DETERMINATION OF SELECTED HEAVY METALS POLLUTANTS AND PHYSIO-CHEMICAL PARAMETERS IN SEDIMENTS AND WATER: A CASE STUDY OF RIVER ATHI MACHAKOS COUNTY

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DECLARATION

Declaration by the student

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ABSTRACT

The study set out to evaluate the effect of industrial activities by analyzing selected heavy metals and physicochemical parameters of water. Chemical survey was conducted in 9 selected sites (potential polluting sites) along Athi river to determine the levels of heavy chemical elements; lead (Pb), Copper (Cu), chromium (Cr), Nickel(Ni) Cadmium(Cd) and to asses water quality based on physicochemical parameters. The variation in concentration of these metals in the water and sediments as well as other water quality parameters was a key factor to establish the pollution levels in different parts of the river. The recommended WHO procedures of water sampling and analyses were followed. Atomic absorption spectrometry analytical technique was used in the determination of the heavy metal levels dissolved in the water and sediments samples. The results obtained in water samples ranged from Pb(0.23-0.54mg/L),Cu(0.0082-0.0163mg/L), Ni(0.0081-0.0284mg/L), Cr(0.1363-0.3255mg/L), Cd(0.0117-0.0240mg/L) and for sediment samples Pb(0.1277-0.3513mg/L), Cu(0.0607-0.1386mg/L),Ni(0.0191-0.0498mg/L), Cr(0.0692-0.1329mg/L) and Cd(0.0108-0.0428mg/L). The values recorded for physicochemical parameters were pH(6.5-7.4), TDS(109-136mg/L), COD(66-102mg/L), BOD(6-15mg/L) and conductivity(155-206 µs/cm). From the results it was evident that the water was heavily polluted and not fit for domestic, agricultural and industrial purposes. Four of the analyzed heavy metals Pb, Cr, Cd and Ni surpassed the recommended WHO maximum permissible limits (0.01mg/L), (0.01mg/L), (0.003mg/L) and (0.001mg/L) respectively. Lead and chromium had the highest levelss in both sediments and water while Cd and Ni had the lowest concentrations. A Kruskal-Wallis test which, was conducted for the mean heavy metal concentrations, BOD, pH, Conductivity, TDS and COD to determine the significant difference of these water quality parameters in the nine different sampling locations showed significant differences between heavy metals in water and sediments and heavy metals in different stations($p<0.05$). ANOVA test on pH did not reveal any significant difference ($p<0.05$) between the means of the various locations sampled and all results obtained fell within national and international standards of ESEPA/WHO. The BOD values were all higher than the normal BOD for unpolluted water of $\leq$ 2mg/L. The variation of electrical conductivity and TDS gradually decreased downstream with a slightly sharp rise at the middle of the sampling points; with observed TDS levels falling below the EPA's recommended maximum of TDS(500mg/L) in water. The COD values obtained were weak < 400mg/L.However, comparing all the observed values with the EPA regulations, the waters of this river is unsafe for domestic, industrial or agricultural use.

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LIST OF ACRONYMS

AAS	Atomic Absorption Spectroscopy
AES	Atomic Emission Spectroscopy
AFS	Atomic Fluorescent Spectroscopy
ANOVA	Analysis of variance
ARBP	Athi River Basin Program
BOD	Biological oxygen demand
CBOD	Carbonaceous biochemical oxygen demand
COD	Chemical oxygen demand
CNS	Central nervous system
DO	Dissolved oxygen
EPA	Environmental protection agency
FAO	Food and Agriculture Organization.
Fig	Figure
HNO_3	Nitric acid
HCl	Hydrochloric acid
IC	Inorganic carbon
ICPMS	Inductively Coupled Plasma Mass Spectrometry
ICPOES	Inductively coupled plasma optical emission spectroscopy.
KEBS	Kenya bureau of standards
km^2	Kilometer squared
L	litre
mg/L	Milligram per litre
NEMA	National environmental management authority
OD	oxygen demand
pH	Potential of hydrogen
PNS	peripheral nervous system
pm	pentometre
ppm	Parts per million

TDS	Total dissolved solids
UNEP	United Nations Environmental Program
USA	United States of America
WHO	World Health Organization

CHAPTER ONE

INTRODUCTION

1.1 General introduction

“Heavy metals" are chemical elements with a specific gravity that is at least 5 times the specific gravity of water. Some well known toxic metallic elements with a specific gravity that is 5 or more times that of water are Cadmium, 8.65; Iron, 7.9; Lead, 11.34; and Mercury, 13.55 (Appelo and Postma, 2005). Some metals are indispensable for the support of daily life and even for sustaining life. For instance, copper, selenium and zinc are essential to maintain the metabolism of the human body (Akpabli and Drah, 2001). However, the presence of high concentrations of heavy metals in the environment is of major apprehension because of their toxicity, bioaccumulation, and threat to human life and environment. Prolonged exposure to heavy metals such as cadmium, copper, lead, nickel and zinc can cause deleterious health effects in humans (Appelo and Postma, 2005). The primary sources of heavy metal pollution are industries and mining sites (Asante *et al.,* 2005). Atmospheric routes have also introduced large quantities of heavy metals to localized area.

Industries which use raw materials containing heavy metals such as smelting industries, hides and skins processing industries, soaps, detergents and perfume producing industries end up disposing their waste in rivers thus contaminating them with heavy metals (Akpabli and Drah, 2001). Such heavy metals lead to biotoxic effects to the aquatic animals in such rivers and also to the people who utilize water from such rivers. Such effects include diarrhea, stomatitis, tremor, hemoglobinuria, rust–red colour to stool, ataxia, paralysis, vomiting and convulsion, depression, renal dysfunction, cancer, teeth staining and Alzheimer’s dementia among other many related effects (Babiker and Mohamed, 2007).

Heavy metals are priority pollutants because of their environmental persistence, biogeochemical recycling and ecological risks (Burton and Liss, 1976). Rivers are the major source of domestic and drinking water supply in the country. Freshwater fish and invertebrates also contribute towards recreation and food supply for locals and hence, bioaccumulation of heavy metals is a serious human health and environmental concern (Gibbs, 1970). The presence of heavy metals in rivers as a result of their uses in modern society is matter of ever-growing concern to politicians, authorities and the public in the Kenya. The strategy for minimization of the effects of heavy metals in waste is partly to reduce today and future environmental and human exposure to the heavy metals in the waste, partly to reduce the content of heavy metals in products marketed (Hesterberg, 1998).

1.2 Statement of the problem

Athi river is increasingly choking with uncollected garbage; human waste from informal settlements; industrial waste in the form of gaseous emissions, liquid effluence and solids waste; agrochemicals, and other wastes especially petrochemicals and metals from microenterprises – the “Juakali”; and overflowing sewers. This situation has occasioned spread of waterborne diseases, loss of sustainable livelihoods, loss of biodiversity, reduced availability and access to safe potable water, and the insidious effects of toxic substances and heavy metal poisoning which affects human productivity (Verma and Srivastava, 1990). Of major concern is the level of heavy metals in this river. Heavy metals enter the river when industrial and consumer waste, or even from the water run – off from the neighbouring mining sites drains directly to the river. These heavy metals have bio accumulated in the river sediments and in the water to dangerous lsevels which pose precarious effects to human health, aquatic life and even the environment. The common polluting heavy metals are lead, cadmium, copper, chromium, nickel, selenium and mercury (Appelo and Postma, 2005).

This actuality has been hypothesized as the core trigger to the numerous heavy metal poisoning effects noted in the Athi River area. Such effects include memory loss; increased allergic reactions, high blood pressure, depression, mood swings, irritability, poor concentration, aggressive behavior, sleep disabilities, fatigue, speech disorders, high blood pressure, vascular occlusion, neuropathy, autoimmune diseases, and chronic fatigue are just some of the many conditions resulting from exposure to such toxins. This has raised hasty concern from diverse environmental and media federations such as National Environmental Protection Agency (NEMA), United Nations Environmental Program (UNEP), Nation Media Group and the Athi River Basin Program (ARBP) among other groups.

As an endeavor to clean this river and thus condense the hypothesized disparaging effects, they have instigated various strategies. There is need to initiate intense research to ascertain the type and magnitude of heavy metal pollution in this river and mainly in the water, sediments on the river banks and in the aquatic animals which subsist in the river. Effects of these heavy metals on the inhabitants of the areas along the river need also to be determined.

1.3 Justification

Heavy metals occur as natural part of the earth's crust, and form persistent environmental contaminants since they cannot be degraded or destroyed (Babiker *et al.*, 2007). They enter the body system through food, air, and water and bio-accumulate over a period of time. In rocks, they subsist as their ores in different chemical forms, from which they are recovered as minerals. Heavy metal ores include sulphides, such as for iron, arsenic, lead, zinc, cobalt, gold, silver and nickel and oxides such as for aluminum, manganese, gold, selenium and antimony (Langmuir, 1997). Some exist and can be recovered as both sulphide and oxide ores such as iron, copper and cobalt. During mining processes, some heavy metals are left behind as tailings scattered in open and partially covered pits; some are, transported through wind and flood, creating various environmental problems (Lester and Birkett, 1999).

Generally, emission of heavy metals occurs during their mining and industrial processing activities. Heavy metals can be released into the environment by both natural and anthropogenic causes (Hesterberg, 1998). In some cases, even long after mining activities have ceased, the emitted metals continue to persist in the environment (Rajendra, *et al*., 2009). It is reported that hard rock mines operate from 515 years until the minerals are depleted, but metal contamination that occurs as a consequence of hard rock mining persist for hundreds of years after the cessation of mining operations (Burton and Liss, 1976).

Apart from mining operations, mercury is introduced into the environment through cosmetic products as well as manufacturing processes like making of sodium hydroxide. Anthropogenic sources of emission are the various industrial point sources including former and present mining sites, foundries and smelters, combustion byproducts and traffics (Lester and Birkett, 1999). Cadmium is released as a byproduct of zinc refining; lead is emitted during its mining and smelting activities, from automobile exhausts (by combustion of petroleum fuels treated with tetraethyl lead antiknock) and from old lead paints; mercury is emitted by the degassing of the earth's crust (Singh, *et al.,* 2008)

Environmental pollution by heavy metals is very prominent in areas of mining and in industrial sites where heavy metals make key raw materials. Heavy metals pollution reduces with increasing distance away from such sites (Rajendra, *et al*., 2009). In mining sites, heavy metals are leached out and in sloppy areas are carried by acid water downstream or runoff to the sea. Through mining activities, water bodies are most emphatically polluted. Water bodies are mainly polluted by heavy metals especially when industries dispose waste containing such metals in water bodies (Asante, *et al*., 2005).

Through rivers and streams, the metals are transported as either dissolved species in water or as an integral part of suspended sediments, (dissolved species in water have the greatest potential of causing the most deleterious effects). They may then be stored in river bed sediments or seep into the underground water thereby contaminating water from underground sources, particularly wells; and the extent of contamination will depend on the nearness of the well to the mining site. Wells located near mining sites have been reported to contain heavy metals at levels that exceed drinking water criteria (Hesterberg, 1998).

1.4 Objectives

1.4.1 General objective

The general objective of the study was to determine selected heavy metal pollutants in sediment, water and some physicochemical parameters in section of Athi river.

1.4.2 Specific objectives

The specific objectives of this research project were to:

1. To determine the levels heavy metals in sediments and water along Athi river.
2. To determine the levels of physicochemical parameters (pH, BOD, COD, TDS and electrical conductivity)
3. To relate the results obtained with permissible limits of environmental protection agencies like EPA, KEBS, WHO and FAO and advice accordingly.

1.4.3 Hypothesis

1. The concentration of heavy metal and the selected water quality parameters varies significantly between the different sampling stations.

2. There is variation between concentration of heavy metals in sediments and that of heavy metals in water.
3. The concentrations of heavy metals are higher than permissible limits of environmental protection agencies like EPA, KEBS, WHO and FAO.

CHAPTER TWO

LITERATURE REVIEW

2.1 Review of related work done

Mulei and Kithiia (2006) investigated on the effects of land use types on the hydrology and water quality of the Upper-Athi river basin, the results of the study indicated a downstream increase in water pollutants and water quality degradation for the three rivers investigated namely Nairobi, Mathare and Ngong rivers which form the main tributaries of Athi River. Heavy metals were detected in water samples but most of them were found to be adsorbed in the river sediments. Concentration values of 1.0 mg/L and 0.1 mg/L for Zn and Pb in water were measured but river sediments had the highest adsorption levels of 700 mg/L and 51 mg/L for Zn and Pb respectively. The dissolved metal ions in water appeared to surpass the recommended WHO and Kenya bureu of standards limits for drinking water of 5m/L and 0.01mg/L respectively. Organic pollution detected was due to frequent sewer bursts and unsewered slum areas with a five day measured value of Biological Oxygen Demand (BODs) and Chemical Oxygen Demand (COD) exhibiting an increasing trend in the three streams. A value of 7.8 mg/L and 123 mg/L in BODs were recorded in Nairobi River at Muthangari and Outering Road Bridge, respectively.

Acording to Ochieng *et al.,* 2009 enrichment factors showed elevated levels of Cd, Pb and Zn in sediment in River Sabaki and River Vevesi that were due to anthropogenic inputs through Athi River. The total dissolved metal concentration ranges for the rivers were comparable with those ranges reported in rivers in South Africa but the sediment concentrations were below those of rivers in Europe and Asia where anthropogenic addition of some of the toxic elements such as Cu, Pb and Cd is evidently higher.

Occupational environmental health associated with both industrial and domestic sewage reuse for food production in AthiRiver town Kenya has been studied. In soils the average levels of lead and cadmium were 0.44mg/g and 0.13mg/g respectively. The crops analysed were selected as root crops, leaf crops and fruits (or seed) crops. The levels of lead found in these crops were 0.06 µg/g, 0.01 µg/g and fruit 0.05 µg/g for root, leaf and fruit crops respectively. Similarly, the cadmium in root, leaf and fruit crops was 0.016 µg/g, 0.03 µg/g and 0.02 µg/g respectively (Kingsley *et al.*, 1999).

In his reseach on Analysis of the levels of heavy metals in plants, and urine samples around the Athi River region. Thuo, (1991) found out that concentrations of metals in plant leaves were found to depend on the levels in the soil, soil type and the organic matter content except for zinc. The metals in the indigenous soil appeared to be more available to plants than those in the dust. Analysis of urine samples from those working in the cement factory had relatively higher concentrations for most of the metals than those not working in the factory (controls) with lead as the only exception (Thuo, 1991).

Lead pollution was fairly high along the three rivers forming the tributeries of Nairobi river with a maximum mean value of 0.58mg/L being recorded along the Ngong River. Domestic and industrial wastes were identified as major sources of pollution. However, urban run-off and leachate from the numerous refuse pits along the rivers contribute a lot to the pollution load in these rivers (Nyikuri *et al*., 2005).

The of concentration of total suspended particulate matter and some gaseous air pollutants in Athi- river urban area showed that the concentrations of Cadmium, Lead and Copper trace metals were practically not affected by seasonal changes. This was partly attributed to their existence in probably small particle sizes for which rainfall washout had minimal or no effect. The prevailing low wind speeds did not favour the dispersion of the pollutants while the characteristic concentration patterns were linked to the production mechanisms, the dominant wind direction (Southeasterly), and the prevailing temperature and relative humidity meteorological conditions. The measured mean concentration values for total suspended particulate matter, Pb and Cd were above the long term WHO standard limits of 0.01mg/L and 0.003mg/L respectively (Mogere, 2005).

2.2 Specific heavy metal sources

The heavy metals sources can be natural and anthropogenic. Rapid population growth, urbanization, intensive agricultural and industrial production, all give rise to increased levels of heavy metal pollutants into the environment(Harrison *et al.,* 2007).

2.2.1 Cadmium

Naturally a very large amount of cadmium is released into the environment, about 25,000 tons a year. About half of this cadmium is released into rivers through weathering of rocks and some cadmium is released into air through forest fires and volcanoes (WHO, 2004). The rest of the cadmium is released through human activities, such as manufacturing. Other sources are airborne industrial contaminants, batteries, candy, ceramics, cigarette smoke, colas, , copper refineries, copper alloys, dental alloys, drinking water, electroplating, fertilizers, food from contaminated soil, fungicides, incineration of tires / rubber / plastic, instant coffee, iron roofs, processed meat, evaporated milk, motor oil, oysters, paint, pesticides, galvanized pipes, processed foods, refined grains / flours cereals, rubber, rubber carpet backing, sea foods (cod, haddock, oyster, tuna), sewage, silver polish, smelters , vending machine soft drinks, tools, vapor lamps, water (city, softened, well), welding metal (USSL, 1954).

2.2.2 Copper

Copper may occur in drinking water either by contamination of the source water used by the later system, or by corrosion of copper plumbing. Corrosion of plumbing is by far the greatest cause for concern (Alkarahi *et al*., 2009). Copper is rarely found in source water, but copper mining and smelting operations and municipal incineration may be sources of contamination. Other sources include birth control pills, congenital intoxication, copper cookware, copper pipes, dental alloys, fungicides, ice makers, industrial emissions, insecticides, swimming pools, water (city / well), welding, beer, bluefish, bone meal, chocolate, corn oil, , lamb, liver, lobster, margarine, milk, mushrooms, nuts, oysters, perch, seeds, shellfish, soybeans, wheat germ and yeast (WHO, 2004).

2.2.3 Lead

Currently lead is usually found in ore with zinc, silver and copper and it is extracted together with these metals. The main lead mineral is Galena (PbS) and there are also deposits of cerrussite and anglesite which are mined (BrodnjakVončina, *et al.,* 2002). Galena is mined in Australia, which produces 19% of the world's new lead, followed by the USA, China, Peru' and Canada. Some is also mined in Mexico and West Germany. World production of new lead is 6 million tonnes a year, and workable reserves total are estimated 85 million tonnes, which is less than 15 year's supply (Lester and Birkett, 1999). Lead occurs naturally in the environment. However, most lead concentrations that are found in the environment are a result of human activities. Due to the application of lead in gasoline an unnatural lead cycle has consisted. In car engines lead is burned, so that lead salts (chlorines, bromines, and oxides) will originate. Lead can also come through ash, auto exhaust, battery manufacturing, bone meal, canned fruit and juice, car batteries, cigarette smoke, coal combustion, cosmetics, eating utensils, electroplating, household dust, glass production, hair dyes, industrial emissions, lead pipes, lead glazed earthenware pottery, metal polish, paint, pencils, pesticides, produce near roads, putty, rain water, PVC containers, refineries, smelters, snow, tin cans with lead solder sealing (such as juices, vegetables), tobacco, toothpaste and toys (Kotti *et al.,* 2005).

2.2.4 Chromium

The two largest sources of chromium emission in the atmosphere are from the chemical manufacturing industry and combustion of natural gas, oil, and coal (Vončina *et al.,* 2007). Other sources of chromium exposure are as follows: cement producing plants, since cement contains chromium; the wearing down of asbestos brake linings from automobiles or similar sources of wind carried asbestos, since asbestos contains chromium; incineration of municipal refuse and sewage sludge; exhaust emission from catalytic converters in automobiles; emissions from air conditioning cooling towers that use chromium compounds as rust inhibitors; wastewaters from electroplating, leather tanning, and textile industries when discharged into lakes and rivers; and solid wastes from the manufacture of chromium compounds, or ashes from municipal incineration, when disposed of improperly in landfill sites (Kotti *et al*., 2005).

Some consumer products that contain small amounts of chromium are: some inks, paints, and paper; some rubber and composition floor coverings; some leather materials; magnetic tapes; stainless steel and a few other metal alloys; and some toner powders used in copying machines (Lester and Birkett, 1999).

2.2.5 Nickel

Nickel is one of many trace metals widely distributed in the environment, being released from both natural sources and anthropogenic activity, with input from both stationary and mobile sources. It is present in the air, water, soil and biological material. Natural sources of atmospheric nickel levels include wind-blown dust, derived from the weathering of rocks and soils, volcanic emissions, forest fires and vegetation. Nickel finds its way into the ambient air as a result of the combustion of coal, diesel oil and fuel oil, the incineration of waste and sewage, and miscellaneous sources (Clayton.and Pattys,1994).

Environmental sources of lower levels of nickel include tobacco, dental or orthopedic implants, stainless steel kitchen utensils and inexpensive jewellery . It has been estimated that each cigarette contains nickel in a quantity of 1.1 to 3.1 μg and that about 10-20% of the nickel inhaled is present in the gaseous phase. According to some authors, nickel in tobacco smoke may be present in the form of nickel carbonyl, a form which is extremely hazardous to human health (Bencko, 1983).

2.3 Health effects of heavy metals

Heavy metals including both essential and non essential elements have a particular significance in toxicology since they are highly persistent and all have potential to be toxic to living organisms. Our bodies require trace amounts of some heavy metals, including copper, zinc, and others, but even these can be dangerous at high levels. Other heavy metals such as mercury, lead, arsenic, and cadmium have no known benefits, and their accumulation over time can cause serious health effects (Lester and Birkett, 1999). There are over 20 different known heavy metal toxins that can impact human health. Heavy metals are in the foods we eat, water we drink, and the air we breathe. The five heavy metals that are focused in this research cause extreme damage to the human body. These are nickel, chromium, lead, cadmium and copper. Contact with nickel compounds can cause a variety of adverse effects on human health, such as nickel allergy in the form of contact dermatitis, lung fibrosis, cardiovascular and kidney diseases and cancer of the respiratory tract (Mcgregor *et al.*, 2000). Chronic noncancer health effects may result from long-term exposure to relatively low concentrations of pollutants. Acute health effects generally result from short-term exposure to high concentrations of pollutants and they manifest as a variety of clinical symptoms (nausea, vomiting, abdominal discomfort, diarrhea, visual disturbance, headache, giddiness, and cough). The most common type of reaction to nickel exposure is a skin rash at the site of contact. Skin contact with metallic or soluble nickel compounds can produce allergic dermatitis. Data indicate that women have greater risk for dermatitis, possibly due to a more frequent contact with nickel-containing items: jewelry, buttons, watches, zippers, coins, certain shampoos and detergents, pigments etc. (Vahter *et al.*, 2002). About 10% of women and 2% of men in the population are highly sensitive to nickel. Sensitization to the metal is generally caused by direct and prolonged skin contact with items that release nickel ions.

The health hazards associated with exposure to chromium are dependent on its oxidation state the hexavalent form being the most toxic compared to chromium (III).Chronic inhalation of hexavalent chromium has been shown to increase risk of lung cancer and may also damage the small capillaries in kidneys and intestines (Lester and Birkett, 1999). Other adverse effects of the hexavalent form on the skin may include ulcerations, dermatitis, allergic skin reactions, skin irritation or ulceration, allergic contact dermatitis, occupational asthma, nasal irritation and ulceration, perforated nasal nosebleed, respiratory irritation, nasal cancer, eye irritation and damage, perforated eardrums, kidney damage, liver damage, pulmonary congestion and edema, and erosion and discoloration of one's teeth. Prolonged industrial exposure to chromium compounds can cause chronic bronchitis and sinusitis (Kotti *et al.*, 2005). Chromium is an acknowledged human carcinogen. Long term effects include increased risk of lung, sinus, and gastrointestinal cancers (Verma and Srivastava, 1990).

Lead on the other hand is a Nero toxin meaning that it is a poison to every living thing on the planet. It is not in any food chain though lead is asymptomatic meaning that not everyone will have the same symptoms or effects. At low levels of exposure to lead, the main health effects are observed in the nervous system; specifically the peripheral and central nervous system (PNS and CNS). Exposure to lead may have subtle effects on the intellectual development of infants and children. Health effects associated with exposure to high levels of lead include vomiting, diarrhea, convulsions, coma or even death. Other effects of Lead include headache, fatigue, nausea, abdominal cramps, joint pain, metallic taste in the mouth, vomiting and constipation or bloody diarrhea (Vončina *et al*., 2007).

The potential for cadmium to harm your health depends upon the form of cadmium present, the amount taken into your body, and whether the cadmium is eaten or breathed. Breathing air with very high levels of cadmium can severely damage the lungs and may cause death. Breathing air with lower levels of cadmium over long periods of time (for years) results in a buildup of cadmium in the kidney, and if sufficiently high, may result in kidney disease (WHO, 2004). Other effects that may occur after breathing cadmium for a long time are lung damage and fragile bones. Some recent studies indicate that a glomerular pattern of dysfunction may also be an early effect of cadmium exposure, as evidenced by an increased excretion of high molecular weight proteins. Later effects on renal function are manifested by aminoaciduria, phosphaturia and glucosuria (Trygg and Wold, 2002). Cadmium is highly toxic and responsible for several cases of poisoning through food. Small quantities of cadmium cause adverse changes in the arteries of human kidney. It replaces zinc biochemically and causes high blood pressures, kidney damage etc (Vahter *et al*., 2002) .

According to the (WHO) and the (FAO), the intake of copper should not exceed 12mg/day for adult males and 10mg/day for adult females (WHO, 2004). Excessive amounts of copper in the body causes liver damage, often with fatal consequences. The symptoms of acute copper poisoning include nausea, vomiting and abdominal and muscle pain, diarrhea, stomach cramps, and nausea. Unlike other heavy metals, acute copper poisoning is a rare event (Lester and Birkett, 1999).

Copper Toxicity or excessive copper levels have also been associated with physical and mental fatigue, sleep disorders, depression and other mental problems, schizophrenia, learning disabilities, hyperactivity, mood swings and general behavioral problems, memory and concentration problems, some dementias, postpartum depression, increased risk of infections, vascular degeneration, hemangiomas, headaches, arthritis, spinal / muscle / joint aches and pains, and several types of cancer (Alkarahi *et al*., 2009).

2.4 Bioaccumulation of heavy metals

Bio-monitoring as indicative of the presence of pollutants is defined as the use of bio–organisms to obtain quantitative information on certain characteristics of the biosphere (Wolterbeek, 2002). Development of indicators of exposure is thus critical to evaluate risk from heavy metals and they are necessary as early warning systems for environmental deterioration. It has the conceptual advantage that biotic responses may provide more direct measures of the biological significance of environmental contaminants (Markert, 1993). In the case of river metal contamination, utilizing macrophytes for bio-monitoring may provide a relatively quick method for determining the spatial extent of metal contamination throughout a large area without the expense. Further, ecological risk assessments call for an understanding of the biological impacts of metal contamination, for which bio-monitoring may provide more relevant information than do metal concentrations alone. Plants play an important role in metal removal via filtration, adsorption, cation exchange, and through plant–induced chemical changes in the rhizosphere (Dunbabin and Bowmer, 1992).

There is evidence that plants can accumulate heavy metals in their tissues. The use of these plants gave birth to a new technology termed phytoremediation, which is one of the most successful techniques that can be used to remove heavy metals. Phytoremediation is the use of plants to remove heavy metals or pollutants from the environment or to render harmless, hazardous material present in the water or soil. The only problem with phytoremediation is that it needs to be done over a long period of time to clean contaminated soil or water properly. Phytoremediation of metal–contaminated water is readily achieved by the use of aquatic and terrestrial plants due to the non–bioavailability of target elements to other organisms. Terrestrial plants must first solubilize the target element in the rhizosphere and then have the ability to transport it to the aerial parts. There are no such problems in plants that grow naturally or are made to grow in or on an aqueous medium.

Macrophytes may concentrate metals in their biomass to a higher level than their ambient environments, and “give a more time–integrated picture of contaminant concentrations” (Markert, 1993). Therefore, macrophytes can be used in ecological surveys as in–situ bio-indicators of water quality due to their ability to accumulate chemicals. Rooted submerged macrophytes taking up pollutants represent the bio-available free–contaminant concentrations in the sediment interstitial water, as well as the contamination in the water column. They have been identified as a potentially useful group for bioremediation and biological monitoring (Salt and kramer, 1998).

2.5 Oxygen Demand

The presence of a sufficient concentration of dissolved oxygen (DO) is critical to maintaining the aquatic life and aesthetic quality of streams and lakes. Determining how organic matter affects the concentration of DO in a river is integral to water quality management. Oxygen demand is a measure of the amount of oxidizable substances in a water sample that can lower DO concentrations.

2.5.1 Biochemical Oxygen Demand (BOD)

The decay of organic matter in water is measured as biochemical or chemical oxygen demand (Kotti *et al.*, 2005). Biochemical oxygen demand, is a measure of the quantity of oxygen consumed by microorganisms during the decomposition of organic matter. BOD is the most commonly used parameter for determining the oxygen demand on the receiving water of a municipal or industrial discharge. BOD can also be used to evaluate the efficiency of treatment processes, and is an indirect measure of biodegradable organic compounds in water (Delzer and McKenzie, 2003). The test for BOD is a bioassay procedure that measures the oxygen consumed by bacteria from the decomposition of organic. The change in DO concentration is measured over a given period of time in water samples at a specified temperature.

It is important to be familiar with the correct procedures for determining OD concentrations before making BOD measurements (WHO, 2004). Biochemical oxygen demand is measured in a laboratory environment. BOD is typically divided into two parts carbonaceous oxygen demand and nitrogenous oxygen demand. Carbonaceous biochemical oxygen demand (CBOD) is the result of the breakdown of organic molecules such a cellulose and sugars into carbondioxide and water. Nitrogenous oxygen demand is the result of the breakdown of proteins. Proteins contain sugars linked to nitrogen (Burton and Liss, 1976). After the nitrogen is "broken off", it is usually in the form of ammonia, which is readily converted to nitrate in the environment. The conversion of ammonia to nitrate requires more than four times the amount of oxygen as the conversion of an equal amount of sugar to carbondioxide and water (Appelo and Postma, 2005).

When nutrients such as nitrate and phosphate are released into the water, growth of aquatic plants is stimulated. Eventually, the increase in plant growth leads to an increase in plant decay and a greater "swing" in the diurnal dissolved oxygen level. The result is an increase in microbial populations, higher levels of BOD, and increased oxygen demand from the photosynthetic organisms during the dark hours. This results in a reduction in DO concentrations, especially during the early morning hours just before dawn. In addition to natural sources of BOD, such as leaf fall from vegetation near the water's edge, aquatic plants, and drainage from organically rich areas like swamps and bogs, there are also anthropogenic (human) sources of organic matter. If these sources have identifiable points of discharge, they are called point sources. The major point sources, which may contribute high levels of BOD, include wastewater treatment facilities, pulp and paper mills, and meat and food processing plants. Organic matter also comes from sources that are not easily identifiable, known as nonpoint sources. Typical nonpoint sources include agricultural runoff, urban runoff, and livestock operations. Both point and nonpoint sources can contribute significantly to the oxygen demand in a lake or stream if not properly regulated and controlled.

2.5.2 Chemical Oxygen Demand(COD)

Chemical oxygen demand (COD) is the amount of oxygen needed to consume the organic and inorganic materials. The industrial and municipal waste water effluents may contain very high amounts of organic matter and if discharged into natural water bodies, it can cause complete depletion of dissolved oxygen leading to the mortality of aquatic organisms (Clair *et al.*, 2003) There exists a definite correlation between the COD and BOD under certain conditions and by determining the COD, the information about the BOD of the water/waste water can be derived. Most applications of COD determine the amount of organic pollutants found in surface water (e.g. lakes and rivers) or wastewater, making COD a useful measure of water quality. It is expressed in milligrams per liter (mg/L), which indicates the mass of oxygen consumed per liter of solution or may express the units as parts per million (ppm). Chemical oxygen demand is a vital test for assessing the quality of effluents and waste waters prior to discharge. The COD is used for the monitoring and control of discharges, and for assessing treatment plant performance. The standard test for COD involves digesting the sample with strong Sulphuric acid solution in the presence of chromium and silver salts. Chemical Oxygen demand testing assesses all chemically oxidizable substances and can be directly related to the true oxygen demand imposed by the effluent if released into the environment. Because each organic compound differs in the amount of oxygen necessary for complete oxidization, the COD test reflects the effect of an effluent on the receiving stream more directly than measurement of carbon content (Moore *et al.*, 1951).

2.6 Total dissolved solids

Total Dissolved Solids (TDS) is a measure of the combined content of all inorganic and organic substances contained in a liquid in: molecular, ionized or micro-granular (colloidal sol) suspended form. Generally the operational definition is that the solids must be small enough to survive filtration through a sieve the size of two micrometer. Total dissolved solids are normally discussed only for freshwater systems, as salinity comprises some of the ions constituting the definition of TDS (Boyd, 1999).. The principal application of TDS is in the study of water quality for streams, rivers and lakes, although TDS is not generally considered a primary pollutant (e.g. it is not deemed to be associated with health effects) it is used as an indication of aesthetic characteristics of drinking water and as an aggregate indicator of the presence of a broad array of chemical contaminants.

Primary sources for TDS in receiving waters are agricultural and residential runoff, leaching of soil contamination and point source water pollution discharge from industrial or sewage treatment plants. The most common chemical constituents are calcium, phosphates, nitrates, sodium, potassium and chloride, which are found in nutrient runoff, general storm water runoff and runoff from snowy climates where road de-icing salts are applied. The chemicals may be cations, anions, molecules or agglomerations on the order of one thousand or fewer molecules, so long as a soluble micro-granule is formed (Ela, 2007). More exotic and harmful elements of TDS are pesticides arising from surface runoff. Certain naturally occurring total dissolved solids arise from the weathering and dissolution of rocks and soils. The United States has established a secondary water quality standard of 500 mg/l to provide for palatability of drinking water (Boyd, 1999).

Total dissolved solids are differentiated from total suspended solids (TSS), in that the latter cannot pass through a sieve of two micrometers and yet are indefinitely suspended in solution. The term "settleable solids" refers to material of any size that will not remain suspended or dissolved in a holding tank not subject to motion, and excludes both TDS and TSS (DeZuane, 1997). Settleable solids may include larger particulate matter or insoluble molecules. High TDS levels generally indicate hard water, which can cause scale buildup in pipes, valves, and filters, reducing performance and adding to system maintenance costs. These effects can be seen in aquariums, spas, swimming pools, and reverse osmosis water treatment systems. Typically, in these applications, total dissolved solids are tested frequently, and filtration membranes are checked in order to prevent adverse effects.

In the case of hydroponics and aquaculture, TDS is often monitored in order to create a water quality environment favorable for organism productivity. For freshwater oysters, trouts, and other high value seafood, highest productivity and economic returns are achieved by mimicking the TDS and pH levels of each species' native environment. For hydroponic uses, total dissolved solids is considered one of the best indices of nutrient availability for the aquatic plants being grown.

Because the threshold of acceptable aesthetic criteria for human drinking water is 500 mg/l, there is no general concern for odor, taste, and color at a level much lower than is required for harm. A number of studies have been conducted and indicate various species' reactions range from intolerance to outright toxicity due to elevated TDS. The numerical results must be interpreted cautiously, as true toxicity outcomes will relate to specific chemical constituents. Nevertheless, some numerical information is a useful guide to the nature of risks in exposing aquatic organisms or terrestrial animals to high TDS levels. Most aquatic ecosystems involving mixed fish fauna can tolerate TDS levels of 1000 mg/l (Boyd, 1999

LD50 is the concentration required to produce a lethal effect on 50 percent of the exposed population. Daphnia magna, a good example of a primary member of the food chain, is a small planktonic crustacean, about 0.5 millimeters in length, having an LD50 of about 10,000 mg/L TDS for a 96 hour exposure (Hogan *et al*., 1973).

Spawning fishes and juveniles appear to be more sensitive to high TDS levels. For example, it was found that concentrations of 350 mg/l TDS reduced spawning of Striped bass (Morone saxatilis) in the San Francisco Bay-Delta region, and that concentrations below 200 mg/l promoted even healthier spawning conditions. In the Truckee River, EPA found that juvenile Lahontan cutthroat trout were subject to higher mortality when exposed to thermal pollution stress combined with high total dissolved solids concentrations (Hogan and Papineu 1987)

For terrestrial animals, poultry typically possess a safe upper limit of TDS exposure of approximately 2900 mg/l, whereas dairy cattle are measured to have a safe upper limit of about 7100 mg/l. Research has shown that exposure to TDS is compounded in toxicity when other stressors are present, such as abnormal pH, high turbidity, or reduced dissolved oxygen with the latter stressor acting only in the case of animalia (Hogan *et al.*, 1973).

2.7 Electrical conductivity

Electrical conductivity: the property of a substance which enables it to serve as a channel or medium for electricity. Salty water conducts electricity more readily than purer water.

Therefore, electrical conductivity is routinely used to measure salinity. The types of salts (ions) causing the salinity usually are chlorides, sulphates, carbonates, sodium, magnesium, calcium and potassium. While an appropriate concentration of salts is vital for aquatic plants and animals, salinity that is beyond the normal range for any species of organism will cause stress or even death to that organism. Salinity also affects the availability of nutrients to plant roots (John, 1990).

Depending on the type of salts present, salinity can increase water clarity. At very high concentrations, salts make water denser, causing salinity gradations within an unmixed water column and slightly increasing the depth necessary to reach the water table in groundwater bores. Electrical conductivity in waterways is affected by land use, such as agriculture (irrigation), urban development (removal of vegetation, sewage and effluent discharges), industrial development (industrial discharges), run-off, groundwater inflows, temperature, evaporation and dilution. Contamination discharges can change the water's electrical conductivity in various ways. For example, a failing sewage system raises the conductivity because of its chloride, phosphate, and nitrate content, but an oil spill would lower the conductivity. The discharge of heavy metals into a water body can raise the conductivity as metallic ions are introduced into the waterway (Lawrence and Don, 1994).

The basic unit of measurement of electrical conductivity is microSiemens per centimetre (µS/cm) or deciSiemens per meter (dS/m). The total dissolved solids (or TDS) content of a water sample, in milligrams per litre (mg/L), is also a measure of salinity. The sample's electrical conductivity can be converted to TDS. The electrical conductivity of water samples should be measured on the spot at the waterbody. Measurement can be delayed by up to 1 month if the sample is refrigerated (but NOT frozen) immediately on being taken, and if the sample bottle is filled completely, with no air gap at the top (John, 1990).

2.8 pH (potential of hydrogen)

pH which is also referred to as the potential of hydrogen is a measure of the acidity or basicity of an aqueous solution. Pure water is neutral, with a pH close to 7.0 at 25 °C (77 °F). Solutions with a pH less than 7 are said to be acidic and solutions with a pH greater than 7 are basic or alkaline. pH measurements are important in medicine, biology, chemistry, agriculture, forestry, food science, environmental science, oceanography, civil engineering and many other applications (Bates, 1973) .

A low pH indicates a high concentration of hydroxonium ions, while a high pH indicates a low concentration. However, pH is not precisely p[H], but takes into account an activity factor. This represents the tendency of hydrogen ions to interact with other components of the solution, which affects among other things the electrical potential read using a pH meter. As a result, pH can be affected by the ionic strength of a solution—for example, the pH of a 0.05 M potassium hydrogen phthalate solution can vary by as much as 0.5 pH units as a function of added potassium chloride, even though the added salt is neither acidic nor basic (Isaac, 1956).

Hydrogen ion activity coefficients cannot be measured directly by any thermodynamically sound method, so they are based on theoretical calculations. Therefore, the pH scale is defined in practice as traceable to a set of standard solutions whose pH is established by international agreement (Bates, 1973). Primary pH standard values are determined by the Harned cell, a hydrogen gas electrode, using the Bates–Guggenheim Convention.

Solubility of heavy metals in surface water is predominately controlled by the water pH (Osmond *et al.*, 1995), the river flow (Neal *et al.*, 2000b; Iwashita and Shimamura, 2003) and the redox environment of the river system (Osmond *et al.*, 1995; Iwashita and Shimamura, 2003). A lower pH increases the competition between metal and hydrogen ions for binding sites. A decrease in pH may also dissolve metal carbonate complexes, releasing free metal ions into the water column (Osmond *et al.*, 1995).

2.9 Methods of heavy metals analysis

ICP-MS (Inductively Coupled Plasma-Mass Spectrometry), Atomic Emission Spectroscopy (AES), Atomic Fluorescent Spectroscopy (AFS) and Atomic Absorption Spectroscopy (AAS) (Carter, 1993).

2.9.1 Inductively Coupled Plasma Mass Spectrometry

Inductively coupled Plasma has been commercially available for over 40 years and is used to measure trace metals in a variety of solutions ICP can be performed using various techniques, two of which are inductively coupled plasma optical emission spectroscopy (ICPOES) and inductively coupled plasma mass spectrometry (ICPMS) (Carter, 1993). Sample solutions are introduced into the ICP as an aerosol that is carried into the center of the plasma (superheated inert gas). The plasma desolvates the aerosol into a solid, vaporizes the solid into a gas, and then dissociates the individual molecules into atoms. This high temperature source (plasma) excites the atoms and ions to emit light at particular wavelengths, which correspond to different elements in the sample solution. The intensity of the emission corresponds to the concentration of the element detected (Montaser, 1998).

2.9.2 Atomic Emission Spectroscopy (AES)

Atomic emission spectroscopy (AES) uses quantitative measurement of the optical emission from excited atoms to determine analyte concentration. Analyte atoms in solution are aspirated into the excitation region where they are desolvated, vaporized, and atomized by a flame, discharge, or plasma (Evans and Giglio, 2000). These high temperature Atomization sources provide sufficient energy to promote the atoms into high energy levels. The atoms decay back to lower levels by emitting light (Carter,1993). Since the transitions are between distinct atomic energy levels, the emission lines in the spectra are narrow. The spectra of multi-elemental samples can be very congested, and spectral separation of nearby atomic transitions requires a high resolution spectrometer.

Since all atoms in a sample are excited simultaneously, they can be detected simultaneously, and is the major advantage of AES compared to atomic absorption(AA) spectroscopy (EURACHEM, 2003).

2.9.3 Atomic Fluorescence Spectroscopy (AFS)

This technique incorporates aspects of both atomic absorption and atomic emission. Like atomic absorption, ground state atoms created in a flame are excited by focusing a beam of light into the atomic vapor. Instead of looking at the amount of light absorbed in the process, however, the emission resulting from the decay of the atoms excited by the source light is measured (Carter, 1993). The intensity of this "fluorescence" increases with increasing atom concentration, providing the basis for quantitative determination. The source lamp for atomic fluorescence is mounted at an angle to the rest of the optical system, so that the light detector sees only the fluorescence in the flame and not the light from the lamp itself. It is advantageous to maximize lamp intensity since sensitivity is directly related to the number of excited atoms which in turn is a function of the intensity of the exciting radiation (EURACHEM, 2003).

2.9.4 Atomic Absorption spectroscopy (AAS)

Atomic absorption spectroscopy (AAS) is a spectro-analytical procedure for the qualitative and quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state. The technique is used for determining the concentration of a particular element (the analyte) in a sample to be analyzed. AAS can be used to determine over 70 different elements in solution or directly in solid samples. The ease and speed at which precise and accurate determinations can be made with this technique have made atomic absorption one of the most popular methods for the determination of metals.

Principles of operation

The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample. It requires standards with known analyte content to establish the relation between the measured absorbance and the analyte concentration and relies therefore on Beer-Lambert Law (Appelo and Postma, 2005). The electrons of the atoms in the atomizer can be promoted to higher orbitals (excited state) for a short period of time (nanoseconds) by absorbing a defined quantity of energy (radiation of a given wavelength). This amount of energy, that is wavelength, is specific to a particular electron transition in a particular element. In general, each wavelength corresponds to only one element, and the width of an absorption line is only of the order of a few picometers (pm), which gives the technique its elemental selectivity. The radiation flux without a sample and with a sample in the atomizer is measured using a detector, and the ratio between the two values (the absorbance) is converted to analyte concentration or mass using BeerLambert Law (Lester and Birkett, 1999).

Instrumentation

The block diagram of the instrumentation involved in AAS is shown in Figure 2.1

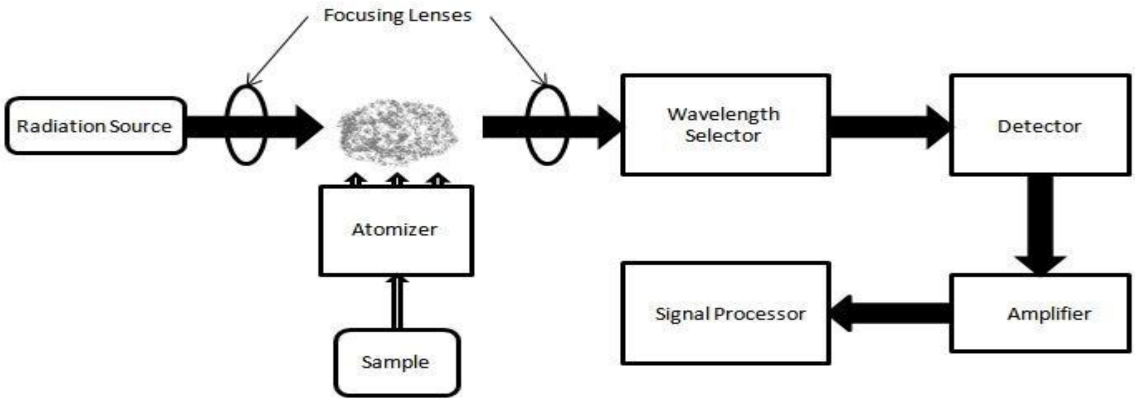

Figure 2. 1: Atomic absorption spectrometer block diagram

Light source

The light source is usually a hollow cathode lamp of the element that is being measured. Lasers are also used in research instruments. Since lasers are intense enough to excite atoms to higher energy levels, they allow AA and atomic fluorescence measurements in a single instrument. The disadvantage of these narrowband light sources is that only one element is measurable at a time (Langmuir, 1997).

Atomizer

Atomic absorption spectroscopy requires that the analyte atoms be in the gas phase. Ions or atoms in a sample must undergo desolvation and vaporization in a high temperature source such as a flame or graphite furnace. Flame AA can only analyze solutions, while graphite furnace AA can accept solutions, slurries, or solid samples (Appelo and Postma, 2005). Flame AA uses a slot type burner to increase the path length, and therefore to increase the total absorbance. Sample solutions are usually aspirated with the gas flow into a nebulizing/mixing chamber to form small droplets before entering the flame (U.S EPA, 1983).

The graphite furnace has several advantages over a flame. It is a much more efficient atomizer than a flame and it can directly accept very small absolute quantities of sample. It also provides a reducing environment for easily oxidized elements. Samples are placed directly in the graphite furnace and the furnace is electrically heated in several steps to dry the sample, ash organic matter, and vaporize the analyte atoms (Lester and Birkett, 1999). Light separation and detection AA spectrometers use monochromators and detectors for UV and visible light. The main purpose of the monochromator is to isolate the absorption line from background light due to interferences. Simple dedicated AA instruments often replace the monochromator with a band pass interference filter. Photomultiplier tubes are the most common detectors for AA spectroscopy (Appelo and Postma, 2005).

Advantages and disadvantages of AAS

Atomic absorbtion spectroscopy present superior advantages over the other techniques notably, solutions, slurries and solid samples can be analyzed much more efficient atomization, high sensitivity [10-10g (flame), 10-14g (non-flame)], smaller quantities of sample (typically 5 – 50 mL), provides a reducing environment for easily oxidized elements, good accuracy (Relative error 0.1 ~ 0.5 %), and Low detection limits. In addition the techniques has a small turnaround time; of the order of few seconds.

However this technique has a number of demerits which include its low precision, requires high level of operator skill, a resonance line source is required for each element to be determined and its high cost of operation which makes it expensive. Due to its simplicity, accuracy and sensitivity among other advantages, AAS will be preferred to the other analytical techniques in this research.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study area

Athi River forms part of Athi-Galana River which is the second longest river in Kenya (after the Tana River). It has a total length of 390 km, and drains a basin area of 70,000 km^2. The river rises in 1° 42' S. as Athi River and enters the Indian Ocean as Galana River (Asante *et al*., 2005). It flows across the Kapote and Athi plains, through the Athi River town, takes a northeast direction and is met by the Nairobi River. Near Thika it forms the Fourteen Falls and turns south-southeast under the wooded slopes of the Yatta ridge, which shuts in its basin on the east. Apart from the numerous small feeders of the upper river, almost the only tributary of significance is the Tsavo River, from the east side of Kilimanjaro, which enters in about 3° S. It turns east, and in its lower course, known as the Sabaki (or Galana), traverses the sterile quartz land of the outer plateau. The valley is in parts low and flat, covered with forest and scrub, and containing small lakes and backwaters connected with the river in the rains. Diring the rainy season the stream, which rises as much as 9 meters. in places, is deep and strong and of a turbid yellow colour; but navigation is interrupted by the Lugard falls, which is actually a series of rapids. Onwards it flows east and enters the Indian Ocean in 30 12' S., just north of Malindi (Akpabli, and Drah, 2001).

This river has numerous uses not only to the habitats of areas around the river banks but also to the industrial sector. For these habitats, the river is useful as a source of water for agricultural irrigation and domestic uses. For industrial purpose, it is used as a major solvent for chemicals; it is also used as coolant especially in the smelter industries. It is used for large scale production of horticultural products (Asante *et al.*, 2005). The river flows through the Tsavo East National Park and attracts diverse wildlife, including hippopotamus and crocodiles.

Athi-Sabaki River basins in general experience two rainfall seasons controlled by the Southern and Northern monsoons (Ojany and Ogendo, 1986). The Southern monsoon is associated with the long rains, which occur between March and June. However, in the Kenya highlands the peak rainfall occurs in April. The Northern monsoon is associated with the short rains that occur in the period between November and December with the peak rainfall occurring in November. However, there are often large inter-annual variations in rainfall, partly due to *El-Nino* and *La-Nina* southern oscillation phenomena. While in Central Kenya highlands the annual rainfall is of the order 1500 mm compared North coast which is in the order 900 mm per annum.

The Athi River basin harbors two of the main urban and industrial and agricultural areas within Kenya.. These are, Nairobi city on the upper catchment areas, which is the heart of industrial activities in Kenya. The second one is Malindi in the southeastern outlet of the basin. In between, there are various economic activities, some of which are potential sources of pollutants. High concentration levels of total suspended particulate matter within the urban commercial area were associated with increased traffic volume.This was in addition to long range transport of the pollutants from Industrial heating processes and power generation at the beginning of industrial operations. The upper catchment area is extensively used for urban settlement, transport and industrial activities while in the southeastern parts it is heavily used for agricultural production especially livestock keeping. The contribution of these land use activities to pollutants generation and hence water pollution and quality degradation is quite enormous. The map of the study area is shown in Figure 1.1.

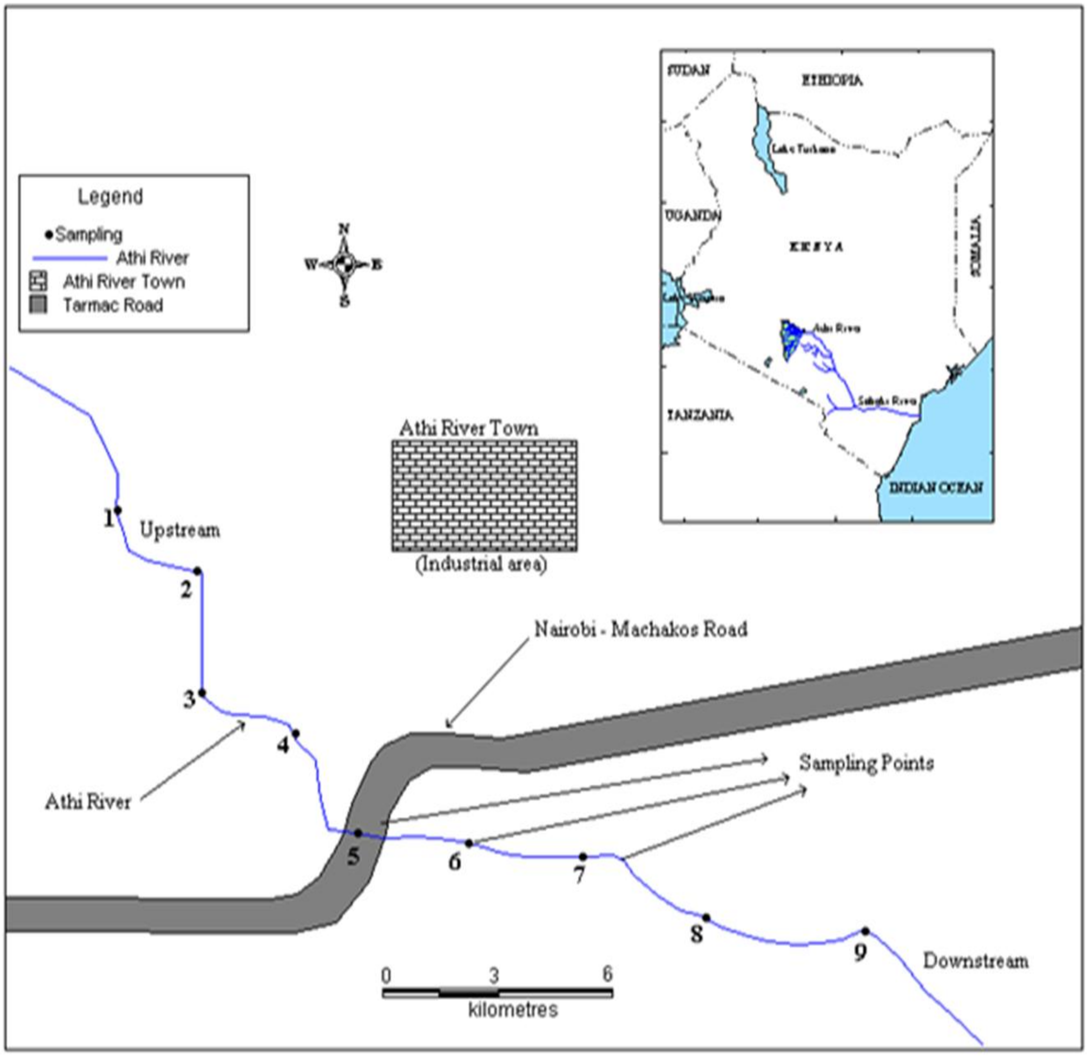

Figure 3. 1: Map of the study area

3.2 Chemicals and reagents

The following are the reagents were used. All the reagents used were analytical grade (A.G):

- Phosphate buffer solution
- Magnesium sulphate, Calcium chloride, Ferric chloride, potassium dichromate, Mercuric Sulphate, Potassium hydrogen phthalate (KHP)
- Sulphuric acid, hydrochloric acid and sodium hydroxide solution.
- Glucoseglutamic acid solution.
- Sample dilution water
- Ferroin indicator solution
- Standard ferrous ammonium sulphate (FAS), titrant

3.3 Materials/Apparatus

- AAS (MA 1700 Atomic Absorption Spectrophotometer)
  Wavelength range: 170nm-900nm. Manufacture Guangzhou Maya equipment co ltd.
- pH Meter (HK-3C Table Model PH Meter (Manufacturer, shenzhen datron electronics co.)
- TDS Meter (Hanna conductivity/TDS meter model HI 9835)
- Conductivity meter (Probe: HI 76300 platinum 4-ring) (manufacture Hanna Hanna labwear)

- Thermometer (digital water Thermometer KT400 (China (Mainland)) manufacture shenzhen datron electronics co.
- BOD bottles, 300 ml, and pointed ground glass stoppers.
- Water bath.
- Reflux flasks, consisting of 250 mL flask with flat bottom and with 24/29 ground glass neck
- Condensers, 24/29 and 30 cm jacket Leibig or equivalent with 24/29 ground glass joint, or air cooled condensers, 60 cm long, 18 mm diameter, 24/29 ground glass joint.
- Hot plate.
- Soil augar.

3.4Sampling

Samples of water and sediments were collected from Athi River, Kenya from samling areas shown in Figure 1.1. The river is located in the heavily industrial region and receives effluents from the .industries. Water was collected for determination of physicochemical parameters and heavy metal contaminations. The sediments were collected for heavy metal contaminations.

3.5 Sample collection

Nine sampling sites in the Athi River ecosystem were selected (S1 – S9). Sediments were collected from targeted sites of Athi River banks, that is, at intervals of three kilometers. Five sediment samples were collected from each site with a 6.5 cm diameter corer to a depth of about 15 centimeters and placed into distinct polythene bags and labeled according to the site of collection. These samples were kept in a deep freezer awaiting analysis. Five water samples from each site were collected into 50 ml acid leached plastic bottles which were then labeled according to the site of collection. Exactly 2ml of conc. nitric acid was added to the water samples to inhibit any process which could change the form of the heavy metals. In-situ measurement of temperature and pH was determined intrusively with appropriate methods. Five water samples from the sampling points were also collected for COD and BOD determinations; they were analyzed within 48 hours of collection to avoid oxygen degradation.

3.6 Preparation of standards

A stock solution of 1000 mg/L containing Pb^{2+}, Cr^{2+}, Cu^{2+}, Cd^{2+} and Ni^{2+} were prepared. They were prepared by dissolving 1.59g, 3.05g,2.67g, 2.1g and 2.103g of $Pb(NO_3)_2$, $CrCl_2$, $CuCl_2$, $Cd(NO_3)_2$ and $Ni(NO_3)_2$, respectively in distilled water. Standards of 0, 2, 3, 4, and 5 mg/L for each metal ion were prepared and their absorbance determined using AAS, from which calibration curve was plotted.

3.7 Sample preparation and experimental procedures

3.7.1 Sediment samples for heavy metal determination

The sediment samples were dried in an oven at 80°C for 24 hours. The dried sediment samples were then ground using pestle and mortar till the desired fineness was achieved; this was be mainly to increase the surface area for extraction of the heavy metals from the sediment samples. The ground samples were then sieved using a sieve of mesh size 72 nm. A 0.5 g of each dry sample was weighed and placed in a clean Kjedahl flask to which

10 ml of aqua – regia solution was added, that is, a mixture of concentrated HNO_3 with concentrated HCl in the ration 1:3 was addeds The samples were digested using an electric digester with glass fume exhaust for a stretch of 2 – 3 hours. The solution was filtered using the normal filter papers (0.45 Whatman filter paper). Each of the resulting clear solution was diluted to 100 ml using distilled water in acid cleaned volumetric flasks. These solutions were ready for AAS analysis of heavy metals.

3.7.2 Water samples for heavy metal determination

Each sample was digested by adding 5ml of concentrated HNO_3 acid in 250 ml beakers. The samples were then digested by electric digester with glass fume exhaust for a stretch of 2 hours after which they were evaporated to near dryness on a hot plate then gradually cooled. After cooling, another 5ml HNO_3 was added to each sample. The solutions were then filtered using the normal filter papers. Each of the resulting clear solution was then diluted to 100 ml using distilled water in acid cleaned volumetric flasks. These solutions were ready for AAS analysis of heavy metals.

3.7.3 Water samples for BOD determination

BOD was determined as described by Sawyer and Mccarty, 1978. Samples can degrade significantly during extended storage. To minimize sample degradation, and thus avoid negative bias in the measurement of BOD, analysis of the water samples was done promptly after sample collection. In order to minimize changes in bacterial concentration. The BOD test procedure was based on DO concentration and required an accurate DO determination. The procedure presented below incorporates the amperometric method for determining DO concentration.

Pre – analysis treatment

Sample dilution water was prepared 3 to 5 days before initiating BOD tests to ensure that the BOD of the dilution water was less than 0.2 mg/L. The sample pH was determined and adjusted to a pH from 6.5 to 7.5 using (H_2SO_4) for samples with pH greater than 7.5 or by use of (NaOH) if the samples had a pH less than 6.5. Sodium sulphide (Na_2SO_3) was then added to remove residual chlorine. Preliminary pretreatment was done to remove any interfering arsenic or cyanide residues. Samples were seeded appropriately after pretreatment.

BOD analysis determination.

A functional constant temperature chamber was turned on and its controlled temperature allowed to stabilize at 20°C ±1°C by use of a thermometer. Dilution was done to obtain samples with a residual DO (after 3 days of incubation) of at least 1 mg/L and a DO uptake of at least 2 mg/L. Several dilutions was done using the recommended sample volumes for the 5-day biochemical oxygen demand test. For preparation of dilution in graduated cylinders, dilution water was siphoned and seeded into a 1 to 2 L capacity cylinder. Siphoning was done slowly without bubbling, using a screw-pin on the tube to regulate the flow. The tip of the tube was kept just below the water surface as it rises. The cylinder was half filled, and a desired quantity of sample added then diluted to appropriate level. The mixed diluted sample was siphoned in three BOD bottles and stopper was tightly placed without entraining any air.

DO determination procedure

Initial DO was determined on one bottle and the other two incubated at 27°C. The final DO was determined) in duplicate after 3 days. The DO was determined as follows: BOD bottle containing the sample was drained off any liquid in the flared tip. The stopper was removed and 1 mL of $MnSO_4$ added followed by 1 mL sodium hydroxide-iodide-azide reagent and then stoppered carefully to exclude air bubbles. The solution was mixed by inverting the bottle a few times. The brown manganese hydroxide floc (white floc which indicates absence of DO) was allowed to settle approximately to half the bottle volume and then 1.0 mL concentrated H_2SO_4 was added and re-stopper. Rapid mixing of the solution was done by inverting several times until dissolution was complete. 20 mL of this standard mixture was titrated with standard sodium thiosulphate.

3.7.4 COD determination

This was determined as described by Munde *et al.,* (2006). 50 ml of sample was taken into a refluxing flask and several boiling stones was added. 0.1 g $HgSO_4$ and 5 ml of concentrated H_2SO_4 was added to the solution. To ensure that $HgSO_4$ dissolved completely, the solution was swirled slowly while adding H_2SO_4 0.1 g of Ag_2SO_4 was added to this solution. Finally 0.2 M potassium dichromate was added. Thorough mixing of the solution was confirmed by swirling the flask in a water bath to recover any volatile substances that may have escaped from the liquid state. The flask was then attached to the condenser and further cooling was done. 20 ml of H_2SO_4 was added to the solution in the flask. The solution was refluxed for 1 hour.

A blank run (using 50 ml distilled water instead of sample) was simultaneously conducted with the same procedure after cooling; the solution was transferred to an Erlenmeyer flask. The reflux flask was rinsed thrice, pouring the rinsing water to the Erlenmeyer flask. The solution was diluted to about 300 ml and about 8 drops of phenanthroline ferrous sulphate was added to the solution as an indicator. The solution was titrated against the Mohr's salt and the titer volume required for the colour change from blue-green to reddish blue was noted. The procedure was repeated for the blank run.

3.7.5 Analysis of pH

The pH was measured using a pH meter of a glass electrode. The pH meter glass electrode was previously immersed in water for several hours. The measurement was started 5 minutes after switching on the meter. The detecting unit was rinsed well with water and water gently blotted with a piece of filter paper. The pH meter was adjusted at one pH value and temperature compensation dial rotated to set to the temperature of the pH standard solution. The detecting unit was then immersed in the pH standard solution which had a pH near that of the sample solution, and after more than 2 minutes, adjusted the zero point adjustment dial so that the reading of the pH meter is set to the pH of the standard solution. The detecting unit was thoroughly washed with water, and gently blotted with a piece of filter paper. The detecting unit was then immersed in the sample solution and the pH value read.

3.7.6 Electrical conductivity

The electrical conductivity and total dissolved salts of the water was determined in a quick and inexpensive way, using portable meters. The procedure as described by Wright (2007), Water sample was collected with the container being entirely filled with the water sample to exclude air and forwarded to a laboratory for testing within 24 hours since delays and high temperatures could change the composition of salts in the sample, affecting the results. The meter was calibrated, and then rinsed with deionized water. The electrode was dipped into the sample and appropriate conductivity range selected. The electrode was moved slowly in a circle for one minute until the digital read-out stabilizes or continually jumped between two numbers. The results were recorded on results sheet.

3.8 Total dissolved solids

Samples were collected and analyzed within 36 hours to reduce biological activity, TDS meter was calibrated rinsed at its tip and with distilled water. Then meter tip was placed into water sample reading meter reading was taken. The meter was allowed to stabilize before taking reading.

3.9 AAS Analysis

Atomic absorption spectrophotometer was used in the analysis. The concentrations of the metals were determined in triplicates. The accuracy and precision of the analytical procedure were determined. A series of standards were prepared for instrumental calibration by serial dilution of working solutions (100 mg/L) prepared from analytical grade stock solutions (1000 mg/L) from BDH Poole, USA. A standard and blank sample was run after every seven samples to check for instrumental accuracy and calibration.

CHAPTER FOUR

RESULTS AND DISCUSSION

The mean heavy metal concentrations sampled in Athi River (in mg/L) was presented for the generalization and therefore evaluation and assessment to be discussed in relation to the findings, the state of this river. Physico-chemical water quality parameters; biological oxygen demand, chemical oxygen demand, total suspended solids, conductivity and pH were also analyzed and discussed.

4.1 Heavy metal analysis

4.1.1 Calibration Curves for Heavy metals

Calibration curves for each heavy metal were set to ensure the accuracy of the Atomic Absorption Spectrophotometer (AAS) and to establish that results of the determination proper were true and reliable. Standards with concentration of 1-5.mg/L were set for the calibration of the AAS. The calibration curve of well-prepared standards and an accurate AAS should present as a linear curve. The data on the calibration for copper, chromium, nickel, lead and cadmium are shown in appendix vi.

4.1.2 Heavy Metals distribution on flowing river water.

The result clearly indicated that heavy metal concentrations were commonly in the same range with world river averages as reported by Martin, and Meybeck, (1979). The trend in concentration of heavy metals along the river is as shown in the Figures 4.4 to Figure 4.6.. The data indicates that the copper concentrations are low. This could be due to low copper concentrations in inflows. Figure 4.1 representing the change in copper concentration from station 1 to station 9; the highest concentration being in station 9(0.0445mg/L) and this decreased to station 7(0.0105 mg/L) and then became gradually constant in the consecutive sampled stations. This possibly could be due to absence of discharge of the metal ions as the river discharge downstream and chemical reaction of copper with water to form its constituent compounds. The sharp increase could signify the discharge point of the metal at station 8. Low copper content is observed in the water generally in all stations; this could be due to the uptake of the labile copper by the thriving water hyacinth and other aquatic plants growing in this region. Generally, this concentration was below the permissible limit; EPA 1.3 mg/L and KEBS, WHO and FAO 1mg/L. This concentration therefore could be deduced not to be a problem in the river.

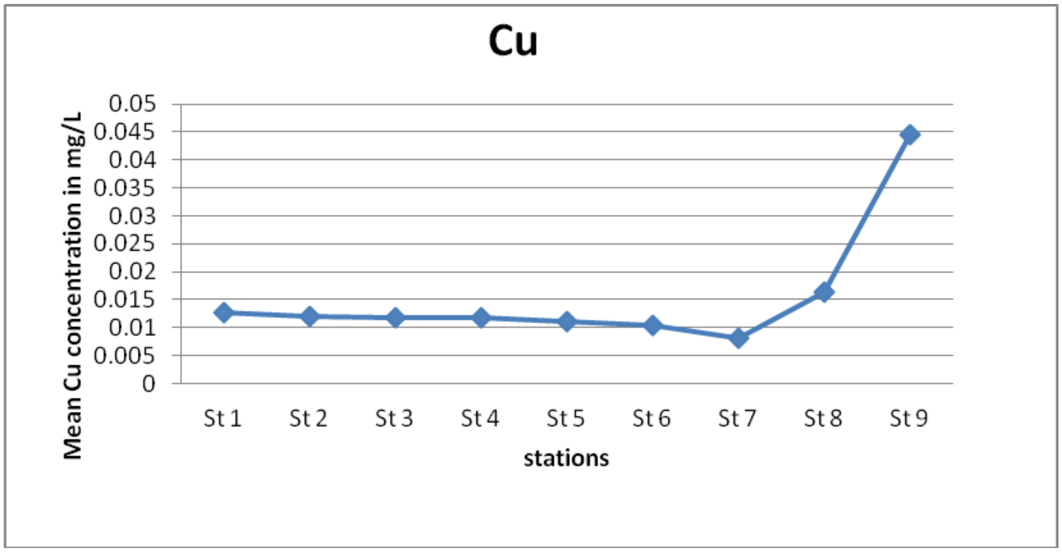

Figure 4. 1: Variation of Copper concentrations in in water in mg/L

The mean concentration of lead at the 9 different stations was as shown in Figure 4.2. This measurement varied by fluctuating among the stations; rising from station 1(0.2444 mg/L) to 2(0.507 mg/L) and then fell to stations 4(0.237 mg/L). It then rose in station 5(0.47 mg/L), dropped in station 6, constant in 6 and 7 and finally rose in station 9(0.0446 mg/L). This fluctuation could probably be attributed to some industrial discharge of their pollutants in the river. There was a battery recycling industry between station 1 and 3, cement industry and steel industry between station 4 and 6 and finally hides and skin between station 7 and 9. This concentration was also observed to be very high compared to copper concentration. The high level of Pb in water of the river could be attributed to the industrial and agricultural discharge as well as from spill of leaded petrol from heavy trucks and dust which holds a huge amount of lead from the combustion of petrol in automobile cars (Hardman *et al.***,** 1994) moreover higher levels of Pb often occur in water bodies near highways and large cities due to high gasoline combustion **(**Banat *et al*., 1998**).**.This concentration was also above the permissible limit for FAO WHO (0.01mg/L) and KEBS (0.1 mg/L). Lead is therefore a pollutant of concern in the river.

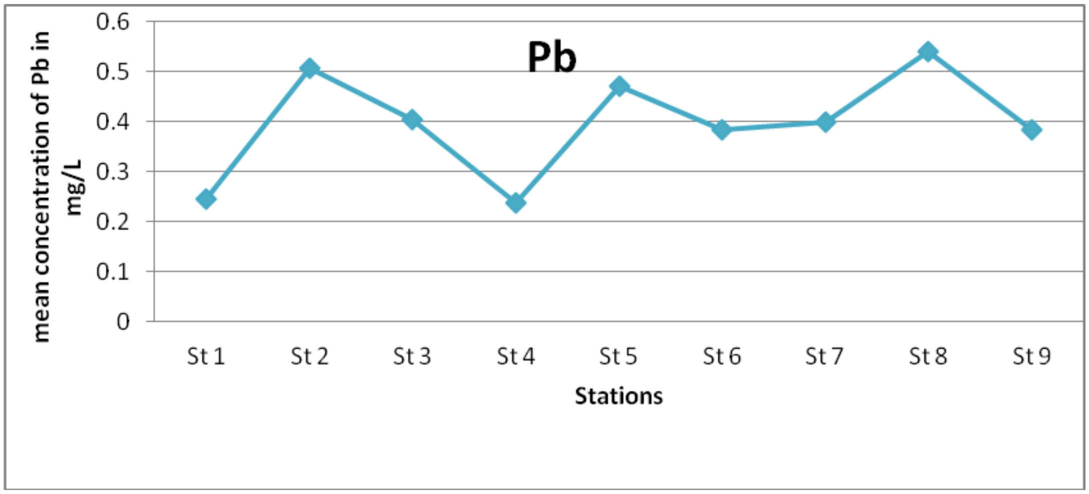

Figure 4. 2: Variation of lead concentrations in water in mg/L

Mean measurement of chromium concentration along the river (Figure 4.3) varied almost similarly to that of lead with some slight increase from station 1(0.1892) to 2(0.2039 mg/L), dropped in station 4(0.1697 mg/L) rose to its highest at station 5(0.3255 mg/L) after which it slightly registered an increase at station 8(0.1725 mg/L). The latter increase can be attributed to effluent. Also, dust which holds a huge amount of lead from the combustion of petrol in automobile cars led to increase Pb content (Hardman et al. 1994).This concentration is higher than the permissible limit for EPA (0.1mg/L), WHO and FAO (0.01mg/L). The mean sampled concentration could also be deduced to be of significant concern in the river in relation to biological communities.

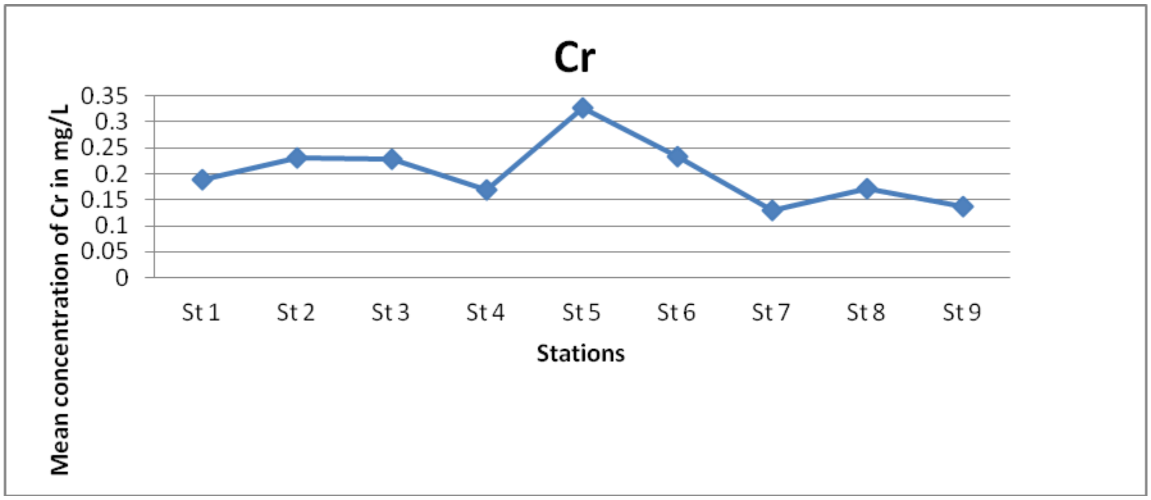

Figure 4. 3: Variation of Chromium concentrations in water in mg/L.

The mean concentration for the sampled cadmium (Figure 4.4) slightly differed from the above two heavy metals registering a decrease from station 1(0.024 mg/L) to station 2(0.011 mg/L) rising to a constant value between 4 and 5(0.095 mg/L) falling to station 7(0.0109 mg/L). It appeared almost similar in nearly all stations; generally indicating approximately three discharge points. The previous industrial discharge influence could be vital in all the stations suggesting a common source. Generally, this concentration was above the permissible limits for EPA (0.005 mg/L), WHO and FAO (0.003 mg/L) and therefore could also be deduced to be pollutant of concern to the environment. Sedimentation could as well account for the low levels of metals observed in different samples from the river.

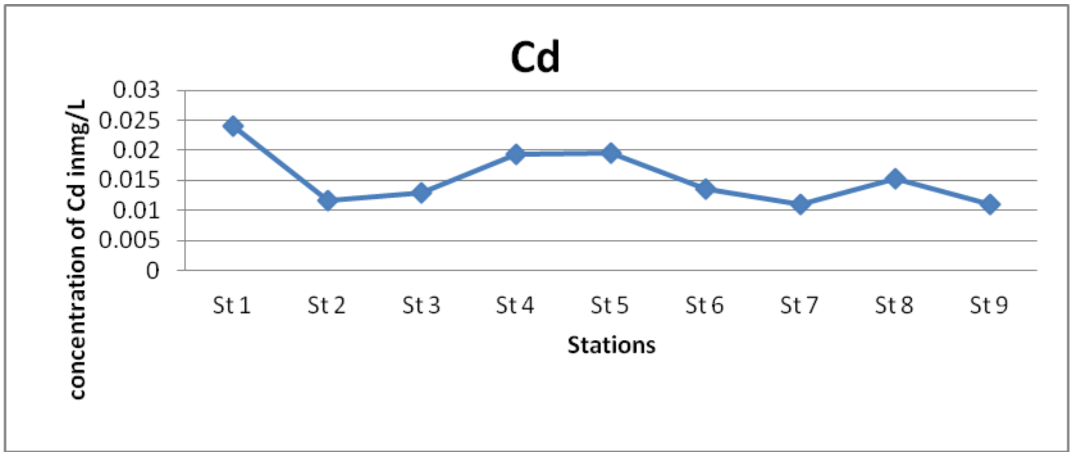

Figure 4. 4: Variation of Cadmium concentrations in water in mg/L.

For nickel concentration, the mean measurements for the samples were as in Figure 4.5. The trend slightly changed at station 7(0.01 mg/L), 8(0.0153 mg/L) and 9(0.0081 mg/L), about similar to that of cadmium. There is a general decrease in concentration downstream. This concentration was also above the permissible limit for EPA (0.001 mg/L) but lower than WHO and FAO (0.02) and KEBS (0.1) and hence inferred to be of concern to the environment and biological communities directly or indirectly associated with the river.

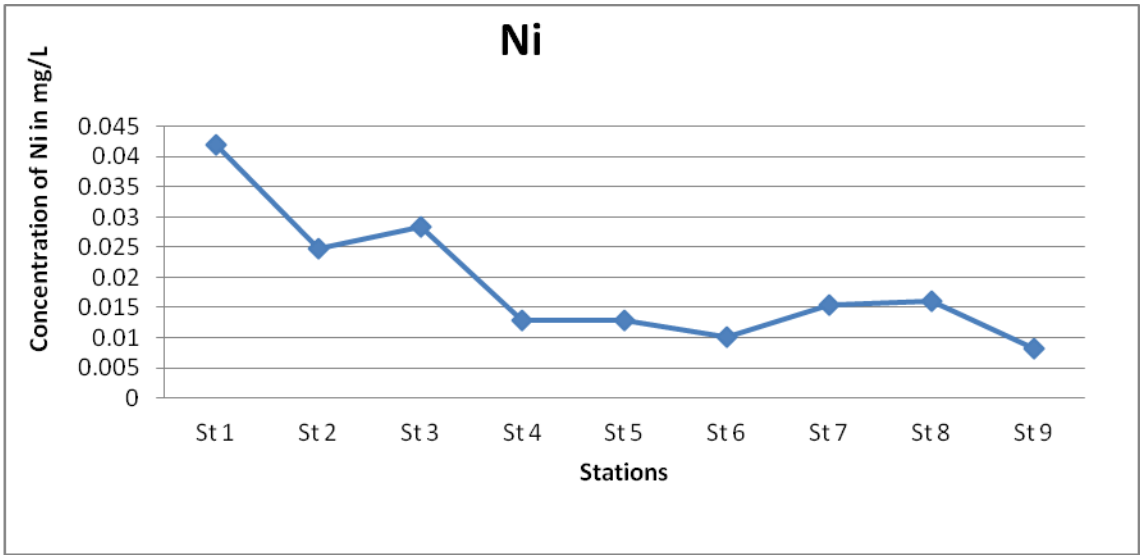

Figure 4. 5: Variation of Nickel concentrations in water in mg/L.

The mean concentrations of heavy metals: Cu Cd, Cr, Pb, and Ni in the river water samples

analyzed are presented in tables 4.1 below.

Table 4. 1: The Mean Variation of heavy metal concentrations in mg/L on river water downstream

Stations	Cu		Pb		Cr		Cd		Ni	
St 1	0.0128	±0.00379	0.2444	±0.0947	0.1892	±0.0596	0.0240	±0.00334	0.0419	±0.0155
St 2	0.0121	±0.00482	0.5071	±0.0989	0.2309	±0.0162	0.0117	±0.00364	0.0248	±0.00913
St 3	0.0118	±0.00353	0.4048	±0.0533	0.2281	±0.0779	0.0129	±0.00558	0.0284	±0.0102
St 4	0.0118	±0.00393	0.2371	±0.0958	0.1697	±0.0286	0.0193	±0.00468	0.0129	±0.00382
St 5	0.0112	±0.00552	0.4700	±0.176	0.3255	±0.0931	0.0195	±0.00354	0.0129	±0.00341
St 6	0.0105	±0.00353	0.3829	±0.0914	0.2337	±0.0586	0.0134	±0.00308	0.0101	±0.00423
St 7	0.0082	±0.00137	0.3980	±0.13	0.1308	±0.0385	0.0109	±0.00379	0.0153	±0.0047
St 8	0.0164	±0.00536	0.5400	±0.143	0.1725	±0.0356	0.0152	±0.00465	0.0159	±0.00275
St 9	0.0445	±0.0262	0.3830	±0.0871	0.1363	±0.0399	0.0109	±0.00322	0.0081	±0.00322

The comparative trend measurement in the sampled concentration of the 5 heavy metals was also evaluated to observe the general change in their concentration from station 1 to station 9 (Figure.4.6). The primary vertical axis having Cu, Cd and Ni (because their concentrations were below 0.1 mg/L) while the secondary vertical axis having Lead and Chromium (because their concentrations were above 0.1 mg/L). from Figure 4.6 it is evident that lead and chromium had the highest concentration in the river water. Copper was generally the least and therefore of no significant value or influence. Possibly this being attributed to minimal industrial discharge of heavy metal pollution in the river water. The presence of elevated levels of Pb and Cr in almost all regions is a serious matter of concern and the potential for human exposure to heavy metals from eating fish caught in the river.

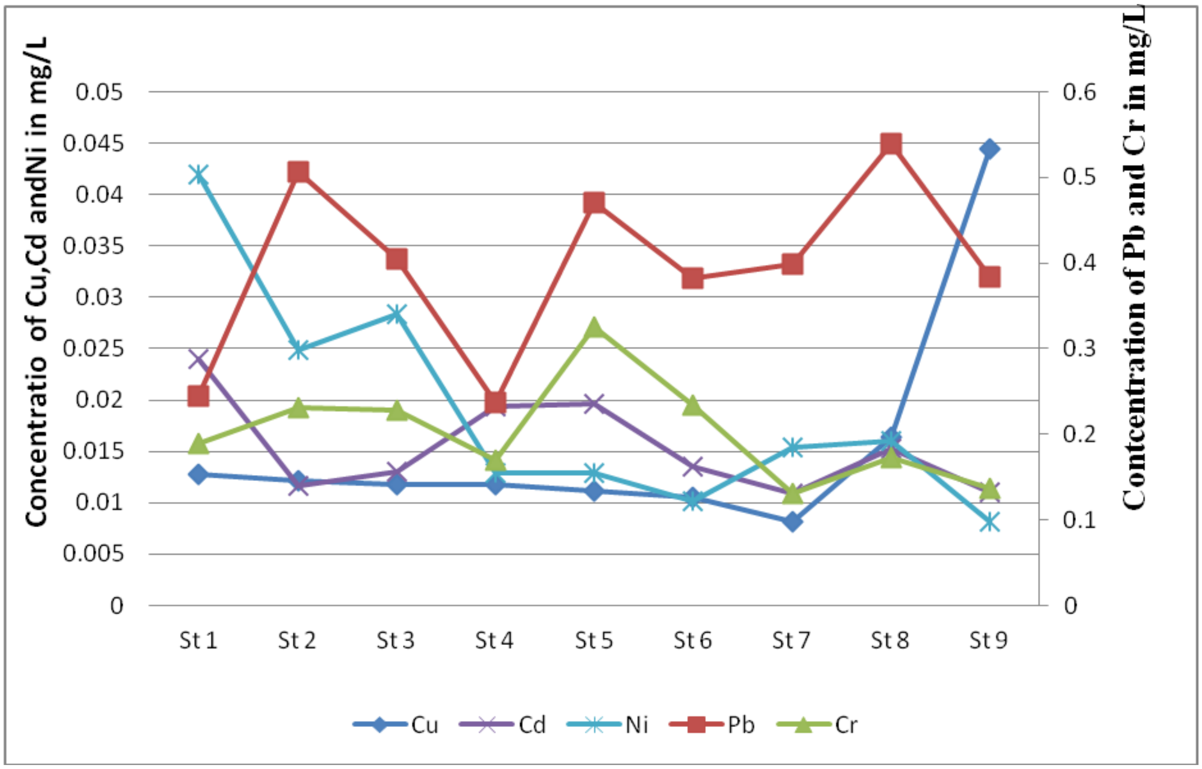

Figure 4. 6: The variation of all the tested heavy metals on river water in mg/L

Single ANOVA test reveal a significant difference in concentration of heavy metals between different stations along the river and also between different heavy metals in the river($p<0.05$). These can be attributed to varying discharge points and difference in the degree of discharge along the river.

4.1.3 Heavy metals in sediments

The mean concentration of copper in sediments was as observed in the Figure 4.7. This was higher than that observed in water. The peaks was observed in station 4(0.1581 mg/L) and 9(0.2475 mg/L), falling through to station 2s while the lowest concentration recorded in station 6(0.0607 mg/L) . The possibility of the observed situation could be due to sediments acting as sinks and therefore adsorbing most of the settled copper in them resulting to the high concentration compared to the flowing water which becomes diluted as the river discharges downstream.

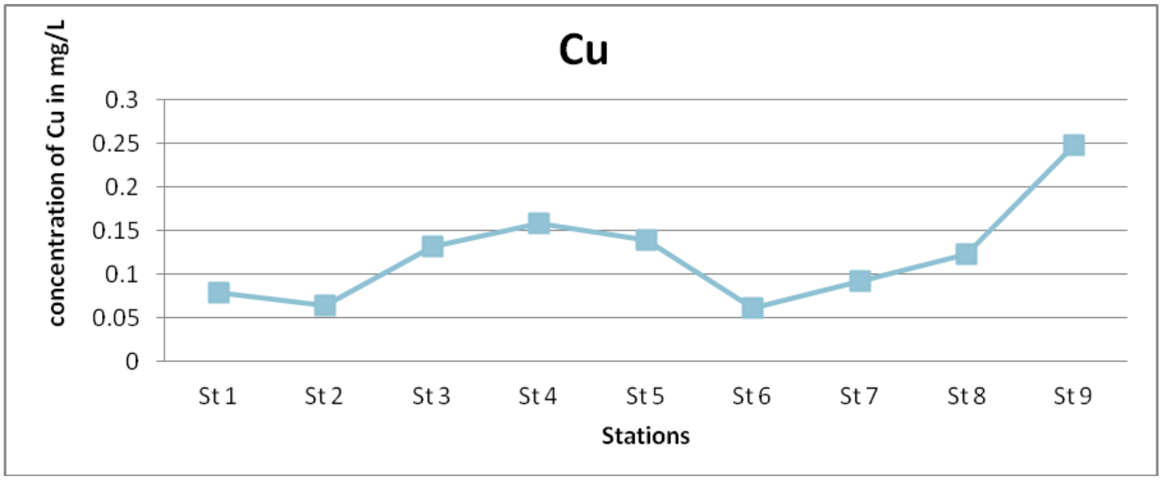

Figure 4. 7: Variation of Copper concentrations in sediments in mg/L along Athi River

Mean lead concentration in sediments did varied very much for the first 5 stations (Figure 4.8). There was however no intense fluctuations from station 5(0.3513 mg/L) to station 9(0.2427 mg/L); with station 5 being the highest. The concentration in water was slightly higher than that in sediments this could be attributed to raw sewage discharge to the river at specific points in to the river. Also, dust which holds a huge amount of lead from the combustion of petrol in automobile cars led to increase Pb content (Hardman *et al.*, 1994). Presence of dry cell battery manufacturing industry from catchment areas of the Athi river might probably responsible for high level of Pb. The level of Pb obtained in the sediment were lower than those in the water, hence the water could be an influencing factor on the level of Pb in the water with other enhancing factor like pH since water acidity is known to influence the solubility and availability of metals.

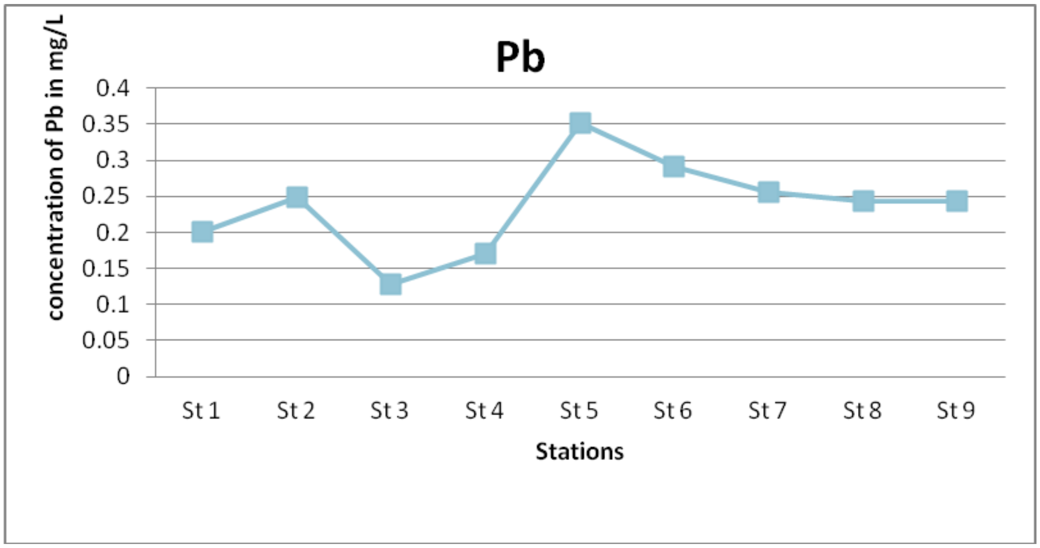

Figure 4. 8: Variation of Lead concentrations in sediments in mg/L along Athi River

Generally, the mean concentration of cadmium was also high in sediment than in water as observed in the Figure 4.9. The peak value of this concentration being in station 5 in water (0.2402 mg/L) which was also the same in sediments concentration. There was however variation due to fluctuation between and among station. As discussed for copper concentration, when water and sediments were compared, the same inference could be drawn for cadmium, sediments acting as sink and therefore retaining much of the settled cadmium. The high level of Cd in the sediment relative to levels in the water is expected since sediments have been described as a sink or reservoir for pollutants in water (Samir *et al*., 2006).

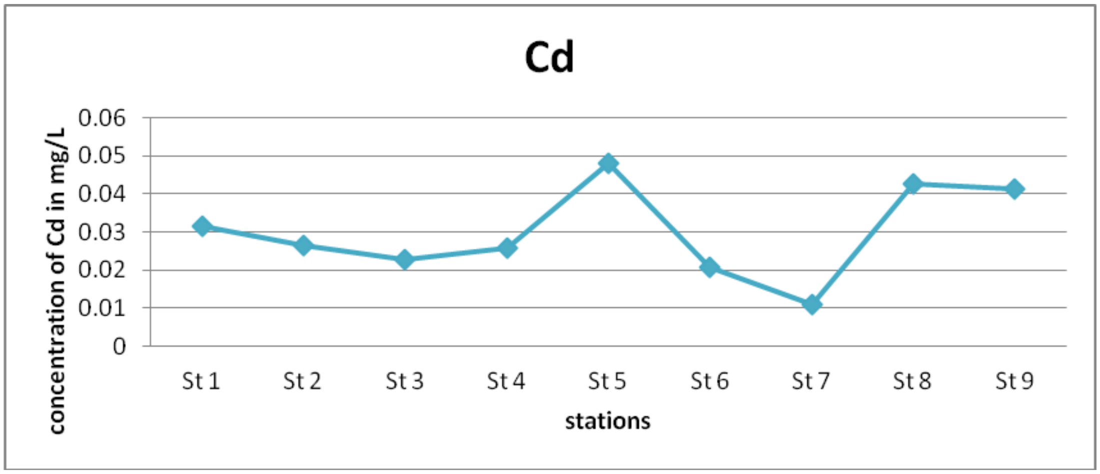

Figure 4. 9: Variation of Cadmium concentrations in sediments in mg/L along Athi River

The mean concentration for chromium in the sediments was lower than that in water (Figure 4.10). The peak measurement in water was 0.3255 mg/L at station 5 and the lowest being 0.1303 mg/L at station 1. Both of the concentration being above the concentration of most stations (except for station 7) measurements at sediment comparison. Possibly this can be attributed to active discharge of this heavy metal and also with the lead above resulting to their concentration being high in water. The industrial discharge could be frequently composed of these two heavy metals and therefore high in water. The high level of Cd and Pb in sediments of Athi-River could be attributed to the industrial and agricultural discharge as well as from spill of leaded petrol from transportation lorries. Apparently the Cr-containing chemicals used for skin tanning ends up in the environment the skin tunneling factory is located within two kilometers from the river..

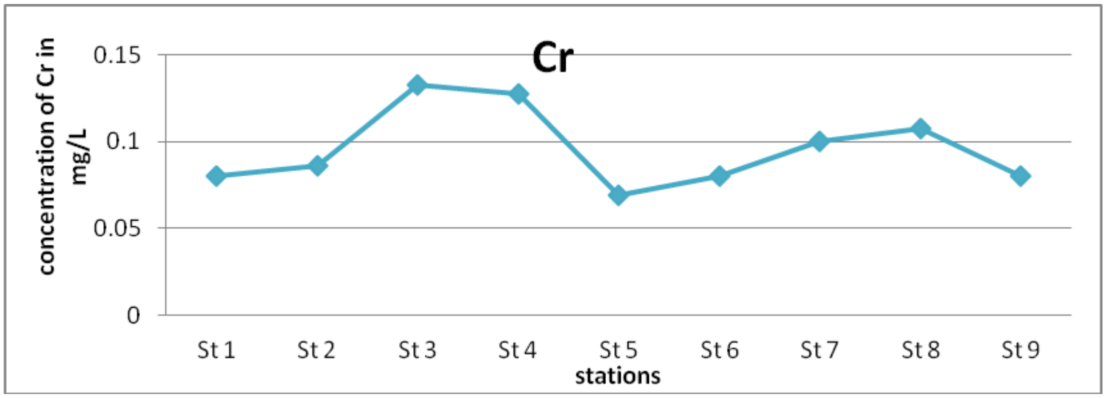

Figure 4. 10: Variation of Chromium concentrations in sediments in mg/L

Mean Nickel concentration was also low in water compared to sediment concentration (Figure4.11). Only in the last three stations where the mean concentration in water was some comparatively equal to some of the mean concentration in sediment. The same deduction as that in copper and cadmium could be attributed to this difference. It was evident that copper, cadmium and nickel are more concentrated sin sediment than in the flowing river water, minimal rate of discharge compared to other metal ions, chemical and physical characteristics of individual heavy metal ions like solubility in water and the nature of complexes formed could be responsible for these observed phenomenon.

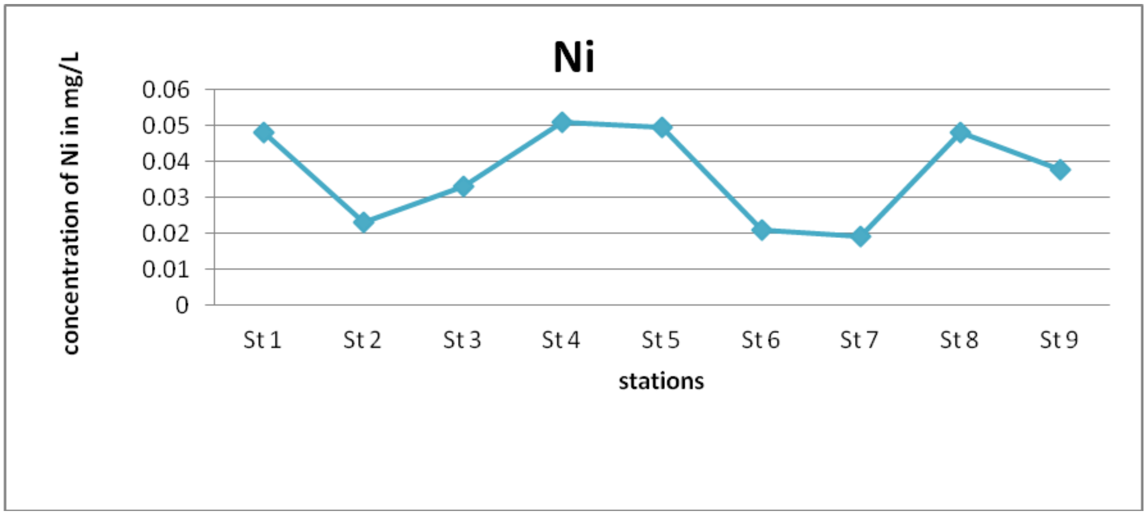

Figure 4. 11: : Variation of Nickel concentrations in sediment in mg/L

Comparison showing variation in concentration of the five tested heavy metals revealed that lead and chromium had the highest concentrations while cadmium had the least, difference in bio-adsorption of heavy metals by sediments was noted (Figure 4.12). The maximum concentrations observed were for Pb both in flowing river water and sediments, while the minimum was Cu in flowing river and Cd in sediments.

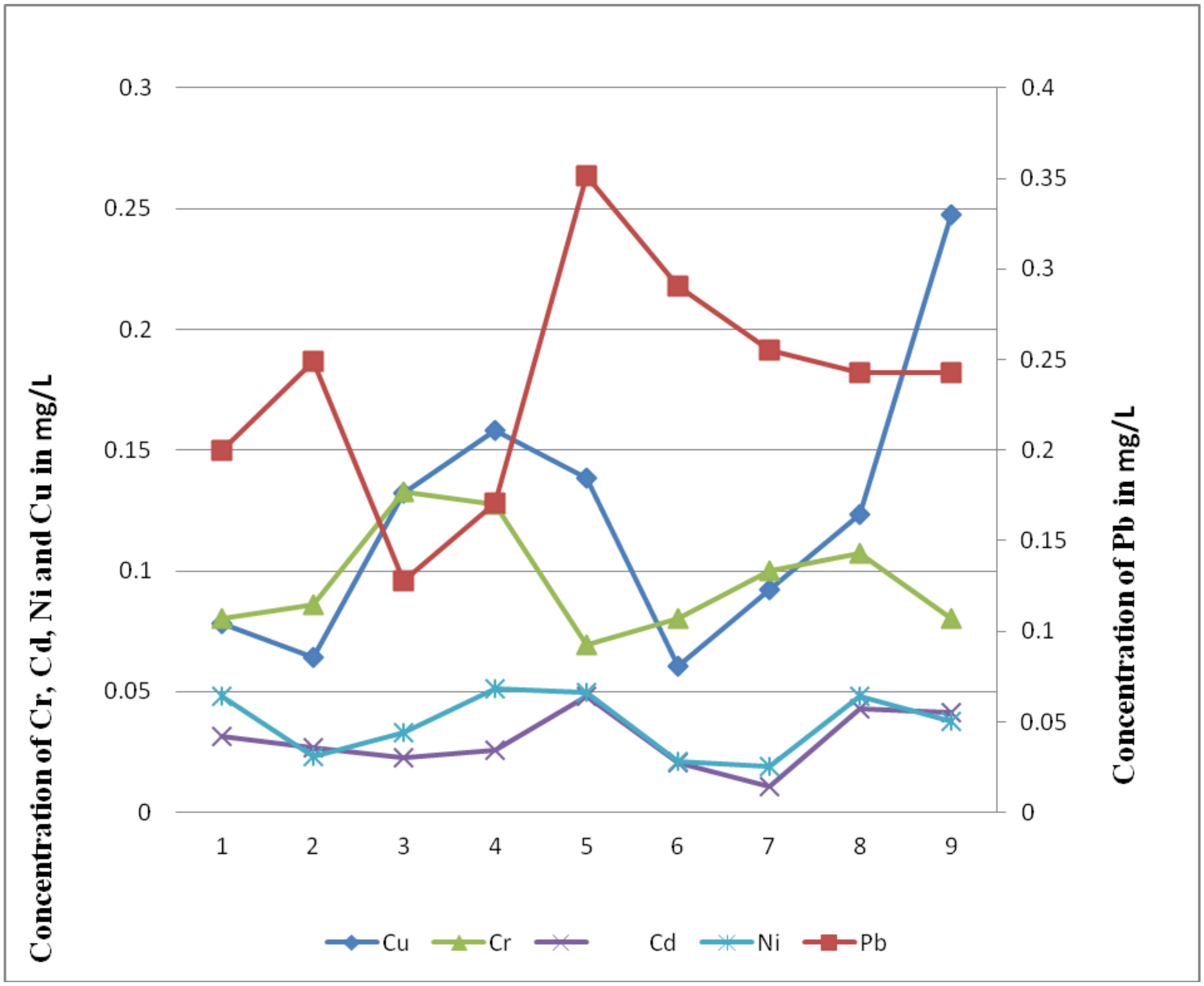

Figure 4. 12: Comparative line graph showing the variation of all the tested heavy metals on sediments in mg/L along the river

Table 4. 2: Mean Variation of Heavy metal concentrations in sediments in mg/L downstream

Station	Cu		Pb		Cr		Cd		Ni	
St 1	0.0782	±0.00858	0.2	±0.113	0.0803	±0.0181	0.03158	±0.00964	0.0483	±0.0165
St 2	0.06436	±0.0096	0.249	±0.106	0.0859	±0.0212	0.0266	±0.0132	0.02324	±0.00711
St 3	0.1322	±0.00708	0.1277	±0.0457	0.1329	±0.0194	0.02274	±0.00806	0.0331	±0.016
St 4	0.1581	±0.00719	0.1708	±0.0422	0.1273	±0.0357	0.0258	±0.00411	0.0511	±0.0212
St 5	0.13866	±0.00346	0.3513	±0.073	0.0692	±0.02	0.0482	±0.01	0.0498	±0.0148
St 6	0.0607	±0.00705	0.2905	±0.0433	0.0804	±0.0127	0.0208	±0.00617	0.02092	±0.00771
St 7	0.09246	±0.00555	0.2555	±0.0186	0.1002	±0.0178	0.01082	±0.00276	0.01912	±0.00236
St 8	0.12336	±0.00616	0.2427	±0.0515	0.1074	±0.0398	0.0428	±0.0131	0.0483	±0.0264
St 9	0.2475	±0.0234	0.2427	±0.0441	0.0803	±0.0307	0.04122	±0.00643	0.0379	±0.0127

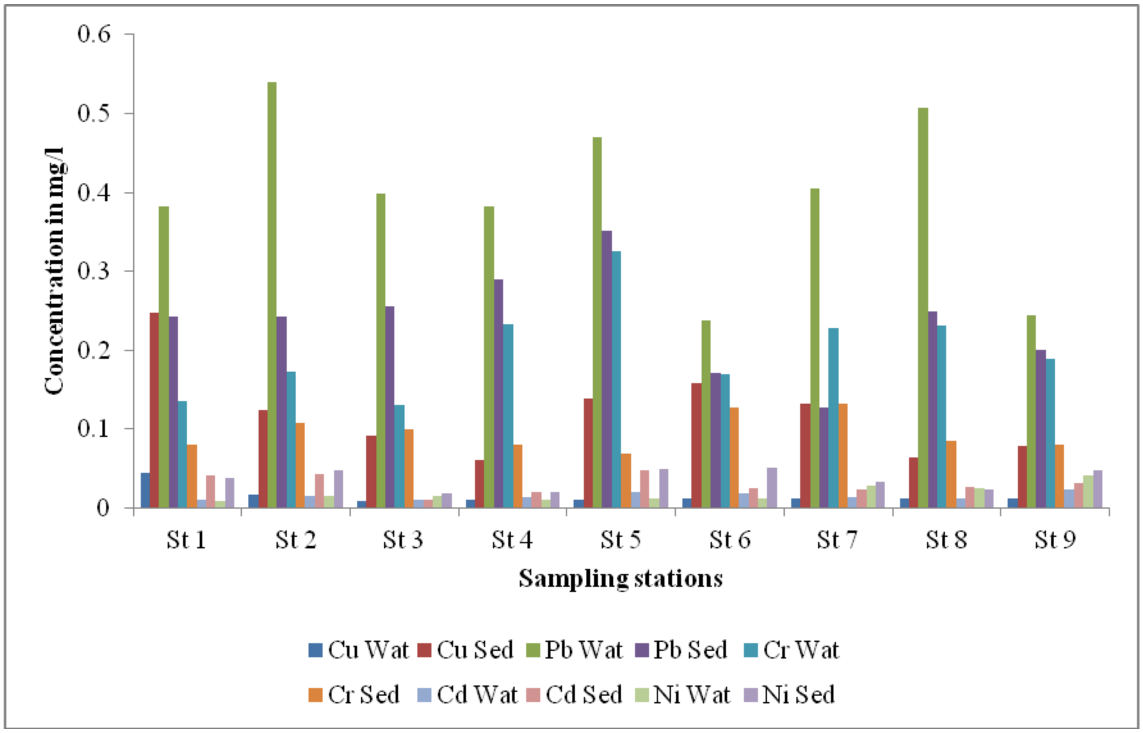

Figure 4. 13: Bar-graph showing the comparative concentrations between water and sediments in mg/L for the 5 heavy metals in the 9 sample stations from station 1to station 9

Sed stands for sediments and wat stands for water in reverse order from station 1 to station 9

There was a great significant difference between concentration of heavy metals in water and concentration of heavy metals in sediments as evident by the ANOVA test h $p>0.05$. This is possibly due to the different complexes formed by metal ions in sediments which makes them immobile (Hamed, 1998). sewage discharge could also play a role since they are discharged in the river before eventually getting in to the sediments. In general, metal content in sediments is indicative of the degree of pollution and serves as a source of solubilization into water depending on the physicochemical circumstances specifically pH and temperature conditions and the uptake by benthic organisms (Ogoyi1, *et al.*, 2011). By comparing the accumulation of heavy metals in water and sediments, it can be concluded that the heavy metals are highly accumulated in sediments than water, since the sediments act as reservoir for all contaminants and dead organic matter descending from the ecosystem above. Similar findings were reported by other authors (Hamed, 1998 and Nguyen *et al.*, 2005). The positive correlations observed between most of the metals in water, especially in Malindi, suggest relative uniformity of the sources of the metal pollutants, as previously reported (Onyari and Wandiga, 1999). However, lack of a similar degree of correlation among metals in the sediments of the habitats suggests that the metals are retained differentially in the sediments. The high levels of metals in the sediments and low level in the water at sites may be due to the calm (undisturbed) nature of the area and therefore the particles are bound to settle.

4.1.4 Physicochemical parameters

Water quality was evaluated based on five parameters namely pH, conductivity, biological oxygen demand (BOD) and chemical Oxygen demand (COD). Solubility of heavy metals in surface water is predominately controlled by the water Ph, the river flow and the redox environment of the river system. A lower pH increases the competition between metal and hydrogen ions for binding sites. A decrease in pH may also dissolve metal carbonate complexes, releasing free metal ions into the water column (Osmond *et al.*, 1995). Although the pH was relatively stable (Figure 4.14), it may have played a significant role in the dissolved heavy metal concentrations. According to WHO and EPA pH between 6.5-8.5 is desirable and pH standard for agricultural use is set as 6.5-7.5. EPA guidelines=6.5-8.5. In general the pH of Athi river water was neither strongly alkaline nor acidic (Figure 4.14).

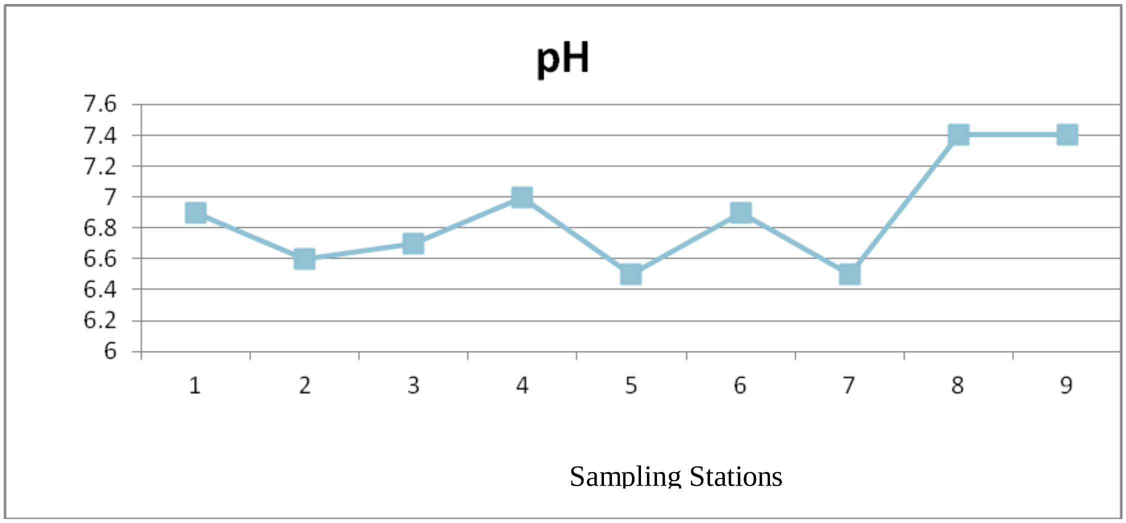

Figure 4. 14: Variation of pH along the river

The was no significant difference in pH ($p<0.05$) among the sampling locations. The pH values of the various samples investigated ranged between 6.5 to 7.4. The results showed both alkaline and acidic points along the river. This notwithstanding all results obtained fell within national and international standard, EPA/WHO (6.5-8.5)

The BOD values (Figure 4.15) are all higher than the normal BOD for unpolluted water of 2mg/L or less, a decreased redox potential, as is often seen under oxygen deficient conditions, will change the composition of metal complexes and release the metal ions into the overlying water. There was a positive correlation between heavy metal concentration and BOD along the river possibly because metal ions consume oxygen during the oxidation process. This variation in the rivers sediment was reflected on the metals distribution. This in agreement with Franc *et al*., 2005 and Tsai *et al.*, 2003 who mentioned that sediments contain more sand and lower values of organic matter exhibit low metals enrichment. They also observed from their findings that the pollutant concentrations in sediments increased with decreasing the particle size in sediments. Sediment has certain limited capacity to absorb different ions from waters percolating through it. This capacity is lowest for carbonate-sandy fractions of sediments (Lake-sea area), and highest for organic matter rich sediments. As the river re-aerates due to atmospheric mixing and as algal photosynthesis adds oxygen to the water, the oxygen levels will slowly increase downstream. The World Health Organization recommended a BOD limit of 6 mg/L and 3 mg/L in urban areas for drinking water. The BOD values in this study ware all beyond this requirement possiply due to high concentrations of metal ion which consume oxygen during the oxidation process.

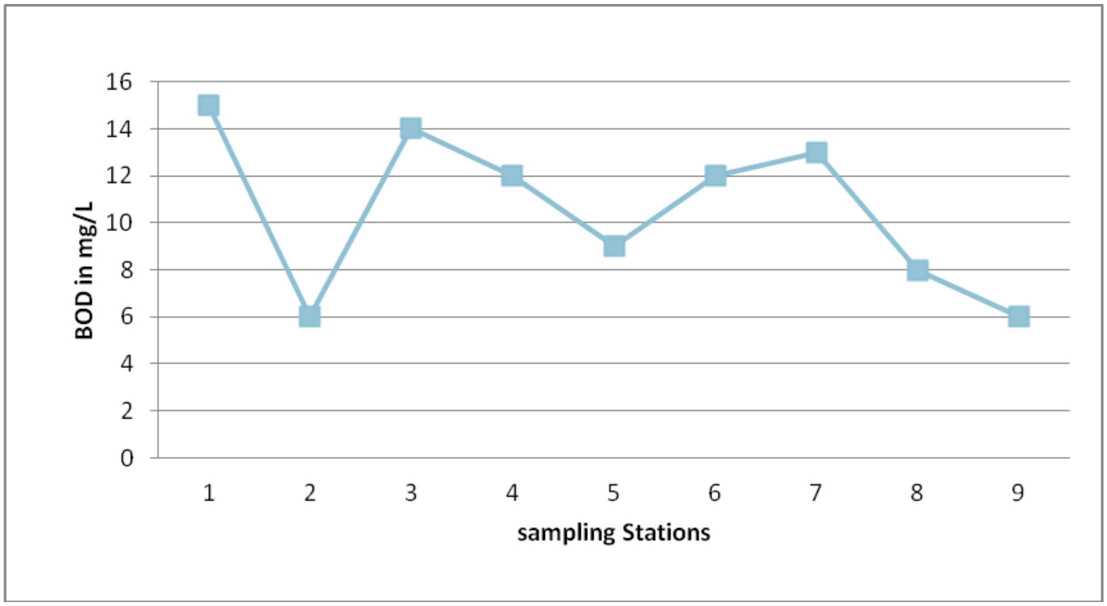

Figure 4. 15: Variation of BOD along the river in mg/L

The variation of electrical conductivity (Figure 4.16) and TDS (Figure 4.17) concurrently gradually decreased downstream with a slightly rise at the middle of the sampling points. Higher conductivity values indicate higher concentrations of free metal ions in water (Chronopoulo *et al.*, 1997). WHO and EU guidelines give 400 µS/cm as the guide level for potable water therefore all the station recorded a lower value than the permissible limit.

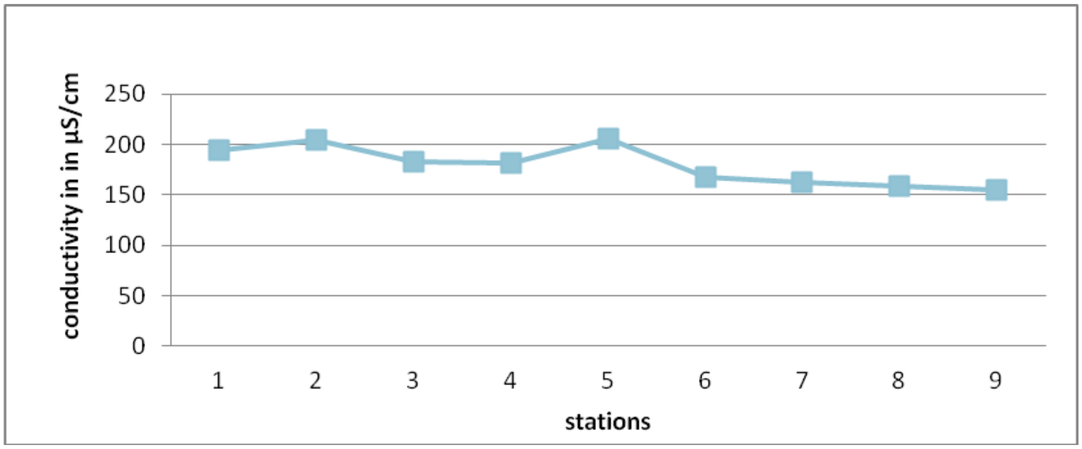

Figure 4. 16: Variation of conductivity along the river in µS/cm

The observed TDS levels can be described as falling below the EPA's recommended maximum of TDS in water is 500 mg/L (Appendix xiv). However, comparing the observed values with the EPA regulations on TDS (appendix xiv), the waters from this river is unsafe for domestic use Figure 4.17 . The TDS and conductance results showed consistent vertical and longitudinal profiles, which indicated that chemo-stratification, was existent as reflected also in the pH.

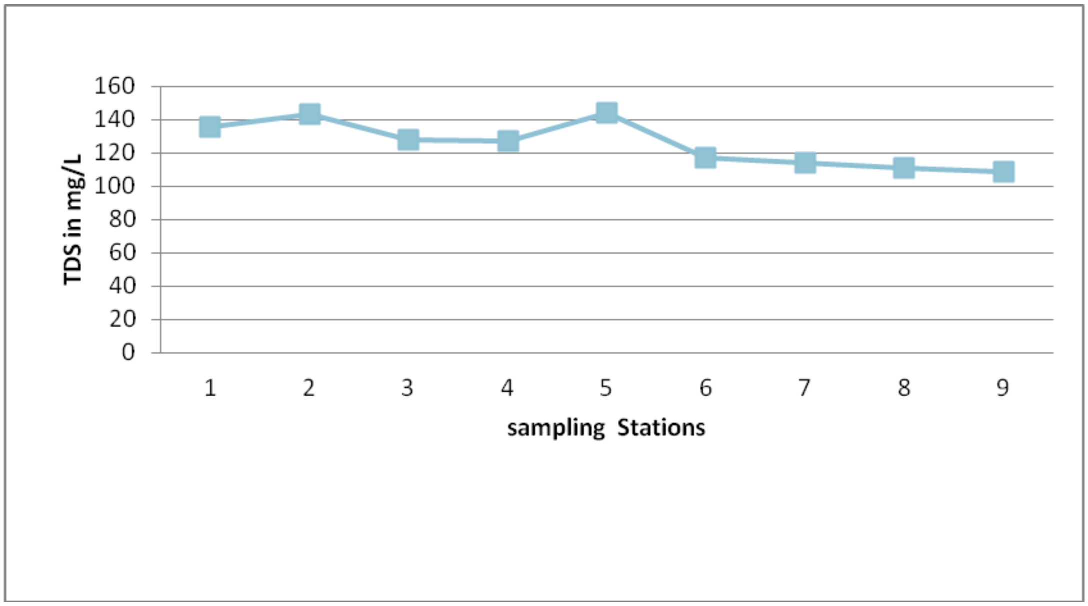

Figure 4. 17: Variation of TDS along the river mg/L

From the COD values (Figure 4.18), the waters of Athi river can be described as having a weak COD (<400). COD testing assesses all chemically oxidizable substances and can be directly related to the true oxygen demand imposed by the effluent if released into the environment. Nevertheless, a sharp increase of COD concentration at sampling station 2 and station 8 is probably attributed to inflows that have strong organic loading. Because each organic compound differs in the amount of oxygen necessary for complete oxidization, the COD test reflects the effect of an effluent on the receiving stream more directly.

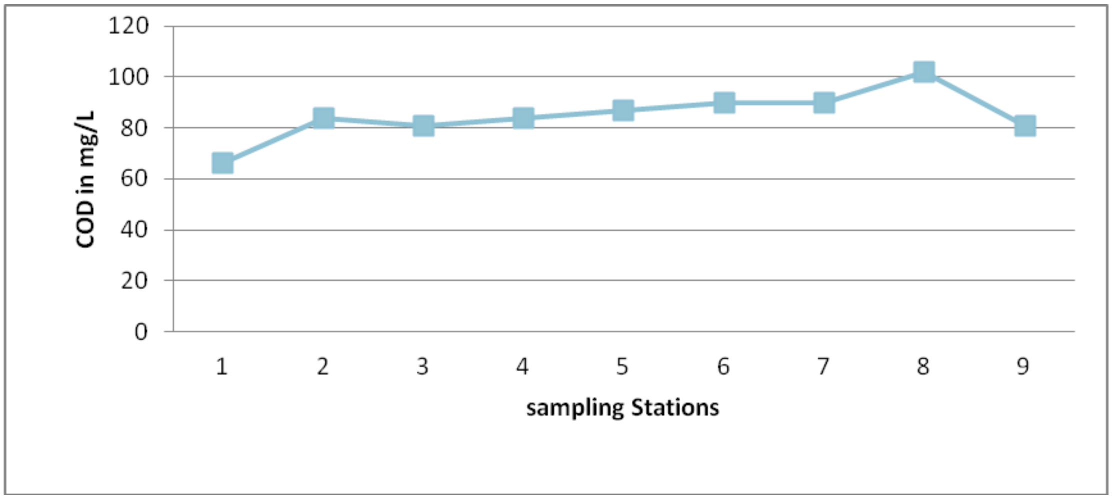

Figure 4. 18: Variation of COD along the river mg/L

The environmental quality standards for surface water demands COD value to be < 30 mg/l. and therefore the athi river water were all above the recommended COD value.

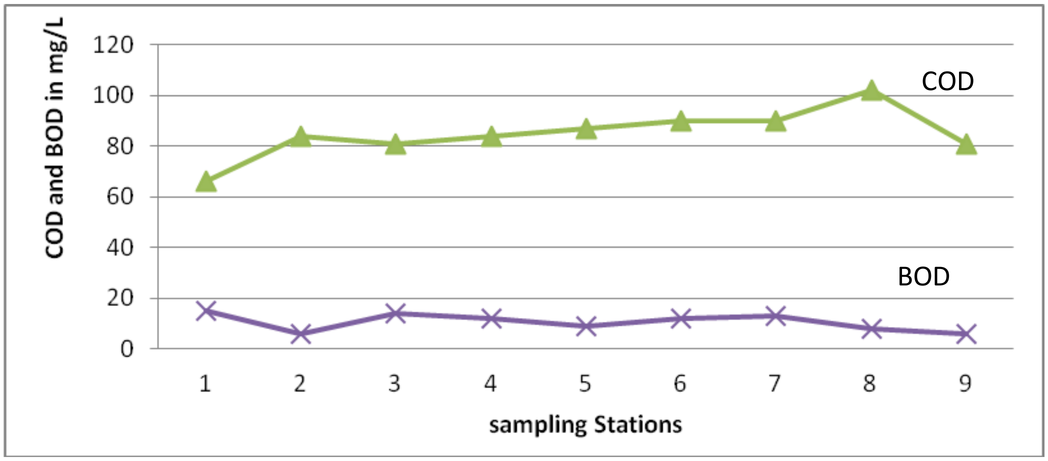

Figure 4. 19: Comparison between BOD and COD in mg/L

The COD values ware higher than BOD values (figure 4019). The difference is not surprising since COD measures both oxidizable organic and inorganic substances while

BOD measures only biologically active oxidizable substances. COD can also be used to evaluate BOD these can be deduced from the general trend above. s

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.0 Conclusion

The investigation of heavy metal pollutants in Athi river namely Pb Cd, Cr, Cu and Ni in free flowing water and within sediments of Athi River revealed that Pb was highest in concentration in both free flowing water and sediments ranging from 0.2371 mg/L to 0.54 mg/L for water and 0.1277mg/L to 0.3513mg/L for sediments. The presence of other heavy metals was also prominently observed.

Variation of average total dissolved solids, chromium, and lead concentrations ware highest at industrial area. Copper mean concentration values were higher in sediments ranging from 0.0643 mg/L to 0.2475 mg/L and lower free flowing water ranging from 0.0082 mg/L to 0.0445 mg/L .TDS and conductivity, had significant difference ($P<0.05$). This implies that TDS and conductivity were the parameters of water quality of the river that had been significantly affected by pollution. Most of the parameters in Athi River are above those recommended by WHO, EPA and KEBS. The results of the study show that although Athi River is already polluted from upstream activities, there is a significant increase in the levels of BOD and TDS. This suggests strongly that human activities along this river are partially contributing to its pollution thereby endangering the health of the people who rely on the river as their water source and affecting the ecosystem too.

5.2 Recommendations

To improve the water quality and environment in the Athi River Basin, the following should be done:

1. Rehabilitate and restore the river
2. Develop and implement water quantity and quality measuring protocols.
3. Enhance service delivery, environmental conservation, and sustainable use of resources.
4. More of the untested heavy metals' concentration should be conducted.
5. It is recommended that further periodic research should be done to continuously monitor these indicators of pollution.

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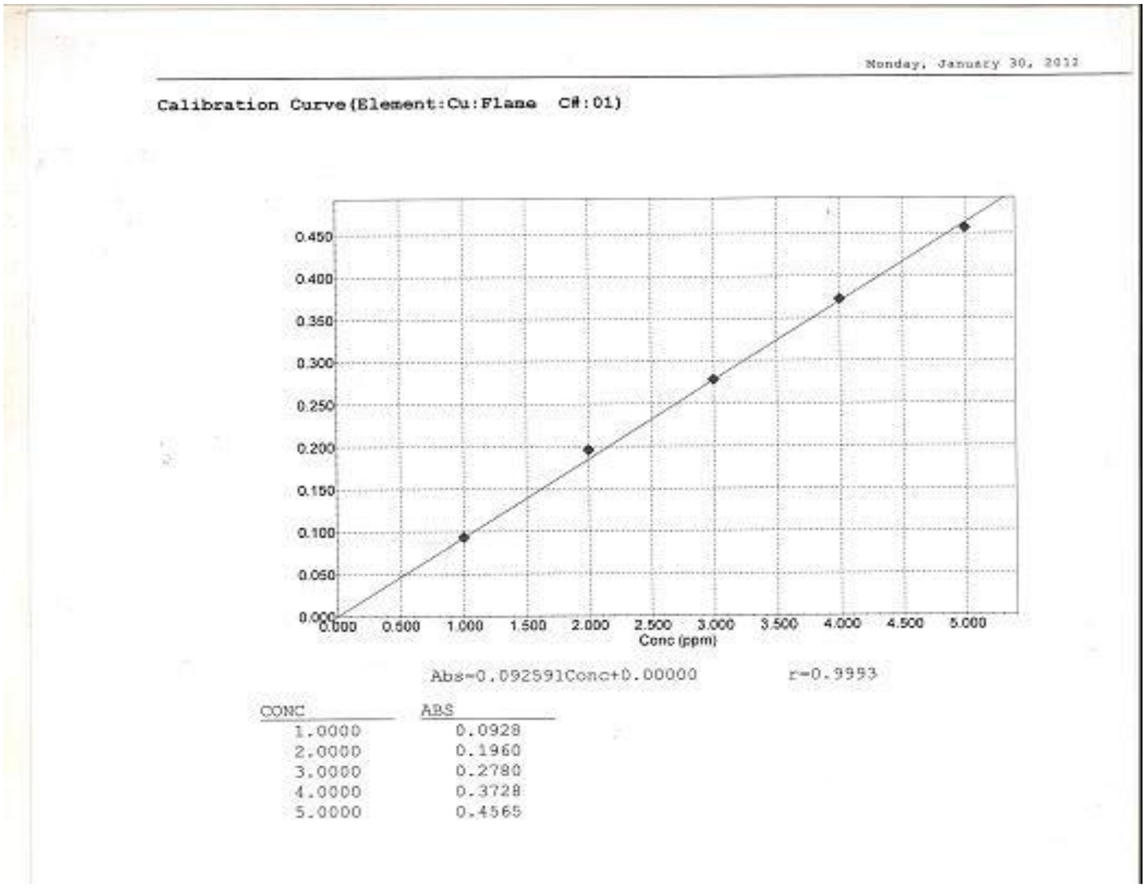
APPEDICES

Appendix 1: Cu calibration curve



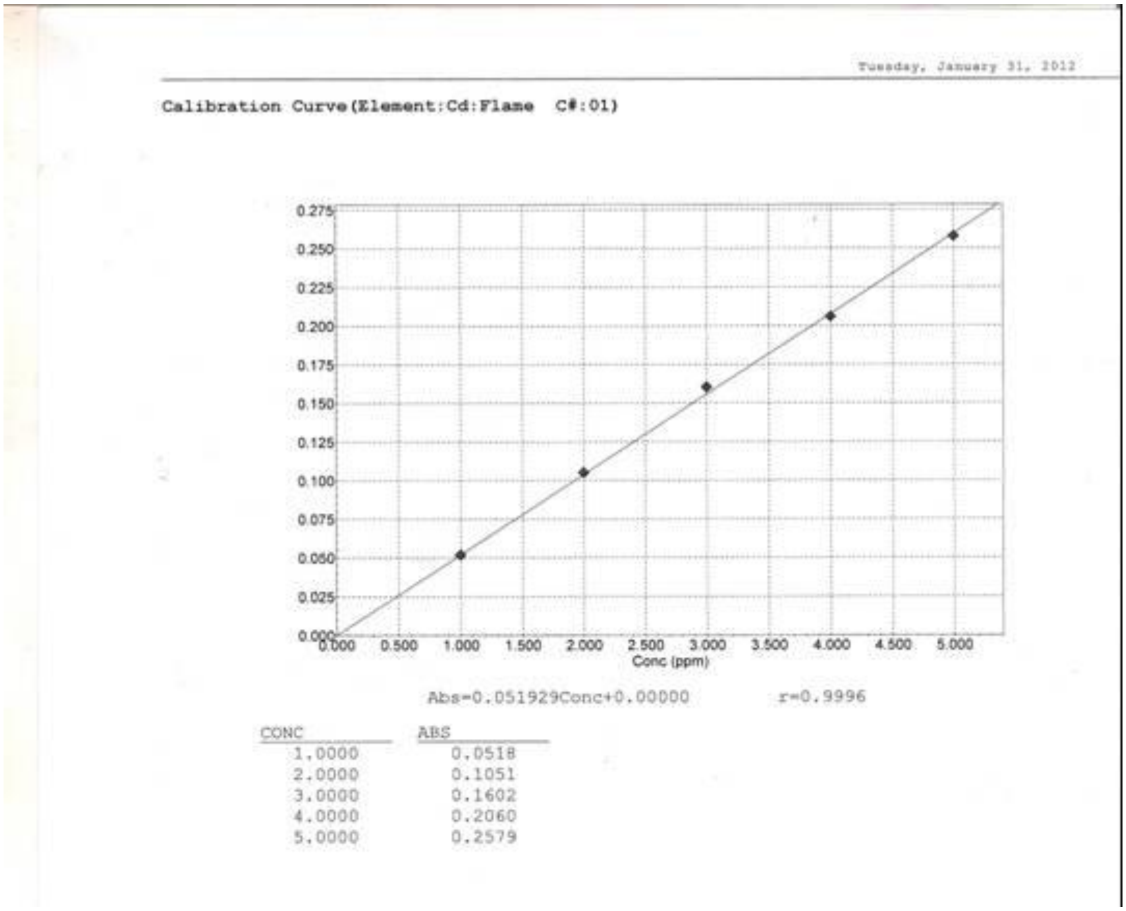
Monday, January 30, 2012

Calibration Curve(Element:Cu:Flame C#:01)

Abs=0.092591Conc+0.00000 r=0.9993

CONC	ABS
1.0000	0.0928
2.0000	0.1960
3.0000	0.2780
4.0000	0.3728
5.0000	0.4565

Appendix 2: Cd calibration curve



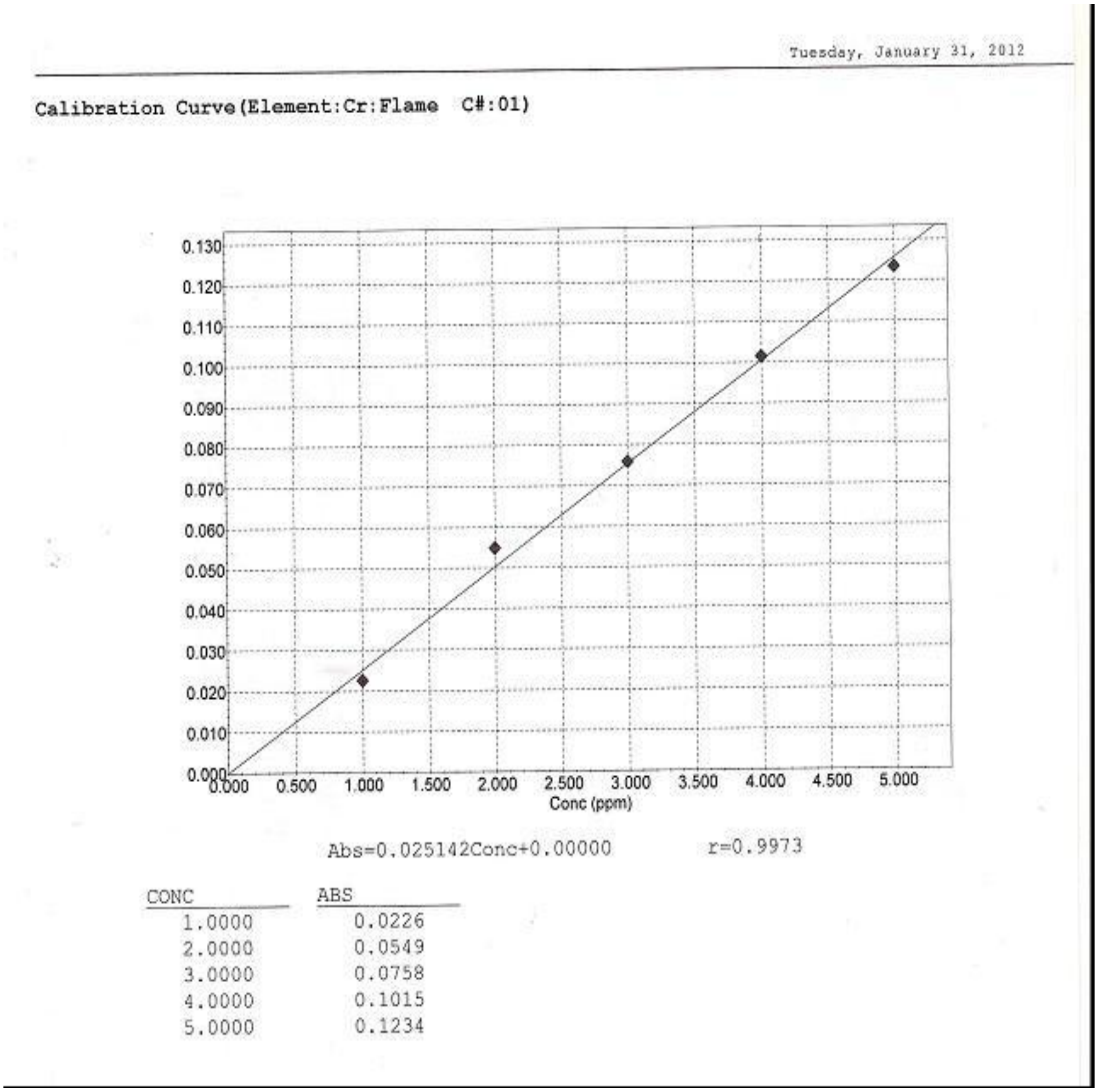
Tuesday, January 31, 2012

Calibration Curve(Element:Cd:Flame C#:01)

Abs=0.051929Conc+0.00000 r=0.9996

CONC	ABS
1.0000	0.0518
2.0000	0.1051
3.0000	0.1602
4.0000	0.2060
5.0000	0.2579

Appendix 3: Cr calibration curve



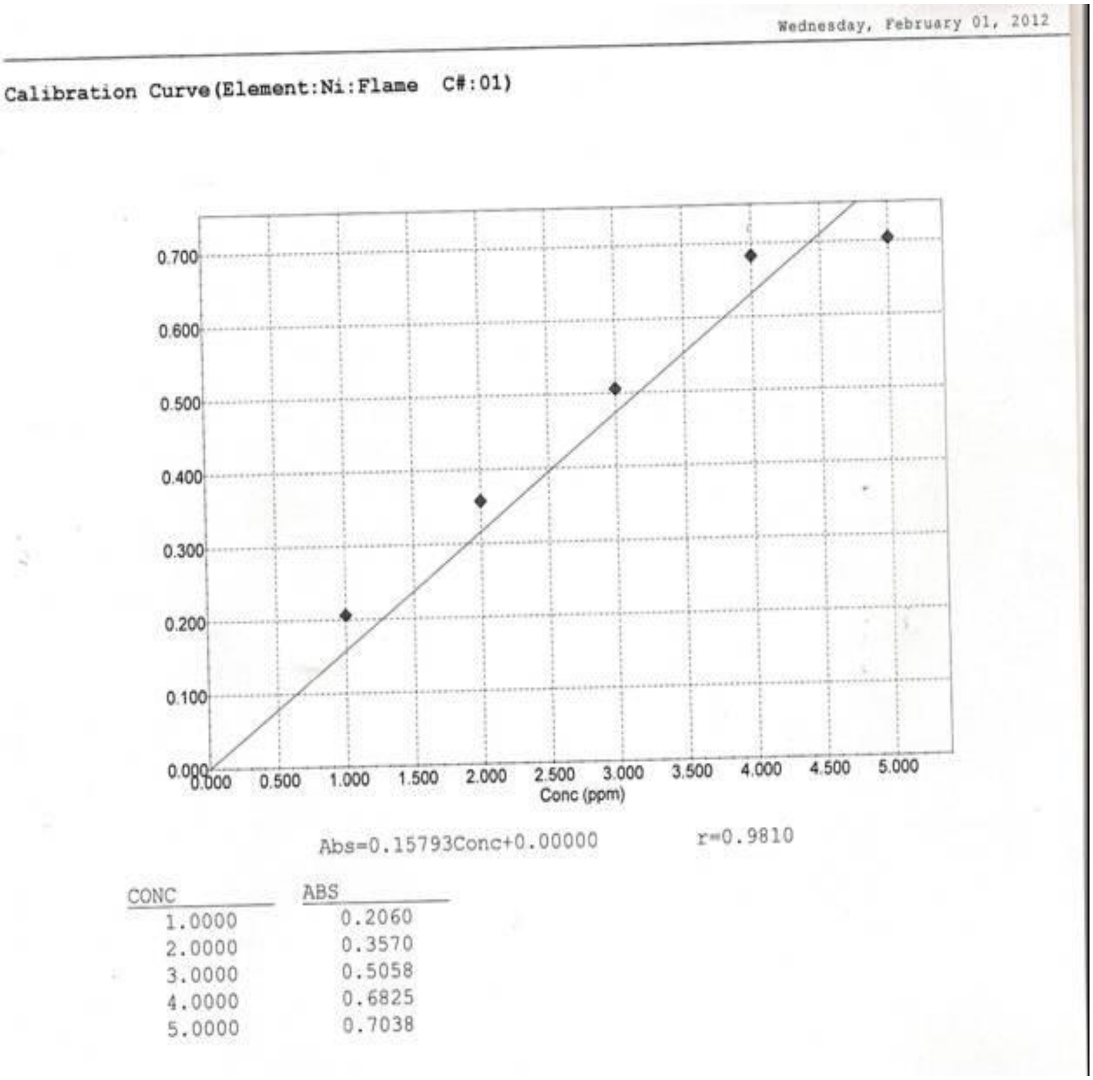
Tuesday, January 31, 2012

Calibration Curve(Element:Cr:Flame C#:01)

Abs=0.025142Conc+0.00000 r=0.9973

CONC	ABS
1.0000	0.0226
2.0000	0.0549
3.0000	0.0758
4.0000	0.1015
5.0000	0.1234

Appendix 4: Ni calibration curve



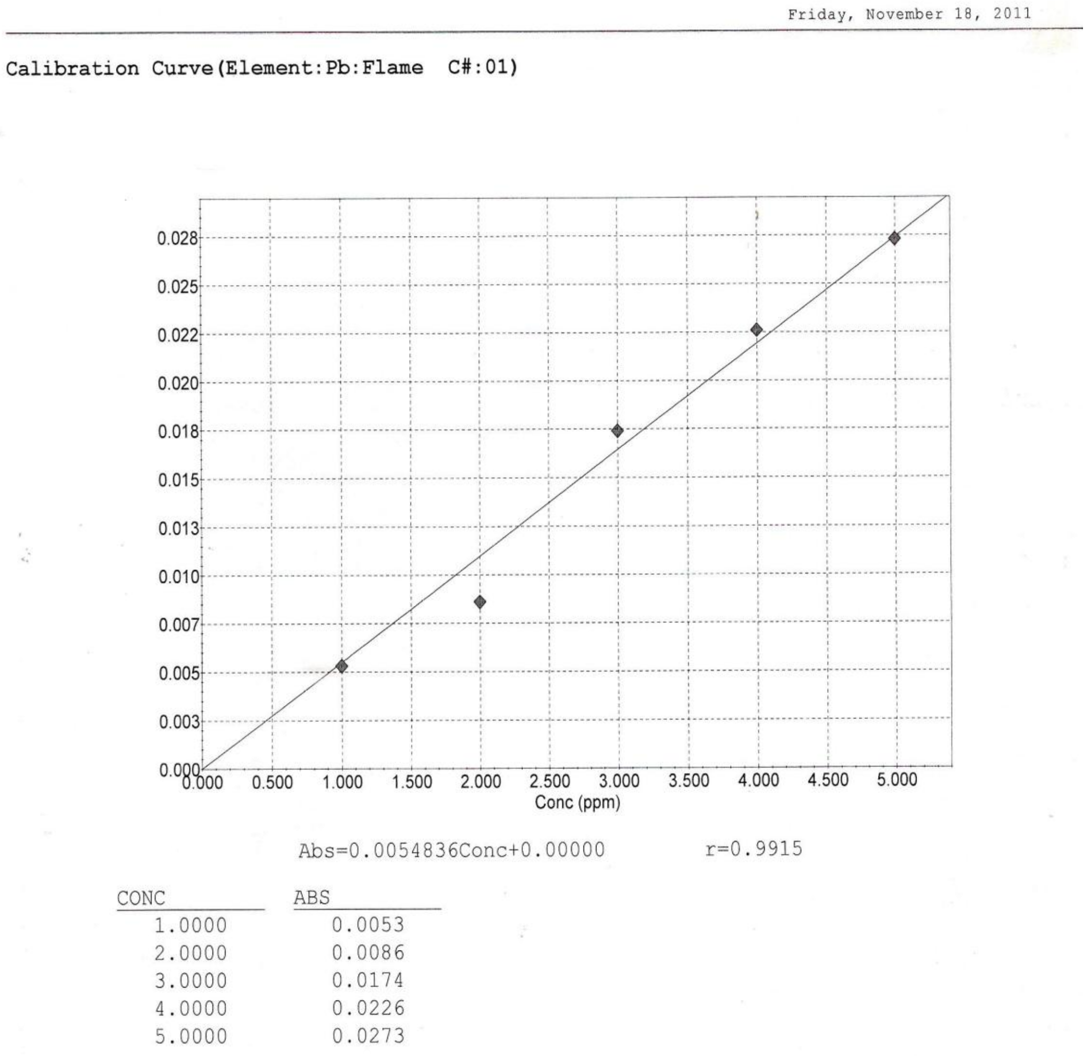
Wednesday, February 01, 2012

Calibration Curve(Element:Ni:Flame C#:01)

Abs=0.15793Conc+0.00000 r=0.9810

CONC	ABS
1.0000	0.2060
2.0000	0.3570
3.0000	0.5058
4.0000	0.6825
5.0000	0.7038

Appendix 5: Pb calibration curve



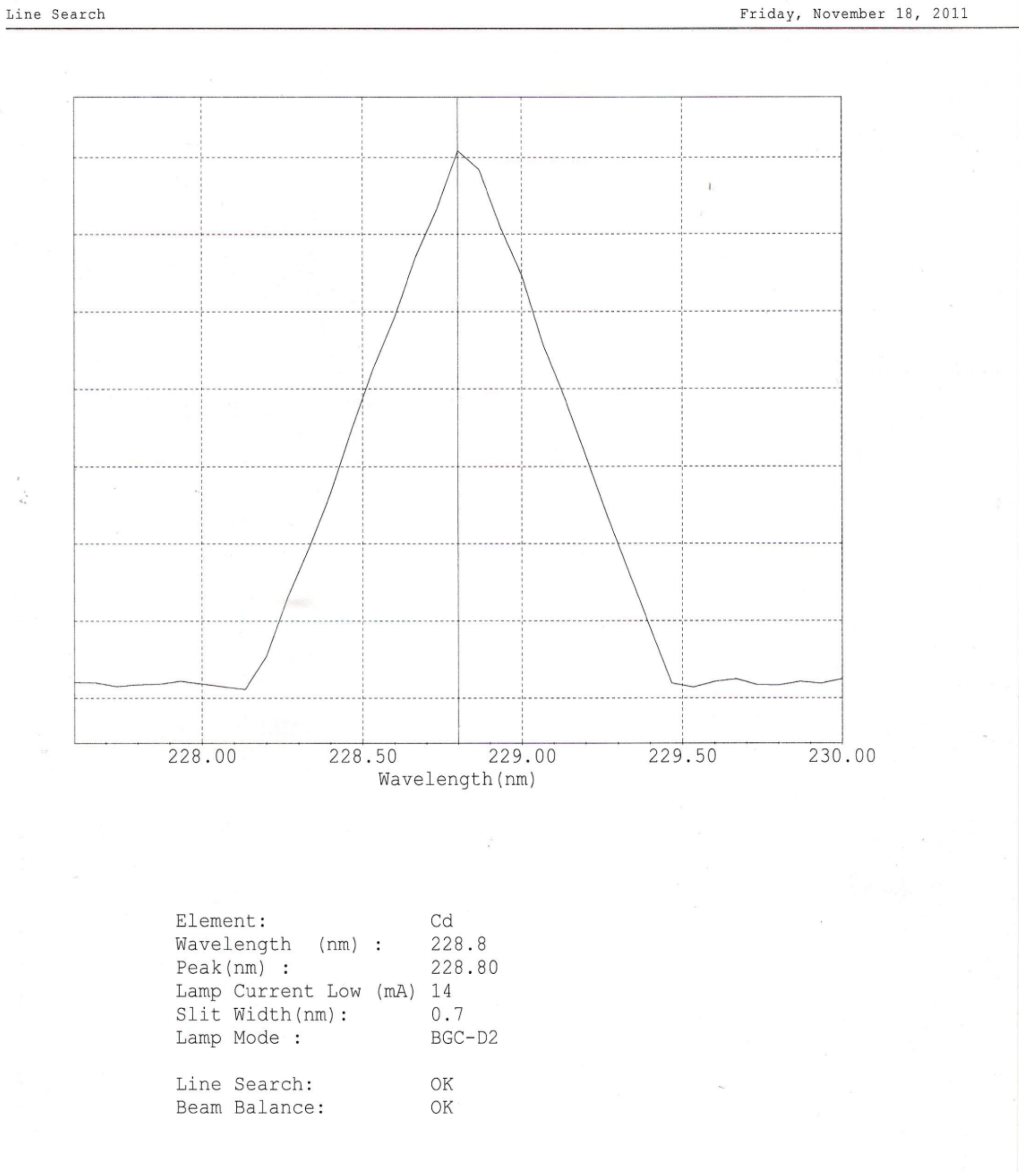
Friday, November 18, 2011

Calibration Curve(Element:Pb:Flame C#:01)

Abs=0.0054836Conc+0.00000 r=0.9915

CONC	ABS
1.0000	0.0053
2.0000	0.0086
3.0000	0.0174
4.0000	0.0226
5.0000	0.0273

Appendix 6: Cd absorbance peak

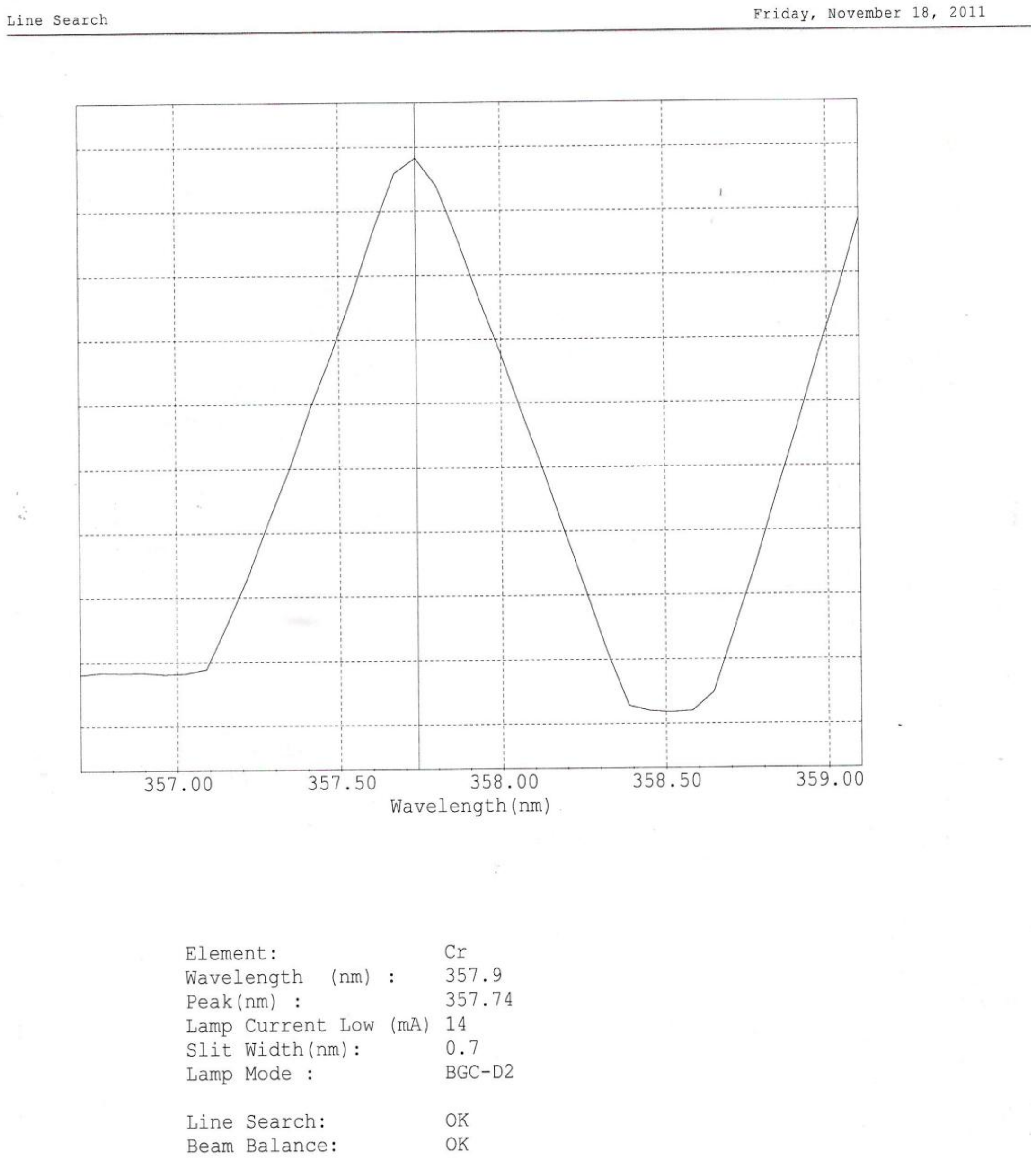


```
Line Search                                          Friday, November 18, 2011
```

```
Element:                  Cd
Wavelength  (nm) :        228.8
Peak(nm) :                228.80
Lamp Current Low (mA)     14
Slit Width(nm):           0.7
Lamp Mode :               BGC-D2

Line Search:              OK
Beam Balance:             OK
```

Appendix 7: Cr absorbance peak



Line Search

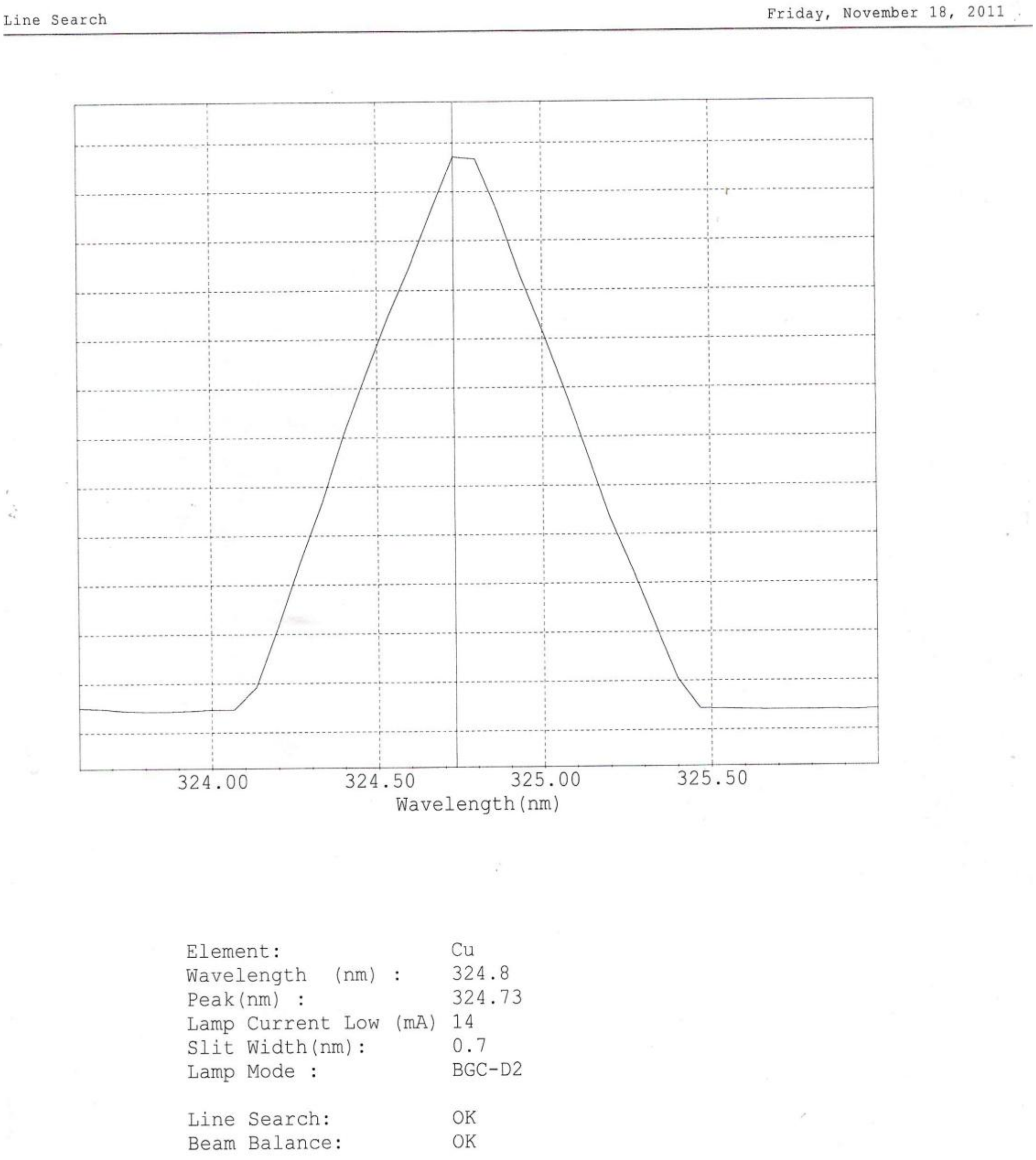
Friday, November 18, 2011

Element: Cr
Wavelength (nm) : 357.9
Peak(nm) : 357.74
Lamp Current Low (mA) 14
Slit Width(nm): 0.7
Lamp Mode : BGC-D2

Line Search: OK
Beam Balance: OK

s

Appendix 8: Cu absorbance peak



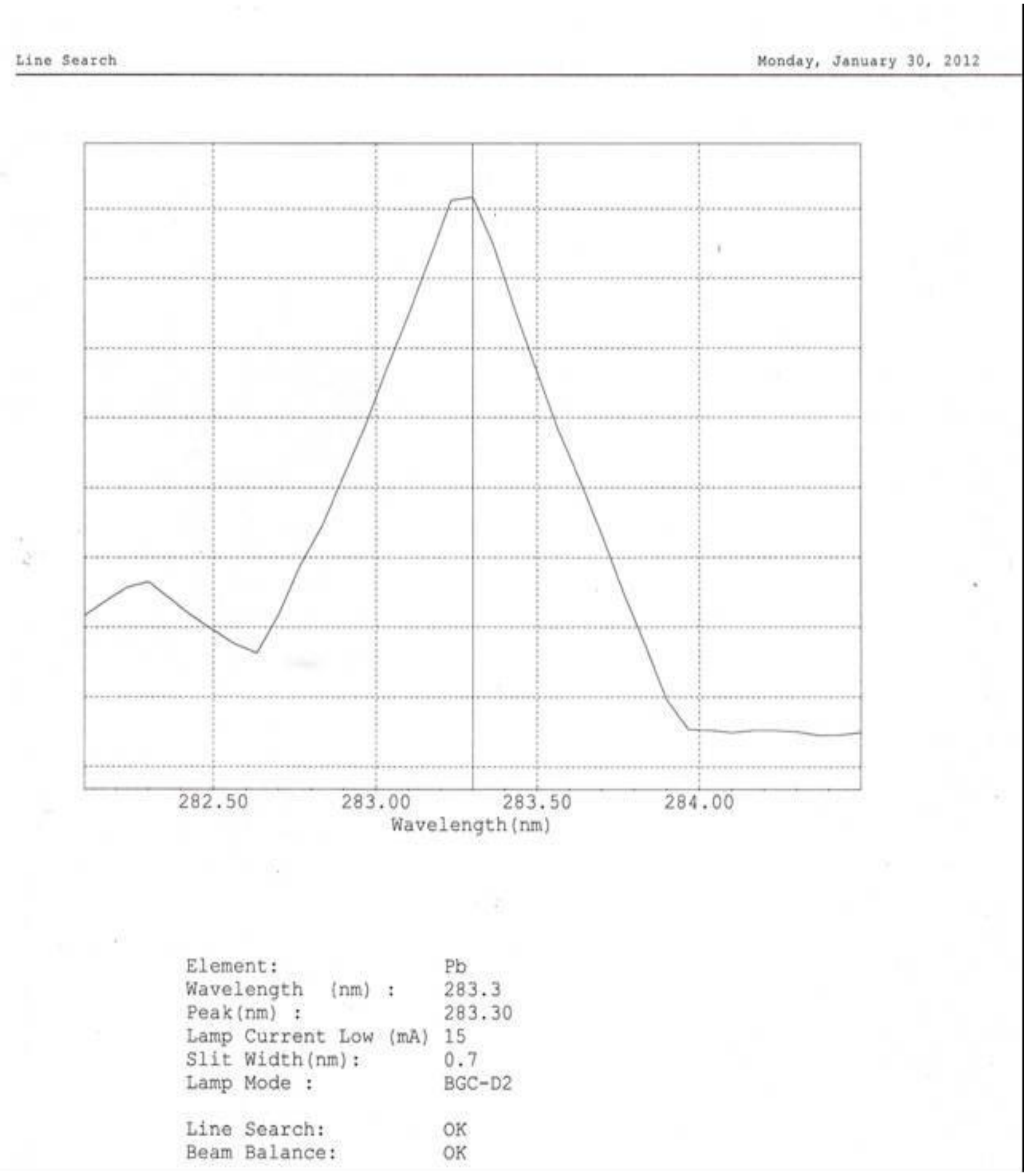
Line Search

Friday, November 18, 2011

```
Element:                  Cu
Wavelength  (nm) :        324.8
Peak(nm) :                324.73
Lamp Current Low (mA)     14
Slit Width(nm):           0.7
Lamp Mode :               BGC-D2

Line Search:              OK
Beam Balance:             OK
```

Appendix 9: Pb absorbance peak



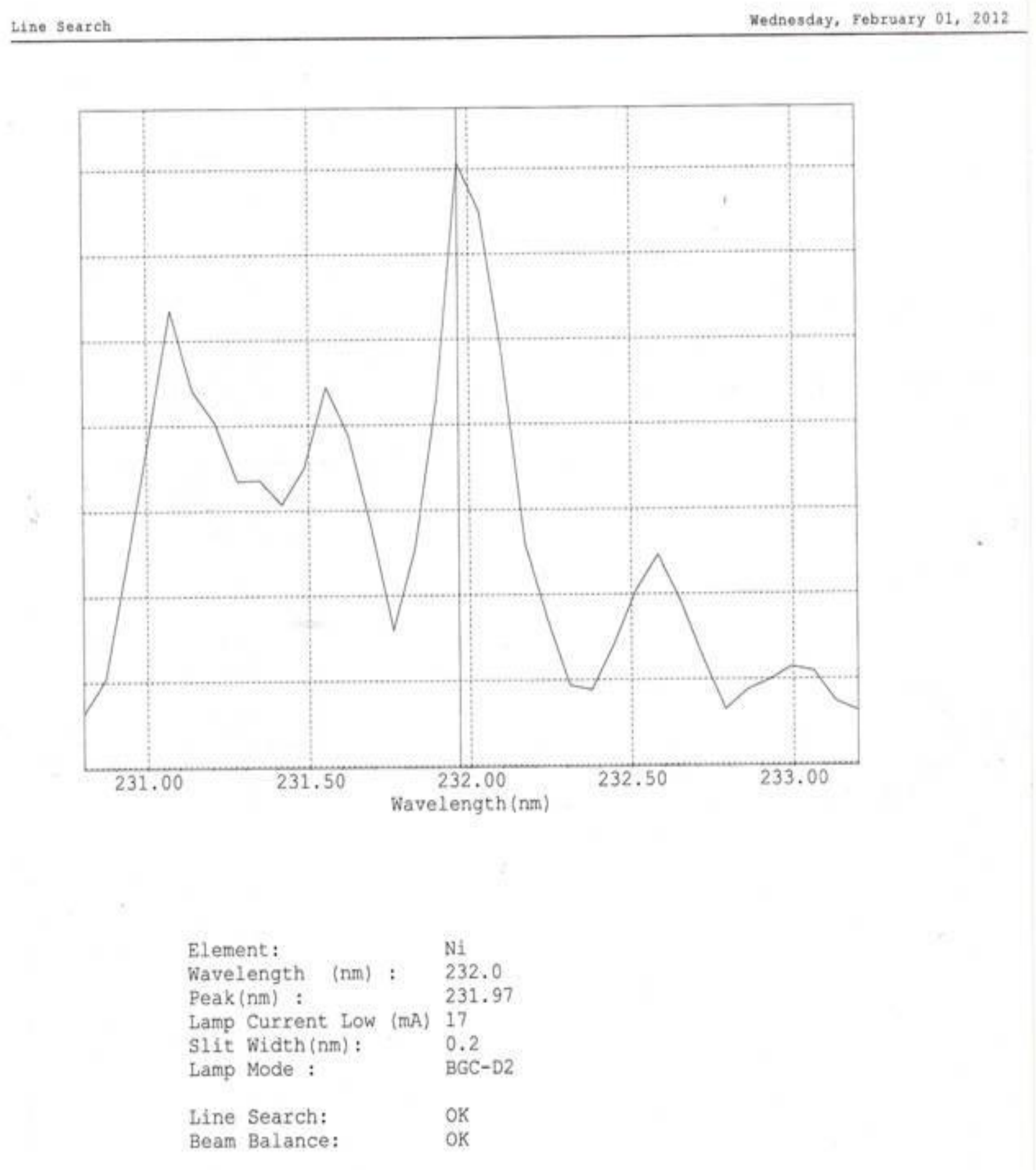
Line Search

Monday, January 30, 2012

Element: Pb
Wavelength (nm) : 283.3
Peak(nm) : 283.30
Lamp Current Low (mA) 15
Slit Width(nm): 0.7
Lamp Mode : BGC-D2

Line Search: OK
Beam Balance: OK

Appendix 10: Ni absorbance peak



```
Line Search                                      Wednesday, February 01, 2012

Element:                    Ni
Wavelength   (nm) :         232.0
Peak(nm) :                  231.97
Lamp Current Low (mA)       17
Slit Width(nm):             0.2
Lamp Mode :                 BGC-D2

Line Search:                OK
Beam Balance:               OK
```

Appendix 11: EPA maximum limits for different heavy metals

Heavy metal	Concentrations(mg/L)
Chromium	0.1
Lead	Zero
Cadmium	0.005
Copper	1.3
Nickel	0.001

Extracted from 31st session, Geneve Switzerland, 30th july 2008

Appendix 12: WHO, FAO and KEBS maximum limits for different heavy metals

Element	WHO and FAO maximum permissible	KEBS maximum permissible limits (mg/L)limits (mg/L)
Pb	0.01	0.1
Cd	0.003	0.005
Cr	0.01	0.05
Cu	1.0	1.0
Ni	0.02	0.1

Permitted levels of some of these heavy metals in drinking water according to: EPA, WHO, FAO and KEBS. From national drinking water regulation.

Appendix 13: EPA regulations on TDS

Description	Conc.(mg/L=ppm)
Ideal Drinking water from reverse osmosis, distillation, deionization, microfiltration, etc..	050
Often considered acceptable range for carbon filtration, mountain springs or aquifers.	50-140
Average tap water.	140-400
Hard water.	170 or above
Less desirable	200-300
Unpleasant levels from tap water, aquifers or mountain springs.	300-500
The EPA's maximum contamination level.	500

Tolerance limits of TDS by KBS is 250 mg/L and pH 6.0-9.0, WHO TDS limits500 mg/L
Extracted from 31st session, Geneve Switzerland, 30th july 2008

Appendix 14: EPA classification of water COD

Water Classification	**COD**
Weak	< 400
Medium	700
Strong	1000
Very Strong	1500