to the nitrate form during nitrification and that nitrification has a net acidifying effect on soil (Table 2.1).

Adequate oxygen levels are necessary to provide for aerobic life forms which carry on natural stream purification processes (Hutchinson, 1957). As DO levels in water drop below 5.0 mg/L, aquatic life is put under stress (Hutchinson, 1957). The lower the concentration, the greater the stress (Hutchinson, 1957). Oxygen levels that remain below 1-2 mg/L for a few hours can result in large fish kills (Tchobanoglous and Shroeder, 1985). Fish in waters containing excessive dissolved gases may suffer from "gas bubble

disease"; however, this is a very rare occurrence. The bubbles or emboli block the flow of blood through blood vessels causing death (Tchobanoglous and Schroeder, 1985). Aquatic invertebrates are also affected by gas bubble disease but at levels higher than those lethal to fish (Tchobanoglous and Schroeder, 1985). There also exists a direct relationship between DO in water and dissolved heavy metals (Duinker *et al.* 1982). Duinker *et al.* (1982) writes that this is due to reoxidation of the metals that make DO consequently reduce with increase in dissolved heavy metals.

Electrical Conductivity is a measurement of the ability of an aqueous solution to carry an electrical current. It is used to determine mineralization which is commonly called total dissolved solids. Total dissolved solids information is used to determine the overall ionic effect in a water source (<http://kywater.org/ww/ramp/rmcond.htm> 9/15/2009 4:59 pm). Certain physiological effects on plants and animals are often affected by the number of available ions in the water. Elevated dissolved solids can cause "mineral tastes" in drinking water. Corrosion or encrustation of metallic surfaces by waters high in dissolved solids causes problems with industrial equipment and boilers as well as domestic plumbing, hot water heaters, toilet flushing mechanisms, faucets, and washing machines and dishwashers (<http://kywater.org/ww/ramp/rmcond.htm> 9/15/2009 4:59 pm). Water quality criteria have been established only for the mainstream of the Ohio River. The limit is 800 $\mu\text{ohms/cm}$ or 500 mg/L total dissolved solids. (<http://kywater.org/ww/ramp/rmcond.htm> 9/15/2009 4:59 pm).

Chemical oxygen demand (COD) is a measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals such as ammonia and nitrite. Measurements of COD are commonly made on samples of waste waters or of natural waters contaminated by domestic or industrial wastes. Chemical oxygen demand is measured as a standardized laboratory assay in which a closed water sample is incubated with a strong chemical oxidant under specific conditions of temperature and for a particular period of time (David, 2006). A commonly used oxidant in COD assays is potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) which is used in combination with boiling sulfuric acid (H_2SO_4) (David, 2006). Because this chemical oxidant is not specific to oxygen-consuming chemicals that are organic or inorganic, both of these sources of oxygen demand are measured in a COD assay (David, 2006).

Chemical oxygen demand is related to biochemical oxygen demand (BOD), another standard test for assaying the oxygen-demanding strength of waste waters. However, biochemical oxygen demand only measures the amount of oxygen consumed

by microbial oxidation and is most relevant to waters rich in organic matter (David, 2006). It is important to understand that COD and BOD do not necessarily measure the same types of oxygen consumption. For example, COD does not measure the oxygen-consuming potential associated with certain dissolved organic compounds such as acetate. However, acetate can be metabolized by microorganisms and would therefore be detected in an assay of BOD (David, 2006). In contrast, the oxygen-consuming potential of cellulose is not measured during a short-term BOD assay, but it is measured during a COD test (<http://science.jrank.org/pages/1388/Chemical-Oxygen-Demand.html>)> Chemical Oxygen Demand 8/15/2009 3:50).

In conclusion, use of nitrogenous fertilizers in sugarcane farming affects soil acidity. No work has been done in Nzoia Nucleus estate farms on the effect of this acidity on availability, solubility and mobility of heavy metals. Apart from bioaccumulation in aquatic animals and plants, presence of bioavailable heavy metals in aquatic environments is correlated with and affects other physicochemical parameters like dissolved oxygen, chemical oxygen demand and conductivity which in turn will affect the aquatic environment. There is therefore need to monitor these physicochemical parameters and heavy metals before serious health and environmental problems arise from intensive farming activities and nitrogenous fertilizer application in large scale farming systems such as Nzoia sugarcane farms.

Chapter 3

Materials and methodology

3.1. Study area

The study area was the nucleus of Nzoia Sugar Company Limited that is located in Bungoma District, Western Province and is within Kenya's sugar belt. It lies between $34^{\circ} 50'49''\text{E}$ - $35^{\circ} 35'41''\text{E}$ longitudes and $0^{\circ}4'55''\text{N}$ - $0^{\circ}20'11''\text{S}$ latitudes. There is heavy sugarcane farming in the nucleus farms where nitrogenous fertilizers such as Diammonium phosphates (DAP) and urea are applied during the onset of the long rains (Table 1.1 and 1.2). The nucleus farms have black nitrosol soils that are deep and well drained (DDP, 1996). The factory draws water from River Kuywa, which passes within the nucleus estate farms, and discharges back its effluent to the same river downstream before it joins River Nzoia. Most of the rainfall is received during the long rain season which is from April to June while the short rains season is from September to November (Table 1.1) and the annual temperature ranges from 15°C minimum to 30°C maximum (DDP, 1996; DDP, 2002). During the rains several canals carry with them residues of chemicals that may be changing physical chemical parameters of water and causing accumulation of heavy metals in River Kuywa, which is a tributary to River Nzoia that drains its water into Lake Victoria. These canals contain perennial water that flows within the nucleus estate farms and are linked to River Kuywa. Although the water volume within the canals drops during the dry season and increases during the wet season, the canals do not dry up. A site outside the nucleus where there is no farming (a football pitch within Nzoia sugar belt, specifically Kanduyi District Education Board Primary School football pitch which lies within the same geographical region as Nzoia Sugar Company) was chosen as a control for soil analysis. A point in the river (sampling a in the river) before it enters the nucleus was chosen as a control for the river samples and a canal (sampling 1 in plot number 9053) that originated from a tree plantation within the nucleus was chosen as a control for the canals (Figure 3.1).

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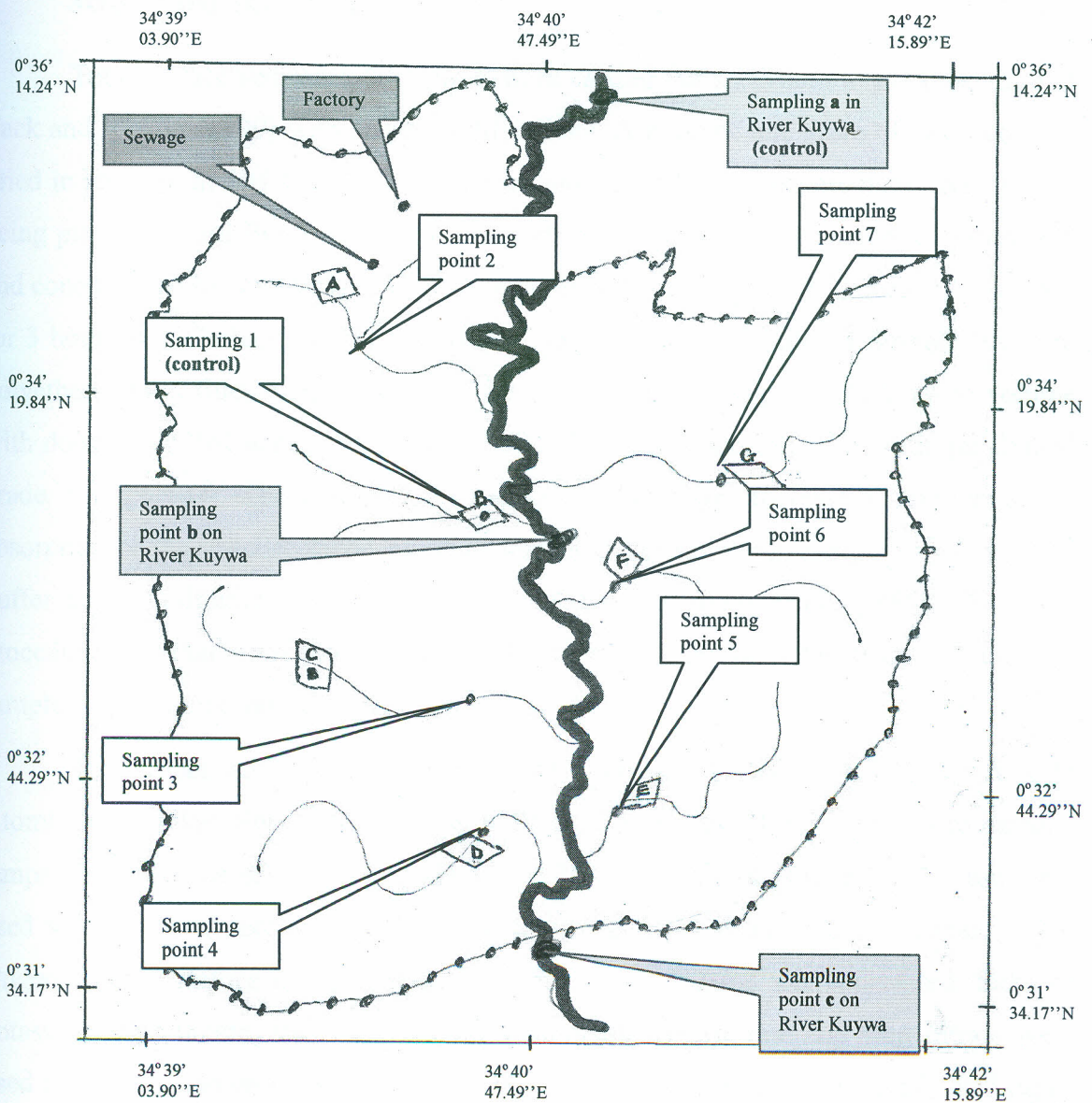
3.2. Sampling and sampling design

Two factor completely randomized block design was used in sampling where the nucleus estate farms were considered as a block and sampling sites located within the nucleus' canals, farms and at three points along River Kuywa as shown in Figure 3.1 in order to give trends of analyte levels and to establish potential point sources. Sampling plots were chosen out of their history in nitrogenous fertilizer applications (Table 1.2) while plot 8071 was chosen due to its use as a dump site. In all the sampled plots, a canal passed near, in the middle or next to them. Soil was sampled in the farm while water and sediments from the canal and River Kuywa as shown below.

3.3. Sampling and Sample preparation before extraction

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 one of the sampling sites per trip were taken. 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 treated as triplicates with one back up. Sampling was done during the dry season - 15/3/2009 and wet season - 21/5/2009. Four samples each measuring 100 g of each type of fertilizers used namely DAP and Urea were picked at random from the 50 bags of fertilizers sampled at random in the nucleus stores and kept in plastic bags ready for analysis

Once collected, the surface water samples were transported in an icebox at 0°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°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 motor 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. Fertilizer samples were dried at room temperature and ground in a pestle and motor in order to normalize for variations in grain size distribution. They were then sieved through a 45 µm mesh sieve and kept in clean plastic containers ready for analysis.



Key

Sampling point: **1 (A)** - Plot 9053, **2 (B)** - Plot 8071, **3 (C)** - Plot 243, **4 (D)** - Plot 125, **5 (E)** - Plot 616, **6 (F)** - Plot 429, **7 (G)** - Plot 413. : Canals. Kuywa River

A – G: Sampling points for soil in the indicated plots.

1 – 7: sampling points for canals.

a – c: sampling points in River Kuywa.

Sampling 1 – control for the canals (a canal drawing its water from a tree plantation).

Figure 3.1. A sketched map of Nzoia Sugar Company Nucleus estate farms and sampling points.

3.4. Determination of heavy metals in surface sediments, top soils and fertilizers

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°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 regia digestion) added. Following digestion for 3 hours in a Gerhardt digester at 100°C, the contents were filtered through 0.45 µm polyethersulfoen 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, SrCl₂.6H₂O). 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 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; Onger, 2008). Before analysis was done, the AAS machine was calibrated. Salts of potassium dichromate, lead nitrate, copper sulphate, zinc nitrate and iron nitrate were used to prepare known concentrations of 0 µg/L, 20 µg/L, 40 µg/L, 80 µg/L, 100 µg/L, 120 µg/L, 160 µg/L and 250 µg/L per salt in 100 ml flasks after additions of 1.5 mg/ml of strontium chloride. These salts were used as standards and a calibration curve was drawn from them in the instrument before unknown samples were read.

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°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; Onger, 2008). Before analysis was done, the AAS machine was calibrated. Salts of potassium dichromate, lead nitrate, copper sulphate, zinc nitrate and iron nitrate were used to prepare known concentrations of 0 µg/L, 20 µg/L, 40 µg/L, 80 µg/L, 100 µg/L, 120 µg/L, 160 µg/L and 250 µg/L per salt in 100 ml flasks after additions of 1.5 mg/ml of strontium chloride. These salts were used as standards and a calibration curve was drawn from them in the instrument before unknown samples were read.

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. Determination of total phosphates

A method as described by Anil (1994) for total phosphates was adopted. The total phosphate content of a water sample includes all of the o-phosphates and condensed phosphates, both soluble and insoluble and organic species. A digestion method with $\text{HNO}_3\text{-H}_2\text{SO}_4$ was necessary to oxidize organic-bond P by rupturing both C-P and C-O-P bonds and releasing P as soluble PO_4^{3-} . In a dilute o-phosphate solution, ammonium molybdate reacts in acidic medium to form molybdo-phosphoric acid. The latter reacts with vanadium to form yellow vanadomolybdophosphoric acid which is measured at 460 nm.

A volume of 100 ml of water sample in a beaker was digested at 150°C with 1 ml concentrated sulfuric acid (H_2SO_4) + 5 ml concentrated nitric acid (HNO_3) and evaporated to dryness. The residue was leached with 5 ml 1 N HNO_3 and transferred to a 50 ml volumetric flask. A volume of 5 ml of 10% ammonium molybdate was added followed by addition of 5 ml of 0.25% ammonium vanadate in 6 N HCl . The mixture was diluted to the mark with distilled water and left to cool for 10 minutes. Absorbance was measured using an ultra violet spectrophotometer (UV-1650 PC-UV-Vis spectrophotometer, Shimadzu) machine of the yellow reaction product, vanadomolybdophosphate, at 460 nm. Absorbances of a blank and calibration standards that were prepared from solutions of phosphate, 220 g $\text{KH}_2\text{PO}_4/\text{L}$; 1 ml = 50 μg PO_4 carried through the same steps were measured. A calibration curve was prepared and total concentration of phosphates per litre determined.

3.8. Determination of Nitrate-Nitrogen

Ultraviolet spectrophotometric screening method of Franson (1995) was used to determine nitrate-nitrogen present in the filtered water samples. Measurement of UV absorption at 220 nm enabled rapid determination of NO_3^- . Because dissolved organic matter also may absorb at 220 nm and NO_3^- does not absorb at 275 nm, a second measurement made at 275 nm was used to correct the NO_3^- value. Sample filtration was intended to remove possible interference from suspended particles. Acidification with 2 ml of 1 N HCl was designed to prevent interference from hydroxide or carbonate concentrations of up to 1000 mg CaCO_3/L . Chloride has no effect on the determination

(Ioather and Rackman, 1959; Goldman and Jacobs, 1961; Armstrong, 1963; Navone 1964).

Double distilled and deionized water of highest purity was used to prepare all solutions and dilutions. Potassium nitrate (KNO_3) was dried in an oven at 105°C for 24 hours then 0.7218 g dissolved in water and diluted to 1000 ml to make a nitrate stock solution. Then a volume of 100 ml stock nitrate solution was diluted to 1000 ml with double distilled water to make intermediate nitrate solutions for calibration.

Samples measuring 50 ml were filtered and 1 ml concentrated HCl solution added and mixed thoroughly. The machine (UV-1650 PC-UV-Vis spectrophotometer, Shimadzu) was calibrated using standards of $\text{NO}_3\text{-N}$ prepared in the range of 0 to 7 mg $\text{NO}_3\text{-N}$ /L by diluting to 50 ml the following volumes of intermediate nitrate solution: 0, 1.00, 2.00, 4.00, and 7.00 ml. The standards were treated in the same manner as samples. Absorbance against redistilled water set at zero absorbance were read using a wavelength of 220 nm to obtain $\text{NO}_3\text{-N}$ reading and a wavelength of 275 nm to determine interference due to dissolved organic matter (UV-1650 PC-UV-Vis spectrophotometer, Shimadzu).

In calculating the $\text{NO}_3\text{-N}$ values, for samples and standards, two times the absorbance reading at 275 nm was subtracted from the reading at 220 nm to obtain absorbance due to $\text{NO}_3\text{-N}$. A standard curve was constructed by plotting absorbance due to $\text{NO}_3\text{-N}$ against $\text{NO}_3\text{-N}$ concentration of standard. Using corrected sample absorbance, sample concentrations were determined from the standard curve.

3.9. Determination of Chemical Oxygen Demand

Closed Reflux colorimetric method described fully in standard methods of Franson (1995) was adopted. In this method, to 500 ml distilled water, 10.216 g of $\text{K}_2\text{Cr}_2\text{O}_7$, primary standard grade, previously dried at 103°C for 2 hours was added, then 167 ml of conc. H_2SO_4 and 33.3 g of HgSO_4 added and dissolved before cooling to room temperature and diluting to 1000 ml in order to make a digestion solution. A powder of Ag_2SO_4 , technical grade, was added to conc. H_2SO_4 at the rate of 5.5 g Ag_2SO_4 /kg H_2SO_4 and left to stand for a day in order to dissolve so as to make a sulfuric acid reagent. Potassium hydrogen phthalate ($\text{HOOC}_6\text{H}_4\text{COOK}$) was used as a standard.

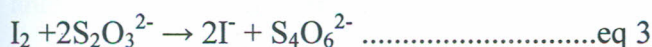
The samples were treated by taking 5.0 ml of water sample into a digestion vessel

and 3.0 ml of digestion solution added followed by careful addition of 7.0 ml sulfuric acid so that an acid layer was formed under the sample and the digestion solution layer and mixed thoroughly. Ampule tubes were placed in a block digester preheated to 150°C and refluxed for two hours. After two hours the samples were cooled and put in 50 ml flasks ready for analysis. A blank and four standards were prepared in the same manner. Cooled samples, blank, and standards were inverted several times and solids allowed to settle before measuring absorbance. Solids that adhered to container wall were dislodged by gentle tapping and settling.

Absorbances were measured using a spectrophotometer (UV-1650 PC UV-Vis spectrophotometer Shimadzu) set at 600 nm. Absorbance was compared to a calibration curve by the machine and concentrations of unknown samples read directly. In preparing the calibration curve, at least eight standards from potassium hydrogen phthalate solution with COD equivalents of 20, 100, 300, 500, 700 and 900 mg O₂/L were prepared. Volume was made to the mark with distilled water; same reagent volumes were used, tube, or ampule size, and digestion procedure followed as for the samples and COD calculated as mg O₂/L = (mg O₂ in final volume x 1000) / ml sample

3.10. Analysis of Dissolved Oxygen (DO)

The Winkler method as outlined by Anil (1994) was used to analyze dissolved oxygen, in which DO was allowed to react with I⁻ to form I₂, which was then titrated with standard Na₂S₂O₃ solution. A fast quantitative reaction was ensured by addition of Mn(II) salts in strongly alkaline medium:



5 ml of 0.025 M Na₂S₂O₃ ≡ 1 mg L⁻¹ DO

A volume of 50 ml of sample was put in a 250 ml bottle, 2 ml of 40% potassium fluoride (KF) (to mask Fe³⁺) was added, and 2 ml of 36% MnSO₄ plus 2 ml of alkaline iodide-azide solution (50 g NaOH + 13.5 g NaI + 1.0 g NaN₃ diluted to 1 L.) was also added (eq 1). The mixture was shaken well and the precipitate allowed to settle then 6 ml of 12 N H₂SO₄ added (eq 2). The mixture was shaken well until the precipitate dissolved. (Interference due to oxidizing agents such as NO₂⁻ and SO₃²⁻ present in waste water were eliminated by addition of NaN₃ to alkaline I⁻ solution. The liberated iodine was titrated

with 0.025 M Na₂S₂O₃ solutions (eqn 3) and the results calculated: 5 ml of 0.025 M Na₂S₂O₃ \equiv 1 mg L⁻¹ DO (Anil, 1994)

3.11. 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 raised slowly 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.

3.12. Statistical analysis

The means and ranges of the data collected were determined in this study. Confidence limit of 5% was applied to test the significance of the analytical results. Analysis of variance (ANOVA) ($p \leq 0.05$) (two factor experiment) and students T-test ($p \leq 0.05$) were used to check the variations. Statistical analysis was performed using MSTATC two factor completely randomized design. With factorial ANOVA for the factors such that Replication was with values from 1 to 3, Factor A (SEASON) with values from 1 to 2 (1- dry season and 2 – wet season) and Factor B (SITE) with values from 1 to 7 for soil and canals. The results have been presented in four categories; thus heavy metals in water and sediments, physicochemical parameters in water, Nucleus soil analysis and fertilizer analysis. The LSD values were calculated using the formula: $\sqrt{2} \times s/y \times t$ whereby s/y value was given by the ANOVA program results and t is the significant level ($P \leq 0.05$) obtained from the t-distribution table.

Chapter 4

Results and Discussion

4.1. Nucleus Soil Analysis

The results for nucleus soil analysis are recorded in Tables 4.1.1. – 4.1.6. The AAS analysis gave mean % recovery values for extraction of the spiked soil samples of Cr, Pb, Cu, Zn and Fe as 93, 89, 94, 88 and 84, respectively, with detection limits of 0.001 ng/mL, 0.001 ng/mL, 0.003 ng/mL, 0.008 ng/mL and 0.01 ng/mL respectively. For soils from the nucleus estate farms, the wet weight to dry weight ratio was 1.015 ± 0.014 and from the control site was 1.029 ± 0.009 .

Table 4.1.1. Mean site variations of selected physicochemical parameters and heavy metals in top soils from the nucleus of Nzoia Sugar Company and a control farm between the long wet and dry seasons.

Mean Total Organic Carbon (%) in soils from the nucleus and from a control farm within Nzoia sugar belt												
Sites (in plot numbers from the nucleus and a control farm)												
	A. (9053)	B (8071)	C (243)	D (125)	E (616)	F (429)	G (413)	Site mean	Control x	Control y	Control z	Control mean
Dry season	6.24	7.28	6.6	9.35	10.89	10.67	9.4	8.63	4.17	5.18	4.92	4.76
Wet season	7.34	8.24	6.35	5.17	11.27	10.28	10.38	8.43	6.31	4.4	4.38	5.03
Mean	6.79	7.76	6.48	7.26	11.08	10.47	9.89	8.53	5.24	4.79	4.63	4.89
Lsd $P \leq 0.05$									0.462			0.30
Interaction						0.65						
CV%						4.76						

Mean pH in soils from the nucleus and from a control farm within Nzoia sugar belt												
Sites (in plot numbers from the nucleus and a control farm)												
	A. (9053)	B (8071)	C (243)	D (125)	E (616)	F (429)	G (413)	Site mean	Control x	Control y	Control z	Control mean
Dry season	6.62	5.08	5.34	5.25	5.27	5.15	5.54	5.46	7.407	7.5	7.46	7.46
Wet season	6.60	5.00	5.25	5.15	5.16	5.00	5.10	5.32	7.19	7.08	7.20	7.16
Mean	6.61	5.04	5.30	5.20	5.22	5.08	5.32	5.39	7.30	7.29	7.33	7.31
Lsd $P \leq 0.05$						0.161						0.096
Interaction						0.335						
CV%						7.94						

Mean Chromium concentration (mg/Kg) in soils from the nucleus and from a control farm within Nzoia sugar belt												
Sites (in plot numbers from the nucleus and a control farm)												
	A. (9053)	B (8071)	C (243)	D (125)	E (616)	F (429)	G (413)	Site mean	Control x	Control y	Control z	Control mean
Dry season	90.2	130.05	147.85	184.66	143.53	178.95	160.98	148.03	105.08	122.34	121.17	116.20
Wet season	86.425	130.29	161.58	186.59	145.95	171.05	134.63	145.22	90.61	118.2	81.85	96.89
Mean	88.31	130.17	154.71	185.62	144.74	175.02	147.81	146.63	97.85	120.27	101.51	106.54
Lsd $P \leq 0.05$						22.288						9.967
Interaction						33.52						
CV%						12.68						

Key:

A – G: Soil sampling points in the indicated plots as illustrated in figure 3.1 within Nzoia nucleus estate farms.

Control xyz: Soil samples taken from a football pitch of Kanduyi primary school within Nzoia sugar belt.

Table 4.1.2. Mean site variations of heavy metals in top soils from the nucleus of Nzoia Sugar Company and a control farm between the long wet and dry seasons.

Mean Copper concentration (mg/Kg) in soils from the nucleus and from a control farm within Nzoia sugar belt

Sites (in plot numbers from the nucleus and a control farm)

	A. (9053)	B (8071)	C (243)	D (125)	E (616)	F (429)	G (413)	Site mean	Control x	Control y	Control z	Control Mean
Dry season	46.01	83.36	75.95	71.08	93.52	84.51	67.31	74.53	71.7	67.6	51.75	63.68
Wet season	51.55	83.33	90.62	81.45	75.33	57.09	65.64	72.14	67.45	60.32	70.54	66.10
Mean	48.78	83.35	83.29	76.27	84.42	70.8	66.48	73.34	69.57	63.96	61.15	64.89
Lsd P≤ 0.05												6.124
Interaction												
CV%												

Mean Zinc concentration (mg/Kg) in soils from the nucleus and from a control farm within Nzoia sugar belt

Sites (in plot numbers from the nucleus and a control farm)

	A. (9053)	B (8071)	C (243)	D (125)	E (616)	F (429)	G (413)	Site mean	Control x	Control y	Control z	Control Mean
Dry season	120.32	134.39	132.02	116.11	104.34	110.71	96.02	116.2729	124.65	131.6	114.22	123.49
Wet season	119.95	186.34	154.86	152.45	182.65	161.38	154.05	158.8114	97.12	116.85	130.05	114.67
Mean	120.14	160.36	143.44	134.28	143.5	136.05	125.03	137.5429	110.88	124.23	122.13	119.08
Lsd P≤ 0.05												8.327
Interaction												
CV%												

Mean Iron concentration (mg/Kg) in soils from the nucleus and from a control farm within Nzoia sugar belt

Sites (in plot numbers from the nucleus and a control farm)

	A. (9053)	B (8071)	C (243)	D (125)	E (616)	F (429)	G (413)	Site mean	Control x	Control y	Control z	Control Mean
Dry season	310.61	334.71	215.63	424.05	533.49	684.81	373.59	410.9843	251.65	336.99	260.26	282.96
Wet season	225.05	250.27	320.24	404.87	263.12	467.73	650.52	368.8286	225.27	160.38	115.38	167.01
Mean	264.83	292.49	267.94	414.56	398.3	576.27	512.06	389.4929	238.46	248.69	187.82	224.99
Lsd P≤ 0.05												23.11
Interaction												
CV%												

Mean Lead concentration (mg/Kg) in soils from the nucleus and from a control farm within Nzoia sugar belt

Sites (in plot numbers from the nucleus and a control farm)

	A. (9053)	B (8071)	C (243)	D (125)	E (616)	F (429)	G (413)	Site mean	Control x	Control y	Control z	Control Mean
Dry season	56.08	53.21	55	63.41	63.38	71.09	51.66	59.12	48.72	65.14	61.75	58.54
Wet season	55.59	51.32	49.99	51.6	52.05	36.18	55.32	50.30	47.52	47.52	56.99	50.68
Mean	55.84	52.27	52.49	57.51	57.72	53.64	53.49	54.71	48.12	56.33	59.37	54.61
Lsd P≤ 0.05												4.456
Interaction												
CV%												

Key:

A – G: Soil sampling points in the indicated plots on figure 3.1 within Nzoia nucleus estate farms.

Control xyz: Soil samples taken from a football pitch of Kanduyi primary school within Nzoia sugar belt.

Table 4.1.3. Correlation matrix of selected physicochemical parameters and heavy metals in top soils from the nucleus of Nzoia Sugar Company and a control farm between the long wet and dry seasons.

	TOC %	pH	Cr	Pb	Cu	Zn	Fe
TOC%	1.000						
pH	-0.668	1.00					
Cr	0.475	-0.471	1.000				
Pb	0.693	-0.680	0.095	1.000			
Cu	0.512	-0.493	0.331	0.530	1.000		
Zn	0.468	-0.473	0.139	-0.250	0.182	1.000	
Fe	0.667	-0.584	0.535	0.237	0.236	-0.001	1.000

Table 4.1.4. This study in comparison with international standard on heavy metals in soils (mg/kg of dry soil).

Heavy Metals	Control ^f soil (Kenya)	Nucleus ^f soil (Kenya)	Normal range in soils ^b	Critical soil total concs. ^{hh}	Reference Values in Neths. Soil Standards ^e	Reference Values in Taiwan Soil Standards ^e	Reference Values for Dutch soil standard ^e
Chromium	142 [#] /144 ^{##}	117 [#] /108 ^{##}	5-1500	75-100	100 [*] /250 ^{**}	100 ^a /400 ^b	100 ^c /380 ^d
Copper	73 [#] /72 ^{##}	64 [#] /66 ^{##}	2-250	60-125	50 [*] /500 ^{**}	120 ^a /200 ^b	36 ^c /190 ^d
Lead	59 [#] /50 ^{##}	62 [#] /51 ^{##}	2-300	100-400	200 [*] /500 ^{**}	50 ^a /500 ^b	85 ^c /530 ^d
Zinc	116 [#] /158 ^{##}	124 [#] /114 ^{##}	1-900	70-400	50 [*] /150 ^{**}	35 ^a /500 ^b	140 ^c /720 ^d
Iron	409 [#] /368 ^{##}	283 [#] /167 ^{##}	NG	NG	NG	NG	NG

Key

NG - Not Given in the literature.

£: This study 2010 Kenya (Number of examined samples 42), #: This study dry season value, ##: This study wet season value, ^b: Alloway (1995a), ^{hh}: Alloway (1995a): The critical soil total concentration is the range of values above which toxicity is considered to be possible, ^e: Zuengsang, (2000); Chen, and Lee, (1995).

*: Tentative soil quality standards for the (Neths.) Netherlands, **: Reference value for good soil quality, a: Taiwan's standard values to assess soil quality, b: The upper limit of the background concentration, c: Natural level, d: Cleanup level.

Table 4.1.5. Heavy metal loads in fertilizers used in the farms of Nzoia nucleus estate farms (mean \pm SD mg/kg dry weight) in comparison to international standards.

	Cr	Pb	Cu	Zn	Fe
UREA ^a	5.170	61.380	36.980	32.050	4536.947
DAP ^a	13.407	247.117	49.070	57.947	3113.48
USEPA ^b standard	NG	300	1500	2800	NG
Canadian ^c standard	NG	500	NG	1850	NG
RCRE ^c Suggested Limits for Sewage Sludge	1200	300	1500	2800	NG

Key

NG - Not Given in the literature.

a: This study 2010 Kenya (Number of examined samples 150)- b: USEPA, 1999, c: The soil profile 2006, RCRE: Rutgers Cooperative Research and Extension

Table 4.1.6. Risk based analysis of DAP fertilizer used in the farms of Nzoia nucleus estate for 50 years (in Kg/Ha) in comparison to international standards.

Heavy Metal	Risk based assessment load ¹	USEPA ² standard	AAPFCO ³ standard	OSDA ⁴ standard	CDFA ⁵ standard
Cr.	0.128	0.6	NG	NG	NG
Cu.	0.4677	NG	NG	NG	NG
Pb.	2.355	2.8	463	340	61
Zn.	0.552	NG	2900	NG	420
Fe.	29.676	NG	NG	NG	NG

Formula: Kg/Hectare = (ppm metal/1,000,000) \times %Ph \times Application Rate Fertilizer \times 0.454 kg/lb \times 2.47 Ac/hectare \times 50 years (USEPA 1999).

Key

NG - Not Given in the literature.

%Ph – percent phosphate in the fertilizer, Ac – Accumulation.

1 – This study 2010 Kenya (Number of examined samples 150), 2 – USEPA 1999, 3 – The Association of American Plant Food Control Officials, 4 – Oregon standards, 5 – California Code of Regulations section 2302 and 2303,

4.1.1. Discussion

All the studied parameters differed significantly from the control sites at $P \leq 0.05$ (Tables 4.1.1 and 4.1.2). This was an indication that the anthropogenic activities taking place in the Nzoia nucleus (sugarcane farming) were the ones responsible for the changes in the concentration of the studied parameters. Soil pH in the nucleus soils

(5.39 ± 0.31) was lower compared to soil pH from the control site (7.306 ± 0.052). This kind of pH behavior in sugarcane plantation is typical and comparable with other areas such as Papua New Guinea recording a reduction of soil pH from 6.5 to 5.8 between 1997 and 1996 (Oliver, 2004). 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 (Oliver, 2004; Woods *et al.*, 2003).

The reduction in soil pH between the two seasons was not significantly different probably due to the fact that it takes time to raise/reduce soil pH in the soil and that the slight difference in water content may not affect the pH much. However the pH was significantly different between the nucleus soils and the control farm soils, indicating the fact that the anthropogenic activity in the farms was affecting the soil pH. From literature, the main culprit in pH change in sugarcane farming is the use of nitrogenous fertilizers. Most of the research done on acidification of sugarcane plantations with nitrogenous fertilizers has been on production line and very little work has been done to evaluate the effect of this soil pH reduction to other physicochemical parameters like heavy metals, chemical oxygen demand, dissolved oxygen and others.

Reduction in soil pH has been found to be a predominant player in solubility of heavy metals (Alloway, 1995a). Most heavy metals will become soluble at pH values less than 6.0 and the lower the pH value, the more the solubility (Alloway, 1995a). Comparing the nucleus and the control soils, total organic carbon and soil pH had a nearly 50 % positive and 50% negative correlations with heavy metals respectively (Table 4.1.3). This was an indication that reduction in soil pH due to use of nitrogenous fertilizers and increase in total organic carbon due to use of biosolids affected availability and solubility of heavy metals. Apart from possible plant uptake of the heavy metals, once they are soluble in the soil water, they become available for transport from one place to another especially with surface runoffs during the long wet seasons.

Most of these heavy metals are naturally occurring in the soils but they are attached to soil matrix and unavailable to plants and transport under neutral soils (Alloway, 1995a). However some of the heavy metals are introduced to the soil through anthropogenic activities like fertilizer application (Mortvedt, 1995). The nitrogenous fertilizers used in Nzoia sugarcane plantations were found to contain pollutants of these heavy metals (Tables 4.1.4,) which are believed to accumulate in the soils with time. However Risk based analysis of the DAP fertilizer for 50 years use (Table 4.1.6) showed

the nucleus only; not to be contaminated with the heavy metal residues in the fertilizer used, though extrapolation to the whole sugar belt region may prove otherwise.

There was sites variation in heavy metal concentrations (at $p < 0.05$) within the nucleus soils, a situation that arose due to different agronomic practices at each site as is seen in Table 1.2 - of history in nitrogenous fertilizer applications. Of interest is site A (plot 9053), which was a tree plantation that had no nitrogenous fertilizer application hence its high value of soil pH and low concentration of Heavy metals. However, leaching and deposition from nearby farms may have affected the values hence use of a football pitch that was at an elevated area as the control. All the same the point that nitrogenous fertilizers affect soil pH can also be seen from the fact that sampling plot A had a higher soil pH compared to other plots where fertilizers were being applied. In addition, factory activities may also be affecting soil pH as can be seen from plot 8071 that was adjacent to the factory, bear and with no fertilizer application (Table 1.2).

Once the soil pH has reduced to below 6.0, heavy metals become soluble and readily transported by surface runoffs and leaching to the aquatic environments where they accumulate in sediments and other sinks like rivers and lakes (Ongeri 2008). Accumulation of heavy metals in aquatic environment raises a number of healthy issues including aquatic animals like fish bioaccumulating them hence being burnt in international markets (Ongeri, 2008).

Generally, the average heavy metal concentrations in both the nucleus soils and the control farm soils were above international standards (Table 4.1.4). There are no regional set standards for heavy metals in Kenyan soils hence using these international standards, we recommend that mitigation measures be put in place to farms using nitrogenous fertilizers such that they do not affect soil pH as such for these has other repercussions like affecting bioavailability, solubility and hence mobility of heavy metals to the aquatic environments.

4.2. Heavy metals in water

The AAS analysis gave mean% recovery values for extraction of the spiked water samples of Cr, Pb, Cu, Zn and Fe as 90, 79, 84, 88 and 94 respectively with detection limits of 0.001 ng/ml, 0.001 ng/ml, 0.003 ng/ml, 0.008 ng/ml and 0.01 ng/ml respectively. The results are recorded in the Tables 4.2.1 – 4.2.5 below.

Table 4.2.1.a. Mean site variations of heavy metal loads in surface water from canals within Nzoia nucleus estate farms (in µg/L) between the long wet and dry seasons.

Chromium								
	Sites							
	1(control)	2	3	4	5	6	7	Mean
Dry Season	0.09	0.42	2.40	0.90	0.80	2.36	0.97	1.133
Wet Season	0.60	2.31	3.12	1.11	1.58	0.96	2.20	1.697
Mean	0.34	1.36	2.76	1.00	1.19	1.66	1.59	1.414
Lsd $p \leq 0.05$				0.250				0.133
Interaction				0.353				
Cv%				12.93				

Lead								
	Sites							
	1(control)	2	3	4	5	6	7	Mean
Dry Season	1.16	3.82	1.40	1.47	1.72	1.80	1.72	1.87
Wet Season	4.717	5.35	4.59	5.78	5.15	5.49	5.46	5.22
Mean	2.94	4.59	3.00	3.63	3.43	3.64	3.59	3.54
Lsd $p \leq 0.05$				0.416				0.222
Interaction				0.588				
Cv%				8.55				

Copper								
	Sites							
	1(control)	2	3	4	5	6	7	Mean
Dry Season	2.39	2.60	2.72	1.81	2.26	3.39	3.08	2.606
Wet Season	11.34	6.07	7.94	19.08	16.72	19.52	14.27	13.56
Mean	6.86	4.34	5.33	10.44	9.492	11.46	8.68	8.09
Lsd $p \leq 0.05$				0.724				0.387
Interaction				1.024				
Cv%				6.56				

Key:

Canal sampling points **1** - Plot 9053, **2** - Plot 8071, **3** - Plot 243, **4** - Plot 125, **5** - Plot 616, **6** - Plot 429, **7** - Plot 413 as illustrated in figure 3.1.

Control: A canal draining water from a farm within the nucleus without sugarcane plantation (tree plantation) thus there was no nitrogenous fertilizer application.

Table 4.2.1.b. Site variations of heavy metal loads in surface water from canals within Nzoia nucleus estate farms (in $\mu\text{g/L}$) between the long wet and dry seasons.

Zinc								
	Sites							
	1(control)	2	3	4	5	6	7	Mean
Dry Season	31.18	63.19	46.92	33.88	41.93	88.44	33.92	48.49
Wet Season	131.37	242.00	327.37	194.77	132.00	178.19	181.67	198.20
Mean	81.28	152.59	187.15	114.32	86.96	133.32	107.79	123.34
Lsd $p \leq 0.05$				23.755				12.70
Interaction				33.60				
Cv%				4.25				

Iron								
	Sites							
	1(control)	2	3	4	5	6	7	Mean
Dry Season	101.03	91.47	80.77	112.23	114.38	69.98	131.04	100.13
Wet Season	133.52	151.21	174.57	114.14	190.28	255.38	206.98	175.16
Mean	117.28	121.34	127.67	113.18	152.33	162.68	169.01	137.64
Lsd $p \leq 0.05$				9.63				5.15
Interaction				13.62				
Cv%				10.94				

Key:

Canal sampling points **1** - Plot 9053, **2** - Plot 8071, **3** - Plot 243, **4** - Plot 125, **5** - Plot 616, **6** - Plot 429, **7** - Plot 413 as illustrated in figure 3.1

Control: A canal draining water from a farm within the nucleus without sugarcane plantation (tree plantation) thus there was no nitrogenous fertilizer application.

Table 4.2.2. Correlation matrix of heavy metal loads in water samples from canals within Nzoia Sugar Company nucleus estate farms.

	Cr $\mu\text{g/L}$	Pb $\mu\text{g/L}$	Cu $\mu\text{g/L}$	Zn $\mu\text{g/L}$	Fe $\mu\text{g/L}$
Cr $\mu\text{g/L}$	1.000				
Pb $\mu\text{g/L}$	0.455	1.000			
Cu $\mu\text{g/L}$	0.161	0.849	1.000		
Zn $\mu\text{g/L}$	0.153	0.738	0.498	1.000	
Fe $\mu\text{g/L}$	0.129	0.674	0.720	0.487	1.000

Table 4.2.3.a. Site variations of heavy metal loads in surface water from River Kuywa within Nzoia nucleus estate farms (in $\mu\text{g/L}$) between the long wet and dry seasons.

Chromium				
	1(control)	Sites 2	3	Mean
Dry season	0.35	0.207	0.50	0.352
Wet season	0.68	0.820	0.95	0.819
Mean	0.515	0.513	0.728	0.586
Lsd $p \leq 0.05$		0.067		0.054
Interaction		0.094		
Cv%		6.220		
Lead				
	1(control)	Sites 2	3	Mean
Dry season	1.62	1.84	1.89	1.783
Wet season	4.70	3.56	5.44	4.570
Mean	3.162	2.698	3.670	3.177
Lsd $p \leq 0.05$		0.445		0.360
Interaction		0.629		
Cv%		27.51		
Copper				
	1(control)	Sites 2	3	Mean
Dry season	1.87	2.40	2.53	2.268
Wet season	4.41	6.41	8.90	6.573
Mean	3.140	4.403	5.718	4.421
Lsd $p \leq 0.05$		0.538		0.440
Interaction		0.761		
Cv%		16.560		
Key				
1 – Inlet of River Kuywa to the Nzoia nucleus sugarcane estate farms (used as a control so as to give the impact of the nucleus).				
2 – A point in the river at the middle of the Nzoia nucleus sugarcane farms.				
3 – Outlet of River Kuywa from Nzoia nucleus estate farms (subtract from the control to get the impact of the nucleus).				

Table 4.2.3.b. Site variations of heavy metal loads in surface water from River Kuywa within Nzoia nucleus estate farms (in $\mu\text{g/L}$) between the long wet and dry seasons.

Zinc				
Sites				
	1(control)	2	3	Mean
Dry season	17.20	26.31	28.13	23.880
Wet season	41.85	65.49	66.18	57.809
Mean	29.53	45.85	47.16	40.844
Lsd $p \leq 0.05$			4.352	3.553
Interaction			6.155	
Cv%			5.740	

Iron				
Sites				
	1(control)	2	3	Mean
Dry season	66.72	81.30	97.80	81.942
Wet season	92.72	108.42	154.94	118.697
Mean	79.72	94.87	126.37	100.320
Lsd $p \leq 0.05$			7.365	6.009
Interaction			10.410	
Cv%			5.170	

Key

- 1 – Inlet of River Kuywa to the Nzoia nucleus sugarcane estate farms (used as a control so as to give the impact of the nucleus).
- 2 – A point in the river at the middle of the Nzoia nucleus sugarcane farms.
- 3 – Outlet of River Kuywa from Nzoia nucleus estate farms (subtract from the control to get the impact of the nucleus).

Table 4.2.4. Correlation matrix of trace metal loads in water samples from River Kuywa.

	Cr $\mu\text{g/L}$	Pb $\mu\text{g/L}$	Cu $\mu\text{g/L}$	Zn $\mu\text{g/L}$	Fe $\mu\text{g/L}$
Cr $\mu\text{g/L}$	1.000				
Pb $\mu\text{g/L}$	0.911	1.000			
Cu $\mu\text{g/L}$	0.887	0.989	1.000		
Zn $\mu\text{g/L}$	0.904	0.911	0.902	1.000	
Fe $\mu\text{g/L}$	0.793	0.770	0.794	0.781	1.000

Table 4.2.5. Comparing with some international standards on domestic water and data from other studies for heavy metals.

	Cr µg/L	Pb µg/L	Cu µg/L	Zn µg/L	Fe µg/L
This study ^a dry season canals	1.131	1.870	2.606	48.491	100.13
This study ^a wet season canals	1.697	5.219	13.564	198.20	175.16
This study ^a dry season Kuywa	0.352	1.760	2.268	23.95	81.94
This study ^a wet season Kuywa	0.819	6.338	6.240	57.81	100.3
KEBS ^b Standard	NG	50	100	5000	300
WHO ^c standard	NG	10	1000	5000	300
Waterquality 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
Dil 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 Turkey 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. World average ^l	NG	0.2	1.00	10	NG

Key

NG – Not Given in literature. **a** – This study 2010 Kenya (number of examined samples: 18 for river and 42 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** – Ongeru (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.

4.2.1. Discussion

The amount of heavy metals in a water system is subject to local and international standards and regulations due to the health effects they pose to human beings in the higher food chain and the aquatic animals in the lower food chains. Nzoia sugar plantations were used to find the effect that arises due to use of nitrogenous fertilizers in sugarcane plantation which is a major cash crop in Bungoma, Lugari and Kakamega Districts from Western Kenya. From the results the nucleus estate farms that are a total of 4000 ha contributed positively to the total heavy metal (Cu, Cr, Zn, Pb and Fe) burden in River Kuywa (Table 4.2.3a&b). Extrapolating the results to out growers (approximately 16500 ha) makes the contribution enormous. Although Table 4.2.5 indicates that the values of heavy metals in water are within limits, considering the impact on out growers in the three Districts as a whole and relating the concentrations to River Nzoia that traverses the Districts may make the concentrations found to be of considerable concern. Continuous accumulation of heavy metals and soil pH reduction may make the values to increase, though there is need for monitoring the values for a longer period of time to validate this claim.

Heavy metals (Cr, Pb, Cu, Zn and Fe) concentrations in water samples differed greatly from the control site in the canals (Table 4.2.1 a&b) and the nucleus contribution to River Kuywa was statistically significant at $P \leq 0.05$ (Table 4.2.3 a&b). This was probably due to the fact that the solubility of all the studied heavy metals increase with reduction in pH (Alloway, 1995a) and as already discussed, the pH of the soils was way below 6.0 a value at which the heavy metals start being soluble hence easily transported to the aquatic environment. The same results can also be supported by the fact that the heavy metals correlated with each other positively further indicating their common origin (Tables 4.2.2 and 4.2.4). The increase in the concentrations during the long wet season was attributed to surface runoffs that acted as transport agent of the heavy metals from the farms to the aquatic environment. Furthermore, soil erosion and leaching also aid in heavy metal transport from the sugarcane plantations to the aquatic environments hence there increased concentrations in water samples during the wet season.

According to Turkish environmental guidelines (1988), water samples fall under class (i) of domestic water indicating the water to be within allowable limits with heavy metal concentrations (Table 4.2.5). Other Rivers like Sondu Mirio, Nyamasaria, Nyando and Winam Gulf have higher heavy metal concentrations (Ongeri, 2008, Table 4.2.5) as

compared to River Kuywa partly because of the distance traversed by these rivers as compared to the short Distance traveled by River Kuywa. All the same, the contribution of the nucleus to heavy metal burden into River Kuywa is significant making sugarcane farming a major contributor of Heavy metals to the water system. River Kuywa drains its water into River Nzoia that finally drains into Lake Victoria. Heavy metals in River Nzoia are already above international standards (Lalah *et al.*, 2008), probably due to the fact that the river basin of River Nzoia comprises mostly of sugarcane plantations.

There is therefore need to monitor soil pH which is a major factor in heavy metal mobility from the farms so as to avoid there accumulation into aquatic environments.

4.3. Heavy metals in Sediments

The AAS analysis gave mean % recovery values for extraction of the spiked sediments samples of Cr, Pb, Cu, Zn and Fe as 93, 89, 94, 88 and 84, respectively, with detection limits of 0.001 ng/ml, 0.001 ng/ml, 0.003 ng/ml, 0.008 ng/ml and 0.01 ng/ml respectively. The wet weight for sediments was 1g per sample while the dry weight averaged to 0.968 ± 0.019 g giving an average of wet weight to dry weight ratio as 1.036 ± 0.024 .

Table 4.3.1.a. Mean site variations of heavy metal loads in surface sediments from canals within Nzoia nucleus estate farms in mg/kg between the long wet and dry seasons.

Chromium								
Sites								Mean
	1(control)	2	3	4	5	6	7	
Dry Season	14.20	64.27	51.63	51.80	59.53	48.61	14.66	43.53
Wet Season	84.65	58.02	94.52	74.53	52.82	106.30	86.10	78.22
Mean	49.42	61.15	72.62	63.17	56.19	73.19	50.38	60.87
Lsd $p \leq 0.05$				5.97				3.77
Interaction				8.44				
Cv%				7.18				

Lead								
Sites								Mean
	1(control)	2	3	4	5	6	7	
Dry Season	19.81	23.42	25.44	29.04	30.95	33.67	26.20	26.93
Wet Season	52.42	51.45	54.16	50.79	56.46	51.14	51.13	52.506
Mean	36.12	37.44	39.80	39.91	43.71	42.40	38.66	39.72
Lsd $p \leq 0.05$				7.06				3.77
Interaction				9.98				
Cv%				13.01				

Copper								
Sites								Mean
	1(control)	2	3	4	5	6	7	
Dry Season	31.67	34.26	31.69	25.04	15.75	18.12	24.70	25.89
Wet Season	45.46	74.87	81.78	56.41	18.58	20.26	55.58	50.42
Mean	38.58	54.57	56.74	40.73	17.16	19.19	40.14	38.16
Lsd $p \leq 0.05$				5.96				3.18
Interaction				8.421				
Cv%				11.43				

Key:

Canal sampling points **1** - Plot 9053, **2** - Plot 8071, **3** - Plot 243, **4** - Plot 125, **5** - Plot 616, **6** - Plot 429, **7** - Plot 413 as illustrated in figure 3.1.

Control: A canal draining water from a farm within the nucleus without sugarcane plantation (Tree plantation) thus there was no nitrogenous fertilizer application.

Table 4.3.1.b. Mean site variations of heavy metal loads in surface sediments from canals within Nzoia nucleus estate farms in mg/kg between the long wet and dry seasons.

	Zinc							Mean
	1(control)	2	3	4	5	6	7	
Dry Season	98.01	92.60	84.88	86.38	110.67	62.92	128.30	94.82
Wet Season	112.39	133.53	87.09	97.48	95.99	80.23	182.71	112.78
Mean	105.20	113.06	85.99	91.93	103.33	71.58	155.51	103.80
Lsd $p \leq 0.05$				12.207				6.53
Interaction				17.260				
Cv%				8.610				

	Iron							Mean
	1(control)	2	3	4	5	6	7	
Dry Season	147.23	111.79	186.75	184.09	215.35	255.76	211.53	187.50
Wet Season	210.28	312.22	360.68	222.52	439.19	324.55	216.31	297.97
Mean	178.76	212.01	273.71	203.30	327.72	290.16	213.92	242.73
Lsd $p \leq 0.05$				8.82				4.71
Interaction				12.47				
Cv%				2.66				

Key:

Canal sampling points **1** - Plot 9053, **2** - Plot 8071, **3** - Plot 243, **4** - Plot 125, **5** - Plot 616, **6** - Plot 429, **7** - Plot 413 as illustrated in figure 3.1.

Control: A canal draining water from a farm within the nucleus without sugarcane plantation (Tree plantation) thus there was no nitrogenous fertilizer application.

Table 4.3.2. Correlation matrix of heavy metal loads (mg/kg of dry weight) in sediments samples from canals within Nzoia Sugar Company nucleus estate farms.

	Cr	Pb	Cu	Zn	Fe
Cr	1.000				
Pb	0.675	1.000			
Cu	0.426	0.473	1.000		
Zn	0.068	0.207	0.360	1.000	
Fe	0.328	0.713	0.173	-0.082	1.000

Table 4.3.3.a. Mean site variations of heavy metal loads in surface sediments from River Kuywa within Nzoia nucleus estate farms in mg/kg between the long wet and dry seasons.

Chromium					
		Sites			
	1(control)	2	3	Mean	
Dry season	29.19	46.45	48.78	41.47	
Wet season	50.34	59.76	63.38	57.83	
Mean	39.76	53.11	56.08	49.65	
Lsd $p \leq 0.05$		4.55		3.72	
Interaction		6.44			
Cv%		4.99			

Lead					
		Sites			
	1(control)	2	3	Mean	
Dry season	28.22	37.33	44.72	36.77	
Wet season	65.91	69.78	83.05	72.92	
Mean	47.07	53.56	63.89	54.84	
Lsd $p \leq 0.05$		11.67		9.53	
Interaction		16.51			
Cv%		11.59			

Copper					
		Sites			
	1(control)	2	3	Mean	
Dry season	35.27	38.27	45.91	39.82	
Wet season	65.62	66.75	67.40	66.59	
Mean	50.44	52.51	56.66	53.20	
Lsd $p \leq 0.05$		6.497		5.30	
Interaction		9.190			
Cv%		6.650			

Key

- 1 – Inlet of River Kuywa to the Nzoia nucleus sugarcane estate farms (used as a control so as to give the impact of the nucleus).
- 2 – A point in the river at the middle of the Nzoia nucleus sugarcane farms.
- 3 – Outlet of River Kuywa from Nzoia nucleus estate farms (subtract from the control to get the impact of the nucleus).

Table 4.3.3.b. Mean site variations of heavy metal loads in surface sediments from River Kuywa within Nzoia nucleus estate farms in mg/kg between the long wet and dry seasons.

Zinc				
	1(control)	Sites 2	3	Mean
Dry season	104.23	132.42	129.93	122.19
Wet season	122.86	147.55	162.06	144.16
Mean	113.54	139.98	146.00	133.17
Lsd $p \leq 0.05$		17.26		14.09
Interaction		24.41		
Cv%		7.05		
Iron				
	1(control)	Sites 2	3	Mean
Dry season	353.31	384.09	420.73	386.04
Wet season	398.90	414.57	467.64	427.04
Mean	376.107	399.33	444.19	406.54
Lsd $p \leq 0.05$		13.85		11.31
Interaction		19.58		
Cv%		1.85		

Key

- 1 – Inlet of River Kuywa to the Nzoia nucleus sugarcane estate farms (used as a control so as to give the impact of the nucleus).
- 2 – A point in the river at the middle of the Nzoia nucleus sugarcane farms.
- 3 – Outlet of River Kuywa from Nzoia nucleus estate farms (subtract from the control to get the impact of the nucleus).

Table 4.3.4. Correlation matrix of heavy metal loads (mg/kg of dry weight) in sediments from River Kuywa.

	Cr	Pb	Cu	Zn	Fe
Cr	1.000				
Pb	0.873	1.000			
Cu	0.821	0.919	1.000		
Zn	0.867	0.760	0.621	1.000	
Fe	0.870	0.810	0.700	0.806	1.000

Table 4.3.5. Comparing with some studies done on sediments from other rivers

RIVER	Cr	Pb	Cu	Zn	Fe
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
This study ^a dry season canals	43.53	26.93	25.89	94.82	197.0
This study ^a wet season canals	79.57	52.51	50.42	112.8	298.0
This study ^a dry season R.Kuywa	41.47	36.75	39.81	122.2	386.1
This study ^a wet season R.Kuywa	57.83	72.92	66.59	144.2	427.1
Sio River Kenya ^b	NG	8.10	18.50	37.70	9.60
Sondu Mirio River Kenya ^b	NG	25.10	20.90	258.40	651.40
Nyamasaria River Kenya ^b	NG	25.10	28.30	131.80	418.30
Nyando River Kenya ^b	NG	17.00	56.30	172.20	685.60
Buyuk Menderes River Turkey ^c	165 ± 7	54.00	137 ± 5	120 ± 10	NG
Gediz River Turkey ^c	200 ± 6	128 ± 15	140 ± 3	160 ± 15	NG
Lake Boeuf Lousiana ^e	11.70	21.00	10.90	64.70	NG
Lake Malawi ^f	NG	14.60	37.30	0.05	NG
PEC ^g	111.00	158.00	111.00	459.00	NG
Dipsiz Stream ^d	19.700	83.60	13.00	370	NG
Lake Tanganyika ⁱ	NG	14.00	20.81	28.36	NG
Back ground concentrations ^h	17.00	14.00	17.00	67.00	NG

NG – Not Given in literature.

a – This study 2010 Kenya (number of examined samples: 18 for river and 42 for canals), **b** – Ongeru (2008), **c** – Akcay *et al.* (2002), **d** – Ahmet *et al.* (2005), **e** – Aucoin *et al.* (1999), **f** – Kidd *et al.* (1998), **g** – PEC: Probable effect concentrations (Mac Donald *et al.*, 2000), **h** – Background concentrations (Bervoets and Blust, 2003), **i** – Charle (2002).

4.3.1. Discussion

In a river system, sediments have been widely used as environmental indicators and their chemical analysis can provide significant information on the assessment of anthropogenic activities (Shriadah, 1999; Singh *et al.*, 2002; Gaur *et al.*, 2005; Valdés *et al.*, 2005). Thus, in water bodies, sediments form an important repository of heavy metals (Ravanelli *et al.*, 1997; Ranjbar, 1998; Fabbri *et al.*, 2001; Kamau, 2001; Mathew *et al.*, 2003; Sekhar *et al.*, 2003; Panda *et al.*, 2006; Nemr *et al.*, 2006; Veen *et al.*, 2006), and the heavy metal pollution of aquatic ecosystems is often most obviously reflected in high metal levels in sediments, other than in elevated concentrations in underlying water (Linnik and Zubenko, 2000; Badran and Zibdah, 2005; Jain *et al.*, 2005).

In the current study therefore, the high concentration of heavy metals (Tables 4.3.1a&b, 4.3.3 a&b) in the river and canals sediments that increased downstream River Kuywa was an indication of pollution loading due to sugarcane farming and nitrogenous fertilizer application in the nucleus estate farms. As indicated earlier, the main factor in the mobility and subsequent accumulation of heavy metals in the river sediments is the reduced soil pH due to use of nitrogenous fertilizers. The heavy metals studied (Cr, Pb, Zn, Cu, and Fe) were above background values (Chale, 2002, Table 4.3.5). Furthermore, heavy metal loads correlated with each other positively further indicating their common source (Tables 4.3.2 and 4.3.4). In canals and river sediments, the values increased drastically during the wet season probably due to surface runoffs in the sugar plantations (Figure 4.3.1, 4.3.3.)

Heavy metal loads in the nucleus sediments (both river and canals) were above other studied Rivers like Nyamasaria, Sio, Nyando and Sondu Mirio within Lake Victoria basin (Ongeri, 2008). Though this can be attributed to the fact that this was a point source and the reported values are assumed to be the average for the entire river.

4.4. Physicochemical parameters in water

Table 4.4.1. Mean site variation of some water quality physicochemical parameters in canals inside the nucleus estate farms of Nzoia Sugar Company between the long wet and dry seasons.

Temperature (°C)								
	Sites							
	1(control)	2	3	4	5	6	7	Mean
Dry season	27.00	26.00	28.00	25.00	24.00	24.00	31.00	26.43
Wet season	26.00	24.00	24.00	25.00	21.00	20.00	23.00	23.27
Mean	26.50	25.00	26.00	25.00	22.00	22.00	27.00	24.86
Lsd $p \leq 0.05$				0.166				0.136
Interactions				0.235				
CV%				0.050				
Conductivity ($\mu\text{S/cm}$)								
	Sites							
	1(control)	2	3	4	5	6	7	Mean
Dry season	88.33	73.70	42.50	54.60	60.68	52.00	33.867	57.95
Wet season	308.00	260.33	256.33	158.67	183.00	353.67	207.00	246.71
Mean	198.17	167.02	149.42	106.63	121.83	202.83	120.43	152.33
Lsd $p \leq 0.05$				9.340				3.3400
Interactions				8.920				
CV%				3.030				
pH								
	Sites							
	1(control)	2	3	4	5	6	7	Mean
Dry season	6.76	6.61	7.04	6.23	6.86	7.01	8.13	6.951
Wet season	4.20	5.53	5.53	4.40	5.73	4.80	4.13	4.91
Mean	5.48	6.07	6.29	5.32	6.30	5.91	6.13	5.93
Lsd $p \leq 0.05$				0.25				0.134
Interactions				0.36				
CV%				3.11				
Turbidity (NTU)								
	Sites							
	1(control)	2	3	4	5	6	7	Mean
Dry season	105.33	116.67	69.22	224.67	61.00	32.41	52.28	94.51
Wet season	811.00	708.33	565.67	533.63	631.90	674.33	956.70	697.37
Mean	458.17	412.50	317.45	379.15	346.45	353.37	504.49	697.37
Lsd $p \leq 0.05$				31.77				16.98
Interactions				44.92				
CV%				5.88				
Dissolved Oxygen (mg/L)								
	Sites							
	1(control)	2	3	4	5	6	7	Mean
Dry season	3.21	4.92	5.08	6.14	5.12	3.84	5.11	4.78
Wet season	4.04	3.35	4.92	4.52	4.12	2.03	4.86	3.975
Mean	3.63	4.14	5.00	5.33	4.62	2.94	5.00	4.376
Lsd $p \leq 0.05$				0.062				0.033
Interactions				0.088				
CV%				3.79				

Key:

Canal sampling points **1** - Plot 9053, **2** - Plot 8071, **3** - Plot 243, **4** - Plot 125, **5** - Plot 616, **6** - Plot 429, **7** - Plot 413 as illustrated in figure 3.1.

Control: A canal draining water from a farm within the nucleus without sugarcane plantation (Tree plantation) thus there was no nitrogenous fertilizer application.

Table 4.4.2. Mean site variation of some water quality physicochemical parameters in canals inside the nucleus estate farms of Nzoia Sugar Company between the long wet and dry seasons.

Chemical Oxygen Demand (mg/L)								
	Sites							
	1(control)	2	3	4	5	6	7	Mean
Dry season	382.67	455.56	368.22	454.28	372.03	508.41	287.47	404.09
Wet season	625.38	723.09	818.61	768.91	868.26	975.74	881.81	808.83
Mean	504.02	589.32	593.42	611.60	620.14	742.08	584.64	606.46
Lsd $p \leq 0.05$				31.086				16.616
Interactions				43.962				
CV%				3.75				

Total Phosphates (mg/L)								
	Sites							
	1(control)	2	3	4	5	6	7	Mean
Dry season	0.91	0.95	0.95	0.85	0.71	1.182	0.425	0.85
Wet season	10.20	7.63	6.50	5.25	4.47	12.20	7.43	7.67
Mean	5.55	4.29	3.73	3.05	2.59	6.70	3.93	4.26
Lsd $p \leq 0.05$				0.321				0.172
Interactions				0.455				
CV%				5.530				

Total Nitrate-Nitrogen (mg/L)								
	Sites							
	1(control)	2	3	4	5	6	7	Mean
Dry season	6.95	4.79	4.25	3.44	2.20	3.50	3.04	4.024
Wet season	25.12	27.71	26.84	24.53	21.40	22.78	27.70	25.152
Mean	16.03	16.25	15.54	13.98	11.80	13.14	15.37	14.59
Lsd $p \leq 0.05$				5.694				3.044
Interactions				8.052				
CV%				3.35				

Key:

Canal sampling points **1** - Plot 9053, **2** - Plot 8071, **3** - Plot 243, **4** - Plot 125, **5** - Plot 616, **6** - Plot 429, **7** - Plot 413 as illustrated in figure 3.1.

Control: A canal draining water from a farm within the nucleus without sugarcane plantation (Tree plantation) thus there was no nitrogenous fertilizer application.

Table 4.4.3. Correlation matrix of physicochemical parameters of water samples from canals within Nzoia nucleus estate farms.

	Temp °C	pH	Cond μS/cm	Turb NTU	DO mg/L	COD mg/L	TP mg/L	NO ₃ -N mg/L
Temp	1.000							
pH	0.583	1.000						
Cond μS/cm	-0.596	-0.800	1.000					
Turb NTU	-0.563	-0.899	0.872	1.000				
DO mg/L	0.456	0.550	-0.794	-0.600	1.000			
COD mg/L	-0.802	-0.812	0.831	0.861	-0.643	1.000		
TP mg/L	-0.576	-0.834	0.978	0.885	-0.695	0.828	1.000	
NO ₃ -N mg/L	-0.481	-0.843	0.906	0.929	-0.624	0.817	0.903	1.000

Table 4.4.4. Correlation matrix of heavy metal loads and physicochemical parameters in water samples from canals in Nzoia nucleus estate farms.

	Cr μg/L	Pb μg/L	Cu μg/L	Zn μg/L	Fe μg/L
Temp	-0.130	-0.532	-0.621	-0.358	-0.631
pH	-0.368	-0.844	-0.785	-0.681	-0.552
Cond	0.390	0.839	0.713	0.763	0.753
Turb	0.424	0.879	0.764	0.759	0.731
DO	-0.356	-0.751	-0.539	-0.692	-0.530
COD	0.189	0.840	0.868	0.716	0.789
TP	0.360	0.830	0.757	0.691	0.746
NO ₃ -N	0.342	0.819	0.648	0.867	0.687

Table 4.4.5. Mean site variation of some water quality physicochemical parameters from River Kuywa inside the nucleus estate farms of Nzoia Sugar Company between the long wet and dry seasons.

	Temperature °C			
	Sites			Mean
	1(control)	2	3	
Dry season	24.50	25.17	26.00	25.22
Wet season	21.50	22.00	22.00	21.83
Mean	23.00	23.58	24.00	23.53
Lsd $p \leq 0.05$		0.166		0.136
Interactions		0.235		
CV%		0.50		

	Conductivity ($\mu\text{S/cm}$)			
	Sites			Mean
	1(control)	2	3	
Dry season	42.60	52.43	61.63	52.22
Wet season	93.33	106.00	115.33	104.89
Mean	67.97	79.22	88.48	78.56
Lsd $p \leq 0.05$		6.40		5.23
Interactions		9.06		
CV%		4.44		

	pH			
	Sites			Mean
	1(control)	2	3	
Dry season	7.30	7.03	6.94	7.090
Wet season	6.27	6.16	5.80	6.078
Mean	6.783	6.598	6.370	6.584
Lsd $p \leq 0.05$		0.523		0.428
Interactions		0.740		
CV%		3.54		

	Turbidity (NTU)			
	Sites			Mean
	1(control)	2	3	
Dry season	58.73	62.36	65.54	62.21
Wet season	956.70	966.17	983.64	968.83
Mean	507.72	514.27	524.59	515.52
Lsd $p \leq 0.05$		17.52		14.307
Interactions		24.781		
CV%		0.97		

Key

- 1 – Inlet of River Kuywa to the Nzoia nucleus sugarcane estate farms (used as a control so as to give the impact of the nucleus).
- 2 – A point in the river at the middle of the Nzoia nucleus sugarcane farms.
- 3 – Outlet of River Kuywa from Nzoia nucleus estate farms (subtract from the control to get the impact of the nucleus).

Table 4.4.6. Mean site variation of some water quality physicochemical parameters from River Kuywa inside the nucleus estate farms of Nzoia Sugar Company between the long wet and dry seasons.

Dissolved Oxygen (mg/L)				
	Sites			
	1(control)	2	3	Mean
Dry season	14.40	10.93	9.51	11.612
Wet season	10.40	7.99	6.76	8.381
Mean	12.40	9.46	8.133	9.997
Lsd $p \leq 0.05$		0.261		0.213
Interactions		0.369		
CV%		12.90		

Chemical Oxygen Demand (mg/L)				
	Sites			
	1(control)	2	3	Mean
Dry season	1213.33	1303.33	14.86.67	1334.44
Wet season	1584.33	1656.68	1710.33	1650.44
Mean	1398.83	1480.00	1598.50	1492.44
Lsd $p \leq 0.05$		81.938		66.902
Interactions		115.878		
CV%		1.64		

Total Phosphates (mg/L)				
	Sites			
	1(control)	2	3	Mean
Dry season	0.82	1.23	1.39	1.148
Wet season	8.26	8.44	10.26	11.655
Mean	4.54	4.84	9.82	6.401
Lsd $p \leq 0.05$		1.143		0.933
Interactions		1.616		
CV%		0.40		

Total Nitrate Nitrogen (mg/L)				
	Sites			
	1(control)	2	3	Mean
Dry season	1.28	2.25	3.45	2.327
Wet season	14.703	17.853	20.717	17.758
Mean	8.00	10.05	12.18	10.042
Lsd $p \leq 0.05$		5.450		4.450
Interactions		14.148		
CV%		6.62		

Key

- 1 – Inlet of River Kuywa to the Nzoia nucleus sugarcane estate farms (used as a control so as to give the impact of the nucleus).
- 2 – A point in the river at the middle of the Nzoia nucleus sugarcane farms.
- 3 – Outlet of River Kuywa from Nzoia nucleus estate farms (subtract from the control to get the impact of the nucleus).

Table 4.4.7. Correlation matrix of physicochemical parameters of water samples from River Kuywa.

	Temp	pH	Cond	Turb	DO	COD	TP	NO ₃ -N
Temp	1.000							
pH	0.811	1.000						
Cond	-0.843	-0.833	1.000					
Turb	-0.952	-0.847	0.962	1.000				
DO	0.515	0.524	-0.547	-0.547	1.000			
COD	-0.018	0.083	-0.276	-0.134	-0.695	1.000		
TP	-0.814	-0.796	0.951	0.916	-0.732	-0.476	1.000	
NO ₃ -N	-0.899	-0.824	0.981	0.976	-0.634	0.972	-0.297	1.000

Table 4.4.8. Correlation matrix of heavy metal loads ($\mu\text{g/L}$) and physicochemical parameters in water samples from River Kuywa.

	Cr	Pb	Cu	Zn	Fe
Temp °C	-0.775	-0.797	-0.747	-0.775	-0.427
pH	-0.726	-0.772	-0.764	-0.797	-0.623
Cond $\mu\text{S/cm}$	0.949	0.931	0.895	0.955	0.819
Turb NTU	0.908	0.896	0.862	0.914	0.656
DO mg/L	-0.602	-0.711	-0.682	-0.630	-0.324
COD mg/L	-0.341	-0.472	-0.478	0.433	-0.370
TP mg/L	0.923	0.991	0.950	0.941	0.764
NO ₃ -N mg/L	0.942	0.957	0.898	0.942	0.731

Table 4.4.9. Comparing with some international standards on domestic water and levels of metals reported in other studies for physicochemical parameters.

	Temp	pH	Cond	Turb	DO	COD	TP	NO ₃ -N
	°C		µS/cm	NTU	mg/L	mg/L	mg/L	mg/L
This study ^a dry season canals	26.42	6.96	57.9	94.4	4.770	405.5	0.949	3.95
This study ^a wet season canals	23.28	4.90	246.7	697.0	3.975	808.8	7.668	25.15
This study ^a dry season R. Kuywa	25.16	7.090	52.22	59.61	11.61	1197.0	1.149	2.326
This study ^a wet season R. Kuywa	21.83	6.356	104.8	945.7	8.381	1226.0	12.76	44.20
KEBS ^b Standard	NG	6.5-8.5	NG	5.000	NG	NG	NG	NG
WHO ^c standard	NG	6.5-8.5	NG	NG	NG	NG	NG	10.000
USEPA ^d standard	NG	6 - 9.5	NG	NG	4 - 5	NG	0.100	10.000
EMCA(WQ) ^g 2006 std	NG	6.5-8.5	NG	NG	NG	NG	2.000	NG
Egyptian standard ^f	NG	6 - 9	NG	NG	10.00	NG	NG	NG
Winam Gulf ^e	NG	7.8	145.30	190.40	4.96	NG	NG	NG
Lake Victoria ^e	NG	7.7	129.80	10- 37	7.48	NG	NG	NG
Sio River ^e	28.00	8.5	76.000	33.00	5.85	NG	NG	NG
Nyamasaria River ^e	28.00	7.3	143.00	202.00	5.08	NG	NG	NG
Nyando River ^e	26.00	7.5	230.00	980.00	4.20	NG	NG	NG
Sondu mirio River ^e	28.00	7.6	170.00	410.00	4.65	NG	NG	NG

Key

NG – Not Given in literature.

a – This study 2010 Kenya (number of examined samples: 42 for canals and 18 for river water),

b – KEBS (1996) maximum permissible limits, **c** – WHO (1993) maximum permissible limits, **d** –

USEPA (1979) permissible limits, **e** – Onger (2008) downstream for rivers, **f** – ECS (Egyptian

chemical standards) (1994) permissible limits, **g** – Kenyan EMCA (WQ) (2006) Standards.

4.4.1 Discussion

Canal water temperature ranged between 20°C to 31°C with a mean of 26.429 ± 2.378°C and 23.286 ± 0.028°C during the dry and wet seasons respectively (Table 4.4.1.), while for River water it ranged between 24.50°C and 26.00°C with a mean of 25.222 ± 0.667°C and 21.833 ± 0.250°C during the dry and wet seasons, respectively (Table 4.4.5). There is no set standard for temperature on drinking or domestic water; maybe due to the

fact that there is no scientific evidence on effect of temperature in drinking water. The null hypotheses for temperature were not rejected at all levels ($P \leq 0.05$). That notwithstanding the observed differences in temperature per site remains to be out of contingency and that of seasons does not depend on sugarcane farming in Nzoia nucleus estate farms but maybe out of other factors not studied; for example time of the day during sampling.

Canals Electrical Conductivity ranged from $33.867 \pm 5.426 \mu\text{S/cm}$ to $353.667 \pm 5.508 \mu\text{S/cm}$ with means of $57.957 \pm 17.722 \mu\text{S/cm}$ dry and $246.714 \pm 65.967 \mu\text{S/cm}$ wet seasons (Table 4.4.1.), while that of River Kuywa ranged from $42.600 \pm 2.740 \mu\text{S/cm}$ to $115.33 \pm 4.163 \mu\text{S/cm}$ with means of $62.212 \pm 3.779 \mu\text{S/cm}$ dry and $104.88 \pm 0.252 \mu\text{S/cm}$ wet seasons (Table 4.4.5.). The variations in conductivity were statistically significant from the control site, between seasons and even in interactions (Table 4.4.1, 4.4.5). Conductivity increased drastically during the wet season with the distribution showing positive skewness. All the null hypotheses were rejected for conductivity at all the significant levels ($P \leq 0.05$ Table 4.4.1, 4.4.5.) and the alternative hypothesis adopted. Increase in conductivity is an indication of increased loads of metallic ions in the water during the wet season. Increased conductivity means that heavy metals become bioavailable hence readily absorbed by aquatic plants and animals in essence affecting the food chains (Wang, 1987; Gough and Herring, 1993; Driscoll *et al.*, 1994; Ongley, 1996). Conductivity levels in the wet season was above other studied Rivers like Sondu Mirio, Nyamasaria, Lake Victoria and Sio in Lake Victoria basin (Ongeri 2008).

Canal turbidity site mean ranged from 32.407 ± 1.112 NTU to 956.700 ± 3.315 NTU in both seasons with seasonal means of 94.480 ± 61.824 NTU for dry season and 697.410 ± 141.618 NTU for wet season (Table 4.4.1) while, river turbidity site mean ranged from 58.733 ± 1.430 NTU to 983.63 ± 5.188 NTU in both seasons with seasonal means of 62.212 ± 3.779 NTU for dry season and 968.83 ± 13.119 NTU for wet season (Tables 4.4.5.). There was drastic increase in turbidity during the wet season (Figures 4.4.3. and 4.4.1.), an indication of runoffs from the fields during the rainy season. Site and seasonal variations were also statistically significant from the control site (Tables 4.4.1 and 4.4.5). Turbidity correlated with most of the other physicochemical parameters for it had nearly perfect positive linear correlations with chemical oxygen demand, total phosphates, and $\text{NO}_3\text{-N}$ (Table 4.4.3. and 4.4.7). This was an indication of surface runoffs and erosion in the farms contributing positively to the above mentioned physicochemical parameters. Generally the null hypothesis was rejected significant level $P \leq 0.05$ (Table

4.4.1 and 4.4.5). Turbidity levels in the water within the canals and River Kuywa were above international standards hence it was not suitable for domestic use as residents downstream River Kuywa. (KEBS, 1996). The turbidity levels compared to that of River Nyando that had been reported to have a value of 980 NTU. In addition, turbidity correlated positively with heavy metals (Tables 4.4.4 and 4.4.8) an indication that the heavy metal loads in water samples were directly linked to surface runoffs and erosions in the sugarcane plantation fields.

The pH site values in water ranged between 8.130 ± 0.010 to 4.133 ± 0.208 in both seasons with seasonal means of 6.968 ± 0.565 for dry season and 4.905 ± 0.682 for wet season in canals water (Table 4.4.1). For river water, the mean values were 7.09 ± 0.170 dry season and 6.356 ± 0.309 wet season (Table 4.4.5). Surface water runoffs into the river and the canals could be the one responsible for the low pH values in the wet seasons. This could be so due to the fact that the nitrogenous fertilizers have affected the soil pH in the farms and hence the same is replicated in the water system. Reduced water pH accelerates solubility of heavy metals from the sediments into water making them bioavailable hence bioaccumulating into aquatic animals and (Alloway, 1995b; Ford *et al.*, 2001). pH gave a very strong negative linear correlations with conductivity, Chemical Oxygen Demand, Total Phosphates, and $\text{NO}_3\text{-N}$, (Table 4.4.3 and 4.4.7). From these correlations we clearly observe that an increase in $\text{NO}_3\text{-N}$ results in reduction in pH values as it had earlier on been reported by Dobermann and Fairhurst (2000).

Water from canals and River Kuywa within Nzoia nucleus estate farms should not be used for domestic purposes in the wet season because its pH is not within the permissible limits of 6.5 - 8.5 (WHO, 1993; KEBS, 1996; EMCA, 2006), 6 - 9.5 (USEPA, 1979) and 6 - 9 (Egyptian Chemical Standards, 1994). The pH value for the river during the wet season was below other rivers like River Sio, Nyando, and Nyamasaria (Ongeri, 2008).

Dissolved oxygen was high during dry season (mean of 4.770 ± 0.954 mg/L canal and 11.612 ± 2.397 mg/L river water) as compared to the wet season (mean of 3.975 ± 0.964 mg/L canal and 8.381 ± 2.019 mg/L river water). This observed difference is due to reoxidation of the high metal concentrations during the wet season (Table 4.2.1 and 4.4.3) as compared to the dry season where the concentration of the metals is low (Table 4.2.1 and 4.2.3). Hence this makes dissolved oxygen reduce with increase in dissolved metals. Thus an increase in dissolved oxygen also increases dissolved metals hence promoting mobilization (Duinker *et al.*, 1982). The net effect is that a high concentration

of heavy metals reduces oxygen concentrations in the water. This phenomenon is seen from the negative linear correlations of dissolved oxygen with heavy metals in Table 4.4.4 (Cr: -0.356, Pb: -0.751, Cu: -0.537, Zn: -0.692, Fe: -0.530 canals) and Tables 4.4.8 (Cr: -0.602, Pb: -0.711, Cu: -0.682, Zn: -0.630, Fe: -0.324 river water). From this observations, the null hypotheses was rejected at significant levels tested ($P \leq 0.05$) (Table 4.4.1 and 4.4.5) hence the adoption of the alternative hypotheses. The dissolved oxygen in canals water wet season (3.975 mg/L) was well below the international standard mark of 4 – 5 mg/L (USEPA, 1979) hence making the water not suitable for domestic use or unsuitable for aquatic plants and animals.

Chemical Oxygen Demand increased rapidly during the wet season with means of 405.521 ± 75.241 mg/L dry season and 808.827 ± 110.482 mg/L wet season canals water (Table 4.4.1) and 1197.556 ± 354.002 mg/L dry season, 1226.778 ± 46.743 mg/L wet season, Table 4.4.5). All the null hypotheses were rejected at all significant levels ($P \leq 0.05$) (Tables 4.4.1 and 4.4.5). Clearly there was increase in chemical parameters in the water in the wet season leading to high oxygen demand. These chemical activities can easily be seen from the positive linear correlations between COD and conductivity (0.861), turbidity (0.861), total phosphates (0.861) and $\text{NO}_3\text{-N}$ (0.903) canal water (Table 4.4.7). Generally rain water runoffs in the farms carry with them contaminants like phosphates and nitrates that increase biological activities in the canals water hence increasing COD levels.

There were very little phosphates in the canals water during the dry season (mean: 0.949 ± 0.335 mg/L) but the concentration rose sharply during the wet season (mean 7.668 ± 2.586 mg/L) (Figures 4.4.1 and 4.4.1, Tables 4.4.1). The same observation is seen in River Kuywa with concentrations of 1.149 ± 0.251 mg/L dry season and 12.767 ± 4.538 mg/L wet season, values which were above USEPA (1979) and EMCA (2006) standards especially in season two (Table 4.4.5). The distribution was skewed to the right (wet season). The null hypothesis was rejected at testing level ($P \leq 0.05$) (Tables 4.4.1, 4.4.2 and 4.4.5). Total phosphates had a nearly perfect positive linear correlation with conductivity (0.978), $\text{NO}_3\text{-N}$ (0.903), turbidity (0.885), and COD (0.828) (Table 4.4.3). There was an indication of these contaminants being products of intensive farming in the farm where runoff water carry them to the canals that finally deposit them into River Kuywa during the wet season. Since second season sampling was done just two weeks after nitrogenous fertilizers had been applied in the farms, it is assumed that they were the major source of the phosphates. Except for the dry season samples, concentration of

phosphates in the canals water is beyond international standards of 2.00 mg/L (EMCA, 2006) and 0.100 mg/L (USEPA, 1979).

The concentration of $\text{NO}_3\text{-N}$ varied in a similar manner as that of total phosphates (Figure 4.4.1 and 4.4.3); a clear indication that they came from similar origin. Its mean concentration was 3.957 ± 1.517 mg/L dry and 25.152 ± 2.356 mg/L wet seasons canals water and for river water it was 2.326 ± 0.978 mg/L dry and 44.202 ± 8.952 mg/L wet seasons (Table 4.4.3). The variations per site and between seasons were significant at all the tested levels (Table 4.4.1 and 4.4.3). It correlated strongly with conductivity (0.906), turbidity (0.929), COD (0.817), and total phosphates (0.903) canals water showing their interrelationships. This was an indication that they all came from similar origin. All the null hypotheses were rejected at all significant levels (Table 4.4.1, 4.4.2, 4.4.3 and 4.4.5). The canals water was extremely polluted with $\text{NO}_3\text{-N}$ at all times since the permissible limit of 10.00 mg/L (WHO, 1993 and USEPA, 1979) was way far below the seasonal means.

The data obtained show that the nucleus estate farms of Nzoia are a point source of nutrients into River Kuywa which finally will find its way into Lake Victoria through R. Nzoia.

Chapter 5

5.1. Summary

Use of nitrogenous fertilizers in sugarcane farming reduces the soil pH in the farms. These findings were supported with the use of a control farm (a football pitch) within the same geographical region that did not practice sugarcane farming.

Reduction in soil pH within sugarcane plantations created an acidic environment that was evident in the aquatic systems and the analyzed soils within the nucleus resulting in high concentrations of heavy metals in wet season. This acidic environment accelerated heavy metal solubility, bioavailability and mobility from one point to another. Surface runoffs, leaching and erosion within the sugar plantations during the wet season acted as a transport media of the available heavy metals to the aquatic systems.

Once in the aquatic systems the heavy metals contributed to increased electrical conductivity, chemical oxygen demand and reduced dissolved oxygen of the water systems beyond allowable limits in some areas.

Finally, the nitrogenous fertilizers themselves also found their way into the aquatic environment as was evident from high quantities of nitrate-nitrogen and total phosphates during the wet season. These quantities were above allowable limits hence posing a great threat to the environment as water systems may become eutrophic leading to serious problems like algal blooms and hyacinth growth.

5.2. Conclusions

The use of nitrogenous fertilizers in sugarcane farming in Nzoia nucleus estate farms reduced soil pH that created acidic environment promoting heavy metal mobility, solubility and bioavailability in the aquatic environment.

The heavy metals themselves are naturally occurring in Nzoia sugar belt as shown in the control site though the fertilizers used also contain contaminants of these heavy metals.

The heavy metal burden in the aquatic environment within Nzoia Nucleus estate farms were within allowable limits as shown by levels in water and surface sediments in canals and River Kuywa.

The presence of heavy metals in the aquatic environment increased the chemical oxygen demand, electrical conductivity and reduced the dissolved oxygen level during the wet season.

Surface runoffs and erosion in the sugarcane farms is responsible for transportation of heavy metals and nutrients from the farms into the aquatic systems making the system polluted with total phosphates and nitrate nitrogen

5.3. Recommendations

The agricultural activities of sugarcane farming in Nzoia nucleus farms should go on but measures to be put in place to control acidification of the soil for this is affecting heavy metal burdens in the surrounding aquatic environments especially water quality in River Kuywa which is a source of domestic water.

Heavy metals in the aquatic environment within the nucleus estate farms did not go beyond international standards.

During the wet season, residents downstream River Kuywa are advised to avoid using the river water directly for domestic use for it is contaminated with physicochemical parameters including nitrate nitrogen, total phosphates and turbidity.

5.4. Recommendations for future research

There is need to screen sugarcane plants, finished products from the factory, aquatic plants and animals from the farms in order to ascertain their heavy metal burden and potential effects so as to avoid intoxication in higher animals of the respective food webs.

Other toxic heavy metals especially cadmium which is common in fertilizers to be studied so as to have a clear heavy metal burden of the River.

5.5. References

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