ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES

PHYSICO-CHEMICAL CHARACTERISTICS AND POLLUTION LEVELS OF TRACE METALS IN THE LITTLE AKAKI AND BIG AKAKI RIVERS

GRADUATE PROJECT (Chem.774)

BELACHEW TOLLA

JULY, 2006

PHYSICO-CHEMICAL CHARACTERISTICS AND POLLUTION LEVELS OF TRACE METALS IN THE LITTLE AKAKI AND BIG AKAKI RIVERS

A Graduate Project Submitted to Addis Ababa University
School of Graduate Studies

In Partial Fulfillment of the
Requirements for the Degree of
Master of Science in Chemistry

BELACHEW TOLLA

JULY, 2006

ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES

PHYSICO-CHEMICAL CHARACTERISTICS AND POLLUTION LEVELS OF TRACE METALS IN THE LITTLE AKAKI AND BIG AKAKI RIVERS

Belachew Tolla
Department of Chemistry
Science Faculty

APPROVED BY	DATE	SIGNITURE
Prof. B.S.Chandravanshi Advisor	________________	____________________
Prof. Hailemichael Alemu Examiner	________________	____________________
Dr. Mesfin Redi Examiner	________________	____________________

AKNOWLEDGEMENTS

For all their sincere, faithful and immense devotion to help me for the accomplishment of this work much appreciation is expressed for my instructors and advisors Prof. B.S.Chandravanshi and Dr.Feleke Zewge.

I also gratefully acknowledge Dr. Mesfin Redi and Dr. Yonas Chebude for their unlimited assistance and support during the study.

I would also like to express my gratitude for financial support provided by Addis Ababa University School of Graduate Studies.

Special thanks are due to Fasil Beyene who is the student of GIS and Remote Sensing for assisting me towards assigning the geographical locations of the sampling areas. Also I can’t forget the help of Ato Belete Yitayal for providing me transportation service during sampling and also the faithful corporation of W/t Buzayehue Taddese and W/t Tigist Tolla for the accomplishment of this work is printed in my heart.

In addition, the generous support and contribution of all my colleagues, friends and families are deeply acknowledged and emphasized in all cases of my future life.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ACRONYMS AND ABBREVIATIONS

ASTM	American Society for Testing Materials
ASV	Anodic Striping Voltammetry
BAR	Big Akaki River
CCME	Canadian Council of Minster for Environment
DPV	Differential Pulse Voltammetry
EC	Electrical Conductivity
ECM	Electro Chemical Methods
EPA	Environmental Protection Authority
FAAS	Flame Atomic Absorption Spectroscopy
GFAAS	Graphite Furnace Atomic Absorption Spectroscopy
GPS	Global Positioning System
ICMR	Indian Council of Medical Research
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ISO	International Standard Organization
IUPAC	International Union of Pure and Applied Chemistry
LAR	Little Akaki River
NAA	Neutrons Activation Analysis
SD	Standard Deviation
TDS	Total Dissolved Solid
TQWR	Tentative Quality South African Target Water Ranges
WHO	World Health Organization

PHYSICO-CHEMICAL CHARACTERISTICS AND POLLUTION LEVELS OF TRACE METALS
IN THE LITTLE AKAKI AND BIG AKAKI RIVERS

By: Belachew Tolla

Advisors: Prof. B.S.Chandravanshi and Dr. Feleke Zewge

ABSTRACT

In the present work, physico-chemical variables (temperatures, pH, TDS, and conductivity) and some selected trace metals (Cd, Cu, Co, Ni, Pb, and Zn) analysis of the water and surface sediments from river Big Akaki and Little Akaki were conducted with a view to asses the quality of the rivers as well as to identify the potential contaminated areas. The results of physico-chemical parameters revealed that the mean values of temperature reading, pH, conductivity, and TDS along LAR varied between 19 to 21 ^{o}C, 6.59 to 7.71, 661 to 1790 μS/cm and 317 to 881 mg/L, respectively and the ranges of these values along BAR are 17 to 21 ^{o}C, 369 to 749 μS/cm, 176 to 316 mg/L. Trends of these variables showed an intimate relation with anthropogenic activities along both rivers. Trace metals in sediment and water samples were determined by FAAS. The levels of dissolved trace metals in these rivers were found to be below the detections limit of the method except for Zn and indeed Ni and Co in some sampling sites of the rivers. The levels of dissolved metals in both rivers are below the South Africa guidelines fixed for irrigational, domestic and livestock watering purposes. In contrast to water samples significant amount of metals were found in both river sediment samples at all sampling stations. The concentration ranges of the metals in LAR sediments were: 0.43 to 1.45,30 to 89, 18.32 to 44.02, 119 to 73, 55.73 to 320, and 205 to 730 mg/L for Cd, Cu, Co, Ni, Pb, and Zn, respectively also the mean range of these metals in BAR sediments are 0.31 to 0.59, 30.5 to 89.41, 18.33 to 30.47, 119 to 62, 35.67 to 71.75, 172.89 to 288 mg/L, respectively. Levels of Cd and Co were found to be low in both river sediments and they are below EPA sediment quality guidelines (SQG). Cu in both river sediments was found to be below SQG except at one site along LAR. Both rivers sediments were found to be enriched with Ni and all sampling sites of LAR and 80% of BAR sites surpassed

SQG for Ni. The levels of Zn and Pb along BAR sediments are below SQG while 30% of sites along LAR contain Pb above SQG and one site along LAR surpassed the SQG for Zn content. Pair wise comparison of the two rivers revealed that generally the levels of trace metals and the values of physico-chemical variables in LAR are higher than that of BAR. The levels of Cd, Pb and Zn in the sediments of LAR showed a significant positive correlation with each other.

Key words: Little Akaki River, Big Akaki River, Water pollution, Sediment, Trace metals, Flame atomic absorption spectroscopy

1. INTRODUCTION

Trace metals have been referred to as common pollutants, which are widely distributed in the environments with sources mainly from anthropogenic activities and from the withering of minerals and soils [1]. The presence of toxic metals such as Cd and Pb in the environment has been a source of concern to environmentalist, governmental agencies, and health practitioners. This is mainly due to their health implication since they are toxic above a certain tolerable level to human, animals and plants [1-5]. Some trace metals such as copper and cobalt are essential for enzymatic activities, acting as enzymatic inhibitors at higher concentrations [5-8]. The pollution of surface water by trace metals is a worldwide problem, and the situation is aggravated by the ability of these metals to accumulate in the sediments and food chain (fish and vegetables) [2-4, 8]. Although Ethiopia does not have the industry that flourishes in developed countries due to the absence of a satisfactory waste management system the water bodies in Addis Ababa are being threaten seriously by human activities.

1.1 The Pollution Status of Rivers in Addis Ababa

Addis Ababa is a typical example of developing countries city where the rate of urbanization and availability of waste removal facility are not equivalent. According to Addis Ababa City Council 2004 [9] the daily waste generation is estimated about 0.252kg/capita/day, 65 % (1,482m^3)/day of municipal waste is collected in the city, surface water bodies receive the major parts of waste produced by the residents and various factories [10-11]. The main surface water system in the city includes Akaki River and various reservoirs [11]. Akaki River, which has two main branches: Big Akai and Little Akaki is the most polluted surface water system in the city. The following general sources can be identified for the pollution observed in the river water and sediment: (1) domestic pollution: untreated liquid and solid waste produced by the inhabitants of the city, supplied by the sewage network and small creeks; (2) industrials pollution: untreated liquid and solid waste produced by various industrial centers, also supplied by the sewage net work and small creeks (this effect is more pronounced along Little Akaki river system)[12]; (3) atmospheric pollution: particulate emissions by vehicles and motors, by product of open air burning of municipal and industrial solid waste and garbage, all of eventually transported to the inner and central Akaki Rivers by precipitation and drainage.

The most important sources of pollution for rivers water in Addis Ababa are industrials and domestic pollution. For example, the western part of Addis Ababa is an industrial estate along Little Akaki; each factory thus pours a lot of chemical pollutants, which affect the gardens down the stream. Though an important information campaign has never been launched, the inhabitants do know the situation of Little Akaki. The general slaughterhouses of Addis Ababa to get rid of their wastes also use the river. The river is also used in this area to irrigate some vegetable gardens [13-15]. Behind the psychiatric center, Saint Emanuel, next to the cereal market to be precise, Little Akaki goes through highly populated areas. There, the river is used as toilets and to wash. The biggest problem as the area is formed of very dense shantytowns comes from garbage. Little Akaki is used there as a public dump for thousands of inhabitants. In fact, and according to many authors [10, 15], the whole stream down to Kaliti is subject to all kind of waste disposals. In some localities sludge water and human faces and other are also dumped to these rivers. Bigi Akaki also crosses the highly populated region in the eastern part of the city where it receives any kinds of wastes from the residents.

Figure 1. Vegetables farm beside Addis Ababa Winery irrigated with water contaminated with the effluent (Photo EPA, 1997).

Figure 2. The Little Akaki River loaded with suspended particles, solid wastes, and toxic industrial and domestic effluents.

Little Akaki is being used to get rid of industrial wastes. If we consider the down stream we can observe different sources of pollution, cement, leather, and beverage production and municipal wastes. Exposure to these wastes which contain toxic components such as trace metal ions, is of great concern, as it poses not only health risks to human but also potentially unacceptable ecological risks to plants which are produce by intensive agricultural practices along the river sides, animals and microorganisms [13-15]. The problem aggravated in some of the rivers catchments area where there is no potable water supply, hence dependence on water sources mainly from surface water for domestic, swimming, washing, lives stock activities, and irrigational activities despite their foul odor, black color and high toxicity.

The pollution status of a river would have its influence on the receiving land, which might possibly reflect on the product cultivated on such land. For example, Royal Crown, a mineral water manufacturer almost faced bankruptcy because they have allegedly proposed pumping spring waters on a soil drained by Little Akaki. Vegetables are grown on the embracement along LAR and BAR within Addis Ababa town and the neighboring town such as Akaki, Alem Gena, and Sebeta [15]. Some studies indicated that 40% of the vegetable supplied to Addis Ababa city and animal feed comes from the suburb directly irrigated by these water or fields flushed from waste water during the heavy rainy season or during the dry season. The vegetables farm at Kera and the Peacock Park are among the biggest farms in the capital city where substantial amount of vegetables are being produced seasonally. These farms are irrigated with the wastewater from river Kera and Bulbula, respectively. For these reasons, the investigation of trace metals in sediments, water and vegetables is essential since even slight changes in their concentration above the acceptable levels, whether due to natural or anthropogenic factors can result in serious environmental and cause long-lasting health problems.

1.2 Objectives and Scope

This study reports the input and distribution of Cd, Pb, Zn, Cu, Ni and Co in Little Akaki and Big Akaki Rivers water and sediment together with the values of pH, conductivity, salinity and total dissolved solid of the water bodies. Also, it aims at estimation of the impact of industrialization by comparing the pollution statues of Little Akaki River, where many factories dominate in the city and Big Akaki River with relatively less industrialization is observed. For comparison purpose from the two rivers, sampling sites with similar latitude were compared towards their metal contents and physico-chemical properties.

Specific objectives

- To collect water and sediments samples from some selected site on Little and Big Akaki river systems.
- To develop a procedure for digestion of sediment samples.
- To determine trace metals (Cd, Pb, Zn, Cu, Ni and Co) contents of the collected water and sediment samples and physico-chemical properties of water bodies.
- To evaluate the degree of pollution of water and sediments collected and evaluate the distribution of those metals along the two rivers.
- Compare the two rivers with their metal contents and physico chemical properties.

2. LITERATURE REVIEW

Over the past two decades, the term “heavy metals” have been used increasingly in various publications and legislation related to chemical hazards and the safe use of chemicals. It is often used as a group of name for metals and metalloids that have been associated with contamination and potential toxicity and ecotoxicity. Usually the term heavy metals used inconsistently to replace the name of trace metals. So it is instructive to see the difference between the two terms. According to IUPAC the term “trace metals” is defined as a metal in low concentration, in mass fractions of ppm or less, in some specified source, e.g., soil, plant, tissue, ground water, etc. [16] while heavy metals is defined based on the following properties: (1) definitions in terms of density (specific gravity): metal with a density above 3.5–5 g/cm^3; (2) definitions in terms of atomic weight (relative atomic mass): metal with a high relative atomic mass. The term is usually applied to common transition metals such as copper, lead or zinc; (3) definitions in terms of atomic number: metal with an atomic number between 21 (scandium) and 92 (uranium); (4) definitions without a clear basis other than toxicity: element commonly used in industry and generically toxic to animals and to aerobic and anaerobic processes, but not every one is dense nor entirely metallic. Includes As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Zn. In this study, all the metals are considered as trace metals other than heavy metals to avoid confusion.

2.1 Trace Metals in Surface Water

Interest in trace elements in water has grown markedly over the decades or so, mainly through increasing concern about the many undesirable effect known or suspected to be caused by certain elements. Analysis of lake sediments, ice sheet, museum specimens, peat and other materials with chrononological significance has indicated increasing concentration of some of certain toxic elements, for example Hg and Pb [17]. It has also been suggested that man’s global activities now lead to greater input of Cd, Cr, Cu, Hg, Pb and Zn than the amount of safely disposed of naturally, mainly by deposition in the oceans [17]. Metals are distributed in the water bodies in different forms of species. Table 1 summaries the different forms of metals that present in water.

Table 1. Trace metal species in water (Source from Wilson *et al.* [17])

Metals species	**Example**	**Metal species**	**Example**
Free metal ions	$Cu(H_2O)_6^{2+}$	Metals bound to organic materials of high molecular mass metal species	Pb-fluvic acid polymers
Simple radicals	UO_2^+, VO_3^-	Coloid	FeOOH
Inorganic complexes	$CdCl^+$,$CuCO_3$, $Pb(CO_3)_2^{2-}$	Metals sorbed on colloids	Pb on clays
Organic complex and chelate compounds	$Cu\text{-}COC.CH_3^+$, $Hg(CH_2)_2$	Precipitates, minerals particles	$PbCO_3$, PbS

In addition to the species shown in Table 1, many metals can exist in different oxidation states that commonly show markedly different speciation. Thus, the oxidation state may govern whether the metal is present as an anionic or cationic species, for example Mo, V and Cr [1-2, 8]. The solubility and the tendency to complexation of the metal may also depend on its oxidation state, fore example Mn and Fe [17]. Interconversion of the various species may occur, and the nature and extent of such conversions depends on the pH, the inorganic and organic constituents of particular water. Such effect may have many important consequences. For example, discharge of an effluent into a river may, if the pH is changed or if the affluent contains metal-complexing substances, affect the equilibria between the metals in the sediments and in the overlying water [8]. The mobility effect of the metals in rivers may be markedly affected by such process (section 2.4).

Metals in the water usually determined as (i) dissolved metals: those metals in an acidified sample that pass through a 0.45-µm membrane filter; (ii) Total metals: the concentration of metals determined in an unfiltered sample after vigorous digestion, or the sum of the concentration of metals in the dissolved and suspended fractions. Usually the metals are defied operationally by the digestion procedure [18]; (iii) acid–extractable metals: the concentration of metals in solution after treatment of unfiltered sample with hot dilute mineral acid [18].

2.2 Trace Metal Analysis Methods

The measurement of specific metallic ion constituents in water is used in two ways: to provide direct determination of the speciation of various molecular or valence forms of an element and to provide elemental analysis either directly or after chemical conversion into a measurable form. Modern analytical laboratories use single- element or multi-element analytical techniques for the determination of trace levels of elements in sediments and water samples.

FAAS, GFAAS, ICP-OES, ICP-MS, NAA, and Electrochemical methods (ECM) are the major techniques used in official methods for water analysis e.g. ASTM, EPA, and ISO [19]. A brief description of each technique is presented below.

Neutron Activation Analysis (NAA): In neutron activation analysis (NAA) a sample (solid or liquid) is interrogated with neutrons and the induced radioactivity is measured and related to isotopic (elemental) concentrations of the elements present in the sample. NAA is a multi-element analysis technique, often non-destructive in nature where approximately 75 elements can be measured with the detection limits ranging from 10^{-6} to 10^{-12} g of element in a sample. Quantization is accomplished by comparison with standards prepared from pure elements or compounds that are irradiated and measured under the same conditions as the samples. Typical sample sizes range from 1mg to 1 g, however in principle much larger samples (10 kg) can be activated and the size is only limited by the capacity of the neutron irradiation facility [19].

Atomic Absorption Spectrometry (FAAS/GFAAS): AAS is generally recognized a powerful technique with low detection limit in the range of μg/L for FAAS [19-21]. Instruments equipped with a graphite furnace vaporization source can achieve detection limits in the range of 10^{-9} to 10^{-12} g in a 10–50 µL aliquot for elements such as Zn, Se, Cd, Hg and Pb. AAS technique is used for single element analysis of aqueous samples and on solid samples, which are introduced in the form of slurry. Quantitation is performed using single element standard solutions from which calibration curves are prepared. One disadvantage of this technique is its limited linear dynamic range (typically one order of magnitude), which often requires the analyst to perform serial dilutions to quantify those elements whose concentrations fall outside the linear range. The additional operations increase the uncertainty of the final results and also reduce the productivity (output). The advantages of the technique are the low capital cost and simplicity of operation, and its specificity and sensitivity for some elements, which can be, volatilized (e.g. Hg) or chemically converted to a volatile hydride (e.g. As, Sn). The detection limits of AAS commonly improved with preconcentration of anlytes to ppm or above levels by chemicals and physical procedures. The most suitable techniques of the preconcentartion are solvent extraction, sorption on solid sorbent, coprecipitation, and electrodeposition [20-21].

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES): This technique is used for multi-element analysis of aqueous samples. Quantitation is accomplished using multi-element standard solutions from which calibration curves are prepared. These instruments have a wide linear dynamic range (typically 3 to 5 orders of magnitude) that permits the analyst to measure both major and trace elements in the same solution without dilution. The technique has one major disadvantage as it yields very complex spectra with many overlapping lines, which may introduce a bias or increase the uncertainty in the final results. Detection limits range from 10^{-8} to 10^{-10} g/mL for approximately 70 elements [19, 22].

Inductively Coupled Plasma Source Mass Spectroscopy (ICP-MS): This technique is similar to ICP-OES except that in addition to elemental analysis, it can also determine isotopic abundances and isotopic ratios for each element. It has a wide linear dynamic range (typically 4 to 5 orders of magnitude) and yields simple mass spectra, which can be corrected for isobaric interferences using the natural isotopic abundances of the interfering elements. A disadvantage of the technique is the higher capital cost for the instrumentation compared to either AAS or ICP-OES, especially in the case of a high resolution magnetic sector instrument. Detection limits range from 10^{-11} to10^{-12} g/mL for elements above a mass number of 80 [19, 23].

The quality of the result of all the above methods depends on the availability of purified water for the preparation of reagents, standards, and blanks, for sample pre-treatment and for rinsing components [19].

Electrochemical Methods (ECM): The other technique of trace metals analysis is ECM. Differential pulse voltammetry (DPV) and anodic striping voltammetry (ASV) are the most sensitive methods. The advantages of ECM are sensitivity, convenience, suitable for turbid solution and convenience for sample handling [24].

2.3 Sources of Trace Metals in Surface Waters

The main sources of trace metals are summarized below but the effect of these sources on the concentration of metals in water is also governed by the speciation of the metals in the water.

i. Atmospheric Precipitation

Dust, rain and smokes may represent very important, direct sources of metals to water bodies [18, 25]. For example, lead in rainfall may be one of the dominant factors affecting the concentration of Pb in the rivers of the U.S.A [19]. As might be expected, industrial smelting plan may contribute metals such as Zn and Cd to the near by water bodies, but air borne contaminants may also be transported long distances before precipitation. In addition to direct input of metals, other atmospheric contaminants (e.g. SO_2) may affect the metals in water by decreasing the pH and thereby leaching metals from sediments [26].

ii. Geochemical Sources

Weathering of surface soils and rocks is a potential source of many trace metals to waters. The nature and concentration of these metals depends on the local geological and geochemical factors [27]. Ore bodies and past and present mining activities may cause usually high concentrations of particular metals in surface waters. Spring water of deep-seated origin may contribute elements not usually found in surface waters [28].

iii. Effluents

Generalization of the effect of industrial effluents is impossible because they clearly depend on the nature of the industry and its effluent control procedures [29]. Such effluents can be important sources of metals such as Hg, Cd, Pb, etc. One aspect of that recently received attention is the quality of water draining from urban areas during heavy rainfall. Such water may contain very high concentrations of metals, and particularly those such as Pb that settle on urban surface from the air. Effluent discharge may also release metals from the sediments.

iv. Sediments

Sediments commonly contain much greater concentrations (by mass) of metals than overlying waters [30]. The metals in sediments are generally present in as small minerals particles or are absorbed on, or incorporated with, other undissolved materials. Such undissolved forms of metals usually contribute rather little metal ions to the water, but changes in the water quality, natural or man made, may lead to the realize of metals from sediments. One interesting example is the release of Hg as dissolved chloride complex when high concentration of chloride of from road de-icing enters water body systems [25].

V. Land Use Drainage

The general geochemical effect of the soil is noted in (ii) above, but man's activities may also be important; for example, the use of chemicals in agriculture, deposition of contaminants from the atmosphere, use of sewage sludge as fertilizers and leaching of waste tips may all cause contamination of surface waters [17].

2.4 Exchangeability of Metals between Water and Sediments

Sediment has been described as a ready sink or reservoir of pollutants including trace metals where they concentrate according to the levels of pollution [2]. Indeed, the level of pollutants is not only dependent on the amount of input but also on the strength of the association between the metals and the sediment compounds [1-2]. The sediment environment provides a long-term record of the effects of anthropogenic discharges, such as industrials and domestic effluents and is an area where impacts often occur before effects are manifest in the water column. In contrast to strong temporal and spatial variability in the aqueous concentration of contaminants, sediments integrate contaminants concentrations over time and that by focusing on sediments the number samples needed in contamination assessment can be reduced [2]. Determinations of metal concentrations in suspended and bed sediments are useful in understanding processes that affect metal contamination in rivers.

The availability of sediment-bound trace metals is dependent not only total metal concentration but also on the strength of the association between the metal and sediment compounds, variations in sediment texture, and composition of the sediment. Metals bound to biogenic carbonate and organic matters are much more available than metals strongly bound to other compounds such as iron oxide and sulphides [8]. The proportion of exchangeable metals in a given sediment is also dependent on other environmental variables. These include physical and chemical characteristics of both the overlying water and the sediment pore water. Changes in pH and reduction/oxidation potential, adsorption/absorption, and physical transport or sorting, as well as anthropogenic metal inputs can mobilize metals from sediments to the water column, either by dissolving unstable metals compounds, precipitating metals by favoring the adsorption on to suspended particles surfaces, or through the formation of insoluble metal sulphides [1-2, 8]. As a combined result of the influence of the above processes, fluctuation of the metal concentrations of sediments occurs in time and space; and bioavailability from sediments changes. The relative importance of individual processes is determined by the geochemistry of the specific metal or metalloid and the characteristics of the ecosystem [17].

2.5 Roles of Trace Metals in the Environment

Trace elements, which include all the elements in the periodic system except bulk elements and macro minerals, are best classified as in to two categories: those elements whose essentiality has been established by accepted standards and those for which proof of essentiality does not exist. Research during the past three decades has added Mo, Cr, Ni, V, and As to the list of essential elements. This suggests that additional elements could be proved essential by future research and the number of elements now accepted as essential should not be considered final [6].

By the simplest definition an element is essential when it meets the criteria postulated by author [6]: (i) the element must present be present in all tissues of a given animals; (ii) its concentration in a given tissue must be fairly constant from one animal to the next; (iii) its withdrawals from the diet must lead to a specific deficiency syndrome; (iv) the deficiency syndrome must be associated with pertinent biochemical changes; v, both the syndrome and the biochemical changes be prevented or corrected by administration of the element. Based on the above criteria, the following trace metals are now considered essential in animals: V, Cr, Mn, Fe, Co, Cu, As, Ni, Zn and Mo.

In contrast to the essential elements certain elements are considered as non essential metals and are usually toxic even in very small amounts and have became serious environmental hazards for plants, animals and man alike. The risks are usually local and often confirmed to the vicinity of a smelter or other industrial plant, but these and abandoned mine workings may contaminate the soil and water supplies for a number of years, with adverse effects on the population, including in the incidence of cancer and other diseases. Fears have also been expressed concerning the long-term global effect of these metals such as Pb and Hg in the environment; Cd and As are also important anthropogenic hazards.

Cadmium: The major intentional uses of cadmium are Ni-Cd batteries, cadmium pigments, cadmium stabilisers, cadmium coatings, cadmium alloys and cadmium electronic compounds such as cadmium telluride (CdTe). The major classes of products where cadmium is present as an impurity are non-ferrous metals (zinc, lead and copper), iron and steel, fossil fuels (coal, oil, gas, peat and wood), cement, and phosphate fertilisers [29].

Cd is toxic by whatever route it is administered and some of the changes produced may result from its metabolic antagonism to Cu, Zn, and Fe: these include anaemia, hypertension and skin changes. Hypertensive patients accumulate Cd in the kidney. It has been reported that one cigarette contains about 0.5 - 2 μg of cadmium and that about 10% of the cadmium content is inhaled when the cigarette is smoked [5].

Cadmium emissions to the environment are normally transported continually between the three main environmental compartments, air, water and soils, but a steady state flux is probably achieved and the general levels can reasonably well be established. Cadmium is a natural, usually minor constituent of surface and groundwater. It may exist in water as the hydrated ion, as inorganic complexes such as carbonates, hydroxides, chlorides or sulphates, or as organic complexes with humic acids. Cadmium may enter aquatic systems through weathering and erosion of soils and bedrock, atmospheric deposition, direct discharge from industrial operations, leakage from landfalls and contaminated sites, and the dispersive use of sludge and fertilisers in agriculture. Much of the cadmium entering fresh waters from industrial sources may be rapidly adsorbed by particulate matter, and thus sediment may be a significant sink for cadmium emitted to the aquatic environment [29, 8]. Some data shows that recent sediments in lakes and streams range from 0.2 to 0.9 ppm in contrast to the levels of generally less than 0.1 ppm cited above for fresh waters. Partitioning of cadmium between the adsorbed-in-sediment state and dissolved-in-water state is therefore an important factor in whether cadmium emitted to waters is or is not available to enter the food chain and affect human health.

Rivers containing excess cadmium can contaminate surrounding land, either through irrigation for agricultural purposes, dumping of dredged sediments or flooding. It has also been demonstrated that rivers can transport cadmium for considerable distances, up to 50 km, from the source [17]. Nonetheless, studies of cadmium contamination in major river systems over the past twenty to thirty years have conclusively demonstrated that cadmium levels in these rivers have decreased significantly. The average cadmium content in the world's oceans has variously been reported as low as < 5 ng/L and 5-20 ng/L to as high as 110 ng/L, 1 00 ng/L and 10 to 100 ng/L [31].

Copper: Copper is a reddish metal that occurs naturally in rock, soil, water, sediment, and air. Its unique chemical and physical properties have made it one of the most commercially important metals. Since copper is easily shaped or molded, it is commonly used to make pennies, electrical wiring, and water pipes. Copper compounds are also used as an agricultural pesticide, and to control algae in lakes and reservoirs.

Copper also occurs naturally in plants and animals. It is an essential element for all known living organisms, including humans [6]. However, very large single or long-term intakes of copper may harm health. Some one may be exposed to copper by breathing air, eating food, or drinking water containing copper or may also be exposed by skin contact with soil, water, or other copper-containing substances.

Most copper compounds found in air, soil, and water are strongly attached to dust or embedded in minerals, and cannot easily enter the body [32]. These forms are not likely to affect health. Other forms become dissolved in water and are not attached to other particles. In this form, copper is more likely to affect our health. Levels of copper found naturally in surface water are generally very low; about 4 micrograms of copper in one liter of water (4 μg/L) or less [31]. However, drinking water may contain higher levels of a dissolved form of copper. High levels of copper occur if corrosive water comes in contact with copper plumbing and copper-containing fixtures in the water distribution system. If corrosive water remains motionless in the plumbing system for six hours or more, copper levels may exceed 1,000 μg/L. The level of copper in drinking water increases with the corrosivity of the water and the length of time it remains in contact with the plumbing. Drinking water normally contributes approximately 150 μg/day and on the average, drinking water accounts for less than 5% of our daily copper intake. Immediate effects from drinking water which contains elevated levels of copper include vomiting, diarrhea, stomach cramps and nausea [31].

Cobalt: Cobalt is a metal that may be stable (non-radioactive, as found in nature), or unstable (radioactive, man-made). The most common radioactive isotope of cobalt is cobalt-60. The non-radioactive cobalt is a naturally occurring element found in rocks, soils, water, plant, and animals in small amount. The largest uses of non-radioactive metallic cobalt are for production of pigments in glass, ceramics, and paints; as catalysts in the petroleum industry; as paint driers; as trace element additives in agriculture and medicine.

The major biological role of cobalt is as a continent of corrin rings in vitamins B_{12}. It is an essential element, required for good health in animals and humans, and therefore, it is important foodstuffs to contain enough amount of cobalt. The major sources in diet are meat, milk and liver. Shortage of cobalt results in deficiency of vitamin B_{12}, which is common in vegetarians due to low vitamin B_{12} intake from their diets [6].

Sources of cobalt in the atmosphere are both natural and anthropogenic. Natural sources include wind-blown continental dust, seawater spray, volcanoes, forest fires, and continental and marine biogenic emissions. Atmospheric cobalt concentrations are much higher near cobalt manufacturing and production facilities. Concentrations of cobalt in uncontaminated freshwater have been reported to range from 0.1 to 10 μg/L [17]. Cobalt that realize in to the water will stick to particles in the water column or to the sediment at the bottom of the body of water in to which it was realized, or remain in the water column in ionic form. Eventually, most pats of it end up in the soil or sediment. Exposure to high levels of the non-radioactive cobalt results in lung and heart defect and dermatitis. Liver and kidney effects have also been observed in animals. The health effect of radioactive cobalt is known to cause cancer. Therefore, exposures to gamma radiation from cobalt-60 result in an increased risk of cancer.

Nickel: Nickel is a metal found in natural deposits as ores containing other elements. The greatest uses of nickel are in making stainless steel, tubing made of a copper-nickel alloy, coinage, Armour plate, colorant for glass, batteries, catalyst for hydrogenating vegetables oils and electroplating.

Nickel is an essential trace element for many plant and animal species with function of interaction with iron absorption. Small amount of nickel is essential for normal growth and reproduction in some species of animals, plant and microorganisms [6]. Nickel ion (II) under various conditions could either activate or inhibit several enzymatic reactions, which are considered to be of crucial importance in humans and other animals, and that interference with these reactions could have severe deleterious effects [5,7]. Taking very small amount nickel results in growth depression, anemia, ultrastructural change in liver and impaired reproduction [6].

Nickel compounds are very toxic for plants and animals [33-34]. The highly volatile nickel carbonyl $[Ni(CO)_4]$ is extremely toxic. It is possible that the tumors seen in rats exposed to this compound were generated as a consequence of a particle effect rather than by a direct effect of Ni^{2+} ion. Nickel compounds can be made as a by-product during various industrial processes that use nickel catalysts, such as coal gasification, petroleum refining, and hydrogenation of fats and oils. They have also been identified in residual fuel oil and in atmospheric emissions from nickel refineries. The amount t of nickel in seawater and streams is normally 2 and 0.3 respectively μg/L [17].

Lead: Lead, a very soft, blue-gray, metallic element has been used since antiquity. Because it is so soft, lead is usually alloyed with other elements. Combined with other elements, it forms a variety of interesting and beautiful minerals, all of which are heavy due to their lead content. The most significant lead mineral is galena (PbS, lead sulfide). $PbCO_3$ and $PbSO_4$ are two other lead-based minerals. Lead had been recognized as an industrial hazard before it was appreciated that house dust is a profile source of the elements from paint, the street, old batteries, solder from cans and toothpaste tube.

Lead has no known nutritional and physiological function and it is usually toxic for organisms. Pb impends the synthesis of heme and accumulates within the red cells as well as the bones to give rise to anemia, headache, dizziness, and damage to the digestive and nervous systems, so its use in some applications has been discontinued [5]. Wrist drop and coils in adults as well as encephalopathy in children are also features of chronic Pb poisoning [35].

Lead is rarely found in source water, but lead mining and smelting operations may be sources of contamination. When released to land, lead binds to soils and does not migrate to ground water. In water, it binds to sediments. Lead may occur in drinking water either by contamination of the source water used by the water system, or by corrosion of lead plumbing or fixtures. Corrosion of plumbing is by far the greatest cause for concern. All water is corrosive to metal plumbing materials to some degree. Grounding of household electrical systems to plumbing may also exacerbate corrosion. Over time, lead-containing plumbing materials will usually develop a scale that minimizes further corrosion of the pipe. World average Pb concentration unpolluted rivers is 4.0μg/L [31].

Zinc: Zinc is one of the most common elements in the earth's crust. It is also an essential element for all living things [6]. Pure zinc is a bluish-white, shiny metal. Zinc has many commercial and industrial uses. A large proportion of all zinc, perhaps more than a third, is used to galvanize metals such as iron so as to prevent corrosion. Zinc metal is used for dry batteries, roof cladding, and to protect iron structures from corrosion by attaching zinc as sacrificial anodes [29]. Zinc is mixed with other metals to form alloys such as brass and bronze, and pennies are made from a copper-zinc alloy. The oxide (ZnO) is also combined with other elements such as chlorine, oxygen, and sulfur to form zinc compounds used to make white paints, ceramics, rubber, wood preservatives, dyes, and fertilizers. Zinc compounds are also used in the drug industry as ingredients in common products like sun blocks, diaper rash ointments, deodorants, athlete's foot preparations, acne and poison ivy preparations, and anti-dandruff shampoos. The sulphide (ZnS) is used in making luminous dials, X-ray and TV screens, paints and fluorescent lights.

Zinc is one of the most abundant trace elements in the human body [6]. It is typically taken in by ingestion of food and water, although it can also enter the lungs by inhaling air, including that contaminated with zinc dust or fumes from smelting or welding activities. Zinc is an essential element in our diet, but too little or too much can be harmful. Without enough dietary intake, people can experience a loss of appetite, decreased sense of taste and smell, decreased immune function, slow healing of wounds, skin sores, and may increase the toxic effects of arsenic, copper, cadmium and lead; thus an adequate amount of zinc can be considered protective against the toxicity of these elements. Eating large amounts of zinc can cause stomach cramps, nausea, and vomiting.

Zinc is found throughout the environment in air, soil, and water, and it is present in all foods. Natural processes, but most results from human activities can release it. Releases to air, water, and soil are common in areas where ores are mined, processed, and smelted for zinc. Because cadmium and lead are commonly present in zinc containing ores, they are also typically released during these processes and so areas are often jointly contaminated. Zinc can be releases to the atmosphere during the production of steel and burning of coal or waste. Surface water can be impacted by discharges of metal manufacturing and chemical industry wastes, and also by run-off following precipitation on soils high in zinc, either due to the natural setting or human applications, including use of zinc fertilizer on agricultural soils.

The average concentration of zinc in air (as fine dust particles) is typically less than 1 microgram per cubic meter ($\mu g/m^3$), although concentrations of 5 $\mu g/m^3$ have been measured near industrial sources. In lakes and rivers, some zinc remains dissolved in water or as fine suspended particles, while other zinc settles to the bottom in association with heavier particles. Average concentration range from 0.02 to 0.05 mg/L in surface water and 0.01 to 0.1 mg/L in drinking water [29]. Concentrations of zinc in sandy soil particles are about 200 times higher than in the water between the soil particles, and concentration ratios are even higher (over 1,000) in both loam and clay soils [26].

3. MATERIALS AND METHODS

3.1 General Description of the Study Areas

To investigate the degree of pollution of rivers in Addis Ababa with trace metals two rivers were considered and compared. The criteria for consideration of sampling sites in each river are based on topographical, industrial, accessibility of the sampling site, and purpose of the study [36].

Location and Topography: Addis Ababa city is the capital of Ethiopia. The population of the city is over 3 million and live in 10 sub-cities and 204 districts divided for administrative purposes. The ten sub-cities are: Arada, Addis Ketema, Lideta, Cherkos, Yeka, Bole, Akaki Kaliti, Nefas silk, Kolfe Keranio and Gulele each with an average of 300,000 people. It covers 540 km^2 of which 18.2 Km^2 are rural. It is situated at 9 ^oN and 38 ^oE and lies between 2200 and 2500 meters above see levels on a well-watered plateau surrounded by hills and mountains [9]. Addis Ababa is Ethiopia's largest city and it is administrative and communications center. It is the main trade center for coffee, the country's chief export for tobacco, grains, and hides. The major industries produce food, beverages, processed tobacco, plastics, chemical products, textiles, cement and leather. In addition, the city is the center of the nation's service and finance sectors. Addis Ababa has a large tourist industry. The African Union and the UN Economic Commission on Africa are headquartered in Addis Ababa, which also hosts numerous international conferences. It is the hub of a highway network and a terminus of a railroad that runs to Djibouti, making Addis Ababa an important distribution center. The well known international airport is in Addis Ababa.

Climate: The lowest and the highest annual average values of temperature are between 10 and 25 ^oC. April and May are the driest months. The main rainy season, which is characterized by intense rainfall of short duration, is responsible for 70% of the annual average rainfall of 1400 mm [37].

Geological setting: Geologically, the city lies on volcano rocks with basaltic lava flows and welded tuffs found at different localities and ages and minor amounts of fluvial sediments [37]. It is rambled with across many wooden hillsides and gullies cut through with fast flowing streams. Little Akaki and Big Akaki River and various streams flow through out the year.

The main study areas are Little Akaki, Big Akaki River, which drain the city from north to south. The streams serve as natural sewerage lines for domestic and industrial wastes, hence making them known for their offensive odor. Eutrophication process in the streams is a result of water pollution.

Little Akaki basin with a catchments area of about 540 km^2 is a very polluted river. It flows through western part of the city (Fig. 1) and has attracted early an important number of industries which use the river to get rid of their industrial wastes. The river starts near to Gefersa and crosses the central city before reaching the Abasamuale Lake, Akaki. Big Akaki River system with a catchments area of 900 km^2 covers eastern parts of the city (Fig. 1). Ten sample stations were selected from each river: LA1 up to LA10 along Little Akaki and BA1 up to BA10 along Big Akaki River based on criteria described in the discussion part. All the sites locations are given in Table 2.

The source of LAR was no accessible during the sampling period. Sampling site LA1 that is down stream of Anbesa Garage was chosen to monitor the impact of the garage on the river water quality. Site LA2, which has a common name of Shankila Wonze and located around at Kolfe bridge, was selected to see the effect of the near by marble factory in the up stream. LA3 to LA5 are located along the mid section of the river. Sample site LA3 receives discharges from the St. George Brewery Factory and National Alcohol Factory and intersect the stream containing LA4 that receives discharge from East Africa Bottling and Awash Wineries. LA5 is located at Evancalical Theological College down stream of the intersection of LA3 and LA4. LA6 is located around Gofa Vegetable Farm. This river is polluted from discharges from Addis Ababa Abattoir and Chora Chemical Manufacturing Enterprise. LA7 located near to Awash Wineries (Mekanisa Branch) receives the urban runoff, municipal wastes, and discharges from various factories. The site LA9, located at Saris was chosen to establish the effect of discharge from Awash Tannery. Sampling station LA10 down stream the Little Akaki at Kaliti Vegetables Farm was selected to see the degree of pollution of the river and sediment where there are extensive agricultural activities.

Also the source of BAR was not accessible, instead sampling point BA7 was considered as reference site because it is contained on the stream that flows over the rural region of the city (Fig. 1) before mixing with the main BAR system. BA1 on the Kebena stream located around German Embassy is believed to be less affected by anthropogenic pressure relatively. Sampling point BA2 located down stream of European Union was chosen where population density is very high. BA3 beside Peakock Park on Bulbula stream was chosen to see the quality of water where there is extensive irrigational activity. This site is located on the stream that crosses the highly populated region of the city. BA4 is down the stream from the mixing point of BA2 and BA3. BA5 is at Bole Michael Church was selected to establish the effect runoff from the local pre-urban settlement on the local river water quality. BA6 located at Saris Abo was selected to compare it with the corresponding site on LAR that is highly affected industrial discharge. BA7 originates from less urbanized region of the city hence it is expected to reflect the natural effect on the quality of the river water. The site was considered as reference point. BA8 is located on the same stream where BA6 is situated. BA9 is down stream of the mixing point of BA8 and BA7 was selected to see the effect the dilution effect of the polluted water stream containing BA8 by stream containing BA7. BA10 is the point around Kaliti Total where it is used for the purpose of washing, swimming, cattle watering, fisheries and irrigational activities.

Table 2. Location of sampling Sites on LAR and BAR Catchments

Site	Locations	River	Elevations (m)	Latitude /Longitude
LA1	Down to Anbesa Garage	--	2465	N 09 ^{0} 02.94' E 038 ^{0}41.61'
LA2	Kolfe Bridge	Shankila Wonze	2420	N 09 ^{0} 02.53' E 038 ^{0}41.61'
LA3	Down Stream of East Africa Bottling and Awash Wineries	Tinishu Akaki	2360	N 09 ^{0} 01.22' E 038 ^{0}42.09'
LA4	Near to OAU	--	2345	N 09 ^{0} 01.13' E 038 ^{0}42.09'
LA5	Evangelical Theology college	Tinishu Akaki	2329	N 09 ^{0} 00.43' E 038 ^{0}59.26'
LA6	Kera	Tinishu Akaki	2317	N 08 ^{0} 59.94' E 038 ^{0}58.34'
LA7	Mekanisa Bridge	Akaki	2221	N 08 ^{0} 58.34' E 038 ^{0}57.45'
LA8	Gofa Vegetables Farm	Tinishu Akaki	2197	N 08 ^{0}57 .45' E 038 ^{0}41.61'
LA9	Down Stream of Awash Tannery	Tinishu Akaki	2175	N 08 ^{0} 55.86' E 038 ^{0}41.61'
LA10	Kalit Vegetable farm	Tinishu Akaki	2160	N 09 ^{0} 02.94' E 038 ^{0}41.61'
BA1	Germany Embassy	Kebena	2406	N 09 ^{0} 02.94' E 038 ^{0}41.61'
BA2	Peacock Park (Kebena stream)	Kebena	2340	N 09 ^{0} 02.94' E 038 ^{0}41.61'
BA3	Peacock Park (Bulbula Stream)	Bulbula	2370	N 09 ^{0} 02.94' E 038 ^{0}41.61'
BA4	Down to Peacock park	Bulbula	2300	N 09 ^{0} 02.94' N 038 ^{0} 41.83’
BA5	Up Stream of Bole Michael Bridge	Kebena	2231	N 0 9^{0}01.00' E 0 38^{0}43.8'7'
BA6	Saris Abo	Bulbula "	2196	N 0 8^{0}58.96' E 0 38^{0}43.87'
BA7	--	"	2137	N 0 8^{0}58.37' E 0 38^{0}43.87'
BA8	Beside Kaliti Driver Training Center	Akaki	2150	N 0 8^{0}57.23' E 0 38^{0}44.20'
BA9	‘’	"	2100	N 0 8^{0}55.95' E 0 38^{0}44.79'
BA10	Down to Kaliti Total	"	2021	N 0 8^{0}54.30' E 0 38^{0}45.53'

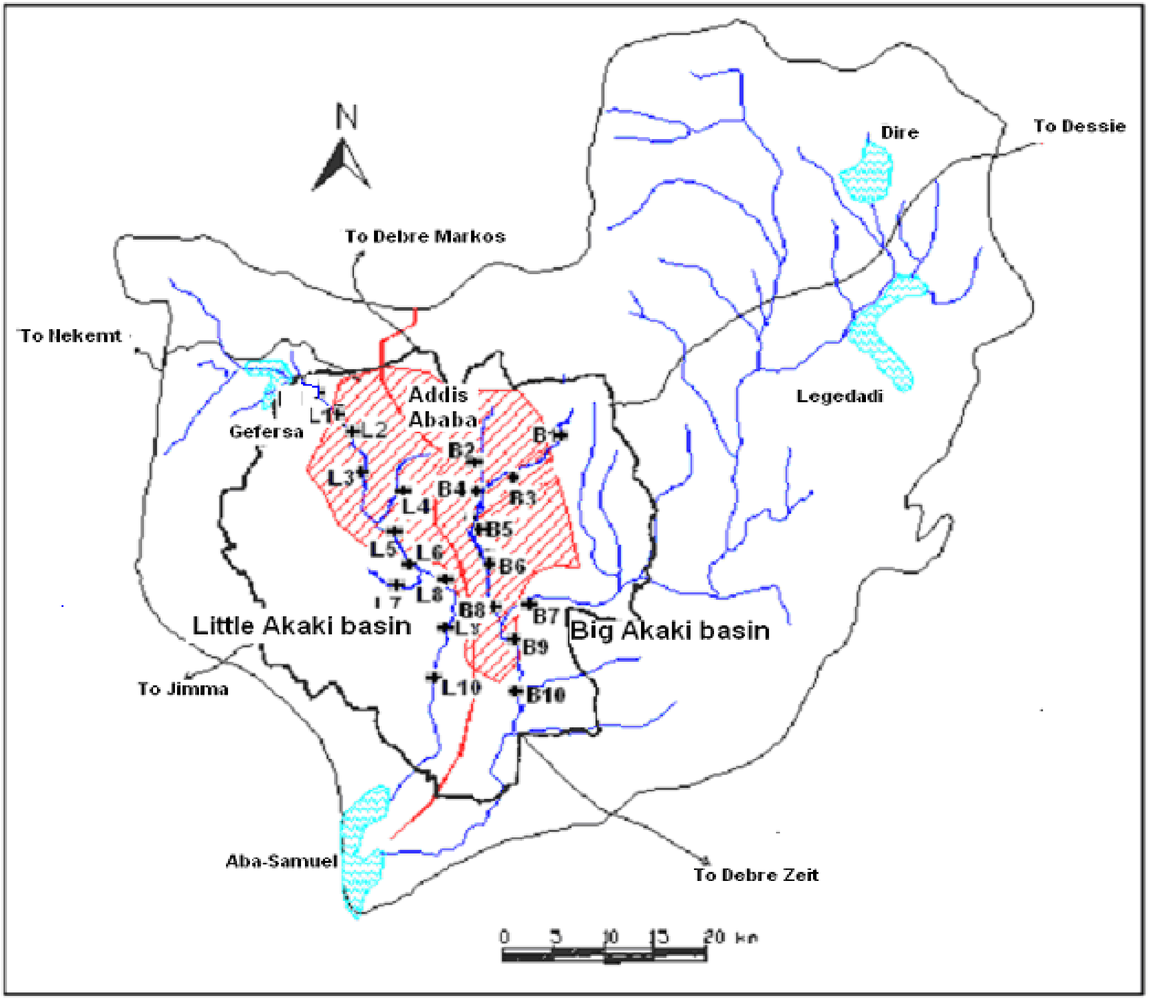


Figure 3. Little and Big Akaki basins, showing the locations of sampling sites used in this study (Source: http//: www.un.urbanwater.net/cities/addababa.html after some modifications).

3.2 Instrumentation and Apparatus

LABOTEC-Model 145 condactometer (UK) was used to measure conductivity, total dissolved substance, and salinity in the laboratory. The pH of water samples was measured by pH/Ion – Meter, WTW, Inolab (Germany) in the laboratory. During the field observation, temperatures were measured using a mercury thermometer (0-50 ^{o}C) and geographical locations of the sampling sites were determined by GPS, etrecs (Thailand). DIGITHEAT DRY OVEN (J.P.SELECTA, s.a., BARCELONA, SPAIN) was used to dry sediment samples and for trace metal analysis BUCK SCINTIFIC 210VGP Atomic Absorption Spectrometer (Norwalk, USA) was used.

3.3 Reagents and Standard Solutions

70% HNO_3 (Spectra$^{®}$, BDH, England), 70% $HClO_4$ (Aldrich, A.C.S. Reagent, Germany), 37 % HCl (Riedel-deHaën), 30% H_2O_2 (ALDRICH, A.C.S. Reagent, Germany) and Buck Scientific puro graphics calibration standards (Norwalk, USA) for Cd, Co, Cu, Ni, Pb and Zn were used as received. All samples were diluted with 3 % acidified dionized water with HNO_3 and the standards were diluted with only dionized water.

3.4 Sampling and Pre-treatments of Samples

A preliminary survey of sampling stations was done for one day to select the appropriate sampling sites based on the access, objectives of study and the potential sources of pollution. Sampling of water and sediments were done on March 10, 2006 and March 12, 2006 for LAR and BAR, respectively.

3.4.1 Cleaning Procedures of Sampling Equipments

Sediment and water samples being tested for inorganic metals constituents should be collected in contaminant-free plastic. Glass containers have the disadvantage of breaking during the transport and interaction with inorganic constituents of the samples. Cleaning was done according to the procedure described in [38]. All plastic bags, polyethylene bottles, plastic bottles, plastic scoops were thoroughly washed with detergent, rinsed with water and then with distilled water before soaking in 10% HNO_3 for about 24 hours. Containers were finally rinsed with deionized water before being used for sampling.

3.4.2 Water Sampling and Transportation

Water samples from sampling stations were collected with 1 L-capacity polyethylene bottles, which have a large lid allowing for easier filling and removal of the sample, by composite sampling technique according to the procedure [38]. Using this procedure, a small portion of water samples were collected from different spots by tilting the bottle against the direction of the stream flow without filling up to the neck of the bottles. Finally the samples were stored in icebox and transported into the laboratory.

3.4.3 Sediments Sampling and Transportation

Composite sampling technique was used [38]. Accordingly, surface sediments were collected from the same sampling locations and at the time as water samples were collected at all sampling locations, a total of about 200 grams of sediments were taken at several spots from the bottom of the river 0-10 cm depth using a hand held polyethylene scoop. After the sediments were transferred to polyethylene plastic bags shortly the samples were stored frozen in icebox until they were transported to the laboratory.

3.4.4 Water Samples Pre-Treatments

In the laboratory the contents of the bottles were divided in to two equal parts. Half part was reserved for physico-chemical analysis and the rest was treated for dissolved metals analysis according to the procedure [18]. In this method, 100 mL of water was centrifuged and filtered using 0.45 μm type membrane filter in to a beaker. The filtrate samples were collected in pre-cleaned polyethylene bottles and acidified to $pH < 2$ with concentrated nitric acid (3 mL). Finally all the samples were stored at 4 ^{o}C until analysis in a refrigerator for maintaining the sample in a state that minimizes change in the composition or concentration of the components in the time between collection and analysis.

3.4.5 Sediments Samples Pre-Treatments

For sediments samples preparation, each composite sample was, homogenized properly. Then, samples were dried in an oven at 90 ^{o}C for 3 days. A drying step is usually required because most concentrations of contaminants in sediments are reported on a dry-weight basis. After drying, the sediments were disaggregated and grounded in an agate mortar using a pestle then, sieved using a 0.5 mm sieve. The dried sediments leaching were stored in pre-cleaned and dried plastic bags.

3.4.6 Digestion of Sediments Samples

In order to develop an optimum procedure for the analysis of sediment samples, different digestion methods were tasted and the procedures that produce white pure silicate residue, consumed minimal reagent volumes, and required shorter digestion time was selected from the different alternatives. The different alternatives procedures tasted are given in Table 3. During the optimization of the procedure a part of the powdered sieved grain size fraction of 0.5 g was weighted directly in to 250 mL beaker and various acid combinations were added (Table 3). For procedure A ($HNO_3/HClO_4$) and B ($HNO_3/HCl/H_2O_2$) 6 mL of conc. HNO_3 was added in to beaker A and B, and then evaporated to semi-dryness on hot plate at low temperature. The residues in beaker A and B were dissolved in 4 mL conc. $HClO_4$ and 4 mL conc. HCl, respectively, and then the mixture again evaporated to semi-dryness. The residue in the beaker B was further dissolved in 3 mL of 30% H_2O_2 then left for 5 min, finally after cooling the residues in A and B were dissolved in 3% HNO_3 acid solution. In both cases clear silica residue was not seen. For producer C ($HNO_3/HClO_4/$ H_2O_2) after dissolving 0.5 g of sample in 6 mL conc. HNO_3 the mixture was heated until semi-dry and then the residue was dissolved in 4 mL conc. $HClO_4$ and heated to semi-dry then the residue was dissolved in 30% H_2O_2. In this procedure white silica residue was obtained. After cooling the mixture was dissolved in 30% HNO_3 acid and filtered using Whatman type # 41 filter paper to remove silicate residue, then the mixture was diluted to 50 mL by 3% HNO_3 in volumetric flask.

Table 3. Optimization procedure for routine sediment sample digestion

Steps	Amount of sample (g)	Reagents used	Duration of time	Condition of digest	Remarks
Procedure A					
1	0.5	6 mL HNO_3	Until semi-dry	Gray residue	Rejected
2		4 mL $HClO_4$	Until semi-dry		
Procedure B					
1	0.5	6 mL HNO_3	Until semi-dry	Gray residue	Rejected
2		4 mL HCL	Until semi-dry		
3		3 mL H_2O_2	5 min		
Procedure C					
1	0.5	6 mL HNO_3	Until semi-dry	White silicate residue	Selected
2		4 mL $HClO_4$	Until semi dry		
3		3 mL H_2O_2	5 min		

3.5 Physico-Chemical Analysis

In all sampling stations of the rivers temperatures were measured on-sites with a mercury thermometer (0-50 ^{o}C). In the laboratory pH was measured with pH/Ion-Meter, WTW, Inolab, Germany. Total dissolved solids, conductivity and salinity measurements were made in the laboratory for all samples using LABOTEC-Model 145, conductometer UK after calibrating with distilled water in the beginning.

3.6 Analytical Procedures for Trace Metals Analysis by FAAS

Water samples and extracted solution of surface sediments were analyzed for trace metals using FAAS. In the use of FAAS for trace metal analysis optimization of the operating conditions is very critical [20, 21]. Wavelength, energy, lamp and burner alignment and slit width were optimized for Cd, Pb, Zn, Cu, Ni and Co analysis (Table 4). Standards used in establishing the analytical curve for trace metal determinations were prepared from standard 1000 mg/L stock solutions (Buck Scientific puro graphics calibration standards, USA). The working solutions (10 mg/L) of each metal were then freshly prepared by diluting the stock solution in 100 mL volumetric flask with deionized water. For water samples and sediments samples four standard solutions were made (Table 5). A rinse blank (deionized water) was used to flush the uptake system to reduce memory interferences. The laboratory fortified blanks, which are made of 1 mL fortifying 1000 mg/L standard metal solutions (Buck Scientific puro graphics calibration standards), were used to assess routine instrument performance. Statistical calculations and graphing were made using Origin Software [54].

Table 4. Operational parameters

Element	**Wavelength (nm)**	**Current (mA)**	**Slit width (nm)**	**Oxidant/Fuel**
Cd	228.9	2.0	0.7	Air-C_2H_2
Co	240.7	4.5	0.2	Air-C_2H_2
Cu	324.8	1.5	0.7	Air-C_2H_2
Pb	217.0	3.0	0.7	Air-C_2H_2
Ni	231.0	7.0	0.2	Air-C_2H_2
Zn	213.9	2.0	0.7	Air-C_2H_2

Table 5. Standard Concentration for Metals Analyzed

Water analysis	**Concentration of standards (mg/L)**	**Sediment analysis**	**Concentration of standards (mg/L)**
Cd	0.005, 0.05, 0.10, 1.00	Cd	0.005, 0.05, 0.10,1.0
Co, Ni, Cu	0.05, 0.10, 0.50, 1.00	Co, Ni, Cu	0.10, 0.50, 1.00, 2.00
Pb, Zn	0.10, 0.50, 1.0, 2.0	Pb, Zn	0.10,0.50, 2.0, 4.0

3.6 Recovery of Sediment Samples

Since there was no standard reference sediment in the laboratory, spiking experiments were employed to validate the digestion procedures. Accordingly, known amount of mixed standard solution containing 10 mg/L of each element was added in to 0.5 g sediment samples. The resulting spiked samples were digested with the method described in section 3.4.6, diluted, and analyzed for total trace elements.

4. RESULTS AND DISCUSSION

4.1 Selection of Sampling Sites

Sampling sites were selected based on the potential sources of pollution, agricultural activities, population density and the aim of the study. Sites where extensive irrigation activities are observed were selected to see the quality of water as it influences plant grown locally. Due to topographical location of the city the rivers and streams are fast flowing especially during rainy seasons [37] as a result deeper sampling sites were selected where sediments are available. Also the access of the site and safety were taken in to consideration for selecting sampling sites. Sampling sites that can be reached easily were selected preferentially. Generally the sampling sites for LAR were adapted from a previous study Melaku *et al.* [23] with minor modifications and the sampling sites for BAR were fixed so that each site will have similar latitude with the corresponding LAR site for comparison purposes of the two rivers which is one of the objectives of this study.

4.2 Physico-Chemical Analysis

Mean values for physico-chemical variables (pH, temperature, conductivity, salinity and TDS) along LAR and BAR are shown in Table 5 and 6 and Figure 2 and 3, respectively.

Temperature: Temperature readings were made on-site immediately before water and sediment sampling at each sampling site. Determination of temperature of the water body is very important because of its effect on other physical parameters such as pH, redox potentials, solubility of metals, etc. Temperatures vary from 19 ^{o}C up steam of LAR to about 21 ^{o}C down stream and was considered quite high compared maximum permissible limit of CCME guidelines used for aesthetic object (Table 6). Temperatures along BAR ranges between 17 ^{o}C to 21 ^{o}C along up stream to down stream of the river system. This range is also considered as above the maximum limit specified by CCME. The spatial variation of the temperature during the sampling season was small with ranges of 2 ^{o}C and 4 ^{o}C for LAR and BAR, respectively.

Table 6. Recommended water criteria

Parameter	Limits	Maximum Permissible limit	Organization
Temprature,^{o}C	--	15	CCME
pH	7.0-8.5	6.5-9.2	WHO
Conductivity, µS/cm	750	2500	WHO
TDS, mg/L	500	1500	ICMR

pH: Determination of pH is also very important because it influence the other physico-chemical parameters and the availability of metal ion in the water [2]. pH also affects the quality of water directly as a result there are standard guidelines established for optimum quality water for domestic , irrigational and livestock activities. The pH of LAR and BAR ranged between 6.59 to 7.71 and 7.6 to 7.8, respectively. These ranges are within the limit of CCME guidelines for livestock watering and irrigation [40], and WHO (Table 7). From the above results the pH of the rivers water is nearly neutral and slightly basic except at LA7 and LA8 where direct industrial discharge is observed from Awash Wineries (Table 6 and Fig. 2).

Electrical Conductivity (EC): Conductivity is a measure of the ability of aqueous solution to carry an electric current that depends on the presence and total concentration of ions, their mobility and valance and on the temperature [18]. The EC is a valuable measure of the amount of metals ions dissolved in water. Its value ranged from 661 to 1790 µs/cm at LA2 and LA7 respectively along LAR. Its value for BAR water samples ranged from 369 (BA7) to 749 (BA8) µS/cm. The smallest value of EC was recorded at site BA7, which is the tributary of BAR and originate from the rural side of the city around Legedadi. The value from this point can be considered as reference site because it is less affected by anthropogenic pressure. The maximum recommended value for EC for potable water is 2500 µS/cm (Table 6) as a result the range obtained along LAR and BAR fell in this domain. Along LAR the values of EC show increasing trend up to around Gofa Vegetable Farm (LA7) and then slightly decreases due to dilution effect.

The increased values of EC are possibly due to discharge of industrial and domestic wastes and other natural processes. EC value also increases from BA1 to BA6 and decreases down stream due to dilution effect. The trend along LAR shows largely the effect of anthropogenic pressure on the river. EC value was higher where there is high density of population at BA3 around Peacock Park, which receives large amount of domestic discharges and decreases down steam where there is less population pressure. Comparing the two rivers BAR has maximum value (749 μS/cm), which is less than half of the maximum value recorded along LAR (1790 μS/cm). This result shows the adverse effect of industrial discharges from various factories on water quality concentrated along LAR course.

Total Dissolved Solids (TDS): TDS can also be taken as an indicator for general water quality because it directly affects the aesthetic value of the water by increasing turbidity. Solid suspended matters in water bodies have high surface area than the bulk sediments as a result increasing the availability of toxic metals [1, 2]. The range of TDS values along TAR and BAR are 317 (LA2) to 881 mg/L (LA7) and 176 (BA3) to 316 mg/L (BA3) respectively. TDS values for sample site LA3, LA6 to LA9 exceeds the maximum value specified by CCME guidelines for drinking water, i.e. 500 mg/L but all the sites along BAR contain TDS below this limits. The TDS spatial variations along LAR and BAR rivers system are similar with that of EC (Fig. 2 and 3). Comparing the two rivers LAR contains much more TDS than BAR as it is exposed to a verity of industrial discharges.

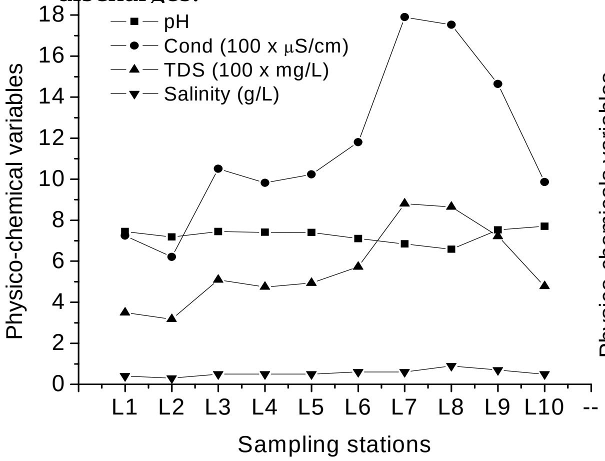


Figure 4. Trends selected physico-chemical variables along LAR.

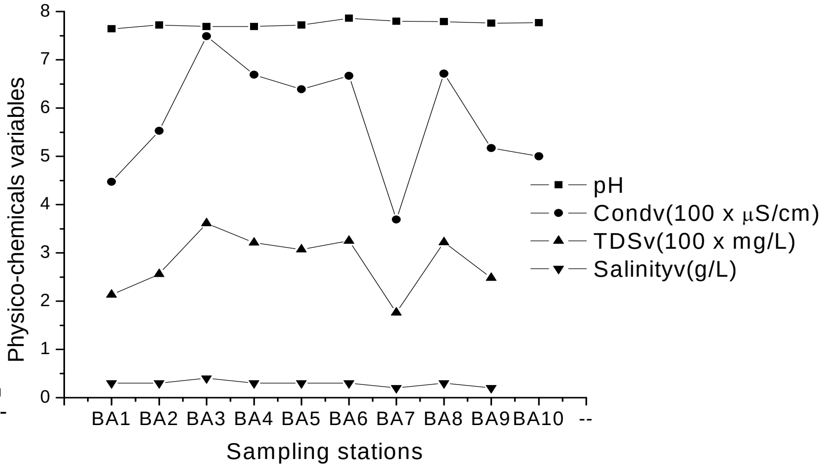


Figure 5. Trends selected physico-chemical variables along BAR.

Table 7. Mean * (± SD) values of Physico-chemical variables for Little Akaki River water samples

Sampling stations	**Temperature (^{o}C)**	**pH**	**Conductivity (10^2 μS/cm)**	**TDS (10^2 mg/L)**	**Salinity ($^0/_{00}$)**
LA1	20.1	7.45 ± 0.01	7.25 ± 0.02	3.50 ± 0.01	0.4 ± 0.00
LA2	20.0	7.19 ± 0.05	6.21 ± 0.01	3.17 ± 0.01	0.3 ± 0.00
LA3	20.1	7.45 ± 0.03	10.51± 0.02	5.09 ± 0.03	0.5 ± 0.00
LA4	19.0	7.42 ± 0.02	9.82 ± 0.01	4.75 ± 0.01	0.5 ± 0.00
LA5	19.1	7.40 ± 0.01	10.24 ± 0.02	4.94 ± 0.02	0.5 ± 0.00
LA6	20.3	7.10 ± 0.08	11.80 ± 0.01	5.73 ± 0.01	0.6 ± 0.00
LA7	20.9	6.85 ± 0.02	17.90 ±0.03	8.81 ± 0.04	0.6 ± 0.00
LA8	20.8	6.59 ± 0.03	17.53 ± 0.05	8.65 ± 0.05	0.9 ± 0.00
LA9	20.3	7.53 ± 0.00	14.64 ± 0.03	7.22 ± 0.03	0.7 ± 0.00
LA10	21.0	7.71 ± 0.01	9.86 ± 0.02	4.78 ± 0.03	0.5 ± 0.00

*Values are means of three determinations.

Table 8. Mean * (± SD) values of Physico-chemical variables for Big Akaki River water samples

Sampling stations	**Temperature (^{o}C)**	**pH**	**Conductivity (10^2 μS/cm)**	**TDS (10^2 mg/L)**	**Salinity ($^0/_{00}$)**
BA1	19.5	7.64 ± 0.08	4.47 ± 0.02	2.13 ± 0.01	0.3 ± 0.0
BA2	17	7.72 ± 0.07	5.53 ± 0.04	2.56 ± 0.02	0.3 ± 0.0
BA3	19.1	7.69 ± 0.01	7.49 ± 0.04	3.61 ± 0.00	0.4 ± 0.0
BA4	19	7.69 ± 0.01	6.69 ± 0.03	3.21 ± 0.01	0.3 ± 0.0
BA5	19.7	7.72 ± 0.01	6.39 ± 0.03	3.07 ± 0.01	0.3 ± 0.0
BA6	19.1	7.86 ± 0.04	6.67 ± 0.03	3.25 ± 0.02	0.3 ± 0.0
BA7	20.3	7.80 ± 0.03	3.69 ± 0.05	1.76 ± 0.01	0.2 ± 0.0
BA8	20.2	7.79 ± 0.01	6.71 ± 0.02	3.22 ± 0.01	0.3 ± 0.0
BA9	20.7	7.76 ± 0.01	5.17 ± 0.04	2.48 ± 0.02	0.2 ± 0.0
BA10	19.5	7.65 ± 0.01	5.63 ± 0.04	2.25 ± 0.03	0.2 ± 0.0

*Values are means of three determinations.

Salinity: Salinity is an important measurement in the analysis of certain industrial wastes and river water [18]. It is defined as the total solids in water after all carbonate have been converted to oxides, all bromides and iodides have been replaced by chlorides, and all organic matter has been oxidized. It is reported as grams per litter or parts per thousands ($^{0}/_{0\,0}$). Along TAR and BAR salinity values have ranges of 0.3 to 0.9$^{0}/_{0\,0}$ and 0.2 to 0.4$^{0}/_{00}$ respectively.

4.3 Validation of Analytical Procedures for Metal Analysis

4.3.1 Analytical Performance of Optimized Digestion Method

The performance of the digestion procedure was estimated using recovery test. Standard metals solutions were used to fortify the sample to the specified level given in Table 9. Percent recovery for each metal analyte was calculated using the following equation:

$$R = \frac{C_S - C}{s} \times 100 \qquad (1)$$

Where: R = percent recovery

C_s = fortified sample concentration

C = sample background concentration

s = concentration equivalent of analyte added to fortify the sample.

Table 9. Recovery of sediment samples from LAR and BAR

Metals	s (mg/L)	C_s-C (mg/L)	% Recovery
Cd	0.5	0.450	90.1 ± 0.1
	0.5	0.426	(85.3± 0.7)
Cu	0.5	0.467	93.5 ± 0.3
	0.5	0.455	(91.0±0.2)
Co	0.5	0.431	86.2 ± 0.2
	0.5	0.443	(88.6± 0.6)
Ni	0.5	0.487	97.5 ± 0.7
	0.5	0.452	(90.4± 0.1)
Pb	0.5	0.943	94.3 ± 0.1
	1.0	0.827	(82.7± 0.9)
Zn	1.0	0.914	91.4 ± 0.3
	1.0	0.953	(95.3 ± 0.1)

The values in the brackets are for sediments from BAR,
Where s, Cs, C as defined in equation 2.

The mean recoveries for all elements are in the range of 80 – 115% thus; the laboratory performance for each analyte is in control [19]. Recoveries values in the above range are acceptable for environmental investigations and the digestion procedure is believed to remove metals fractions associated with carbonate, sulphides, soluble salts, organic mater, and Fe-Mn oxide phase [1, 41-44].

Comparing the recoveries values for sediments from the two rivers Cd, Cu, Ni, and Pb were recovered more sufficiently from sediment taken from LAR and the recoveries values for Zn and Co are better for sediments taken from BAR. The main causes of losses of recoveries could be attributed during the digestion process and could also include systematic and random sources of uncertainty during analysis using AAS. However no exaggerated differences were observed between the recoveries of metals in sediments taken from the two rivers (Fig. 4) and the values for all metals are within the range that is required for environmental investigation.

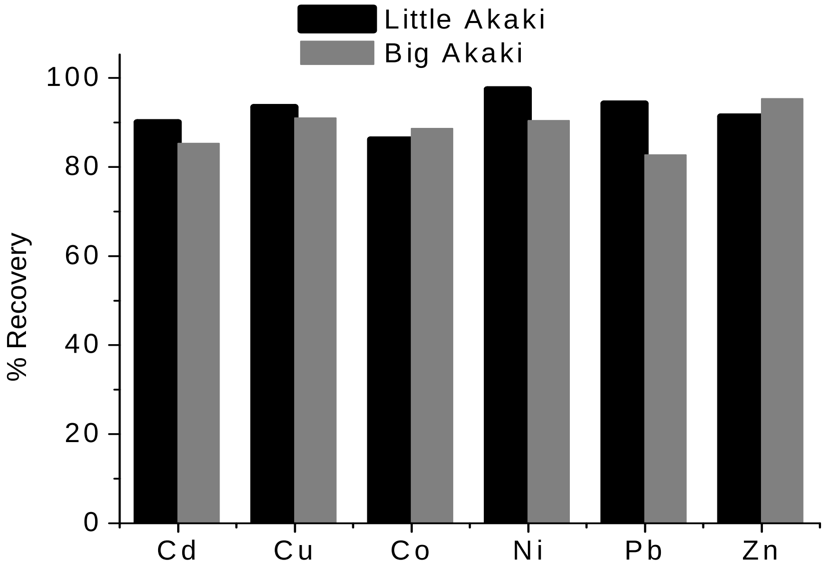


Figure 6. Percent of recoveries metal in LAR and BAR sediments.

4.3.2 Calibration Procedures

The quality of the results obtained for trace metals analysis using AAS are seriously affected by the calibration and standards preparations procedure. The linearity for the calibration lines for Cd, Cu, Co, Ni, Pb and Zn showed correlation coefficients (r^2) of 0.93, 0.97, 0.91, 0.95, 0.99, and 0.94, respectively for measurements of freshly prepared standard metal solutions. The causes of deviation of correlations coefficients from unity include systematic and random errors involved during measurements using FAAS.

4.3.3 Method Detection Limits

Method detection limit is defined as the minimum concentration of analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero [19]. Method detection limits for trace metals will vary with wavelength selected and the spectrometer configuration and operating conditions [20].

MDLs for water samples analysis were tried to be determined using reagent water blank i.e. 0.1 M HNO_3, which was used to preserve water samples. MDLs for total recoverable trace metal determination in sediment were established using blank regent ($HNO_3/HClO_4/H_2O_2$) that was digested in the same condition as sediment samples (section 3.4.6). To determine MDLs values, seven replicate determinations of water and sediment blank were taken for each element. The values for water blank were below the detection limits for the metals hence the instrument detection limits were taken as detection limits for the metals. The MDLs for sediment analysis were calculated as follows:

$$MDL = (t) \times (S) \qquad (2)$$

where: t = Student's value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom (t = 3.14 for seven replicates determinations), S = standard deviation of the seven replicate analyses.

Table 10. Method detection limits of water and sediment analysis

Element	Detection Limits		
	[a] IDLs (mg/L)	[a]MDL $_{water}$ (mg/L)	[b]MDL $_{sediment}$ (mg/kg)
Cd	0.005	0.005	0.02
Co	0.050	0.050	0.07
Cu	0.020	0.020	0.09
Pb	0.100	0.100	0.10
Ni	0.040	0.040	0.10
Zn	0.005	0.005	0.50

[a] Results are obtained from the manual of the instrument,

[b] Results are calculated using equation 1.

4.4 Analysis of Little Akaki and Big Akaki Rivers Water and Sediments

Trace metals (Cd, Cu, Co, Ni, Pb, and Zn) contents of the water and sediments samples taken from both rivers were determined using FAAS. The 6 elements were chosen for analysis taking into consideration the existing analytical methods of determination of these metals and the history of human activity in the city.

4.4.1 Dissolved Metals Concentration in Water

Cadmium: Cadmium concentrations in both river waters are generally below the detection limits (0.005 mg/L) therefore no appreciable amount of cadmium was detected at all sampling sites (Table 13 and 14). The South African Target Water Quality Range (TWQR) for Cd is < 0.005 mg/L in river water for domestic use (Table 11). Therefore Cd will not be a problem if water is used for domestic purpose from both rivers. Also the levels of Cd in both rivers is below the limits of TWQR for irrigation and livestock watering activities for cadmium (Table 11), therefore adverse effect of cadmium will not be expected if water is used for these purpose from both rivers. Recently the amount of Cd in Little Akaki River was reported in the range of 0.005 x10^{-3} to 1.19 x 10^{-3} mg/L using ICP-MS instrumentation Melaku *et al.* [45].

Copper: The concentration of copper in water samples of both rivers is very low which is below the detection limit (0.02 mg/L). The South African guideline for Cu in domestic water supply is < 1.0 mg/L (Table 11). The value obtained for both rivers is low, thus Cu is not supposed to be a problem for domestic use of water from these rivers. The TWQR for Cu in water for livestock watering is < 5 mg/L (Table 11) and the adverse chronic effect may occur at 1 to 10 mg/L Cu, depending on the live stock [4]. Cu in waters of the LAR and BAR did not exceed this level; therefore Cu will not be a problem in the rivers water if used for livestock watering. The TWQR for Cu in water that will be used for irrigation is < 0.2 mg/L (Table 11), so Cu is not also a problem for using water from both rivers for irrigational purposes. In the previous study the amount of Cu in Little Akaki River was reported in the range of 0.001 to 0.021 mg/L using ICP-MS instrumentation Melaku *et al.* [45].

Table 11. Tentative South African Target Water Quality Ranges (TQWR)

Element	Domestic	Irrigation	Livestock watering Activities
Cd	0 to 0.005 mg/L	0 to 0.01 mg/L	0 to 0.01 mg/L
Cu	0 to 1.0 mg/L	0 to 0.2 mg/L	0 to 5.0 mg/L
Co	0 to 2.0 mg/L	0 to 1.0 mg/L	0 to 1.0 mg/L
Ni	--	0 to 0.15mg/L	0 to 0.2 mg/L
Pb	0 to 0.01 mg/L	0 to 0.2 mg/l	0 to 0.1 mg/L
Zn	0 to 3.0 mg/L	0 to 1.0 mg/L	0 to 20 mg/L

Cobalt: In LAR cobalt concentration ranges between trace level (below the detection limit i.e., < 0.05 mg/L) to 0.077 ± 0.005 mg/L (Table 13). Except at LA8 and LA9 with mean concentration of 0.077 ± 0.005 mg/L and 0.062 ± 0.005 mg/L, respectively, cobalt concentration was below the detection limit at all sampling sites. The concentration level of cobalt along BAR was also below the detection limit at all sampling sites (Table 14). The SA guideline for Co is < 3.0 mg/L in water for domestic use (Table 11). The limit was not exceeded in both river and therefore Co is not a problem for using the water from both rivers for domestic purpose. The TWQR for Co in water for livestock watering and irrigational activities is < 20 mg/L and < 1mg/L, respectively (Table 11) therefore Co is not supposed to be a problem using of water from LAR and BAR for the irrigational and livestock watering activities.

Comparing the two rivers with respect to their cobalt content LAR exceeds BAR at some sampling sites. The concentrations of metals in the water bodies are influenced by their levels in the underlying sediment and physico- chemical parameters [42-43]. As it will be seen in the next section sediments of LAR contains generally higher amount of Co, which may be, originated either from natural or anthropogenic sources. In the previous study by Melaku *et al.* [45] cobalt in the Little Akaki River was reported to be in the range 0.00019 mg/L to 0.0046 mg/L by ICP-MS instrumentation.

Nickel: The levels of Ni in both river are generally below the detection limit but an appreciable amount of Ni were detected at two sampling sites LA7 and LA8 with mean values of 0.042 ± 0.001 and 0.036 ± 0.003 mg/L respectively. Also BA4 and BA5 sampling sites along BAR contains significant amount of dissolved Ni with mean value 0.049 ± 0.005 mg/L and 0.053 ± 0.003 mg/L respectively. More attention should be given for dissolved Ni in water because of its high toxicity even in low concentration, such as the fact that Ni can cause allergic reactions. The value in unpolluted water is $5x10^{-4}$ mg/L [31]. The values obtained in this study are generally below detection limit but this does not mean that these values are below the above limit ($5x10^{-4}$ mg/L). In fact in a previous study on Liitle Akaki River water which is the most polluted river in the city Melaku *et al.* [45] found mean concentration of Ni in the range of 0.0011 to 0.019 mg/L which is quite above the above level.

Lead: Levels of lead in both rivers are below the detection limit of the method (0.1 mg/L) hence no appreciable amount of lead was detected at all sampling stations. Melaku *et al.* [45] reported the mean lead concentration in Little Akaki River (the more polluted) in the range of 0.023 ± 0.001 μg/L to 3.28 ± 0.19 μg/L using ICP-MS instrumentation. SA guidelines for Pb in water for use of domestic, irrigation and live stock watering are 0 to 0.01 mg/L, 0 to 0.2 mg/L and 0 to 0.1 mg/L, respectively (Table 11). But the upper limit for domestic use purpose is below the detection limit of the method (0.1 mg/L) hence from the results obtained we can not draw a conclusion about the status of the rivers water in lead content. But the upper limits for irrigation and livestock watering activity are above the detection limit for Pb. Lead concentrations obtained by Melaku *et al.* [45] along LAR are below the upper limits of any of the guidelines based on this Pb may not be a source of worries in using water from LAR and BAR for demotic, irrigation or livestock watering purpose.

Zinc: In contrast to the other metals it was possible to detect an appreciable amount of Zn at all sampling sites of LAR and BAR. Zinc concentration ranges between 0.038 ± 0.001 mg/L to 0.089 ± 0.005 mg/L and 0.023 ± 0.002 mg/L to 0.192 ± 0.009 mg/L in BAR and LAR, respectively (Table 13 and Table 14). It is possible that low cost houses roofed with zinc corrugated sheets may have contributed to the levels of zinc determined in both rivers. Zn may be leached to the water system from the roofs, since the pH of rainwater is acidic. The SA guidelines for Zn in domestic water supply is < 3 mg/L (Table 11), hence adverse effect will not be expected by using water from both rivers for domestic purpose. Also the TWQR levels of Zn in water for irrigation and live stock watering are <1.0 mg/L and 20 mg/L respectively therefore water from both rivers can be utilized for irrigation and livestock watering since the range obtained was much lower than the TWQR values.

30 % of sampling sites along LAR contains higher amount of Zn metal than the maximum value recorded in BAR (0.089 ± 0.005), hence LAR water is more or less exposed to Zn metal pollution compared to that of BAR. It was also detected appreciable amount of Zn in LAR by Melaku *et al*. [45] in the previous study.

4.4.2 Distribution of Total Metal Concentrations in Surface Sediments of the Rivers

The mean concentrations of the metals in surface sediments of LAR and BAR are given in Table 13 and Table 14 and Fig. 5 and Fig. 6, respectively. The amounts of each trace metals detected were compared with literature values and quality guidelines to see the degree of pollution of the sediments of the two rivers.

Cadmium: Cadmium concentration in LAR and BAR sediments varied from 0.43 ± 0.02 (LA1) to 1.45 ± 0.05 mg/kg (LA8) and 0.31 ± 0.194 (BA7) to 0.59 ± 0.268 (BA6) respectively. The level of Cd along LAR sediments was observed to be moderate with the highest value occurring at LA8 indicating a localized effect of the near by battery factory which is located upstream of LA8 also previously it was reported a relatively high levels of Cd near to this sampling site Melaku *et al.* [23]. Generally the level of Cd in BAR sediments is very low. Comparing the levels of Cd in surface sediments of both rivers with interim fresh water sediment quality guideline (Table 12) its value is below the highly polluted sediment level (3 mg/kg). Under normal condition in surface water the pH at which metals are optimally adsorbed Cd is one of the metals which adsorb weakly [8] and also its low concentration in water at all sampling sites signifies the low contribution of anthropogenic and natural sources toward Cd to environment. The distribution of cadmium along both rivers sediment is uniform at 5 % significance level. Itanna *et al*. [15] and W/Gabriel [48] also found quite low level of Cd in vegetables irrigated by these river waters.

Low level of Cd in the sediments is common for example Awofolu *et al.* [1] reported the mean concentration of cadmium in Tyume river sediments, South Africa in the range of trace to 0.005 mg/kg and Neziri [49] reported in the range of 0.2 to 0.9 mg/kg in Drine river, Buna river and Lake Shkodra, Albania although there are rivers which are highly polluted with Cd for example it was reported in Asua, Galindo and Nerbioi-Ibaizabal River sediments, Spain, in the range of 1.2 – 381 mg/kg [50].

Copper: The mean values are significant in surface sediment of LAR and BAR comparing with interim fresh water surface sediment guidelines but quite below from the EPA sediment quality guidelines (Table 12). The levels of Cu varied between 30.5 ± 1.8 (BA1) and 89.41 ± 8.8 mg/kg (BA8) along BAR and 52.41± 3.02 mg /kg and 123.41 ± 9.83 mg/kg along LAR (Table 13 and 14). Most of the levels along the LAR sediments are above the maximum level fixed by the interim guideline, i.e. 86 mg/kg. The elevated level of Cu along LAR was recorded at LA8 which shows the direct discharge of industrial effluent from the near by factory located upstream of this site. Along BAR the highest values were recorded at BA6 and BA8 with values 89.54 ± 8.8 mg/kg and 89.98 mg/kg respectively. These values may be originated from natural mineralization of the soil, since no factory was observed which could be the source of the metal.

Comparing the levels copper with the literature values Neziri [49] recorded mean copper concentration in the range of 10.1 to10.6 mg/kg and Van Aardt *et al.* [51] presented 14 to 23 mg/kg concentration of copper in the sediment of Mooi-river catchments, South Africa. From the above comparison and the guidelines value the two rivers sediments are enriched with Cu metal but any of these levels did not exceed the EPA maximum value.

Cobalt: The mean cobalt values are very low with ranges of 18.32±1.79 mg/Kg to 44.02 ± 2.44 mg/Kg and 18.33 ± 2.02 to30.47 ± 3.04 mg/Kg at LAR and BAR, respectively (Table 13 and 14). The variation of Co level in BAR sediments is low suggesting the absence of significant anthropogenic contributions to its level in the river. In contrast there is a significant variation in the concentration of Co along LAR sediment indicating a significance contribution of anthropogenic activities.

Awolfolu *et al.* [1] reported low level of Co concentration in Tyume rivers sediments which varies between trace to 0.312 mg/Kg and Yasar *et al*. [25] reported a range of 11 to 60 mg/Kg Co concentration in Izmit bay sediments, Turk. EPA and Canadian interim sediment quality guidelines did not fix the maximum tolerable limit for Co but comparing the data with literature values both rivers sediments are moderately enriched by cobalt.

Table 12. Canadian Interim and EPA fresh water sediment quality guidelines for trace metals

Metals	EPA (mg/kg)	Interim (mg/kg)
Cd	--	3
Cu	149	86
Co	--	--
Ni	48.6	61
Pb	128	91
Zn	459	540

Nickel: Nickel concentration range between 119.82 ± 2.27 mg/kg (BA9) to 73.26 ±5.15 mg/kg (BA8) along BAR (Table 13 and Table 14). Fig. 5 and 6 show the spatial distribution along BAR and LAR sediments, respectively. The distribution along BAR is more or less uniform (Fig.5) but there is a variation of concentrations along LAR with the highest value occurring at LA4. Comparing the levels of Ni with the guideline (Table 11) 80% of the sampling site along BAR contain greater amount than the level fixed by EPA for sever toxic effect (48 mg/kg). In the case of LAR the entire sampling sites exceeded up to twice of this level.

The concentration of nickel in Tyume rivers sediments is 0.401 ± 0.006 mg/kg to 0.91 ± 0.007 mg/kg respectively [1], Glasby *et al*. [52] reported mean range of 2 to 50 mg/Kg in Auckland harbors, Newzland and Yasar *et al*. [25] reported mean value of Ni in the range of 24-60 mg/Kg in izmit Bay, Turk. From the above comparison and guideline value the level of nickel is critical in LAR and BAR sediments.

Lead: The mean concentration of lead in BAR and LAR varied between 35.67 ± 3.44 mg/kg and 71.75 ± 11.73 mg/kg and 55.73 ± 7.35 mg/kg and 320.33 ±10.48 mg/kg, respectively. The EPA Upper limit value of sediment quality guidelines is 128 mg/kg (Table 12) so the levels in BAR sediment is below this limits but at three sampling sites along LAR exceeded this value LA8 (320 ± 9.92 mg/Kg), LA9 (142.33 ± 19.32) and LA10 (184.68 ± 8.33 mg/Kg). The highest value observed at LA8 is due to the direct industrial discharge from the battery factory and Awash Tannery. Lead can also be contributed from deposition of Pb particles on the road next to the rivers especially during precipitation, from agricultural activity around the rivers, since the metal can occur as impurity in fertilizers and metal based pesticides and compost and manure.

Ramessur *et al*. [2] reported the mean concentration of Pb in sediment from an urbanized river in Mauritius in the range of 3.8 ± 0.6 to 179.2 ± 60.2 mg/kg and Awofolu *et al.* [1] reported in the range of 0.021 ± 0.004 mg/kg to 0.035 ± 0.001 mg/kg in Tyume River, South Africa. Comparing the situation of LAR and BAR with these literature values there is a significant enrichment of both rivers sediment with lead. Also a recent study by

H/Gebriel [48] shown high levels of Pb in vegetable grown around Gofa Vegetables Farm.

Zinc: The mean level of Zn in LAR ranges from 205.23 ± 17.53 mg/Kg (LA5) to 730 ± 17.59 mg/Kg (Table 13). The presence of marked variability of Zn concentration along the LAR sediments (Fig.5) suggests a possible anthropogenic input of the metal in to the river, mainly at around LA8 where an elevated level of Zn was observed. The mean range of Zn along BAR is 172.89 ± 21.24 to 288 ± 14.61 mg/kg at BA2 and BA10, respectively (Table14). The absence of high variability along BAR possibly suggests the absence of direct industrial discharges in to the river catchments. One common source of Zn in the sediment can be corrosion of zinc corrugated roof from the dominant low cost houses. The levels of Zn in LAR and BAR sediments at all sampling sites are below the interim and EPA guidelines (Table12) except at sampling station of LA8 where industrials discharges are realized in to the river. Previously the mean value of Zn in Tinishu Akaki River sediments was reported in the range of 141.1 to 825.7 mg/kg by Melaku *et al.* [23]

Awofolu *et al.* [1] reported Zn concentration in the range of 0.08 to 0.491 in Tyume Rivers, South Africa and Ramessur *et al.* [2] reported Zn concentration in the range of 134.6 to 179.2 mg/kg in sediments from an urbanized river in Mauritius also Glasby *et al.* [52] reported mean range of 2 to 234 mg/kg in Auckland harbors, Newzland. Comparing the case of LAR and BAR with the above literature values there is a much more enrichments of these sediments with Zn though most of them are below the limit of EPA and interim guidelines.

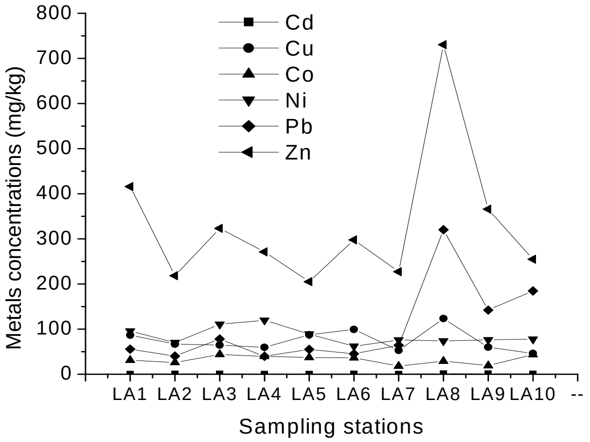


Figure 7. Metal distribution Along LAR.

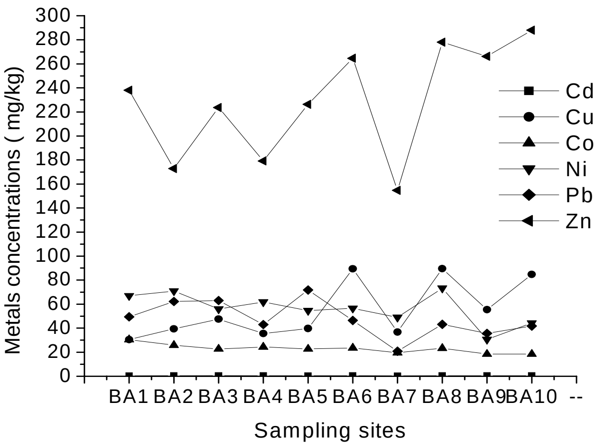


Figure 8. Metals Distribution Along BAR.

Table 13. Mean concentration *(±standard deviation) of trace metals dissolved in water (mg/L) and in surface sediments (mg/Kg) for sampling sites along Little Akaki River

Sites	Elements					
	Cd	**Cu**	**Co**	**Ni**	**Pb**	**Zn**
LA1	nd	nd	nd	nd	nd	0.022±0.002
	(0.43±0.02)	(86.62±0.89)	(31.26±3.04)	(95.77±3.13)	(55.73±7.35)	(415.93±11.43)
LA2	nd	nd	Nd	nd	nd	0.050±0.003
	(0.62±0.01)	(66.90±2.54)	(26.13±1.80)	(70.26 ±1.17)	(40.33±4.13)	(218.41± 12.05)
LA3	nd	nd	nd	nd	nd	0.19±0.009
	(0.69±0.02)	(64.60±5.79)	(44.02±2.44)	(110.80±1.90)	(78.2±11.23)	(323.33±15.35)
LA4	nd	nd	nd	nd	nd	0.053±0.004
	(0.44 ± 0.01)	(59.67±0.95)	(39.72±2.47)	(119.82±2.27)	(39.86±8.73)	(271.29±14.35)
LA5	nd	nd	nd	nd	nd	0.054±0.002
	(0.49 ± 0.01)	(87.96±1.86)	(37.23±1.61)	(89.08±1.30)	(55.19±7.48)	(205.23±17.53)
LA6	nd	nd	nd	nd	nd	0.126±0.008
	(0.54 ± 0.02)	(99.45±1.36)	(36.61±2.41)	(62.10±2.34)	(45.37± 4.17)	(297.83±13.67)
LA7	nd	nd	nd	0.042±0.001	nd	0.0572±0.003
	(0.28 ± 0.05)	(52.41±1.83)	(18.32±1.79)	(76.92±3.76)	(64.33±9.92)	(227.5±17.59)
LA8	nd	nd	0.077± 0.005	0.036 ± 0.003	nd	0.08013±0.004
	(1.45 ± 0.06)	(123.3± 3.02)	(29.12±2.18)	(73.26 ± 2.91)	(320.33±10.48)	(730.34±13.66)
LA9	nd	nd	0.062 ± 0.005	nd	nd	0.0535±0.006
	(1.31 ±0.03)	(59.90±1.32)	(29.21±2.02)	(76.41±3.82)	(142.3 ± 19.32)	(365.84±9.35)
LA10	nd	nd	0.05 ± 0.003	nd	nd	0.09325±0.006
	(0.58 ± 0.02)	(46.04±1.74)	(43.61±1.87)	(77.87±5.12)	(184.68 ± 8.33)	(255.12±15.44)

*Values are mean of triplicate analysis
Values in the parenthesis are for sediment samples
nd = not detected**.**

Table 14. Mean concentration *(± standard deviation) of trace metals dissolved in water (mg/L) and in surface sediments (mg/Kg) for sampling sites along Big Akaki River**.**

Sites	**Elements**					
	Cd	**Cu**	**Co**	**Ni**	**Pb**	**Zn**
BA1	nd (0.37±0.13)	nd (30.51±1.82)	nd (30.47±3.11)	nd (66.97±11.29)	nd (49.44 ± 5.43)	0.038 ± 0.001 (238 ± 24.85)
BA2	nd (0.51±0.21)	nd (39.43±1.41)	nd (25.79±2.13)	nd (70.93 ±11.07)	nd (62.22 ± 5.86)	0.082 ±0.007 (172.9 ± 21.24)
BA3	nd (0.56±0.13)	nd (47.52±1.93)	nd (22.66±0.99)	nd (55.94±9.42)	nd (63.0±6.23)	0.067 ± 0.005 (223.67±25.68)
BA4	nd (0.51±0.12)	nd (35.58±2.52)	nd (24.38±1.39)	0.049±0.005 (61.85 ± 2.88)	nd (43 ± 3.85)	0.058±0.003 (179.22±20.18)
BA5	nd (0.39±0.09)	nd (39.74 ±1.31)	nd (22.68±1.97)	0.053±0.003 (54.63±10.91)	nd (71.75±11.75)	0.056±0.001 (226.33±17.81)
BA6	nd (0.59±0.27)	nd (89.41± 8.82)	nd (23.56±2.57)	nd (56.56±7.75)	nd (46.44 ± 6.26)	0.065±0.004 (264.67±25.13)
BA7	nd (0.31±0.19)	nd (36.76 ±4.83)	nd (19.54±3.69)	nd (49.01±6.31)	nd (20.78 ± 7.08)	0.050±0.005 (154.67±40.86)
BA8	nd (0.51 ± 0.12)	nd (89.54±39.91)	nd (23.32±3.31)	nd (73.26±5.15)	nd (43.22 ± 8.49)	0.061 ± 0.002 (278.11 ± 37.35)
BA9	nd (0.53± 0.33)	nd (55.42± 4.12)	nd (18.43±2.77)	nd (30.64±14.77)	nd (35.67 ± 3.44)	0.064 ± 0.007 (266.26 ± 7.56)
BA10	nd (0.48±0.15)	nd (84.75±4.44)	nd (18.43±4.25)	nd 44.21±9.09)	nd (41.78±8.62)	0.083 ± 0.004 (288.53 ±14.61)

*Values are mean of triplicate analysis
Values in the parenthesis are for sediment samples
nd = not detected

4.4.3 Comparison of LAR and BAR with Metal Contents and Physico Chemical Properties

To compare the two rivers, pair of sampling sites that have similar latitude were compared for physico-chemical characteristics and metal load. The sampling sites were designated by symbol S1 up to S10 for simplicity.

Pair wise comparisons of the two rivers revealed that the physico chemical properties are markedly different statistically (at 5% significant level). All the pH measured values at LAR site are lower than the corresponding BAR site as can be seen from Fig. 9 (a). The slight alkalinity of water samples from BAR could be possibly from calcium carbonate bed rock weathering or may reflect the importance of dissolution of limestone and dolomites in the water shade. Conductance values of water samples along LAR are significantly higher than the corresponding BAR site as shown in Fig. 9 (b). For example the value at LA8 is 2.6 times as that of BA8 and the value at LA10 exceeds by 1.75 times the corresponding value at BA10. 80% of sampling sites along LAR have conductance value above the desired limit i.e. 750 µS/cm (Table 6) while all sites along BAR have values of below this limit. Also the TDS values at all sampling sites are statistically higher than the corresponding sampling site along BAR as shown Fig. 9 (c). 50% of the sites along LAR contain TDS, which is above the desirable limit (500 mg/L) while all the values along BAR are below this limit. Also there was significant difference in the values of salinity the values along LAR exceeds that of BAR up to three times at LA8 as can be seen from Table 7 and 8.

The levels of dissolve metals in both rivers water are below the detection limits of the instrument except for Zn, also for Co and Ni at some sampling stations (Table 13 and 14). Fig. 9 (d) shows the pair wise comparison of dissolved Zn concentration in the two rivers. The result shows that two sampling site along LAR significantly higher than the corresponding BAR sites (LA3 and LA6) which may be due to direct anthropogenic influence. The rest sampling sites contain comparable amount of dissolved Zn, as the main source of Zn is corrosion of galvanized roofs from low cost houses that are dominant in both regions.

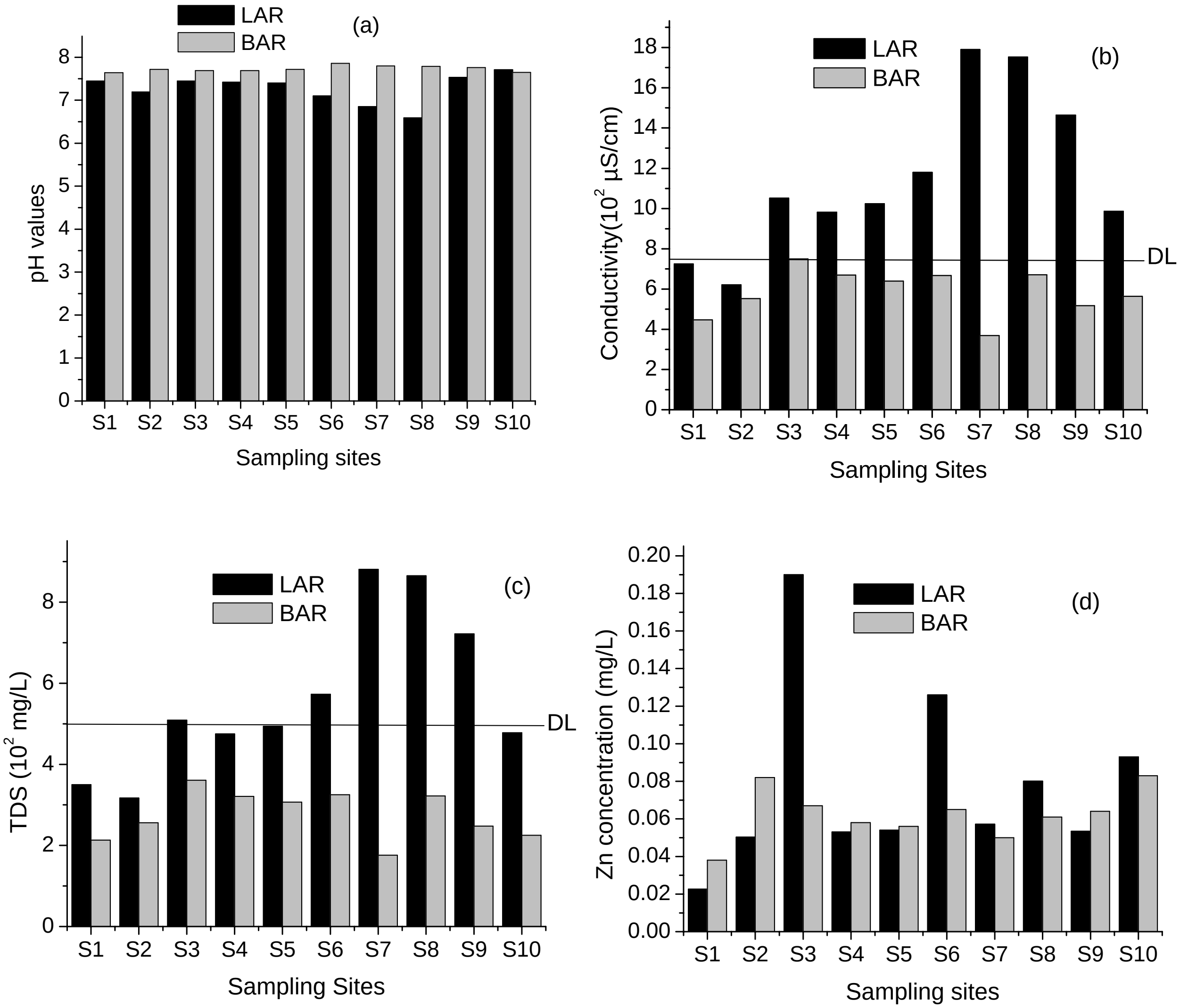


Figure 9. Pair wise comparison of physicochemical properties and dissolved Zn concentration of LAR and BAR sampling sites that have the same latitude (a) pH (b) Conductivity (c) TDS and (d) Dissolved Zn concentration. The horizontal lines are desirable limit of CCME.

Comparison of the rivers sediments with cadmium content reveals that 50 % of sampling sites have no significant difference in Cd content at 5 % significance level (S1, S4, S5, S6 and S7) as shown in Fig.10 (a). Cd contents in LAR sediment at down sites are significantly different with the corresponding BAR sites. The value in LAR at LA8 is three times greater than the value obtained at BA8 in BAR sediment as a result of direct discharge of untreated waste from industries. From the above result LAR sediments are more polluted than the corresponding BAR sediments with cadmium.

The pair wise comparison of copper level in the two river sediments is shown in Fig. 10 (b). It shows that all of the values are statistically different and most of the LAR sediments contain higher amount than the corresponding BAR sites. This is also accounted by the relatively high industrial activities along LAR river course. The possible source of higher copper in LAR may be from corrosion of metal pipes in different industries, agricultural activities, fungicides, and leather preservative. However, the values in both sediments are below EPA guidelines.

Comparison of the sites for Co content revealed that most of LAR sites contain significantly higher concentrations (5% significant level) as shown in Fig.10 (c) this may also be the direct influence of industrial discharges. The levels of cobalt along both rivers were observed to be higher in the up sites indicating the influence of natural factors in combination with anthropogenic effects.

Ni and Zn concentration are also observed to be statistically different in all sampling sites except at S1 for Ni as shown in Fig. 10 (d) and (f). 70% of LAR sites contain higher amount of Ni in the sediment as compared to those of BAR. The mean value of Ni at LA3 for example contains Ni three times as that of BA3 and LA10 contains 1.5 times as that of BA10. The level of Ni in all sampling sites in both sediments are above EPA SQG as shown in Fig. 10 (d) therefore, the load of Ni in both rivers is critical. The level of Zn in LAR sediment are quiet above the corresponding values of BAR in all sampling sites. The levels in LAR exceed up to three times the corresponding BAR sites as can be seen from Fig. 10 (f). Even though both sediments have appreciable Zn load compared to the other metals and some literature values they are below EPA SQG except at LA8.

In the case of Pb 30 % of the sampling sites along LAR contain higher amount of Pb than the corresponding BAR sediments as shown in Fig. 10 (e). Significant differences were observed down stream of the rivers indicating the impact of untreated industrial discharges.

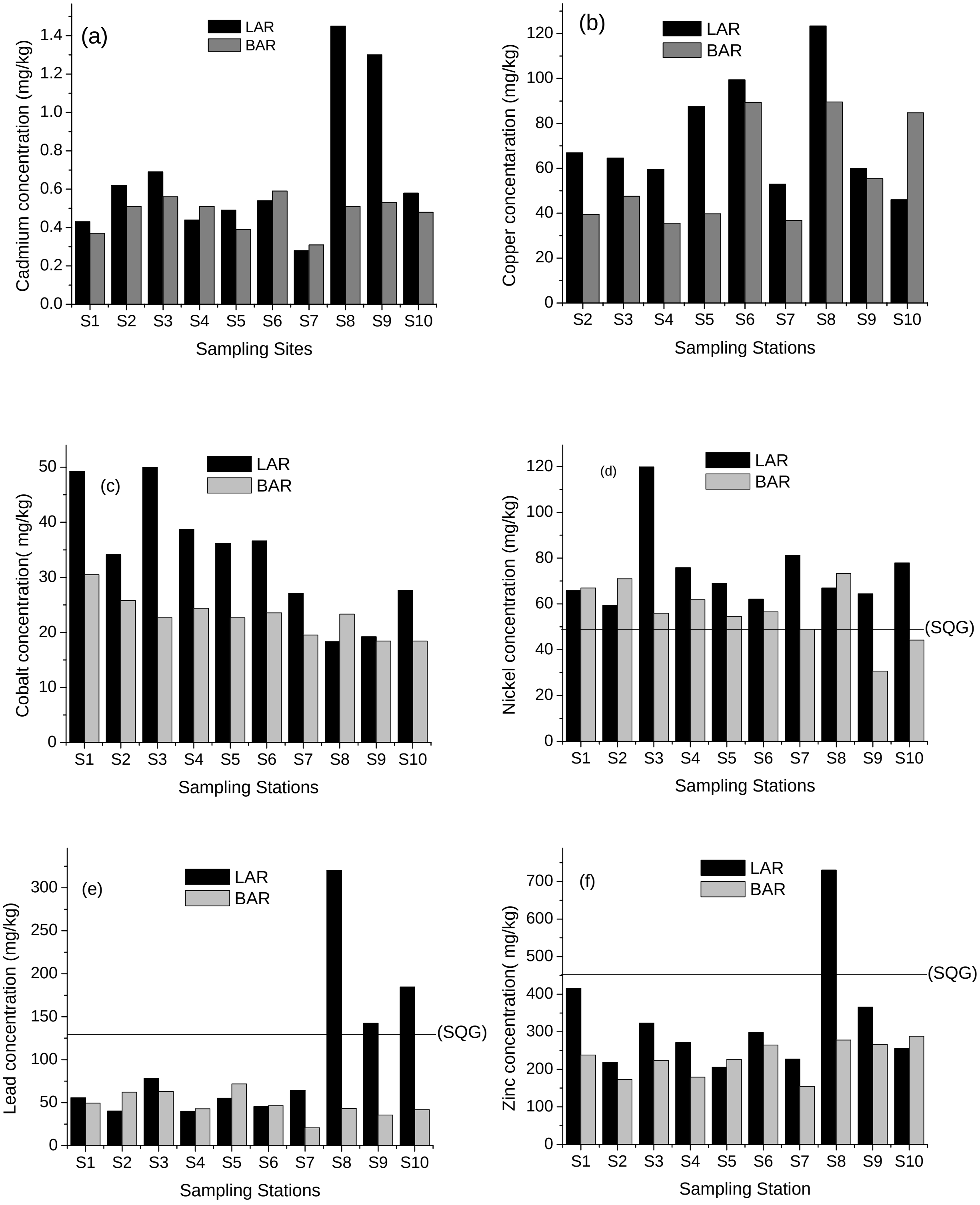


Figure 10. Pair wise comparison of the metal contents of LAR and BAR sediments sampling sites that have the same latitude (a) Cd, (b) Cu, (c) Co, (d) Ni, (e) Pb, and (f) Zn. The horizontal lines are the EPA sediment quality guidelines (SQG) for Cu, Ni, Pb, and Zn.

4.4.4 Correlations of Trace Metals and Physico-Chemicals Variables

Conductivity is directly proportional to total dissolved ions (TDS) like Na^+, K^+, M^{2+}, CO_3^+, HCO_3^-, dissolved trace metals, etc. Table 15 and Fig.11 (b) shows a significant positive correlation of TDS with conductivity. So, usually conductivity is a simple and valuables method to estimate TDS of a water body in field measurements.

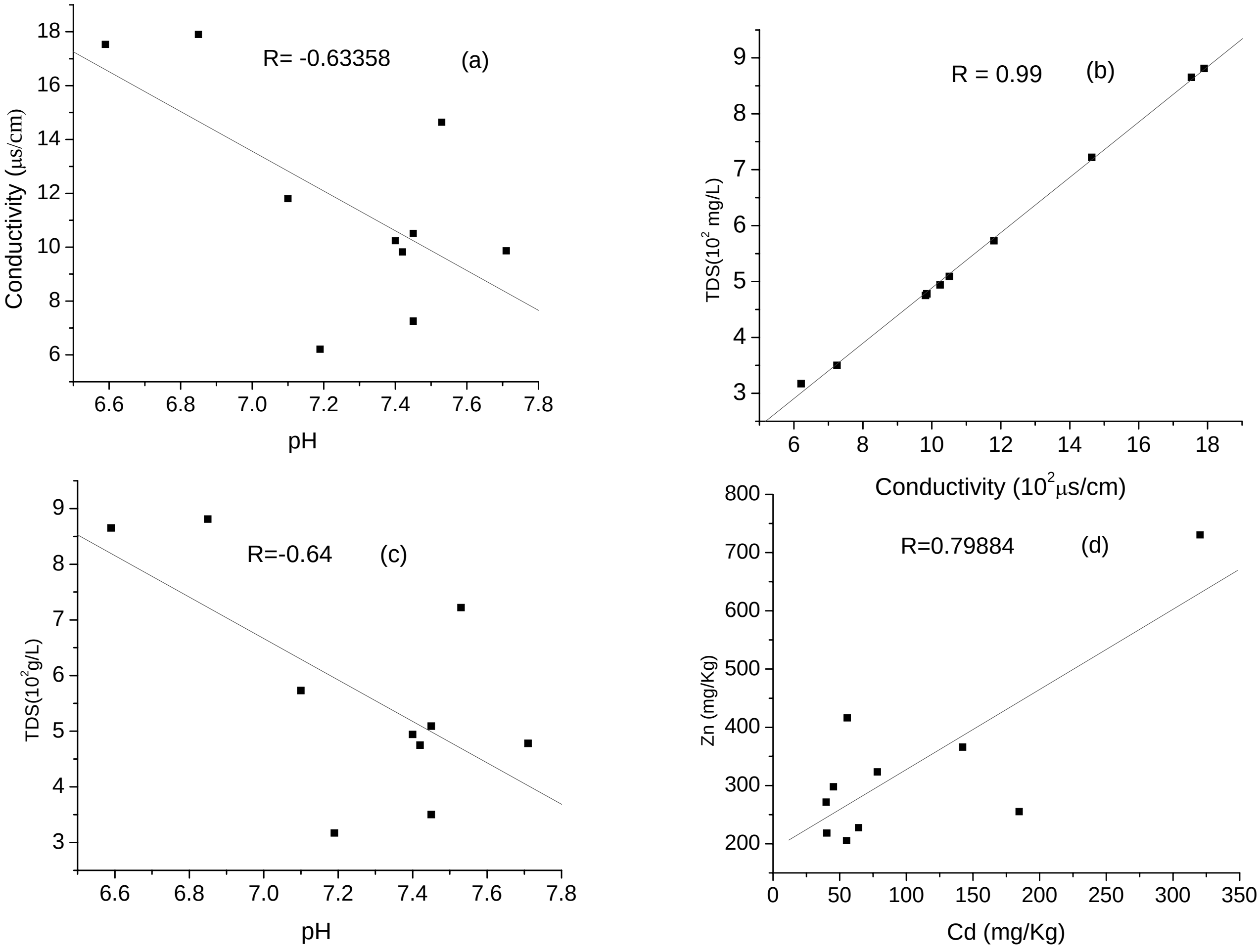
pH and TDS/conductivity were correlated negatively as shown in Fig.11 (a) and Table 15. According to Veado *et al.* [53] most of dissolved ions are favorably adsorb on to the abundant iron and manganese oxide in the surface sediments. Formation these metals oxides were observed to increase from zero to 100% with increasing pH in the range of 5 to 7.5 [29, 53]. Generally oxidizing and alkaline conditions promote precipitation of iron and manganese reducing TDS/conductivity, in contrast acidic and reducing condition promote the solution of iron and manganese decreasing adsorptions of dissolved ions thereby increasing TDS/Conductivity.

Cd, Pb, and Zn in the sediments along LAR showed a significant positive correlation with each other Fig.11 (d), (e) and (f) and Table 15 with correlation coefficient of 0.56, 0.62 and 0.64 for Cd vs. Zn, Cd vs. Pb and Pb vs. Zn, respectively. These positive and similar correlations may have an indication that these metals have a similar source. According to Veado *et al.* [53] these metals have similar properties towards adsorptions on to metal hydroxides and organic matters. Ramesssur *et al*. [2] found significant positive correlation for Zn vs. Pb in sediments from an urbanized river in Mauritius.

No appreciable correlations were observed between metal concentrations in sediments with measured pH values. This may be due to the overwhelming influence of local untreated industrial discharge and uneven sediment composition and structure. In fact a significant negative correlation was observed between dissolved Zn and measured pH value ($r^2 = 0.52$). The same explanation can be applied as pH vs. TDS/conductivity to justify this phenomenon. The pore water concentration in sediment exceeds that of the overlying water at lower pH hence diffusion of the metal will follow to increase the concentration of the overlying water.

Table 15. Correlation matrixes of physico-chemical variables and trace metals in sediments of LAR

	pH	TDS	Cond	Cd	Cu	Co	Ni	Pb	Zn
pH	1								
TDS	-0.64	1							
Cond	-0.63	0.99	1						
Cd	-0.26	0.46	0.45	1					
Cu	0.16	-0.26	-0.26	0.03	1				
Co	0.39	-0.69	-0.68	-0.62	0.44	1			
Ni	0.19	0.04	0.05	-0.15	0.75	0.43	1		
Pb	-0.36	0.55	0.54	0.79	-0.16	-0.66	-0.06	1	
Zn	-0.52	0.45	0.44	0.75	-0.15	-0.10	-0.12	0.80	1



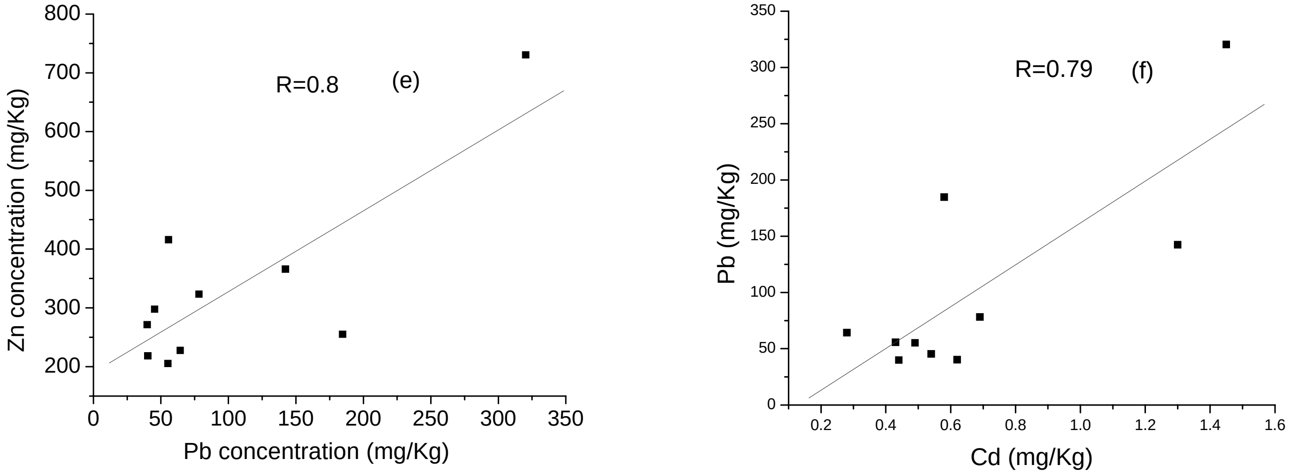


Figure 11. Trace metal and physico-chemical parameters with correlation coefficients for LAR sediments and water samples, (a) pH vs. conductivity, (b) TDS vs. conductivity, (c) pH vs.TDS, (d) Cd vs.Zn, (e) Zn vs.Pb and (f) Cd vs Pb.

5. CONCLUSION AND RECOMMENDATIONS

The present study revealed that open beaker digestion was a reliable method for quantitative determination of trace metals in the sediment samples. The result of recovery test showed that comparable value for each metal in both rivers indicating the two rivers sediments may have similar composition.

Determination of trace metals in the rivers is imperative as the rivers are used for various purposes by the residents. The concentrations of dissolved trace metals in both rivers water were found to be below the maximum permissible limit of TQWR for domestic, irrigational and livestock activities purposes hence, water can be used from both rivers for these purposes without the adverse effect of the metals determined. On the other hand trace metals pollution state of sediments in the rivers is alarming. On the average the degree of pollution the sediments with trace metals in decreasing order is as follows: Zn>Pb>Cu>Ni >Co>Cd.

The present finding showed that water and sediments quality of both LAR and BAR are highly linked to anthropogenic sources with the intensity of human pressure associated with industrial effluent, domestic wastes and agricultural activities. The measured physico-chemical parameters and the distribution of trace metals showed a similar declining quality trend from up to down stream of the rivers. The pollution problem along BAR was observed to be associated mainly with untreated domestic wastes from the residents where as the pollution case of LAR is attributed by the combined influence of domestic waste and more dominantly from industrial sources.

Comparisons of concentration of toxic metals and physico-chemical properties of the water in the two river revealed that LAR is more polluted than BAR. This is consistent with everybody's expectations as Little Akai is a sink for various untreated industrial discharges.

In this study the pollution statues of the rivers with trace metals were assessed and the relative importance of anthropogenic sources have been identified but it was found to be difficult to locate the exact sources of for each pollution component at each sampling site. Therefore, it is recommended that further studies are required to locate and quantify the possible contributing pollution sources. Also it is recommended to asses the correlation of trace metals concentration in sediments with that of the overlying water bodies using low detection limit instruments to predict the potential hazards due to excessive accumulation of metals in the sediments.

6. REFERENCES

1. Awofolu, O.R.; Mbolekwa, Z.; Mtshemla, V.; Fatoki, O.S. Levels of trace metals in water and sediments of Tyume River and its effect on the Irrigated Farmland. *Water SA* **2005**; 31: 87-94.
2. Ramessur, R.T.; Ramjeawon,T. Determination of lead, chromium and zinc in sediments from an urbanized River in Mauritius. *Environ. Int.* **2002**; 28: 315-324.
3. Yah, H.; Gray, N.F. Riverine sediment metal concentration of the Avoca-Avonmore Catchments, South –East Ireland: A base line assessment. *Biology and Environ.* **2005**; 105B (2): 95-106.
4. Davies O. A.; Allison, M.E.; Uyi, H. S. Bioaccumulation of heavy metals in water, sediment and periwinkle (*Tympanotonus fuscatus var radula*) from the Elechi Creek, Niger Delta. *African Journal of Biotechnology* **2006**; 5 (10): 968-973.
5. Goodman and Gilman's. *The Pharmacological Basis of Therapeutics*, McGraw – Hill,Inc: NY; **1990**; pp.1592-1611.
6. Mertz,W. The essential trace elements. *Science* **1981**; 213: 1332-1338.
7. Vallee, B.L. The function trace elements in biology. *Scientific Monthly* **1951**; 72(6): 368-376.
8. Mwashote, B.M. Levels of cadmium and lead in water, sediment and selected fish species in Mombassa, Kenya. *Indian J. Mar. Sci.* **2003**; 2(1): 25-34.
9. AACC (Addis Ababa City Council) 2004. *The Federal Democratic Republic of Ethiopia: Basic Information.* http://www.ethiopar.net/English/basinfo/infoadds.html accessed on May 12, 2006.
10. Bezunesh, T. Water risks and natural heritage elements for research proposals on the urban dynamics of Addis Ababa. http://www.bondy.ird.fr/cvd/mohamed_2004/Site/Ird/scientific1.html accessed on April 25, 2005.
11. Alemayehu, T. The impact of uncontrolled waste disposal on surface water quality in Addis Ababa, Ethiopia. *SINET: Ethiopia.J. Sci*. **2001**; 24(1): 93-104.
12. Tesfay, B. The degradation of the Abo-Kebena River in Addis Ababa. M.Sc. *Thesis*, Addis Ababa University; 1988; pp 1-24.
13. Itanna, F. Metals in leafy vegetables grown in Addis Ababa and toxicological implications. *Ethiopian J. Health Dev.* **2002**; 16(3): 295-302.

14. WIC (Walta Information Center) 2004. *Vegetables cultivated along city's polluted rivers said poisoning danger to health.* WIC, Addis Ababa, Ethiopia. http://www.waltainfo.com/EnNews/2003/Mar/18Mar03/Mar18e7.html accessed on May 19, 2005.
15. Itanna, F. Metal concentration of some vegetables irrigated with industrial liquid waste at Akaki, Ethiopia. *SINET: Ethiopia. J. Sci.* **1998**; 21 (1): 133-144.
16. Duffus, J.H. "Heavy Metals" – a Meaningless Term? *Pure Appl.Chem.***2002**; 74(5): 793-807.
17. Willson, A.L. Trace metals in water. *Phil. Trans. R. Soc. Lond.* **1979**; 288 (1026): 25-39.
18. Clesceri, L.C.; Green berg, A.E.; Eaton, A.D. Standard methods for the examination of water and waste water, 20th ed., *American Health Association:* Baltimore (USA) **1998**; 3-1-3-17.
19. Theodore D. M. Method 200.5: Determinations of trace elements in drinking water by axially viewed inductively coupled plasma-atomic emission spectrometry. *National Exposure Research Laboratory Office of Research and Development U. S. Environmental Protection Agency Cincinnati, OHIO 45268*; **2003**:1-36.
20. Ebdon, L.; Evans, E.H.; Fisher, A.S.Hill, s.J. *An Introduction to Analytical Atomic Absorption spectrometry*, John Wily and Sons: NY; **1998**; pp. 8-50.
21. VanLoo, J.C. *Analytical Atomic Absorption Spectroscopy: Selected Methods*, Academic press: NY; **1980**; pp.200-219.
22. Botes, P.J.; Van Staden, J.F. Investigation of trace element mobility in river sediments using ICP-OES. Water SA .**2005**; 31 (2): 183-194.
23. Melaku, S.; Wondimu, T.; Dams, R.; Moens, L. Multi-element analysis of Tinishu Akaki River sediment, Ethiopia by ICP-MS after microwave assisted digestion. *Can. J. Ana. Sci. Spectrosc.* **2004**; 50(1): 31-40.
24. Bulska, E. Analytical advantage of using electrochemistry for atomic spectrometry. *Pure Appl. Chem.* **2001**; 73(1): 1-7.
25. Yasar, D.; Aksu, A.E.; Uslu, O. Anthropogenic pollution in Izmit Bay: Heavy metals concentrations in surface sediments. *Turk J. Engin. Environ. Sci.* **2001**; 25:299-313.

26. Duchar, P.; Calvert, S.E.; Price, N.B. Distribution of trace metals in the pore of waters of shallow marine sediments. *Limnol .Oceanogr*. **1973**; 18(4): 605-610.
27. Burton, J.D.; Althaus, M.; Millward, G.E.; Morris, A.W.; Statham, T.J.; Tappin, A.D.; Turnner, A. Processes influencing the fate of trace metals in the North Sea. *Phil. Trans. R. Soc. Lond.* **1993;** A345: 557-568.
28. Zinabu, G.M.; Zerihun,D. The chemical composition of the effluent from Awassa Textile Factory and its effect on aquatic biota. *SINET: Ethiopia. J. Sci*.**2002**; 25 (2): 103-144.
29. Wesley.G. Industrial water pollution control 2nd ed., Mc Graw-Hill Book Company: New York; 1986; pp.98-109.
30. Binning, K.; Baird, D.; Survey of heavy metals in the sediments of the Swartkops River estuary, Port Elizabeth South Africa. Water SA. **2001**; 27 (4): 461-466.
31. Okonkwo, O.J.; Mothiba, M. Physico–chemical characteristic and pollution levels of heavy metals in rivers in Thohoyandou, South Africa. *Journal of Hydrology* **2005**; 308: 122-127.
32. Dubiniski, B.J.; Siimpson, R.L.; Good, R.E. The retention of heavy metals in sewage sludge applied to a freshwater tidal wetland. *Estuaries* **1986**; 9(2): 102-111.
33. Bak, J., Jensen, J., Larsen, M. M., Pritzl, G. and Scott-Fordsmand, J. A heavy metal monitoring programme in Denmark. *Sci. Total Environ.* **1997***;* 207: 179-186.
34. Hueper, W. C.; Payne, W. W. Experimental studies in metal carcinogenesis. *Arch. Environ. Health* **1962;** 5:445-462.
35. Guo, Q. Increases of lead and chromium in drinking water from using Cement-mortar-lined pipes: Initial modeling and assessment. *Journal of Hazardous Materials* **1997**; 56: 18 l-213.
36. Egli, H.; Dassenakis, M.; Gerelick, H.; VanGrieken, R.; Peijneburg, W.J.G.M.; Klasinc, L.; Kordel, W.; Prist, N.; and Tarvares, T. Minimum requirements for reporting analytical data for environmental samples. *Pure Appl. Chem.* **2003**; 75(8): 1097-1106.
37. Girmay, H.shallow resistivty investigation in Filwoha Fault. M.Sc. *Thesis,* Addis Ababa University, **1985;** pp.1-10.
38. South Dakota State Department of Environment and Natural Resources Water

Resources Assistance Program **2005**; Standard operating procedures for field samplers Volume I; pp10-40.

39. International Atomic Agency, Collection and Preparation of Bottom Sediment Samples for Analysis of Radionuclids and Trace Elements; July 2003:1-40.
40. Canadian water Quality guidelines. http://www.ccme.ca/assets/pdf/el_062.pdf. accessed on May 12, 2006.
41. Zaranyika, M.F.; Mtet, L.; Zromuya, S.; Gongoraand, G.; Mathuthu, A.S. The effect industrial effluent and leachate from landfill on the levels of selected trace heavy metals in the water of upper and middle Mukuvisi River in Harare, Zimbabuwe. *Bull. Chem. soc. Ethiop.* **1993**; 7(1): 1-10.
42. Zinabu, G. M.; Pearce. G. N. Concentrations of heavy metals and related trace elements in some Ethiopian Rift-Valley Lakes and their in-flows. *Hydrobiologia* **2003**; 429**:** 171–178.
43. Gonzalez, H. Heavy metals surveys in sediments of five Cuba Bays. *Biogeochemistry* **1991**; 14:113-128.
44. Yu, K.C.; Tsai, L.J.; Chen, S.H.; Ho, S.T. Correlation analysis on binding behavior of heavy metals with sediment matrixes. *Water Res.***2001**; 35(10): 2417-2428.
45. Melaku,S.;Wondimu,T.; Dams,R.;Moens,L. Simultaneous determination of trace elements in Tinishu Akaki River water sample, Ethiopia, by ICP-MS *Can .J. Ana. Sci. Spectrosc.* **2004**; 49(6): 374-384.
46. Fatoki, O.S.; Lujifa,N.; Ogunfowokan, A.O. Trace metal pollution in Umtat River. *Water SA* **2002**; 28(2): 183-190.
47. Van Aardt, W.J.; Heavy metals (Cd, Pb, Cu, Zn) in mudfish and sediments from three hard-water dams of the Mooi-River Catchments, South Africa. *Water SA* **2004**; 30(2): 211-218.
48. H/gebrial, Y. Metals in leafy vegetables grown in Addis Ababa. M.Sc. *Thesis*, Addis Ababa University, **2003;** pp.31-39.
49. Neziri, A.; Gössler, W. Determination of heavy metals in water and sediments of Drini River, Buna River and Lake Shkodra, Albania. hhttp://www.balwois.mpl.ird.fr/balwois/administration/full_paper/ffp-541.pdf. Accessed on May 12, 2006.

50. Landajo, A.; Arana, G.; de Diego, A.; Etxebarria, N.; Zuloaga, O.; Amouroix, D. Analysis of heavy metal distribution in superficial estuarine sediments (estuary of Bilbao, Basque Country) by open-focused microwave-assisted extraction and ICP-OES. *Chemosphere* **2004**; 56: 1033-41.
51. Van Aardt, W.J.; Heavy metals (Cd, Pb,Cu, Zn) in mudfish and sediments from three hard- water dams of the Mooi- River Catchments, South Africa. *Water SA* **2004**; 30(2): 211-218.
52. Glasby, G.P.; Stoffers, P.; Walter, P.; Dav9is, K.R.; Renner, R.M. Heavy- metals pollution in Manukau and Waitemata Harbours, New Zealand. *New Zealand journal of marine and fresh water research* **1998;** 22: 595-611.
53. Veado, M.A.R.V.; Pinte, G.; De Oliveira, A.H.; Revel, G. Study of water and sediment interactions in the Das Velhas River, Brazil–major and trace elements. Water SA **2000**; 26 (2): 255-261.
54. Microcal software, inc. *Origion Data Analysis and Technical Graphics Software for Windows Version 6.0*, Microcal Software, inc.: Northampton 1999.