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Levels of potentially toxic elements and polycyclic aromatic hydrocarbons in sediment, Swiss chard and water of Akaki River, Lake Awassa and Lake Ziway, Ethiopia

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Levels of potentially toxic elements and polycyclic aromatic hydrocarbons in sediment, Swiss chard and water of Akaki River, Lake Awassa and Lake Ziway, Ethiopia

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PhD Dissertation

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This is to certify that the thesis prepared by Kebede Nigussie Mekonnen, entitled: *Levels of potentially toxic elements and polycyclic aromatic hydrocarbons in sediment, Swiss chard and water of Akaki River, Lake Awassa and Lake Ziway, Ethiopia* and submitted in fulfillment of the requirements for Degree of Doctor of Philosophy (Analytical Chemistry) complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

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Kebede Nigussie Mekonnen

April 2014

To my beloved family (Tsehaynesh and Yeabsira)

and

My late father Nigussie Mekonnen

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ABSTRACT

Levels of potentially toxic elements and polycyclic aromatic hydrocarbons in Sediment, Swiss chard and Water of Akaki River, Lake Awassa and Lake Ziway, Ethiopia

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Addis Ababa University, 2014

In this work, the levels of potentially toxic elements and polycyclic aromatic hydrocarbons in sediment, Swiss chard and water of Akaki River, Lake Awassa and Lake Ziway, Ethiopia, were determined, employing comprehensive sample volume, effective sample pretreatment and various state-of-the-art instrumentations. The implications of the levels of potentially toxic elements and polycyclic aromatic hydrocarbons were also evaluated based on national and/or international guidelines.

A total of thirty nine sediment and water samples were collected from Akaki River, Lake Awassa, and Lake Ziway, Ethiopia while Swiss chard samples were collected from five farmlands irrigated with Akaki River for determination of potentially toxic elements (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Sn, Hg and Pb) and polycyclic aromatic hydrocarbons. The potentially toxic elements were determined using laser-induced breakdown spectrometry (LIBS), flame-atomic absorption spectrometry (F-AAS), inductively coupled plasma-optical emission spectrometry (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS) and elemental mercury analyzer. The polycyclic aromatic hydrocarbons in sediment samples were determined using gas chromatography-mass spectrometry (GC-MS) after microwave-assisted extraction (MAE) with acetone/n-hexane (1:1, v/v).

External calibrations were used for quantifications of potentially toxic elements and polycyclic aromatic hydrocarbons. The precision and accuracy of the methods were verified using certified reference materials. The results obtained were accurate and precise at the 95% confidence level with recoveries >90% and the average relative standard deviations $\leq$ 10% for most of the quantified species.

In the present study, LIBS has been applied for the determination of levels of Cr, Mn and Fe in sediment samples and the results were compared with those obtained using F-AAS. Fourteen sediment samples were collected from Akaki River, Addis Ababa, Ethiopia. The LIBS results for the elements varied from 0.060–0.707 mg/g for Cr, 0.895–3.64 mg/g for Mn and 26.9–71.8 mg/g for Fe. The F-AAS results varied from 0.061–1.37 mg/g for Cr, 1.24–4.46 mg/g for Mn and 49.0–83.3 mg/g for Fe. With reference to sediment quality guidelines, Akaki River is heavily polluted by Cr.

Using elemental mercury analyzer, the concentration of mercury in sediment samples ranges between 3.9 to 110 µg/kg for Akaki River, 12 to 67 µg/kg for Lake Awassa, and 17 to 110 µg/kg for Lake Ziway. When compared to Lake Awassa, Lake Ziway had a higher concentration of mercury. The average values for the areas are 24 µg/kg for Lake Awassa, 32 µg/kg for Akaki River, and 44 µg/kg for Lake Ziway. The sources of mercury in the present study areas can be related to natural than anthropogenic origin.

The concentration (in µg/L) of the potentially toxic elements in water were in the range of 0.992–18.8, <0.416–83.0, 1.05–1580, <45–1760, <0.109–1.99, 0.432–12.8, 0.765–12.5, 6.00–300, <0.937–1.96, <0.294–1.50, <0.012–0.633, 0.132–4.76, <0.289 and 0.198–7.18 for V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Ag, Cd, Sn, Hg and Pb, respectively. The concentrations of all the

quantified elements in the water, with the exception of Mn are in the range of the permissible limits of the European Community and World Health Organization guidelines for both drinking and irrigation water. In general, lower concentrations were observed for the known toxic elements (such as Hg and Cd) while higher concentrations were observed for Zn, Mn and Fe.

The average concentrations of the potentially toxic elements in sediment of Akaki River follow the pattern: As << Hg < Se < Cd < Ag < Sn < Co < Cu < Ni < V < Cr < Pb < Zn < Mn < Fe. For Lake Awassa, the average concentrations of the potentially toxic elements in sediment follow the pattern: As << Hg < Se < Cd < Co < Sn < Ag < Ni < V < Cu < Cr < Pb < Zn < Fe < Mn. For Lake Ziway, the average concentrations of the potentially toxic elements in sediment in sediment follow the pattern: As << Hg < Se < Cd < Sn < Pb < Co < Ag < Ni < Cr < V < Cu < Zn < Fe < Mn. For both lakes similar pattern in elemental concentration is observed. For the entire sampling areas, the minimum concentration is observed for the known toxic elements (such as As, Hg and Cd) while the highest concentration is observed for Zn, Fe and Mn.

For the vegetable samples based on the elemental concentrations the pattern in leaf is: Ag ≈ Cd << Hg < Se < As < Co < Pb < V < Ni < Cr < Cu < Sn < Zn < Mn < Fe, whereas for stem: Ag ≈ Cd << Hg < Co < As < Se < Pb < V < Ni < Cr < Cu < Sn < Mn < Zn < Fe. For specific sites the potentially toxic elements Cr, Fe, Pb, Zn and As in Swiss chard surpassed the maximum permitted guideline values.

The assessment of sediment pollution on effect based sediment quality guidelines indicate that some of the Akaki River sites are heavily polluted with Cu, Zn and Pb. Moreover, both lakes are heavily polluted with Zn and even some of the sites are heavily polluted with Cu, Ni and Pb. With respect to the ecotoxicological aspect of potentially toxic element contamination, at least *possible contamination for biota could be observed in some of the Akaki River sites with Zn, Ag, Cd, Hg and Pb, which could be an alarm for the responsible personnel. Both lakes have higher concentration of Ag which suggests that the areas could be toxic to aquatic organisms with probable effects, while for Cr, Cu, As and Hg are less than the minimum range. Based on the bivariate correlation procedure, there is significant correlation between the two lakes at the 0.01 level (2-tailed) for the fifteen potentially toxic elements, which shows similar sources for both lakes. In general, when looking the area wise average concentrations of potentially toxic elements in the water and sediment samples, Lake Ziway > Akaki River > Lake Awassa.*

The contents of the fourteen polycyclic aromatic hydrocarbons (dry mass) in sediments were determined. The results obtained ranged from 0 to 3,070 ng/g, 24.9 to 410 ng/g and 15.0 to 310 ng/g for Akaki River, Lake Awassa and Lake Ziway, respectively. Source ratios indicated that the polycyclic aromatic hydrocarbons are mainly from petrogenic sources. Sediment quality guidelines showed that all the sediment sampling sites are of at lesser sediment toxicity risk and should not exert adverse biological effects relative to the quantified polycyclic aromatic hydrocarbons. Though the concentrations of some of the potentially toxic elements as well as PAHs are within the limit proposed by national and/or international guidelines, the history of their level and therefore the anthropogenic effects could not be determined, as there were no reliable data in the literature for the specified sampling areas. Therefore this study can be used as a baseline data for further studies. The qualities of water and sediments of the investigated aquatic system are degrading. Therefore, remediation mechanisms should be implemented and properly practiced around the rivers and lakes catchment areas.

KEYWORDS

Sediment, Swiss chard, water, potentially toxic elements, polycyclic aromatic hydrocarbons, microwave acid digestion, microwave-assisted extraction, laser-induced breakdown spectrometry, flame-atomic absorption spectrometry, inductively coupled plasma-optical emission spectrometry, inductively coupled plasma-mass spectrometry, RA-915+ mercury analyzer, gas chromatography-mass spectrometry, Akaki River, Lake Ziway, Lake Awassa, Ethiopia.

LIST OF ACRONYMS

AA	Addis Ababa
AR	Akaki River
BCR	Community Bureau of Reference (a registered trade mark of the EC)
CCD	Charge coupled device
CRM/RM/SRM	Certified Reference Material/Reference Material/Standard Reference Material
EC	European Commission
ERL	Effects range-low
ERM	Effects range-median
F-AAS	Flame-atomic absorption spectrometry
FAO	Food and Agricultural Organization
FMOWR	Federal Ministry of Water Resources
GC-MS	Gas chromatography-mass spectrometry
GF-AAS	Graphite furnace-atomic absorption spectrometry
ICCD	Intensified charge-coupled detector
ICP-MS	Inductively coupled plasma-mass spectrometry
ICP-OES	Inductively coupled plasma-optical emission spectrometry
IRMM	Institute of Reference Materials and Measurements
LIBS	Laser-induced breakdown spectrometry
LOD	Limit of detection
MAE	Microwave-assisted extraction
MARS	Microwave-assisted reaction system
Nd:YAG	Neodymium-doped yttrium aluminum garnet

NIST	National Institute of Standards and Technology
PAHs	Polycyclic aromatic hydrocarbons
SIM	Selected ion monitoring
SQGs	Sediment quality guidelines
TAR	Tinishu Akaki River
TlAR	Tiliku Akaki River
USEPA	United State Environmental Protection Agency
WHO	World Health Organization
XRF	X-ray florescence spectrometry

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CHAPTER ONE

BACKGROUND AND MOTIVATION OF THE STUDY

1.1. Introduction

In this chapter, environmental pollution, with respect to sediment, plants and water, are discussed. Environmental contamination issues in Ethiopian context are highlighted. In addition, an overview of the research gaps with respect to potentially toxic elements and PAHs, the objectives of the study, the justification towards those selected potentially toxic elements and the overall organization of the dissertation are given in brief.

1.2. Environmental Pollution with respect to Sediment, Plant and Water

Currently, environmental pollution is a major concern because of the continuous growth of urbanization and industrial development. Concerns over the possible ecological effects of the increasing accumulation of potentially toxic elements and PAHs in the environment are growing. These are some of the most serious pollutants in our natural environment. Therefore, knowledge of the change in concentrations and distributions of potentially toxic elements and their compounds, and PAHs in various compartments of the environment is a priority, since such contamination is an environmental problem throughout the world. The source of these known contaminants are both anthropogenic activities and natural processes, but human activities contribute significantly to total environmental exposure to these substances.

There are principally three reservoirs of contaminants in the aquatic environment namely water, sediment and biota, where the sediment is the major repository of the contaminants (Bagheri *et al*. 2011). Sediments[1] consist of a complex mixture of inorganic and organic components. Sediments act as both carriers and source of contamination in an aquatic environment; not only playing an important role in water pollution, but they can also provide a record of pollution history, since they represent long-term sources of contamination to higher tropic levels (Rauf *et al*. 2009; Bagheri *et al*. 2011; Bentum *et al*. 2011). The distribution of contaminants in sediments can provide evidence of the anthropogenic impact on aquatic and other ecosystems, and therefore aid in assessing the risks associated with human induced change (Bentum *et al*. 2011). The contamination of sediment with contaminants, even in low concentrations, may lead to serious environmental problems. In general, contaminated sediments may cause significant damage to ecosystems and decrease biodiversity. Contaminants are not necessarily fixed permanently by the sediment, but may be recycled *via* biological and chemical agents, both within the sedimentary compartment and the water column (Saghali *et al*. 2013).

Plants occupy a special place among the ecological materials usually investigated, since they are responsible for oxygen production. Besides, they are an extremely important link in the food chain, collecting contaminants from the soil, air and water and transmitting further to man and animals. The elemental composition of plants usually reflects the geochemical features of the environment where they grow. That is why some of them are successfully used as biomonitors. Plants are a reasonable source of data relating to soil, water and air pollution, however, to make any comparison then the same species of plant must be sampled from uncontaminated, as well as

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[1] Sediment is the loose sand, clay, silt and other soil particles that settle at the bottom of a body of water. Sediment can come from soil erosion or from the decomposition of plants and animals. Wind, water and ice help carry these articles to rivers, lakes and streams.

from areas thought to be contaminated and analyzed together. The length of the record of pollution determined by plant analysis is only as long as the last growing season. As soon as the plants die back and shed foliage the record is lost, thus, plant samples must be collected at the same time of the year (Ward 2000).

Water is the most essential nutrient for human existence. Due to the movement of water and the diffusion of dissolved substances, different geochemical processes take place in the Earth's crust. To a great extent, they are responsible for the redistribution of chemical elements in soil and further on to the biosphere. Water has been used much as a recipient of toxic and solid waste from domestic, industrial and agricultural runoffs (Aksoy *et al*. 2005). This is one of the reasons that make the determination of the various contaminants in water as one of the important tasks in environmental pollution control. Therefore, the need for the management of water resources is crucial and even more pressing as industrialization and development advances. Running water may only indicate a recent or continued pollution incident, as the contaminant will be diluted with freshwater flow passing the point of the pollution source. However, surface water could be used as a monitor for longer periods of pollution. The problem of water pollution due to potentially toxic elements and PAHs has begun to cause concerns in most metropolitan cities (Lokeshwari and Chandrappa 2006; Sonawana *et al*. 2013). Monitoring contaminant flow is important specifically for health care of the communities and generally for sustainable development.

The potentially toxic elements entering the ecosystem may lead to geoaccumulation, bioaccumulation and biomagnification in biosystems through contaminated water, soil, sediment, air and biota and may have possibilities for environmental transformation into more toxic forms

(Singare *et al*. 2012; Saghali *et al*. 2013; Sonawane *et al*. 2013). These contaminants entering the aquatic environments are adsorbed onto particulate matter, although they can form free metal ions and soluble complexes that are available for uptake by biological organisms, or are deposited in sediments. Once deposited, binding by sulfides and/or iron hydroxides immobilizes potentially toxic elements until a change in redox or pH occurs (Singare *et al*. 2012). Therefore a better understanding of their sources, their accumulation in the various media and the effects of their presence are seen to be particularly important issues of present day research on risk assessment.

The rapid and accurate determination of contaminants in environmental matrices such as sediments, water and plant have led to the development and continuous improvement of various analytical methods, concerning both sample digestion and the choice of the most appropriate instrumental techniques to obtain exhaustive chemical information in the shortest time possible. The determination of the total content of these contaminants in the sediment, water and plant are particularly useful to collect information on the genesis and on the level of contamination. For the potentially toxic elements, the instrumental analysis following digestion procedures has lately evolved from mono-elemental spectroscopic techniques (such as F-AAS and GF-AAS) to multi-elemental ones (such as ICP-OES and ICP-MS), which allow the analysis of a large number of analytes in a reasonably short time and achieve wider sample characterization (Bettinelli *et al*. 2000). Apart from the above spectroscopic techniques, some of the methods (such as LIBS and elemental mercury analyzer) do not require a sample in liquid form, instead direct analysis of solid samples is possible. For the analysis of PAHs, various extraction techniques are used in combination with advanced instrumental analysis techniques, such as gas chromatography- and high performance liquid chromatography-mass spectrometry.

1.3. Environmental Contamination Problems in Ethiopia

The environmental problems in Ethiopia are similar to those in the developing countries and also to countries with economies in transition. Some of these problems are: soil erosion, land degradation, desertification, deforestation, industrial emission and pollution, and wildlife reduction, in which the entire problems are the results of natural and/or anthropogenic phenomena. Due to rapid population and industrial growth in the city of Addis Ababa, the city's environment, particularly the Akaki River, is susceptible to pollution. The Akaki River catchment comprises of numerous small rivers, where the dominant ones are the Tinishu and Tiliku Akaki Rivers. Most of the small and medium scale industries in the country reside in the capital, Addis Ababa. However, most of them are established along either banks of the Akaki River and are mostly with no or non-functioning waste water treatment facilities discharging their wastes to the river and its tributaries. The common contaminants from these industries include solids, oils, detergents, solvents, pesticides, and inorganics such as potentially toxic elements, nitrates, phosphates, sulfates, chloride and others (Itanna 1998a,b; Melaku *et al*. 2005a,b; Xu and Usher 2006; Gebre and van Rooijen 2009; Prabu 2009; Weldesilassie *et al*. 2010).

Yabe *et al*. (2010) reported that the Akaki River is the seventh of fourteen sites in Africa where potentially toxic element pollution exceeding the maximum limits in water, sediments or soils. The inappropriate practices of dumping household and industrial wastes in the river catchments have resulted in the spread of anthropogenic diseases in the city (Mazhindu *et al*. 2012). Itanna (2002) reported that metals in leafy vegetables grown at environmentally contaminated sites in Addis Ababa could be at concentrations that are toxic to human health. Since the 1940s, a variety of vegetables have been produced within and around the city, mainly using water from the Akaki River where the irrigation is carried out informally by smallholder farmers without conventional irrigation infrastructure. They provide about 60% of the vegetables on the cities' vegetable markets, which provides their main source of household income (Gebre and van Rooijen 2009; Weldesilassie *et al*. 2009,2010). The study done by Beyene *et al*. (2009) in the Addis Ababa urban area revealed three biologically highly stressed rivers (including Akaki River) impacted primarily by physical habitat degradation, point and non-point sources of pollution.

Studies made on vegetables and farmlands by Itanna (1998) in the vicinities of old and new industrial sites at Akaki and Awassa indicated the gradual increase of trace elements in soils over time. Alemayehu (2000,2001) reported appreciable amounts of trace elements in lakes and rivers due to the impact of uncontrolled waste disposal on surface water. Itanna (2002), Fitamo *et al*. (2007) and Itanna *et al*. (2008) determined the concentrations of metals in soils and leafy vegetables grown in Addis Ababa so as to assess the toxicological implications of contamination. The result indicated that Kera had considerably higher concentrations of particularly Cr, Cd, Ni, Pb and Zn as compared to Bulbula, because of more industrial effluents from the various industrial sources. Recently, Weldegebriel *et al*. (2012) evaluated the concentrations of metals in vegetables grown in soils irrigated with Akaki Riverr water in areas such as Akaki, Goffa, Kera and Peacok in Addis Ababa. The results indicated that the levels of trace metals Cd, Co, Cu, Mn and Ni in most of the water samples collected from Goffa, Kera and Akaki farms surpassed irrigation water guideline limits.

The limited reports dealing with the amount of the potentially toxic elements in the various compartments of Lake Awassa and Lake Ziway, Ethiopia, make it difficult to assess the extent of pollution and long-term changes in the water quality. Gebre-Mariam and Desta (2002) determined the chemical composition of the effluent of the Awassa textile factory with a focus on its effect on phytoplankton and fried fish. The findings indicated the potential effect of pollutants on the lake ecosystem. Zinabu and Pearce (2003) determined the concentrations of potentially toxic elements and related trace elements in the water bodies of some Ethiopian Rift Valley lakes and their in-flow, to provide baseline data on water quality for comparison with drinking water standards. Ataro *et al*. (2003), Kebede and Wondimu (2004), and Nigussie *et al*. (2010) compared trace element concentrations in tilapia and water of Lake Awassa and Lake Ziway, and stated that tilapia had accumulated potentially toxic elements at levels above the concentrations reported in the lake water. Thus, the above reports provided some ground to conceive of the likely occurrence of chemical pollution by potentially toxic elements and the consequent threat to Akaki River, Lake Awassa and Lake Ziway, Ethiopia.

1.4. Research Gap

A. Research conducted on the presence of potentially toxic elements in water, sediment and water of Akaki River, Lake Awassa and Lake Ziway, Ethiopia is lacking;

B. There is no other work done to determine the levels of PAHs in sediments of Lake Awassa and Lake Ziway; even only one study done on soil around Akaki River;

C. There is no other study that correlates the levels of potentially toxic elements in water, sediment and plant in the aquatic systems of Ethiopia;

D. There is no other research work done that exploits various instrumental methods (LIBS, ICP-OES, ICP-MS, F-AAS and elemental mercury analyzer) for potentially toxic elements analysis;

E. There is limited research work done on the levels of the various toxic elements, particularly those of mercury, in the aquatic system of the Akaki River, Lake Awassa and Lake Ziway;

F. There is no other work done that compares and contrasts the levels of pollution of the freshwater bodies of Ethiopia based on sediment quality guidelines to assess ecological risks of potentially toxic elements and PAHs;

G. There is no other work that could act as a baseline study for the potentially toxic elements and PAHs on sediments, plants and water of Ethiopia.

Therefore, the present study has been undertaken to address the above problems and to fill the research gaps. In this work, the concentrations of selected potentially toxic elements and PAHs in the freshwater bodies of Ethiopia are reported. Here, direct solid analysis techniques (LIBS and elemental mercury analyzer) and aqueous samples analysis techniques (F-AAS, ICP-OES, ICP-MS and GC-MS) are used for identification and quantification. Various sample preparation techniques are also addressed in this work. Moreover, the obtained elemental and PAH levels of pollution are characterized with respect to various guidelines.

Due to the limited comprehensive research works on the potentially toxic elements and even the absence of any other work on PAHs in the Ethiopian context, this study will serve as a baseline data, which will be useful for further studies. Moreover, the various stakeholders directly and/or indirectly working on environmental conservation, policy developers and policy makers in the country, in particular, can use the results as credible inputs.

1.5. Objectives of the Study

1.5.1. General objectives of the study

The main objective of this research work is to determine the toxicity levels of freshwater bodies of Ethiopia (Akaki River, Lake Awassa and Lake Ziway) through the analysis of selected potentially toxic elements and priority listed PAHs in sediment, plant and water samples using LIBS, F-AAS, ICP-OES, ICP-MS, elemental mercury analyzer and GC-MS.

1.5.2. Specific objectives of the study

The specific objectives of this research work are to:

- develop methods for quantification of potentially toxic elements in water, sediment and plant samples employing LIBS, F-AAS, ICP-OES, ICP-MS and elemental mercury analyzer;
- optimize the LIBS method;
- efficiently digest the samples for potentially toxic element analysis using a microwave assisted acid digestion procedure;
- quantitatively extract the PAHs from the sediment samples using microwave-assisted extraction and cleanup steps;
- validate the methods used for the analysis of sediment, water and plant samples (LIBS, F-AAS, ICP-OES, ICP-MS and GC-MS) using CRMs;
- compare the LODs, accuracy and precision determined from LIBS analysis with the values obtained by F-AAS;
- quantify the levels of potentially toxic elements in water, sediment and plant samples using LIBS, F-AAS, ICP-OES, ICP-MS and an elemental mercury analyzer;

- assess the concentration, distribution and sources of PAHs in sediments by GC-MS;
- compare the levels of potentially toxic elements in sediment, water and plants with literature values so as to determine the status of pollution of the freshwater bodies of Ethiopia;
- compare the levels of potentially toxic elements with sediment quality guidelines (SQGs) to assess ecological risks of selected potentially toxic elements;
- compare the levels of PAHs with SQGs to assess ecological risks of PAHs.

1.6. Justifications towards the Selected Potentially Toxic Elements

The phrase "potentially toxic element" is used in this dissertation in preference to "trace elements". The phrase "trace element" is defined as those elements making up between 0.01% and 1% of the Earth's crust. These elements can be divided into three group: the first group comprises essential elements, where both lack of exposure and over-exposure may cause adverse biological effects; the second group are those not considered essential, but which have beneficial effect on metabolism; the last group consists of those widely distributed in living organisms, but having no known beneficial metabolic effect (Mehri and Marjan 2013; Shahid *et al*. 2014). However, all of them may cause a stern menace to plants, animals and humans through the food chain beyond supra-optimal concentrations, so they are potentially toxic (Kisku *et al*. 2000; Shuhaimi-Othman *et al*. 2013; Shahid *et al*. 2014) and therefore the phrase "potentially toxic element" is preferred.

For instance, Fe, Mn, Cu and Zn are micro-elements absolutely necessary for sound growth of plants (Kisku *et al*. 2000; Kukla *et al*. 2011; Saueia *et al*. 2013). However, values below those ranges can lead to deficiencies, and at elevated concentration, they become potentially toxic (Dudka and Miller 1999; Oudeh *et al*. 2002; Fraga 2005; Duval *et al*. 2011; Kodom *et al*. 2012;

Edet *et al*. 2014). Although Co and Se are not essential to plant growth, they are required by animals and humans (Saueia *et al*. 2013). Others, such as Cd, Hg, Pb, have no known beneficial effect, but excessive intake can lead to health problems (Dudka and Miller 1999; Oudeh *et al*. 2002; Kukla *et al*. 2011; Saueia *et al*. 2013). Rather than considering single element contamination, most contamination is multi-elemental, which results in various forms of interactions between the elements (synergistic, additive, independent or antagonistic) and little is known regarding these effects (Macnicol and Beckett 1985; Kukla *et al*. 2011).

With respect to plants, the scarcity of Fe causes disturbances to protein metabolism, whereas superfluous Fe is toxic for plants. Excess Fe inhibits the take up of Ca, Mn, B, and also P and K. On the other hand, an Fe deficit can restrict chlorophyll formation and cause yellowing of the plant leaves (Kukla *et al*. 2011). Superfluous Mn has toxic effects on sensitive plants, while its scarcity is associated with restricted formation of chloroplasts, a lower rate of photosynthetic processes and whitish spots on young leaves, similar to those caused by shortage of Fe (Kukla *et al*. 2011). Cu scarcity is manifested in a lower growth rate, chlorosis and necrotic spots between the leaf veins, while an excess suppress root growth (Kukla *et al*. 2011). Cr is necessary for animals only, but Cr(VI) can be toxic to plants and animals (Kukla *et al*. 2011; Nema *et al*. 2012). When plants absorb Cd, it inhibits physiological processes and results in decreasing productivity of the plants (Nakamura *et al*. 2008).

With respect to humans, at higher levels Mn concentrates in a region of the paleostriatum, the globus pallidus, and produces manganism, a disorder that resembles Parkinson's disease (Aschner *et al*. 2009; Douglas *et al*. 2010; Rivera-Mancia *et al*. 2011). On the other hand, its deficiency can cause birth defects, alterations in bone formation, reproductive disturbances and increased vulnerability to convulsions (Douglas *et al*. 2010; Rivera-Mancia *et al*. 2011). High dietary Fe has been results with haemochromatosis (Fe overload) and also shown to depress Mn absorption and status (Finley 1999; Pietrangelo 2003). At extremely high concentrations, Cr, Zn and Cu can cause nephritis, anuria and extensive lesions in kidneys (Roney *et al*. 2006; Maxwell and Iwegbue 2011; Nema *et al*. 2012). Allergic dermatitis, known as Ni itch, is caused by exposure to high levels of Ni (Nema *et al*. 2012). Although V has beneficial effects on teeth, reduces cholesterol levels and is used to treat certain diseases, including cancers, many of its forms are toxic (Mehri and Marjan 2013).

On the other hand, Cd and Pb cause kidney damage and evoke symptoms of chronic toxicity, including impaired organ function, poor reproductive capacity, hypertension, tumors and hepatic dysfunction. Moreover, Pb can affect brain functions by interfering with neurotransmitter release and synapse function (Maxwell and Iwegbue 2011; Nema *et al*. 2012). Cd causes serious human health problems such as kidney dysfunction, osteomalacia and reproductive deficiencies when it enters the food chain (Nakamura *et al*. 2008; Nema *et al*. 2012). The element As is associated with cancers of the skin and internal organs and is associated with vascular diseases (Nema *et al*. 2012). The element Hg causes neurological disorders and has toxic effect on the kidney (Nema *et al*. 2012). Signs of chronic exposure to excessive intake of inorganic Sn include growth depression and anemia. In addition, Sn also is able to modify the activities of several enzymes and it has been claimed that the element interferes with the metabolism of Zn, Cu and Ca (Mehri and Marjan 2013).

1.7. Significance of the Study

Potentially toxic elements and PAHs in Ethiopia are not regularly monitored; there is the potential for significant accumulation of these species in sediment, soils, plants and water, thereby posing a risk to biota in general and specifically to human beings. Thus, the adverse effects of both potentially toxic elements and PAHs on human health *via* the food chain highlight the importance of monitoring their levels in water, soils, sediments and plants. Based on this fact, analytical procedures that are of academic interest, as well as of practical importance, were developed and communicated to the scientific community. The methods that were developed were applied to monitor the levels of potentially toxic elements and PAHs in environmental samples (sediment, plant and water). In addition to this, the established research collaboration between Tshwane University of Technology, the National Laser Centre (Council for Scientific and Industrial Research, South Africa), Addis Ababa University and Mekelle University could act as a stepping stone for diversified collaboration. The scientific outputs (publications, oral presentations and dissertation) could be helpful for the various stakeholders (government, policy makers, environmentalists, researchers, etc) for further actions in improving the public health and ecological well-being.

1.8. Statement of the Problem

The possible adverse effects of excessive amounts of potentially toxic elements and high PAH concentrations on humans and other biota underscore the significance of the proper assessment of their levels in water, sediments and plants. In this study, the concentrations of potentially toxic elements and PAHs in water, sediment and plant samples were determined to evaluate the degree of pollution of water, sediments and water samples collected from Akaki River, Lake Awassa and Lake Ziway, Ethiopia. For this reason, various analytical methodologies (LIBS, F-AAS, ICP-OES, ICP-MS and elemental mercury analyzer) were validated and used for determination of the levels of potentially toxic elements in environmental samples after appropriate sample preparation protocols. Moreover, GC-MS was used for the identification and quantification of the US EPA “priority list” PAHs in sediment samples after microwave-assisted extraction.

1.9. Organization of Dissertation

In this PhD work, the levels of potentially toxic elements and PAHs in sediment, plant and water samples of Akaki River, Lake Awassa and Lake Ziway, Ethiopia are presented and critically evaluated. It is organized into five main chapters, references and annexures. The organization is as follows:

Chapter One: entitled “***Background and Motivation of the Study***” provides the general background and motivation related to the aforementioned objectives (environmental pollution with respect to sediment, plant and water, and environmental contamination problems in Ethiopia), the research gaps, objectives of the study, justifications towards the selected potentially toxic elements, significance of the study, statement of the problem and the organization of the dissertation.

Chapter Two: entitled “***Review of the Literature***” presents a summary of the available literature to support the overall research objectives and to reinforce the need to address issues as listed: pollutants in freshwater bodies, microwave-assisted acid digestion, microwave-assisted extraction, analytical methodologies for analysis of potentially toxic elements and PAHs.

Chapter Three: entitled "***Experimental***" describes the experimental methods followed in the study and includes a description of the study areas, reagents, chemical and standards, sample collection and preservation, sample preparation, optimization of the instrument, calibration and analysis, preparation of standards, quality assurance, identification and quantification, and statistical analysis.

Chapter Four: entitled "***Results and Discussions***" presents the results obtained. These results are critically discussed in relation to findings of similar research studies works done elsewhere and in the area. The chapter is classified into the following sections: assessment of the levels of potentially toxic elements in sediment using laser-induced breakdown spectrometry; distribution of mercury in the sediments of some freshwater bodies in Ethiopia; potentially toxic elements in freshwater bodies in Ethiopia; assessment of potentially toxic elements in Swiss chard and sediments of Akaki River, Lake Awassa and Lake Ziway, Ethiopia; comparison of the concentrations of potentially toxic elements in sediment and water samples; and distribution of PAHs in some river and lake sediments of Ethiopia.

Chapter Five: entitled "***Conclusions***" provides the concluding remarks and recommendations of this PhD research work with respect to the objectives of the study based on the research findings.

The part titled "***Reference***" presents the literature cited in this dissertation.

Finally in the "***Annex***" part, the publications, oral presentations and trainings that lead to PhD qualification are presented.

CHAPTER TWO

REVIEW OF THE LITERATURE

2.1. Introduction

In this chapter, a brief literature survey of potentially toxic elements and PAHs in sediment, plant and water is presented. An overview of the sample preparation and quantification methods for the potentially toxic elements and PAHs in various matrices is reviewed. Moreover, brief descriptions of the various instrumentations used in this work namely LIBS, F-AAS, ICP-OES, ICP-MS, elemental mercury analyzer and GC-MS are given.

2.2. Pollutants in Freshwater Bodies

The major types of pollutants found in freshwater bodies are nutrients, bulk organics, halogenated hydrocarbons or persistent organics, PAHs and potentially toxic elements (US EPA 1999; US EPA 2005; Rodriguez-Obeso *et al*. 2007). Potentially toxic elements and PAHs can be toxic to various plants and animals, depending on the level of contamination. Some of them can also be toxic to humans and biota depending on their levels. Some of the potentially toxic elements are essential in plant nutrition, but plants growing in the vicinities of industrial areas display increased concentrations, serving in many cases as biomonitors of pollution loads (Naser *et al*. 2012). Many persistent organic contaminants and some potentially toxic elements could biomagnify and bioaccumulate as they travel up the food chain (US EPA 1999; US EPA 2005; Prabu 2009). They are among the conservative pollutants that are not subject to bacterial attack or other break down or degradation processes and are permanent additions to the aquatic environment (Igwe and Abia 2006). Vegetables cultivated in industrially polluted areas take up potentially toxic elements and accumulate them in their edible and non-edible parts in quantities high enough to cause problems both to animals and humans consuming these metal-rich plants.

2.2.1. Potentially toxic elements in freshwater bodies

The source of potentially toxic elements in water bodies can be of natural origin (eroded minerals within sediments, leaching of ore deposits and volcanism products) or anthropogenic (solid waste dumping and industrial or domestic discharge). These potentially toxic elements may present in dissolved form (causing toxic effects on a wide diversity of organisms) and/or particulate form (adsorbed on sediments, suspended particulate matter or colloids in transitional complexes, linked to organic matter and carbonates) (Melaku *et al*. 2007; Nollet 2007; Emeka and Weltime 2008). Industrial effluent, urban run-off, atmospheric deposition as well as upstream run-off are absorbed onto deposits and incorporated into the surface sediments (Kumar *et al*. 2011).

Sediment is the major depository of potentially toxic elements, in some cases, holding more than 99% of the total amount present in the aquatic system (Davies *et al*. 2006). Sediment constitutes the most important sink for metals and other pollutants; it can act as a point and non-point source and has the potential to release the sediment-bound metals and other pollutants to overlying waters, and in turn adversely affects aquatic environment (Soylak *et al*. 2002; Dauvalter *et al*. 2011; Krishna *et al*. 2011; Forghani *et al*. 2012; Hernandez-Crespo *et al*. 2012; Rahman *et al*. 2013; Yohannes *et al*. 2013a). Sediments are important sources of information about the long-term trends in geochemical and ecological conditions of aquatic systems and their catchment areas. Sediments are preferred monitoring tools, since contaminant concentrations are orders of magnitude higher than in water, due to long-term accumulation. Sediment contamination, have less variation in time and space, allowing more consistent assessment of spatial and temporal contamination (Krishna *et al*. 2011; Rahman *et al*. 2013; Zhao *et al*. 2013). The favorable physicochemical conditions of sediment can also remobilize and release the metals into the water column (Youssef and El-Said 2010). The monitoring of potentially toxic elements in sediment is essential, since even slight changes in their concentration levels, whether due to natural or anthropogenic factors, can result in serious environmental and subsequent health problems. Therefore, study of potentially toxic element concentrations in sediment is useful for the estimation of pollution trends (Kumar *et al*. 2011).

Potentially toxic elements are natural constituents of sediments at trace levels. They come from rocks and soils through the processes of erosion, transport and deposition. They can also be derived from anthropogenic sources (such as mining operations, industrial activity and sludge dumping), in which case they are incorporated into sediments as artificial pollutants from industrial or urban releases and wastes (Rodrigues *et al*. 2010; Krishna *et al*. 2011; Hernandez-Crespo *et al*. 2012). These increase their natural concentrations and lead to highly contaminated environments (Rodrigues *et al*. 2010). Elements in sediments may exist in different chemical forms or be bound in different ways (Rodriguez-Obeso *et al*. 2007).

Potentially toxic elements can become part of the sediment mass through precipitation (e.g., carbonates, sulfides, phosphates and hydroxyl complexes) or adsorption (e.g., clay, sediment and organic matter). In most cases, a radical change in the sediment geochemistry (falling pH and change in redox) may result in their re-suspension as ions. Beside natural sources, metals enter the watercourse through runoff and atmospheric deposition. They are adsorbed by suspended particles and settle at the bottom of water bodies and may also be adsorbed directly by the sediments of the water course. Hence, sediments characterize the degree of environmental contamination by contaminants and therefore are suitable target for pollution studies (Dauvalter *et al*. 2011).

The concentrations of potentially toxic elements will show an increase with time, because there is no mechanism to funnel out the sediments and dilute the effects of pollution. This potential increase in concentrations will pose more threats, due to their lateral and vertical movement through the sediments, thereby polluting the riverine and lake water (Rodriguez-Obeso *et al*. 2007). Lakes, unlike a typical riverine system, are static in nature (Gupta *et al*. 2013). Potentially toxic elements in sediments are able to return to the water body via a complex process involving changes in hydrodynamic conditions, bioturbation, as well as physical and chemical conditions. This process pollutes the aquatic system (Zhao *et al*. 2013).

When the distribution of potentially toxic elements in aquatic environments is examined, it is observed that the highest amount of accumulation is in the bottom sediment and the organisms that live in the sediment are seriously affected by this situation. The surface sediments are accumulation zones for contaminants, organic and inorganic materials, and also good food sources for living organisms (Mulayim *et al*. 2012). Sediment not only acts as the carrier of contaminants, but also as the potential secondary sources of contaminants in the aquatic system (Soltan *et al*. 2005).

Water quality and properties will alter with physical, chemical and biological contamination of water and these alterations in the properties of the water affect organisms living in the area (Yilmaz and Sadikoglu 2011; Sehgal *et al*. 2012). Currently, water contamination by potentially toxic elements has become a question of substantial public and scientific concern in the light of the evidence of their toxicity to humans and other biota (Abdul *et al*. 2012). Potentially toxic elements are stable and persistent contaminants of aquatic environments and enter into the aquatic environment, soil and plants through natural and anthropogenic causes (Akbulut and Akbulut 2010). Environmental exposure to these potentially toxic elements over a long period may lead to adverse effects and intensive efforts are needed to explore their levels (Sehgal *et al*. 2012). Though the level of elements in water is typically quite low, mainly because of dilution, the high frequency of consumption makes water a potentially significant source of some low-level potentially toxic elements (Miller-Ihli and Baker 2001). Even though the natural levels of potentially toxic elements are recognized, those from aquatic ecosystems have considerably increased further with increase of industrial and urban development.

2.2.2. The PAHs

The PAHs are a complex class of condensed multi-numbered benzenoid-ring organic compounds containing two or more fused aromatic rings with carbon and hydrogen atoms (Qiao *et al*. 2006; Yim *et al*. 2007; Nikolaou *et al*. 2009; Hahladakis *et al*. 2013). The number and position of the rings as well as the number, position and nature of the atoms that can be present in the molecule affect the physical and chemical properties of PAHs, their environmental behavior and their interactions with biota and human (Nikolaou *et al*. 2009). They are formed from anthropogenic (fossil fuel combustion, municipal and industrial effluents, oil spills, agricultural and urban runoff, vehicle exhausts, asphalt production and waste incineration) and natural sources (all incomplete natural combustion at high temperature and pyrolytic processes involving fossil fuels, forest fires and volcanic eruptions) (Martinez *et al*. 2004; Culotta *et al*. 2006; Li *et al*. 2006; Qiao *et al*. 2006; Liang *et al*. 2007; Yim *et al*. 2007; Orecchio and Papuzza 2009; Hahladakis *et al*. 2013). The important anthropogenic sources of PAHs are petrogenic and pyrolitic. Petrogenic PAHs are mainly derived from spillage of crude oil and its refined products, whereas pyrolytic PAHs are formed as a consequence of incomplete combustion of diesel fuel, engine oil, wood, coal, biomass of forest, grass fires, waste incinerators and fossil fuels, all of which are commonly used in industrial operation and power plants (Chahal *et al*. 2010; Mirza *et al*. 2012; Nasher *et al*. 2013).

The PAHs are ubiquitous persistent environmental contaminants and present in complex mixtures, which practically makes human and environmental exposure to PAHs to be inescapable (Qiao *et al*. 2006; Duke and Albert 2007; Orecchio *et al*. 2009). Since most of them have no practical use and are widespread in all the environmental compartments, the existent level of PAHs in a wide range of environmental samples has attracted interest from analytical chemists (Shu *et al*. 2003). Several PAHs may induce a number of adverse effects, such as, genotoxicity, carcinogenicity and reproductive toxicity (Sverdrup *et al*. 2002; Qiao *et al*. 2006).

The United States Environmental Protection Agency (US EPA) classified 16 of them as priority pollutants because of their carcinogenic and mutagenic properties (Figure 1). Some of the PAHs (in particular benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*a*]pyrene and benzo[*ghi*]perylene) are probable human carcinogens (Duke and Albert 2007; Liang *et al*. 2007; Wang *et al*. 2007; Nikolaou *et al*. 2009). Those PAHs that have not been found to be carcinogenic and mutagenic may, however, synergistically increase the carcinogenicity of other PAHs (Orecchio and Papuzza 2009; Orecchio *et al*. 2009).

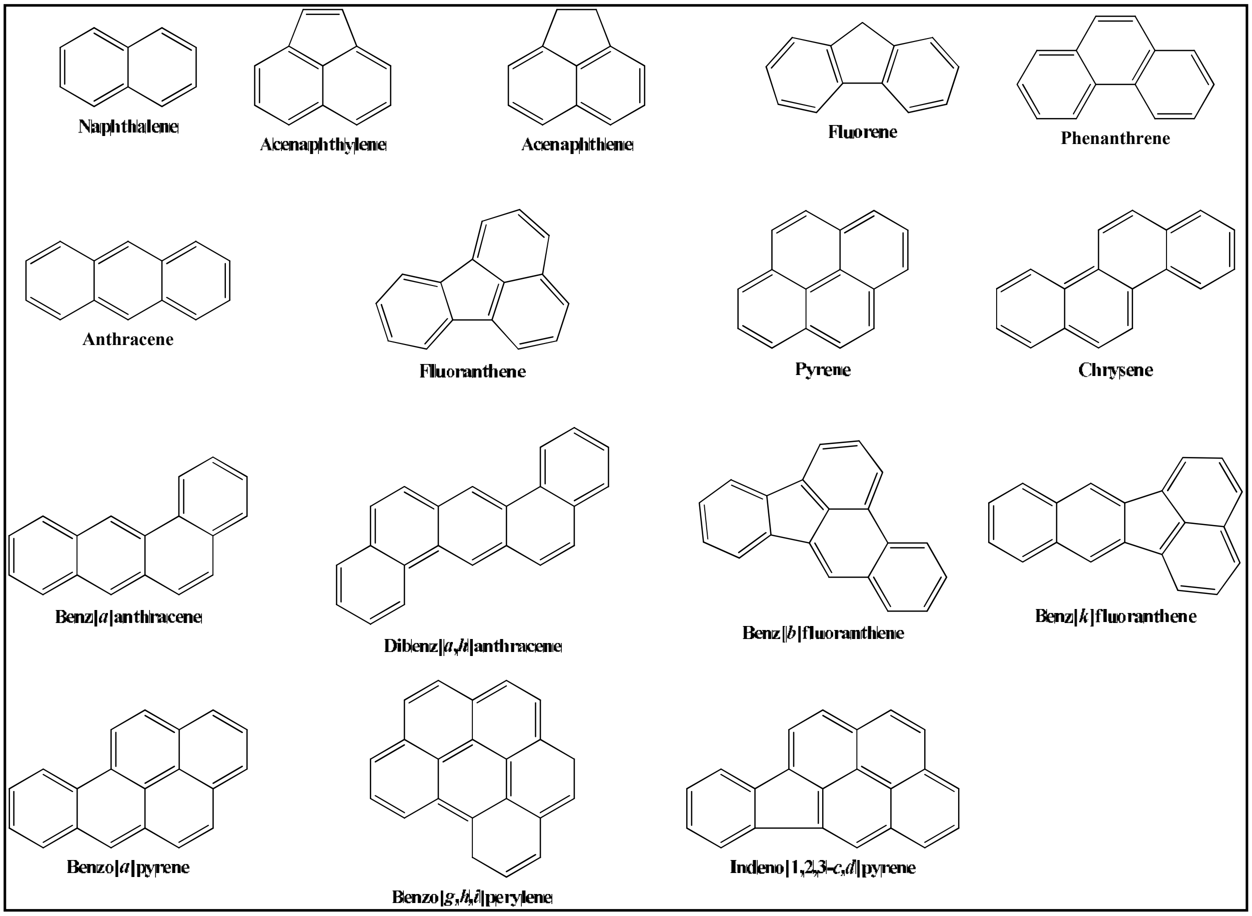

Figure 1. Chemical structures of the US EPA priority pollutant PAHs.

Sediments are usually the ultimate sinks of PAHs and other contaminants discharged into the environment, whose characteristics reflect the inputs from point and non-point sources of contaminants to those systems (Yamada *et al*. 2009; Hahladakis *et al*. 2013; Yohannes *et al*. 2013a,b). The PAHs uniqueness of high toxicity, high stability, high lipophilicity, low water solubility, electro-chemical stability and adsorption to sediments make them a potentially dangerous group of chemicals and thus the sediment become their long-term repository and a steady indicator of environmental pollution (Martinez *et al*. 2004; Villar *et al*. 2004; Duke and Albert 2007; Kumar *et al*. 2008; Nikolaou *et al*. 2009; Hahladakis *et al*. 2013). Total concentrations of PAHs in sediments vary depending on the locations and range, from a few parts-per-billion to several parts-per-million (Kumar *et al*. 2008). Once PAH-enriched particles accumulate in sediments, they may undergo a number of changes caused by chemical, biological and physical activities. As a result, the bound PAHs can be remobilized from the sediment into the water phase and tend to bioaccumulate in aquatic organisms.

2.3. Microwave-Assisted Acid Digestion for Potentially Toxic Elements

For the determination of potentially toxic elements in various matrices, sample preparation is the crucial step. Some of the techniques require direct insertion of solid samples into the analytical instrument, while other techniques require sample digestion prior to analysis. Conventional digestion procedures, such as wet digestion and dry ashing, are frequently the most time consuming stage of the analysis. These methods are labor intensive and tedious, and very often have a high contamination potential (Nemati *et al*. 2010).

Microwave digestion is one of the most powerful methods, since it is less likely to result in sample contamination. In addition, the technique minimizes losses of volatile analytes, requires only small amounts of acids and shortens digestion times substantially, relative to traditional methods. The digestion efficiency depends largely on factors such as the heating method, working pressure, and nature and volume of the acids used to dissolve the sample matrices (Bakkali *et al*. 2009).

In addition to avoiding problems observed in the conventional procedures of digestion, such as incomplete decomposition, risks of contamination, long and exhausting stages of decomposition, microwave digestion in closed vessels prevents losses by volatilization (Sandroni and Smith 2002; Sandroni *et al*. 2003; Esen and Balci 2008; Junior *et al*. 2014). Microwave digestion also tends to yield more controlled and reproducible results than conventional methods. The fact that closed vessels are utilized enables higher temperatures to be reached through increased pressure, which is extremely beneficial for the digestion of samples with refractory matrices, such as sediments, since major components of the sediments are clays, carbonaceous minerals, oxides, and organic matter (Sandroni and Smith 2002; Sandroni *et al.* 2003; Junior *et al.* 2014).

A large number of different acid mixtures have been used for microwave acid digestion such as HNO_3, HNO_3/HCl, HNO_3/HF, $HClO_4/HNO_3$, HNO_3/H_2SO_4, $HF/HNO_3/HCl$ and $HNO_3/HClO_4/HF$ (Bettinelli *et al.* 2000; Sandroni and Smith 2002; Sandroni *et al.* 2003; Soltan *et al.* 2005; Gaudino *et al.* 2007; Esen and Balci 2008; Huang *et al.* 2009; Nigussie *et al.* 2010; Dauvalter *et al.* 2011; Sardans *et al.* 2011; Forghani *et al.* 2012; Mulayim *et al.* 2012; Tsakovski *et al.* 2012; Rahman *et al.* 2013; Zhao *et al.* 2013; Junior *et al.* 2014). In most cases, complete digestion of sample is required to achieve reproducible and accurate results.

Aqua regia digestion with HF and H_3BO_3 is commonly used (Bettinelli *et al.* 2000; Junior *et al.* 2014). The addition of HF strongly influences analyte recoveries in microwave acid digestion, since it breaks down silicates and minerals better than $HClO_4/HNO_3$ and HNO_3/HCl acid combinations. However, HF can damage glassware and of the ICP-MS or ICP-OES torch. This problem can be avoided by using a combination of HF and saturated H_3BO_3 solution, to remove any excess of HF and for dilution of samples prior to analysis (Wilson *et al.* 2006; Hansen *et al.* 2009; Nemati *et al.* 2010; Marin *et al.* 2011; Muller *et al.* 2013).

For plant samples, a combination of HNO_3/H_2O_2 is needed when the sample material is difficult to decompose, since H_2O_2 is considered valuable for digesting food samples high in carbohydrates and/or fats (Itanna 2002; Bakkali *et al*. 2009; Marin *et al*. 2011; Zuluaga *et al*. 2011; Muller *et al*. 2013).

2.4. Microwave-Assisted Extraction for PAHs

The analytical procedure for PAH analysis usually involves sampling, sample preparation (extraction into solution), identification and quantification techniques. The extraction of PAHs from sediments can be achieved with a number of established methods. Traditionally the extraction of PAHs from sediment is carried out by means of Soxhlet extraction, soaking, maceration, water percolation and mechanical shaking. Some of these techniques require a very long extraction time, consume large amounts of organic solvent, are laborious and can degrade thermally labile compounds (Dean and Xiong 2000; Shu *et al*. 2003; Villar *et al*. 2004; Alvarez-Aviles *et al*. 2007; Wang *et al*. 2007; Chan *et al*. 2011).

Currently, advanced extraction techniques, such as supercritical fluid extraction (SFE), accelerated solvent extraction (ASE) and microwave-assisted extraction (MAE) have been established in order to reduce the volume of extraction solvents and extraction times and improve the precision of analytes recoveries (Dean and Xiong 2000; Shu *et al*. 2000; Shu *et al*. 2003; Villar *et al*. 2004; Alvarez-Aviles *et al*. 2007; Wang *et al*. 2007; Nikolaou *et al*. 2009; Chan *et al*. 2011). The MAE utilizes microwave energy, which is a non-ionizing radiation that causes molecular motion by migration of ions and rotation of dipoles. However, it does not induce changes in molecular structure, when heating the solvent and sample for extracting pollutants (Sanchez-Prado *et al*. 2010). Microwave digestion is gaining an important role in sample preparation techniques because it offers greatly reduced usage of organic solvents, reduced extraction times, reduced size of extraction apparatus and allows the simultaneous extraction of multiple samples (Dean and Xiong 2000; Villar *et al*. 2004; Wang *et al*. 2007; Chan *et al*. 2011).

2.5. Analytical Methodologies for Potentially Toxic Element Analysis

The conventional analytical methodologies used for the identification and determination of potentially toxic elements in water, sediment and plants consist of four basic steps: collection of the samples, sample transport and preparation in the analytical laboratory, sample dissolution and finally, analysis by an appropriate technique. The low levels at which potentially toxic element are present and the thin line (small difference which makes hard to distinguish them) between acceptable and dangerous concentrations needs more sensitive and selective methods of analysis. There is an urgent need for rapid and precise determination of the concentrations of contaminants, in particular those of potentially toxic elements in both solid and liquid samples.

Various analytical techniques are available to quantify potentially toxic elements present at trace levels. These techniques include F-AAS, GF-AAS, LIBS, XRF, electrochemical analysis, neutron activation analysis (NAA), ICP-OES and ICP-MS (Bettinelli *et al*. 2000; Beck *et al*. 2002; Sandroni and Smith 2002; Sandroni *et al*. 2003; Becker 2005; Melaku *et al*. 2005a; Soltan *et al*. 2005; Gaudino *et al*. 2007; Nollet 2007; Rodriguez-Obeso *et al*. 2007; Bakkali *et al*. 2009; Chen *et al*. 2009; Hansen *et al*. 2009; Huang *et al*. 2009; Tsakovski *et al*. 2009; Faraji *et al*. 2010; Lepri *et al*. 2010; Nigussie *et al*. 2010; Marin *et al*. 2011; Sardans *et al*. 2011; Zuluaga *et al*. 2011; Forghani *et al*. 2012; Hicsonmez *et al*. 2012; Mihaylova *et al*. 2012; Mulayim *et al*. 2012; Tsakovski *et al*. 2012; Gupta *et al*. 2013; Mekonnen *et al*. 2013; Muller *et al*. 2013; Rahman *et al*. 2013; Yohannes *et al*. 2013a,b; Junior *et al*. 2014).

In the following sections, LIBS, F-AAS, ICP-OES, ICP-MS and the elemental mercury analyzer will be discussed in relation to their application to potentially toxic element analysis in various matrices.

2.5.1. Laser-induced breakdown spectrometry

Laser-induced breakdown spectrometry is an atomic emission technique that is useful for the analysis of various samples of environmental and geological interest. It can be regarded as a universal sampling, atomization, excitation and ionization source, since laser-induced plasmas can be formed in gases, liquids, aerosols, slurries, conducting and non-conducting solid samples (Le Drogoff *et al*. 2001; Miziolek *et al*. 2006; Gondal *et al*. 2007a,b; Mohamed 2008; Gondal *et al*. 2009a).

The stimulus for LIBS is a solid-state, short-pulsed, Nd:YAG laser that is focused on a sample to produce a high-temperature plasma, high electron density laser spark or micro-plasma. Upon cooling, the excited atomic, ionic and molecular fragments produced within the plasma emit narrow radiation, characteristic to the emitting species over a broad spectral range, from ultraviolet through visible to the near infrared. This reflects the elemental composition of the material in the volatilized sample that can be gated off by the detection system (Lal *et al*. 2004; Gondal *et al*. 2006; Miziolek *et al*. 2006; Bakry 2007; Gondal *et al*. 2009a,b). In this technique, powerful laser pulses evaporate a small amount of material (typically a few micrograms) during analysis, thereby creating a plasma plume. The emission from the plasma is spectrally resolved to determine the chemical composition of the sample.

A range of processes such as sample heating, phase change, melting, atomization, excitation, ionization and thermo-ionic emission occurs in LIBS (Miziolek *et al*. 2006; Gondal *et al*. 2007a,b; Gondal *et al*. 2009a; Gondal *et al*. 2011). The technique has been proven capable of detecting many metals of environmental concern (Gondal *et al*. 2009b). The principle of LIBS is similar to that of conventional plasma-optical emission spectrometry, in which the light from an excited sample is spectrally resolved and may be temporally resolved to yield qualitative and quantitative information about elemental constituents. What distinguishes the LIBS technique from conventional plasma-OES is that the sample need not be transported to the plasma source; rather, the plasma is formed within the sample or on the surface of the sample in-situ (Song *et al*. 1997).

The LIBS appears to have significant potential in remote sensing, can be used in a hostile environment, and allows direct use with minimal sample preparation in different phases. It is an inherent multi-element technique (Sneddon and Lee 1997). In principle, LIBS may be used to extract qualitative and quantitative elemental analysis information of any material, irrespective of its physical state. One of the principal advantages of this technique is its independence of the laser source wavelength, since the plasma formation process is mainly related to the high energy of the laser pulse. The major advantages of the LIBS method include: short analysis time (seconds), low analysis cost per sample, high precision sufficient for screening many elements of interest, high sensitivity and possibility of *in-situ* detection from remotely-located samples, versatility in sampling and direct analysis of extremely hard materials that are difficult to solubilize. As only a minute quantity of material is required for the analysis, LIBS is essentially a non-destructive technique (Borgia *et al*. 2000; Wainner *et al*. 2001; Whitehouse *et al*. 2001; Harmon *et al*. 2005; Barnett *et al*. 2008; Gondal *et al*. 2008; Burakov *et al*. 2009; Gondal *et al*.

2009a,b). In addition, LIBS can be used for the analysis of certain elements outside the capability of other current field portable techniques (such as XRF) (Gondal *et al*. 2006; Pace *et al*. 2006; Gondal and Hussain 2007; Rai *et al*. 2007; Santos *et al*. 2009).

The principal advantages of LIBS over spectrochemical techniques, such as ICP-OES, ICP-MS, and GF-AAS, are those of speed and simplicity as well as that the required sample size, analysis time and required sample manipulation are minimal. These advantages are particularly valuable in the analysis of chemically and radiologically hazardous samples. Sample pretreatment procedures for solid analysis (digestion/dissolution) can be time-consuming, tedious, contamination-prone, costly, and frequently generate undesirable and toxic amounts of chemical waste. It has unique significant advantages, which can be adapted especially in direct elemental analysis of environmental samples for field application using portable system (Song *et al*. 1997; Tran *et al*. 2000; Capitelli *et al*. 2002; Lee *et al*. 2004).

Furthermore, LIBS allows non-contact (remote) chemical analysis, without significant requirements for sample preparation. This is especially promising for the analysis of potentially toxic elements in soils and sediments, because no chemical dissolution of sample material is required, which in turn is the case for conventional techniques (Hilbk-Kortenbruck *et al*. 2001). However, LIBS has some limitations in analytical performance characteristics, such as poor LOD, precision, accuracy, etc., and matrix effects can be significant. Moreover, LIBS spectra have relatively high background signals (Arnold 1995; Scaffidi *et al*. 2003; Burakov *et al*. 2009). A major disadvantage of LIBS at present is the more complex (and increased cost) instrumentation to accurately take advantage of the transient plasma, in addition to the lack of suitable standards. These disadvantages render the technique semi-quantitative at this point in time (Sneddon and Lee 1997).

The key factors, which affect the sensitivity of the LIBS system include the laser pulse characteristics (pulse width, energy, etc.), the sample homogeneity and the sampling geometry (distance from the focusing lens to the sample, focal length of the collecting lens, fiber optics, etc.), surrounding atmosphere and the binding material used for the pellet preparation of samples in powder forms (Le Drogoff *et al*. 2001; Bakry 2007; Gondal and Hussain 2007; Gondal *et al*. 2007a,b). In employing LIBS, enough time should be allowed for the plasma to attain equilibrium conditions. The self-absorption effects, due to possible saturation of the signal for high concentration elements, need to be avoided. In analyzing complex and inhomogeneous specimens, possible onset of matrix effects, resulting from complex physical-chemical phenomena involved in the processes of ablation and plasma formation may occur, and therefore appropriate measures should be applied (Gaudiuso 2010).

Direct solid analysis of environmental samples such as sediment by LIBS was selected as an alternative technique to be evaluated for the determination of potentially toxic elements in sediment, since the technique is rapid, requires none or little sample preparation (except homogenization and pellet preparation), and has portable and stand-off detection (Lal *et al*. 2004; Liu and Zhang 2008; Gondal *et al*. 2011). The technique has been employed for the characterization of potentially toxic elements in sediment marine samples such as Cr, Cu, Mn, Fe and Ba (Lazic *et al*. 2001, Barbini *et al*. (2002), Lazic *et al*. (2007)). Further, Mohamed *et al*. (2007), Capitelli *et al*. (2002), Santos *et al*. (2009) and Senesi *et al*. (2009) determined potentially toxic elements (V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Pb and Cd) in soil and sediment using LIBS.

2.5.2. Flame-atomic absorption spectrometry

The F-AAS is one of the most extensively used techniques for determination of metals in different sample matrices. Generally F-AAS is used when concentration of the analyte is high enough, *i.e.* in the ppm range. A specific hollow cathode lamp is required for the determination of each element (Rao and Talluri 2007).

Due to its relatively low cost and good analytical performance, F-AAS has been widely used for the determination of various metals. The conventional way to conduct such determinations involves a mineralization stage for obtaining the sample into a solution, suitable for introduction into the flame nebulizer. The flame is used for the destruction and consequent elimination of the organic matter, which otherwise could cause spectral interferences and may accumulate residues in the burner head and spray chamber (Ioannidou *et al*. 2005; Chen *et al*. 2009).

The F-AAS works by introducing the sample into a flame where it is dissociated into its constituent atoms. Electromagnetic radiation in the ultraviolet-visible region is directed through the flame and is partially absorbed in a manner characteristic of the atoms present. Generally, the technique requires a liquid sample (introduced by nebulizer and spray chamber) to be aspirated, aerosolized and mixed with combustible gases, such as acetylene and air or acetylene and nitrous oxide. The mixture is ignited in a flame with a temperature ranging from 2100 to 2800 °C. During combustion, atoms of the element of interest in the sample are reduced to free, unexcited ground state atoms, which absorb light at characteristic wavelengths. To provide element specific wavelengths, a light beam from a lamp (hollow cathode lamp or electrodeless discharge lamp) of which cathode consists of the element being determined, is passed through the flame. A device such as photo-multiplier tube or solid-state detector detects the amount of reduction of the light intensity due to absorption by the analyte, and this can be directly related to the amount of the element in the sample (Levinson 2001; Dean 2003; Otles 2009).

The F-AAS is relatively inexpensive and simple to operate. It encounters relatively little interference. Nonetheless, some refractory elements may not be determined with good sensitivity, since flame temperatures are often not hot enough to induce complete atomization. It can be used for the analysis of liquid, gas and solid samples. However, when simultaneous determination of elements is required other techniques may be preferred, since in FAAS commonly single elements or a few elements are to be determined at the same time (Brown and Milton 2005; Melaku *et al*. 2005a,b; Chen *et al*. 2007; Lepri *et al*. 2010).

2.5.3. Elemental mercury analyzer

Many of the techniques that exist for mercury determination involve an intermediate stage for mercury pre-concentration in absorption traps. The methods have the limitations that the mercury pre-concentration process is fairly lengthy (from several to tens of minutes); because of the slow pumping rate (Sholupov *et al*. 2004). Generally, the techniques are prone to analyte loss and/or contamination (Grobecker and Detcheva 2006). One of the fastest spectrometric methods for low-cost mercury determination is using a Zeeman atomic absorption spectrometer. In this technique, the risk of contamination and analyte loss is minimized, since addition of chemical modifiers and chemical sample preparations are not required. In addition, fast analysis and superior a LOD over conventional techniques are obtained (Beaulieu *et al*. 2008).

The working principle of the instrument is as follows: mercury, present in various chemical forms, is sublimated and atomized in a two-stage pyrolysis reactor. The first and second chambers of the atomizer are heated independently up to 800 °C. A weighed sample is placed in the atomizer using a special container (sample boat). After inserting the sample boat containing the sample into the atomizer, the less volatile mercury compounds dissociates when heated, whereas more readily volatile species, for example organic mercury compounds, may leave the first chamber unchanged. In addition, the organic materials of the matrix may produce much smoke and other compounds which can give rise to strong background absorption in the analytical cell. All the products are transported from the first chamber to a second one by a carrier gas (ambient air). In the second chamber, all of the mercury compounds are totally dissociated, and the organic matrix of the sample is burnt out, mainly producing CO_2 and H_2O. A metal catalyst improves the efficiency of oxidation and dissociation in the second chamber. Mercury vapor and the remaining smoke are transferred into a multi-path analytical cell and the mercury atoms are detected by a photodetector (RA-915+ analyzer - elemental mercury analyzer). The mercury content in the sample is determined from the integrated analytical signal with due account of the preset calibration coefficient (Sholupov *et al*. 2004; Grobecker and Detcheva 2006; Beaulieu *et al*. 2008; Witt *et al*. 2008).

2.5.4. Inductively coupled plasma-optical emission spectrometry

The instrumental analysis following digestion procedures has lately evolved from mono-elemental spectroscopic techniques (F-AAS and GF-AAS) to multi-elemental ones (ICP-OES and ICP-MS) which allow the simultaneous analysis of a large number of analytes in a reasonably short time and achieve wider sample characterization. The successful use of this technique depends on various factors such as a good LOD, linearity of calibration curves, compatibility with different acid mixtures for sample dissolution and low sensitivity to matrix effects. Various studies have been issued on the use of ICP-OES for the determination of potentially toxic elements in soils and sediments (Bettinelli *et al*. 2000).

The ICP-OES has several advantages, compared with atomic absorption techniques: more complete atomization, the plasma is practically free of background radiation, it is a multi-element technique that combines qualities such as relatively low LOD, rapid analysis and wide linear range, while interferences from ionization of self-absorption are irrelevant (Sapkota *et al*. 2005; Hill 2007; Hicsonmez *et al*. 2009; Bhat *et al*. 2010; Larrea-Marin *et al*. 2010; Qing-hua *et al*. 2012; Zhu *et al*. 2012; Li *et al*. 2013; Muller *et al*. 2013). The selectivity of ICP-OES in analytical spectrometry makes it suitable for elemental analysis in a variety of different matrixes for simultaneous elemental determination over a wide concentration range for about 75 elements in the periodic table (Bettinelli *et al*. 2000; Carrilho *et al*. 2002; Sandroni and Smith 2002; Bhat *et al*. 2010).

For ICP-OES systems, various excitation sources have been used to produce the excited atoms that emit the light used for element measurement. In general, the sample aerosol is desolvated in the plasma, then vaporized and dissociated, followed by excitation of the atoms or ions present in the sample. The element is identified by the specific wavelength emitted and the concentration of the element present is determined by the intensity of the peak. Generation of the plasma is achieved by igniting argon gas in an intense electromagnetic field, causing collisions between neutral argon gas and charged particles. This results in high temperature plasma with temperatures approaching 10,000 °C (Ohlsson 2012; Li *et al*. 2013).

In ICP-OES, the signal is strongly dependent on the sample matrix, nebulization and atomization conditions. Thus, it is important to optimize instrumental variables such as RF power, sample uptake flow rate and nebulizer argon gas flow rate, since the emission intensities are mostly affected by these three variables (Momen *et al*. 2008). In ICP-OES, the light emitted by the excited atoms and ions in the plasma is measured to obtain information about the sample. Because the excited species in the plasma emit light at several different wavelengths, the emission from the plasma is polychromatic. The polychromatic radiation must be separated into individual wavelengths so the emission from each excited species can be identified and its intensity can be measured without interference from emission at other wavelengths. The separation of light according to wavelength is generally done using a monochromator, which is used to measure light at one wavelength at a time, or a polychromator, which can be used to measure light at several different wavelengths at once. The actual detection of the light, once it has been separated from other wavelengths, is done using a photosensitive detector (Hill 2007).

2.5.5. Inductively coupled plasma-mass spectrometry

The ICP-MS is undoubtedly the fastest growing trace element analysis technique available today. Since its commercialization in 1983, ICP-MS has contributed a diverse range of application areas including environmental, geochemical, semiconductor, clinical, nuclear, chemical and metallurgical (Erdogan 2009). At present, ICP-MS is one of the most frequently used atomic spectrometric technique for fast, robust, sensitive and simultaneous multi-element determination at the trace concentration levels for a wide variety of liquid samples in different matrices (Duane and Facchetti 1995; Mannio *et al*. 1995; Bettinelli *et al*. 2000; Falandysz *et al*. 2001; Becker 2002;2005; Ioannidou *et al*. 2005; Melaku *et al*. 2005a,b; Chen *et al*. 2007; Rahmi *et al*. 2007;

Rao and Talluri 2007; Gondal *et al*. 2008; Bienfang *et al*. 2009; Chen *et al*. 2009; D'Ilio *et al*. 2011). In addition, ICP-MS possesses the unique capability of measuring precise and accurate isotope ratios, which is applied in the determination of element concentrations by the isotope-dilution (ID) technique (ID-ICP-MS). However, in addition to the expensiveness of the method, ICP-MS still suffers from several atomic and molecular isobaric interferences, but these can mostly be overcome by careful use of collision-cell (CC) or reaction-cell (RC) technology or high-resolution mass spectrometers (HR-MS) that resolve elements and interferences, which would have previously been co-detected (Brown and Milton 2005).

The ICP-MS ionizes the sample using the same type of intense argon plasma used for ICP-OES, but then detects the various elemental species using conventional MS techniques. A quadrupole, magnetic sector or time-of-flight can serve as the mass filter. The plasma is usually produced in argon at atmospheric pressure, sustained by a high frequency energy field. The temperature in the plasma is suitable for atom excitation and ionization of elemental species. The instrument is fitted with a quartz torch, consisting of three concentric tubes into which different argon flows are introduced (Becker 2002; Rao and Talluri 2007). Here the liquid solution is effectively nebulized and the fine aerosol formed is transported with argon into the ICP torch, where after the chemical compounds (and the water matrix) are evaporated, the molecules are dissociated into their atomic constituents and the neutrals are excited and ionized. The resulting ions are extracted from the argon plasma via an interface between the sampler and the skimmer cones (a series of apertures) into the high vacuum mass analyzer, where the isotopic ions are separated according to their mass-to-charge ratio. Detection of the separated ion beams is achieved by a discrete dynode electron multiplier. The intensity of a specific peak in the mass spectrum is proportional to the amount of the elemental isotope from the original sample (Becker 2005; Hill 2007).

2.6. Analytical Methodologies for PAHs Analysis

The PAHs are commonly determined by capillary gas chromatography with flame ionization detection (in GC-FID) or mass spectrometric detection (in GC-MS) or by high-performance liquid chromatography (HPLC) with ultraviolet (UV) and/or fluorescence (FL) detection (Martinez *et al*. 2004; Denis *et al*. 2012). The use of GC-MS for the determination of PAHs is based on a favorable combination of greater selectivity, resolution and sensitivity (Alvarez-Aviles *et al*. 2007; Yamada *et al*. 2009; Denis *et al*. 2012). However, due to the complex nature of the sediments, prior to introduction into the analytical system, a sample preparation (extraction and cleanup) process is needed to transfer the analytes of interest from their original surroundings into a form suitable for analysis (Shu *et al*. 2000; Alvarez-Aviles *et al*. 2007; Yamada *et al*. 2009). Sample extraction is a critical step in PAHs analysis because these compounds are strongly sorbed to the matrix; consequently, their extraction is time-consuming and in many cases causes quantification errors (Yamada *et al*. 2009).

The GC-MS utilizes a compound's intrinsic affinity for a stationary phase and facilitates the separation of complex sample matrices into their component parts. Essentially, a sample is injected into a hot inlet, which volatilizes the components in the sample. Next, an inert gas carries the volatile compounds through a column. The retention time, which is inherently related to a compound's affinity to the stationary phase, can be used to identify the analyte in question when compared to a reference standard. In addition, detection methods, such as mass detection can provide a secondary means of identification. After separation of the sample matrix, the components are introduced to a mass detector. The mass spectrometry detection is used to identify the various components from their mass spectra. Each compound has a unique or near unique mass spectrum that can be compared with a mass spectral database and thus identified. Through use of reference standards, verification and quantitation are also possible (http://www.chemir.com/gas-chromatography-mass-spectrometry.html accessed on February 2014).

CHAPTER THREE

EXPERIMENTAL

3.1. Introduction

In this chapter, the description of -the study areas, sample collection and preservation, list of reagents stating their purities, list of reference materials, chemicals and standards, sample preparation for the various analytical methodologies, preparation of working standards, quality assurance, identification and quantification of analyte of interest, and statistical packages used in data analysis are given. In addition, the equipment and instrumentation used for sample collection, preparation and quantification of potentially toxic elements and PAHs are described in brief.

3.2. Description of the Study Areas

3.2.1. Akaki River

Addis Ababa (AA), the capital city of Ethiopia, has a fast population growth, uncontrolled urbanization and industrialization, poor sanitation, uncontrolled waste disposal, etc. which causes a serious quality deprivation of surface and groundwater in particular. Two major rivers flow through the city, namely the Tinishu Akaki River (TAR - through the western part of the city) and the Tiliku Akaki River (TlAR - through the eastern part of the city). These rivers, which are tributaries of the Awash River, originate from the Entoto Mountains that are located north of AA and join at the Aba Samuel reservoir (43 km to the south). Many tributaries join the rivers at different localities. Some of these include the Bulbula, Burayu, Gefersa, Gerbaja, Jaja, Kebena, Kera, Kidanemihret, Lafto, Likuanda, Mekannisa, Melkaqurani, Weira, Werenchiti, Zennebework rivers. The rivers are the convergence points of all streams crossing the city from different directions. Local people use water from the rivers for irrigation, drinking, cooking, washing, waste disposal, and other domestic needs (Figure 2) (Fitamo *et al*. 2007; Melaku *et al*. 2007). They serve as a pollutant sink since they carry domestic wastes, rain runoff waters, and untreated industrial discharges of various types, hence making them known for their offensive odor (Xu and Usher 2006; Prabu 2009).

Figure 2. Activities in and around Akaki River (irrigation, solid waste disposal, cattle watering, motor pumps for irrigation, domestic use washing, factory effluents disposal, factory effluent disposal on river, pesticide usage in irrigation on a farm nearby the river).

The most widespread waste disposal mechanisms in the city may be categorized as improper and include defective septic tanks, open dumps, surface impoundments from domestic wastes, street sweepings, commercial wastes and industrial waste (Alemayehu 2001). The common contaminants from the industries include solids, oils, detergents, solvents, pesticides, and inorganics such as nitrates, phosphates, sulfates, chlorides, potentially toxic elements, acids, alkalis and others (Itanna 1998a,b; Melaku *et al*. 2005a,b; Xu and Usher 2006; Gebre and Rooijen 2009; Prabu 2009; Weldesilassie 2010). These, together with waste from hospitals and hotels, which are directly or indirectly dumped in the rivers, change the chemical and physical properties of the water (Alemayehu 2001).

3.2.2. Lake Awassa

Ethiopia has 11 fresh lakes, 9 saline lakes, 4 crater lakes and over 12 major swamps or wetlands. The majority of the lakes are found in the Rift Valley Basin. The Ethiopian Rift Valley lakes are the northernmost of the African Rift Valley lakes. The rift valley splits the Ethiopian highlands into northern and southern halves, and the lakes occupy the floor of the rift valley between the two highlands. The Ethiopian Rift Valley region encompasses seven lakes, namely Lake Abaya (1162 km^2, elevation 1285 m), Lake Chamo (551 km^2, elevation 1235 m), Lake Ziway (485 km^2, elevation 1636 m), Lake Shala (329 km^2, elevation 1558 m), Lake Langano (230 km^2, elevation 1585 m), Lake Abijata (205 km^2, elevation 1573 m) and Lake Awasa (129 km^2, elevation 1708 m) (Awulachew *et al*. 2007). It is an important area for agricultural, commercial and industrial development of Ethiopia, besides acting as center for tourists. The area is densely populated with various agro-industry enterprises and mechanized irrigation farms, and one of the most environmentally threatened areas in Ethiopia (Hengsdijk *et al*. 2009).

Lake Awassa lies to the west of fast-growing Hawassa town, the capital of the Southern Nations, Nationalities, and Peoples (SNNP), and about 275 km south of Addis Ababa. Lake Awassa is located $6^{o}33'$ – $7^{o}33'$N and $30^{o}22'$ – $38^{o}29'$E. The lake is fed by few ephemeral streams on the north-west and western side of the catchment and the Tikurwuha River which, is the only perennial river, enters Lake Awassa draining the Cheleleka (Shallo) swamp on the north-east side (Desta *et al*. 2007). Lake Awassa is endhoric with no surface water outflow or with no outlets from the lake, but water may seep away through the underlying volcanic ash and pumice. Lake Awassa is the smallest (in size) and the highest (in altitude) of the major main Ethiopian Rift Valley lakes with a maximum depth of about 21 m.

Lake Awassa is a freshwater lake inhabited by a rich diversity of birds and fish (Nigussie *et al*. 2010). The lake supplies the town with all its water and supports a thriving local fishery (Nigussie *et al*. 2010) (Figure 3).

Figure 3. Activities in and around Lake Awassa and Lake Ziway (hippopotamuses, birds, fishing (both using fishing net and stick picking), cloth washing, house hold usage, recreation, and cattle watering).

It is highly likely that more domestic and industrial wastes (like waste from the Awassa Textile Factory), solid and liquid wastes generated by different sectors, various agrochemicals in small- and large-scale farming (such as the center for the preparation and expansion of selected seeds) and sewer lines (which end up in the lake) will find their way directly or indirectly into the lake. This would, elevate the levels of potentially toxic elements and other contaminants in the lake system, in addition to those emanating from natural sources (Gebre-Mariam and Desta 2002; Ataro *et al*. 2003; Kebede and Wondimu 2004; Awulachew *et al*. 2007; Nigussie *et al*. 2010; Mekonnen *et al*. 2012a,b).

3.2.3. Lake Ziway

Lake Ziway is the largest and shallowest lake in the Central Main Ethiopian Rift Valley. It is located about 97 km south of Addis Ababa, on the border between the Regions of Oromia and the SNNP. Lake Ziway is located 7°52′ – 8°40′N and 38°40′ – 38°56′E. The fast grown town of Ziway lies on the lake's western shore. It is 31 km long and 20 km wide. It has a maximum depth of 9 m and a mean depth of 2.5 m (Gebre-Mariam and Pearce 2003). Lake Ziway is fed by the two major rivers, Meki and Katar, which drain from Northwestern and Southwestern plateaus, respectively. The lake, in turn, drains toward Lake Abiyata via Bulbula River and is being used for irrigation purposes (Vallet-Coulomb *et al*. 2001; Ataro *et al*. 2003; Kebede and Wondimu 2004; Awulachew *et al*. 2007; Nigussie *et al*. 2010; Mekonnen *et al*. 2012a,b).

It is most likely that more domestic wastes and various agrochemicals from small- and large-scale farming will find their way directly or indirectly into Lake Ziway, elevating the levels of potentially toxic elements and other contaminants in the lake system, in addition to contaminants from natural sources (Ataro *et al*. 2003; Kebede and Wondimu 2004; Nigussie *et al*. 2010). Lake Ziway is surrounded by lands that are under continuous cultivation throughout the year and modern farming practices take place around the lake (Kitata and Chandravanshi 2012). Recently, there has been increased attention for buffer zone along Lake Ziway to combat water level reductions, increase fish yields and improve water quality. However, a number of private enterprises (such as floriculture, horticulture, vegetables and fruits, seed cleaning for export) have been established and have been under development over the last few years (Hengsdijk *et al*. 2009). The lake is known for its population of birds and hippopotamuses and supports a fishing industry (Figure 3).

3.3. Reagents, Chemicals and Standards

All the reagents were of analytical grade and the water used was doubly deionized water using a Millipore purification system (18.2 MΩ/cm) (Millipore, France) for all dilutions. A 65% HNO_3 (Suprapur®, Merck, Germany) was used for cleaning glassware and for preservation of water samples. All the glassware and polyethylene bottles were washed with detergent, rinsed with doubly deionized water and soaked in 10% HNO_3 (v/v) for 24 h. The glassware was rinsed again three times with doubly deionized water and finally dried in oven.

For preparation of the calibration standards, stock solutions of 1000 mg/L single element metal standard solutions of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Ag, Cd, Sn, Hg, Pb, Ga, In and Tl (Spectrascan Teknolab AB, Sweden) were used for ICP-OES and ICP-MS. A 10 µg/L SMART tune solution for mass calibration containing Ba, Be, Ce, Co, In, Mg, Pb, Rh and U was obtained from PerkinElmer (Concord, Ontario, Canada) and used for mass calibration. Argon (99.998% purity) and helium (99.999%, purity) were supplied by Afrox Boc gases (Afrox, South Africa). For construction of calibration curves for F-AAS analysis, 1000 mg/L of standard stock solutions of Cr, Mn and Fe (Spectra AA – 20 plus, Varian Mulgrave Victoria, Australia) were used after appropriate dilution.

The accuracy and precision of the method were evaluated using Channel Sediment CRM BCR®-320R No. 58 (IRMM, Belgium), Apple Leaves Standard Reference Material 1515 (NIST, USA), Standard Reference Material® 1643e (NIST, USA), Standard Reference Material of New York-New Jersey Waterway Sediment, SRM 1944 (NIST, USA), Standard Reference Material® 2587 Trace Elements in Soil containing Lead from Paint (NIST, USA), San Jaoquin Soil Standard Reference Material® 2709a (NIST, USA), Light Sandy Soil – Trace Elements CRM 7002

(Analytika Co. Ltd, Czech Republic), Buffalo River Sediment Reference Material 8704 (NIST, USA), NCS DC 73322 Soil (China National Analysis Center for Iron and Steel, China) CRM Stream Sediment NCS DC 73348 (China National Analysis Center for Iron and Steel, China), NCS DC 73374 Stream Sediment (China National Analysis Center for Iron and Steel, China) and CRM of Tibetan soil, NCS DC 78302 (China) were used. The soil and sediment CRMs were also used for construction of calibration curves for LIBS and elemental mercury analyzer.

The following chemicals were used for digestion of sediment and plant samples: H_3BO_3 (pro analysi, Merck KGaA, Germany), 32% HCl (AAR grade, SMM Instruments, South Africa), 37% HCl (Puriss, Sigma-Aldrich, Germany), 40% HF (AAR grade, SMM Instruments, South Africa), 50% H_2O_2 (Sigma-Aldrich, USA), 65% HNO_3 (Suprapur, Merck, Germany), 69.5% HNO_3 (Scharlau, reagent grade, Spain). The Cr, Mn and Fe metal powders with high purity (99.99%) (Alfa Aesar$^{®}$ A Johnson Matthey Company, USA) were used to identify emission lines of the analytes for LIBS.

A 99.8% acetone and 95% *n*-hexane (HPLC grade, LAB-SCAN Analytical Sciences, Poland) were used as extracting solvents. The Cu metal powder (used for desulfurization of solution prior to determination of PAHS) was obtained from UNILAB (Philip Harris, UK) and activated using 99.9% methanol (HPLC grade, LAB-SCAN Analytical Sciences, Poland), dichloromethane and diethyl ether (AAR grade, SMM Instruments, South Africa). Anhydrous Na_2SO_4 (analyzed reagent > 99.0% UNIVAR) was obtained from Merck Chemicals (Pty) Ltd, Germany. The PAHs kit containing 16 priority pollutants (Supelco Inc., USA) was used for preparation of series of standards for the construction of the external calibration curves for PAHs analysis.

3.4. Instrumentation

A Microwave Accelerated Reaction System, MARS 5 (MARS®, CEM Corporation, Matthews, USA), equipped with Easy Prep™ high pressure digestion vessels, temperature and pressure regulation via a sensor vessel was used for digestion of sediment and plant samples. A Q-switched[2] Nd:YAG laser at 1064 nm (Continuum Powerlite 9010, Continuum Inc., USA), a F-AAS instrument (Varian Atomic Absorption Spectrometer Spectra AA – 20 plus, Australia), an ICP-MS instrument (ELAN DRC-e ICP Mass Spectrometer Axial Field Technology, PerkinElmer, Canada), Spectro-Arcos inductively coupled plasma optical emission spectrometer (ICP-OES) (AMETEK-Spectro Analytical Instruments GmbH & Co.KG, Germany) and RA-915+ mercury analyzer with a PYRO-915 attachment (Lumex, Russia) were used for the determination of potentially toxic elements (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Sn, Hg and Pb) in water, sediment and plant samples.

A CEM MARS Xpress Microwave Accelerated Reaction System (CEM Corporation, USA) was used for extraction of PAHs from the sediment samples. An Agilent 7890A series gas chromatograph interfaced to an inert Agilent 5975C mass selective detector (MSD) (GC-MS) (Agilent Technologies, USA) was used to determine PAHs in sediment samples.

3.5. Sample Collection and Preservation

For sampling, three areas namely Addis Ababa (AA), Awassa and Ziway were selected. A total of thirty nine sampling sites were chosen for sampling sediments and water samples while Swiss chard samples were collected from six farming sites irrigated directly or indirectly with Akaki

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[2] A Q-switch is a device that is similar to a shutter that controls the laser resonator's ability to oscillate. This shutter effect allows one to spoil the resonator's "Q_{factor}" keeping it low to prevent lasing action. Under these conditions, the laser gain material is able to store higher level of energy. The extra stored energy is subsequently extracted as laser light emission in the form of extremely short width, high-peak power pulses.

River. The Swiss chard is selected due to the availability in the entire selected sites and also Itanna (1998a;2002) and Weldegebriel *et al*. (2012) reported higher concentration of metals in the plant than other plants (onion, potato, cabbage, red beet, Ethiopian kale, lettuce and cauliflower). The samples were collected in two campaigns from the entire sampling areas, i.e., first campaign from January 2011 to April 2011, while second campaign from January 2012 to April 2012. The timelines were selected since they were dry season in the entire sampling areas so as dilution due to rain could not be observed.

From Akaki River, seventeen sampling sites (TAR at Biheretsigie, AA Bulbula, AA Entoto, AA Gefersa, AA Kebena, AA Kera, AA Kidanemihret before TAR, AA TAR Alert, AA TAR before Kidanemihret, AA TAR before Melkaqurani, AA TAR Kalti, AA Melkaqurani before TAR, AA TAR Kolfe, AA TAR with Kidanemihret, AA TAR with Melkaqurani, AA TlAR at KK Textile Factory and AA TlAR with TAR at Aba Samuel) (Figure 4) were selected for collecting sediment samples. Similarly twelve sites from Lake Awassa (Amoragedel, Asamaber, Buko, Deset, Fidelserawit, Kereisa, Mezinagna, Muatie, Samijerisa, Shewaber, Tikurwuha and Wondotika) (Figure 5) and ten sites from Lake Ziway (Bochesa, Debresina, Gabriel, Gelila, Korekonch, Mezinagna, Shalo, Sedeicha, Wameicha and Wofdeset) (Figure 6) were selected. The sampling stations were chosen to include hotspots of pollution such as an industrial region, uncontrolled domestic wastewater discharge areas and rivers, and other spots where anthropogenic effects are minimal for comparison purpose.

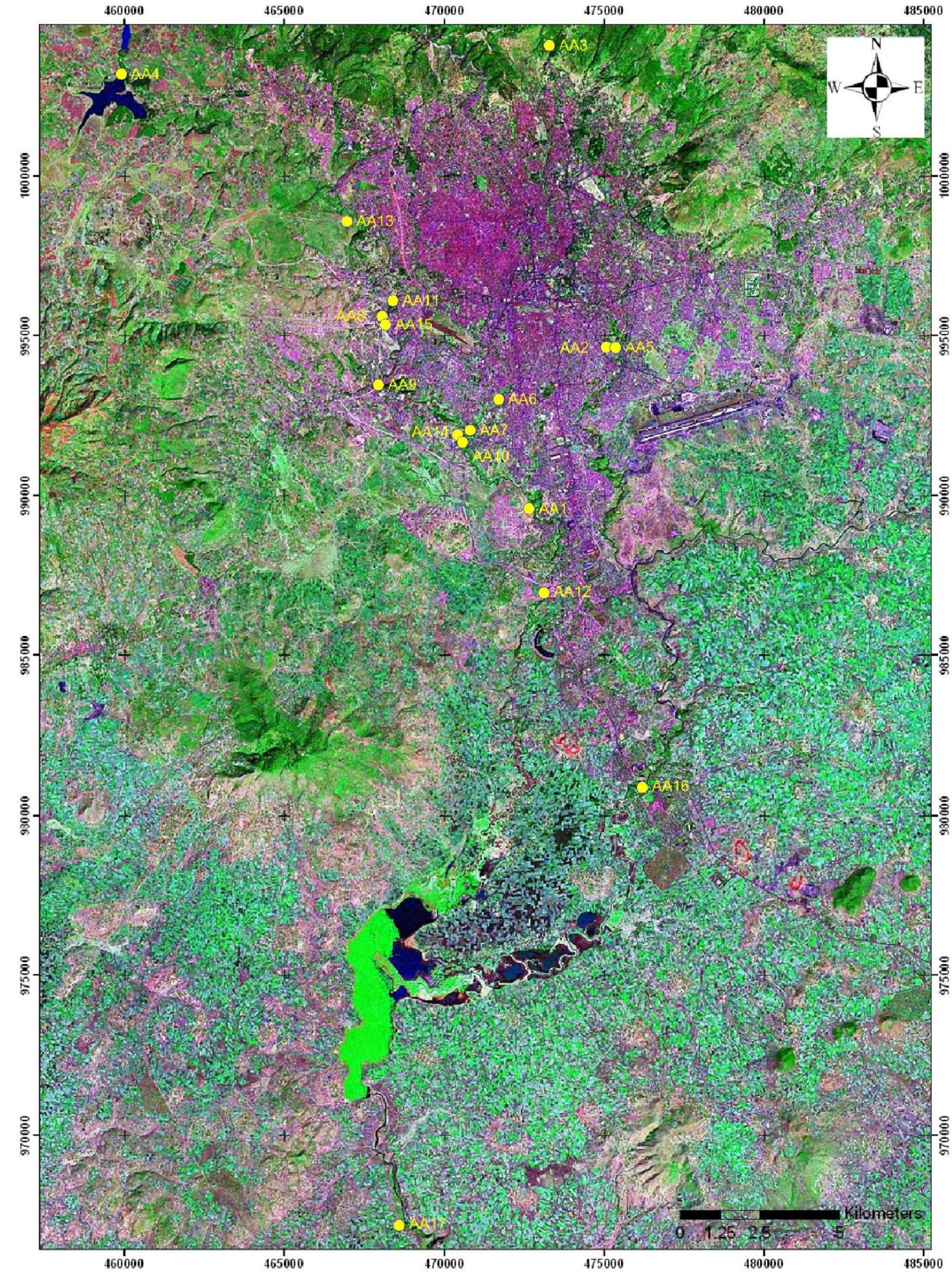

Figure 4. Sampling sites in Akaki River.

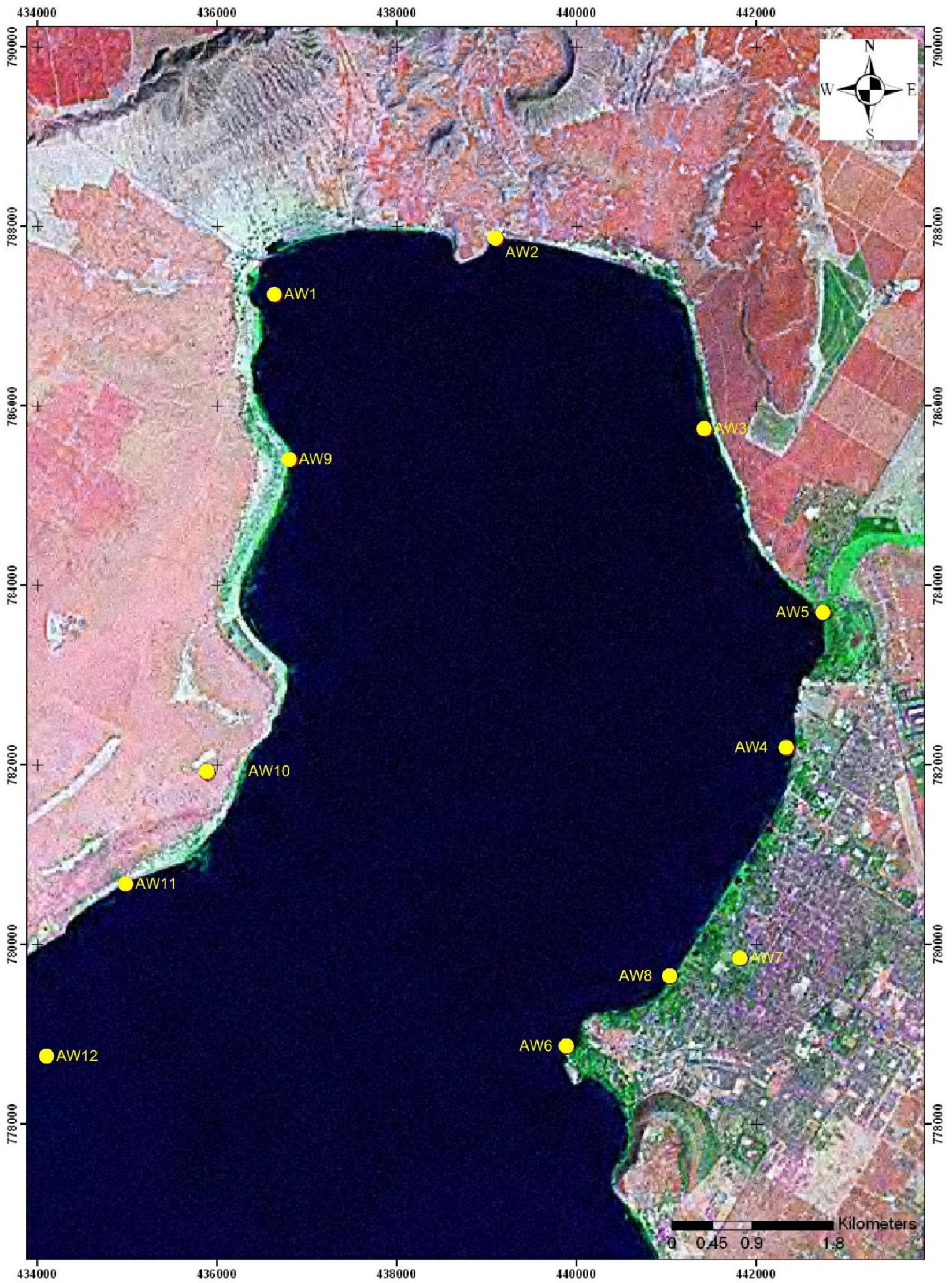

Figure 5. Sampling sites in Lake Awassa.

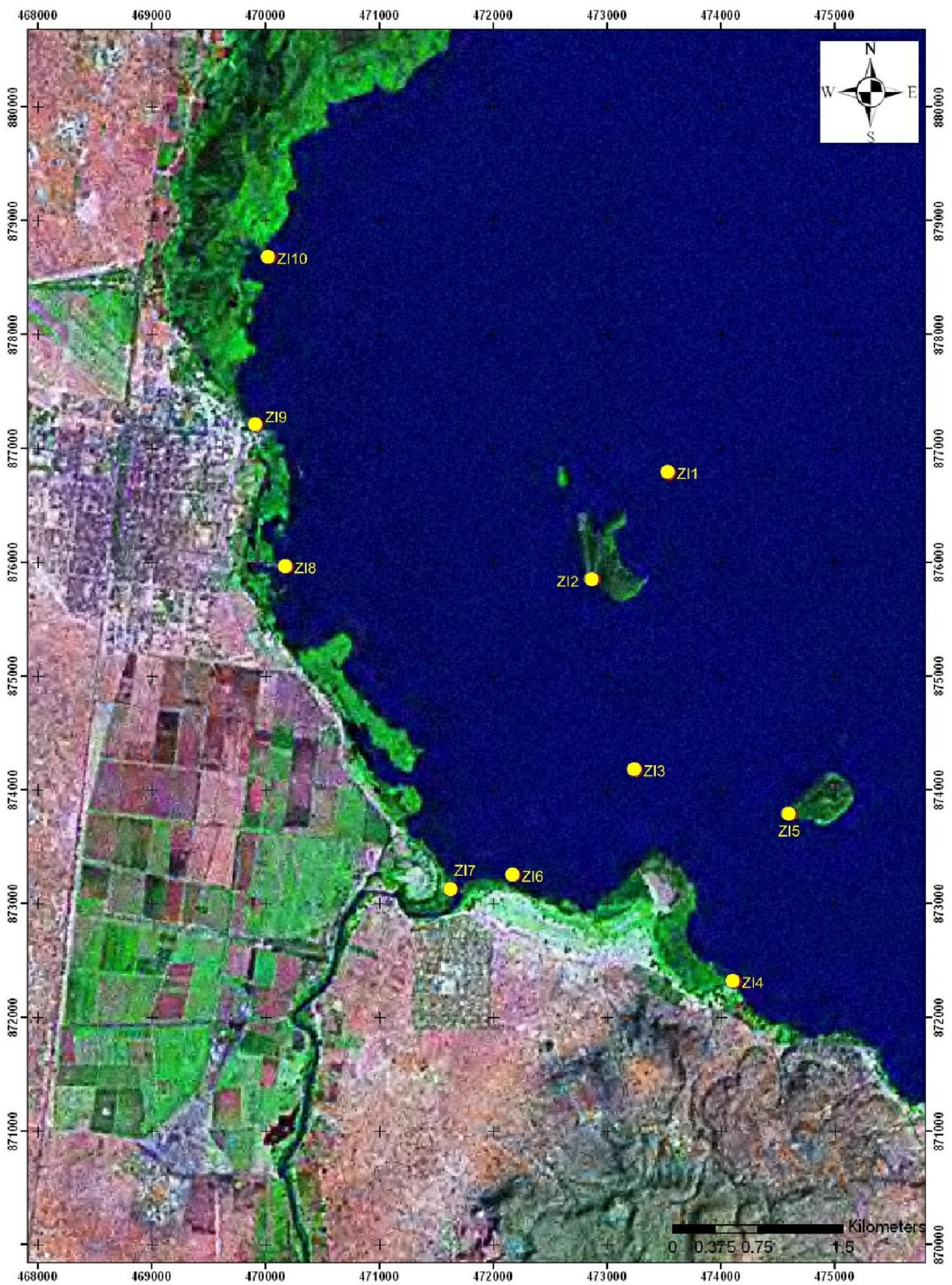

Figure 6. Sampling sites in Lake Ziway.

The top 20 cm of the bottom sediment samples were collected from sampling spots using an Ekman Bottom Grab sampler device (Van Walt Ltd, UK) in 500-mL double-cup polyethylene bottles. Water samples were collected in 1-L polyethylene bottles (with latex gloves and plastic spatula) and kept in an ice box until brought to the laboratory. The samples were placed in double cap polyethylene bottles to avoid any type of external mixing or addition of moisture. The fully grown (ready to be eaten) Swiss chard samples were collected by hand from the vegetable farms. Care was taken so as to get representative samples. Moreover, fallen leaves and leaves starting to wilt were not taken. The samples were kept in plastic bags and then in an ice box until brought to the laboratory. From each sampling area, the entire samples were collected in triplicate.

Once brought to the laboratory, the Swiss chard samples were washed thoroughly with tap water to remove superficial dust, dirt, possible parasites or their eggs, again washed with deionized water and cut into pieces. The plant and sediment samples were spread on plastic trays and allowed to dry at ambient temperature and ground to suitable mesh size using a ceramic coated grinder. Once the samples were powdered and dried, they were kept in 50-mL labeled double-cap polypropylene flasks until analysis. The samples were sieved to remove coarse materials because the particles above the mesh size may consist of shells, rocks, wood, and other detritus materials, and are usually not a source of bioavailable contaminants. Large debris, shells and visible materials were removed prior to grinding. The water samples were filtered through a G4 glass filter, transferred to 100-mL labeled double-cap polyethylene bottles and acidified with HNO_3 kept in refrigerator until analysis.

3.6. Sample Preparation for the Analytical Methodologies

3.6.1. The LIBS sample preparation

For pellet preparation, 4 g of the sediment samples were accurately weighed and mixed thoroughly with 0.3 g of boric acid as binder. Care was taken to avoid any contamination during pellet preparation. The pellets were made in a disc of cylindrical form having diameter 24 mm and 3 to 5 mm thick using a hydraulic press (ENERPAC P142, International Crystal Laboratories, USA) with pressure of 8000 psi. Pellets of pure metal powders and CRMs were also prepared in similar way for identifying the emission lines and the calibration purpose.

3.6.2. Digestion of sediment samples for F-AAS

Samples were prepared in triplicate according to the following procedure: 0.5 g of dried and ground sediment samples was accurately weighed and placed in 100-mL beaker. Freshly prepared *aqua regia* (5 mL) was added. The beaker was left for 20 min until the foam caused by organic matter decomposition disappeared. Then it was refluxed on a hot plate for 2 h at a temperature not exceeding 160 °C. The digest was filtered with No. 42 Whatman filter paper and after cooling the digest was diluted with deionized water to 50 mL and placed in the refrigerator prior to analysis using F-AAS. Blanks and CRMs were prepared in similar fashion.

3.6.3. Digestion of sediment and plant samples by microwave-assisted acid digestion for ICP-OES and ICP-MS

A 0.1000 g of dried and finely ground sediment sample was weighed directly into dry microwave digestion vessel and 3 mL HCl, 1 mL HNO_3 and 1 mL HF was added drop wise into vessel liner (so as the sample will not react violently) in that order, washing down any material on walls. The vessels were left for 20 min until the foam caused by organic matter decomposition disappeared. The vessels were mounted to the microwave digestion system and the digestion started based on the optimized two-stage sediment samples digestion procedure (stage 1: Table 1). When the temperature reading was below 40 °C, the vessels were removed from the microwave system and vented slowly so as to remove the excess pressure. About 1 mL of the filtered saturated H_3BO_3 was added to the reaction mixture in the vessel, which was then capped. The digestion was continued with stage 2 (Table 1). When the temperature reading was less than 40 °C the vessels were removed from the microwave system.

Table 1. Program for the digestion of sediment samples using microwave digestion system.

Parameters	**Digestion stage**	
	1	**2**
Maximum power, W	1600	1600
Maximum control pressure, psi	800	800
Ramp time, min	25	25
Hold time, min	10	5
Cooling time, min	15	15
Control temperature °C	200	150

A 0.2500 g dry matter of Swiss chard (leaves or stems) was measured into dry microwave digestion vessel. Then 4.0 mL HNO_3 and 1 mL H_2O_2 was added drop wise into the vessel liner, washing down any material on walls. The vessels were left for 20 min until the foam caused by organic matter decomposition disappeared, whereafter they were sealed and the digestion program 1 was run (stage 1: Table 1). The digestion was stopped when the temperature reading was less than 40 °C and then the vessels were removed from the microwave system.

The clear digested sediment and plant sample solutions were quantitatively transferred and diluted with deionized water to 50.00 mL in the presence of 50 µL of 10 µg/mL mixed internal standard (Ga, In and Tl). The analytical solutions were transferred to double-cap polypropylene for storage till analysis. All the digestions were carried out in triplicate, including the analytical blanks and CRMs, processed simultaneously with the samples.

3.6.4. Microwave-assisted extraction for PAHs analysis

A 2.000 g sediment sample was weighed into extraction vessel and the extraction of PAHs was done with the optimized method using 30 mL of mixture of *n*-hexane/acetone (1:1, v/v) (Table 2).

Table 2. The MAE parameters for PAHs analysis in sediment samples of Akaki River, Lake Awassa and Lake Ziway.

Parameters	**Description**
Extracting solvent	Acetone (15 mL) + hexane (15 mL)
Time, min	30
Temperature, °C	110
Power, W	200
Vent, min	5

After extraction, the vessels were allowed to cool to room temperature before they were opened. The supernatant was first filtered through pre-cleaned Pasteur's pipette glass filled with solvent-rinsed glass wool, and the solvent was decanted and went through the clean-up procedure. To the extract, 2 g of pre-cleaned anhydrous Na_2SO_4 were added, mixed thoroughly, left overnight and filtered. To the filtrate, 0.2 g of activated copper was added for desulfurization (Ledgard 2007), filtered with premium syringe filter (diameter 0.22 µm, Agilent) and evaporated to near dryness using a Genevac EZ-2 Series Personal Evaporator (Genevac Inc, UK). To the concentrated extract, about 1 mL of dichloromethane was added so as to make the final volume 1.0 mL and transferred to 1.5-mL brown vials for GC-MS.

3.7. Optimization of the Instrument, Calibration and Analysis

3.7.1. The LIBS

A Q-switched Nd:YAG laser that can deliver maximum pulse energy of 1 J, operating at its fundamental wavelength (1064 nm) with pulse duration of 8 ns and 10 Hz pulse repetition rate, was used for generating the sample plasma. The operating conditions for the LIBS system are summarized in Table 3.

Table 3. Operating conditions of Q-switched Nd:YAG laser high power LIBS for the determination of Cr Mn and Fe in sediment samples of Akaki River, Ethiopia.

Operating parameters	**Setting for**		
	Cr	**Mn**	**Fe**
Laser pulse energy, mJ	53.5	53.5	53.5
Gate delay, µs	0.9	1.4	1.0
Gate width, µs	6	6	6
Gain level	150	150	100
Number of accumulation	25	25	25
Grating groove density, lines/mm	2400	2400	2400
Grating blaze, nm	300	300	300
Input side slit width, µm	50	50	50
Wavelength range, nm	423–431	402–406	402–410

An energy meter (FieldMaxII-TOP, COHEREnT®, USA) was used to monitor the dependence of the LIBS signal on incident laser energy (Figure 7).

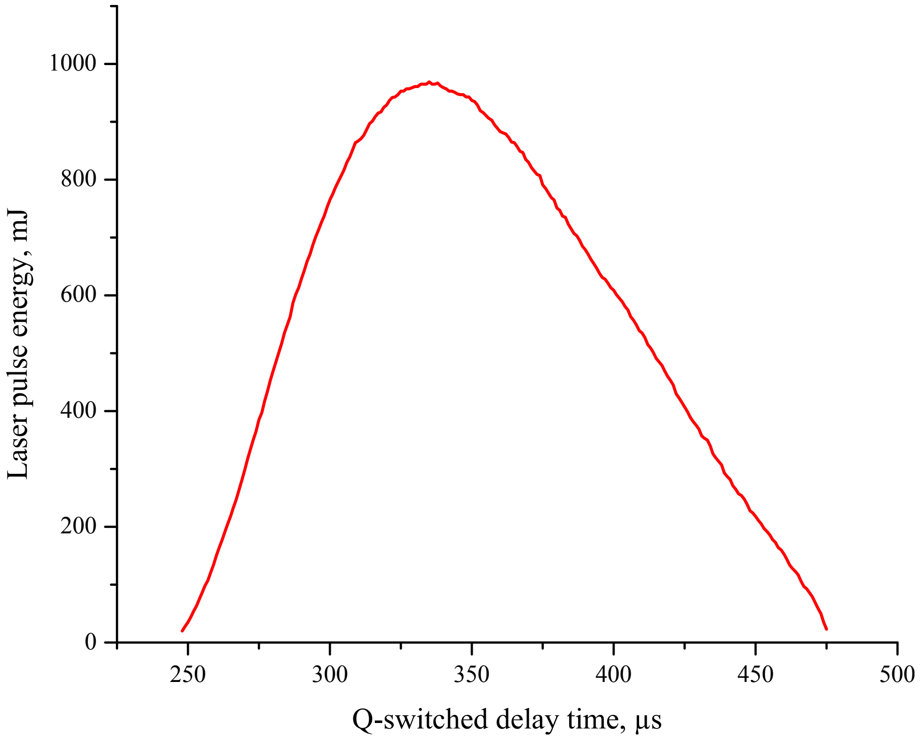

Figure 7. Measurement of laser pulse energy versus Q-switched delay time for LIBS analysis.

The laser beam was focused on the samples using a focusing lens of 25.4 mm diameter and 45 mm focal length to produce the plasma. In this experiment, a 2 mm diameter aperture was placed in the path of the laser beam before the lens in order to obtain a uniform beam shape. The emitted light was collimated by collecting lenses at a 45° angle to the incident laser beam, and thereafter a 2 m length fused-silica optical fiber was used to feed the signal into an Andor Shamrock SR-303i spectrometer (Model SR-3031-A, Andor Technology, Ireland), equipped with an intensified charge coupled device (DH734-18F-03 ICCD, Andor Technology, Ireland) containing three different gratings (300, 1200 and 2400 grooves per mm), each one being blazed at 300 nm, for detection of the dispersed light.

An accumulation of 25 laser shots were recorded to complete one measurement so as to enhance the signal-to-background ratio. Eight spectra of each sample were collected in different test portions of the pellet and averaged to decrease the shot-to-shot variations. All the spectral lines for the Cr, Mn and Fe were recorded for pellets of the metal powders and the CRMs, and were identified using the NIST atomic spectral database. A schematic diagram of the experimental set-up is shown in Figure 8.

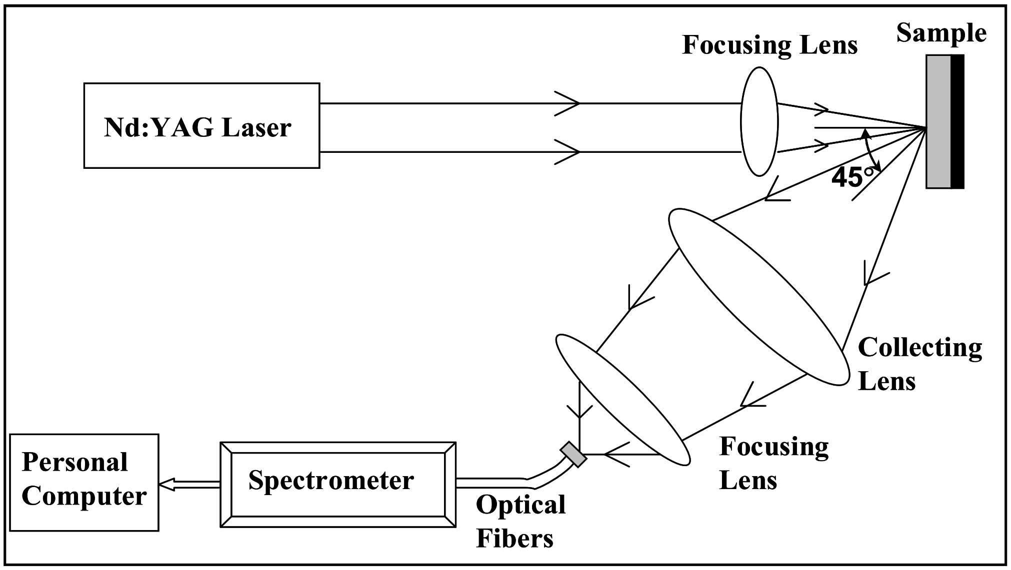

Figure 8. Schematic diagram of LIBS setup for the determination of Cr Mn and Fe in sediment samples of Akaki River, Ethiopia.

Besides the sample homogeneity, the experimental variables that can influence LIBS measurements are laser related (i.e. wavelength, energy, pulse duration and shot-to-shot power fluctuation), focusing spot size, ambient conditions, physical properties of the sample, amplification detector gain, ambient atmosphere, pressure and the detection window (delay time and gate width) (Godoi *et al*. 2009). The spectrometer was wavelength calibrated using mercury-argon lamp. Using metal powders emission lines with no or minimal interferences were selected.

Moreover, pre-exposure was performed to set the response of the ICCD so as to avoid over-saturation.

For each new sample, before spectral collection, 10 laser pulses were performed to clean the sample surface and remove contamination. The delay times were chosen according to the maximum LIBS signal intensity for each element present in the samples. Emission spectra at different laser energies were recorded to study the effect of the laser energy on the line emission intensity at a constant gate width of 6 µs used throughout the study. To study the effect of laser energy on the line emission variation, laser produced plasma emission spectra from sediment samples were recorded from 20–190 mJ at the optimized delay times for each element.

For the quantification of potentially toxic elements in sediment samples, CRMs (CRM 320R, 2709a, 2587 and 8704; NCS DC 73322 and 73374) were employed for construction of the five point calibration curves. The selection of the CRMs was based on the presence of the elements of interest. Care was taken so as to make similar experimental condition to be followed for the CRMs and the analyzed sediment samples and therefore to minimize CRMs matrix effect on sediment samples. The concentration ranges of the CRMs used were as stipulated in the specific CRM's certificate for the specific quantified element.

3.7.2. The F-AAS

Each of the digested sediment sample was analyzed for the selected potentially toxic elements using F-AAS. Three independent replicates were performed for each sample and blanks were measured in parallel. After optimizing the instrument for optimum analytical conditions (energy, calibration curve, etc), the concentrations of Cr, Mn and Fe in the sediment samples were measured at 357.9 nm, 279.5 nm and 248.3 nm, respectively.

3.7.3. The ICP-OES

The determination of Mn, Fe and Zn were performed using Spectro-Arcos ICP-OES equipped with a holographic grating (3600 grooves/mm) and having radial plasma observation with side-on plasma interface. It utilizes 32 linear CCDs for the simultaneous recording of the wavelengths between 130 and 770 nm. The cross flow nebulizer and Scott double pass spray chamber system were used sample introduction. At least four emission lines for each element were tested before selection where the choice of the analytes' spectral lines was based on both the sensitivity and spectral interference obtained. The instrumental parameters are shown in Table 4.

Table 4. Instrument operating parameters of Spectro-Arcos ICP-OES for the determination of Mn Fe and Zn in sediment and plant samples of Akaki River, Lake Awassa and Lake Ziway, Ethiopia.

ICP-OES instrumental setting	**Value**
Radio frequency power, W	1400
Frequency of RF generator MHz	27.12
Plasma gas flow rate, L/min	12.0
Auxiliary gas flow rate, L/min	1.0
Nebulizer flow rate, L/min	1.0
Replicate read time, s	28
Delay, s	15
Sample uptake delay, s	30
Sample uptake, mL/min	1.5
Pump rate, rpm	30
Rinse time, s	30
Replicates	3
Element (λ/nm) (emission lines used for quantification labeled in **bold**)	Mn (257.611, 259.373, 260.569, 294.921 and **403.076** nm)
	Fe (239.562, 259.941, **262.567** and 275.573 nm);
	Zn (202.613, 206.200, **213.856** and 334.502 nm)

3.7.4. The ICP-MS

The various instrumental parameters for ELAN DRC-e ICP-MS were optimized using SMART tune standard solution containing 10 µg/L of Ba, Be, Ce, Co, In, Mg, Pb, Rh and U in 1% HNO_3. The ICP-MS is optimized to provide the maximum ^{238}U intensity for optimal counting statistics (>300,000 cps), as well as minimal values (<0.03 or <3%) of the ratios $^{140}CeO^+/^{140}Ce^+$ (oxides) and $^{138}Ba^{2+}/^{138}Ba^+$ (double charged species) and optimum intensity of the analytes (Mg, In and U). All of the isotopes were chosen as a function of their natural abundance and spectral interference possibility. The instrumental parameters are listed in Table 5.

Table 5. Instrument operating parameters of ELAN DRC-e ICP-MS for the determination of potentially toxic elements in water, sediment and plant samples of Akaki River, Lake Awassa and Lake Ziway, Ethiopia.

Operating parameter	**PerkinElmer SCIEX ELAN DRC-e Setting**
Sample introduction	Cross-flow nebulizer
Spray chamber	Ryton®, double-pass
RF power, W	1100.00 – 1200.00
RF generator frequency, MHz	40.00
Plasma gas flow, L/min	15.00
Auxiliary gas flow, L/min	1.20
Nebulizer gas flow, L/min	0.91-0.96
Autolens	On
Analog stage voltage, V	-1800.00 – -1850.00
Pulse stage voltage, V	800.00 – 900
Main water temperature, °C	16.0 – 18.1
Interface water temperature, °C	27.0 – 31.2
Torch box temperature, °C	32.0 – 38.8
Lens voltage, V	8.00 – 13.50
Interface	Ni sampler and skimmer cones, i.d. 1.1 and 0.9 mm, respectively
Torch	Standard quartz torch
Data acquisition	Peak hopping; dwell time per amu 50 ms, sweeps 20, reading 1, replicates 3
Monitored ions (analytes used for quantification labeled in **bold**)	**^{51}V**, **^{52}Cr**, ^{53}Cr, **^{59}Co**, ^{58}Ni, **^{60}Ni**, **^{63}Cu**,^{65}Cu, **^{75}As**, ^{77}Se, ^{78}Se, **^{82}Se**, **^{107}Ag**, ^{109}Ag, ^{110}Cd, ^{111}Cd, ^{112}Cd, ^{113}Cd, **^{114}Cd**, ^{116}Cd, ^{117}Sn, ^{118}Sn, ^{119}Sn, **^{120}Sn**, ^{198}Hg, ^{199}Hg, ^{200}Hg, ^{201}Hg, **^{202}Hg**, ^{206}Pb, ^{207}Pb, **^{208}Pb**; (**^{55}Mn**, ^{54}Fe, **^{56}Fe**, ^{64}Zn, ^{66}Zn, **^{68}Zn** – for only water samples)

3.7.5. The elemental mercury analyzer

For the determination of mercury in the collected sediment and plant samples, a mercury analyzer with pyrolysis attachment was used. A schematic diagram of the experimental set-up is provided in Figure 9 and the working principle of the instrument has been explained elsewhere (Sholupov *et al*. 2004; Grobecker and Detcheva 2006; Beaulieu *et al*. 2008; Witt *et al*. 2008).

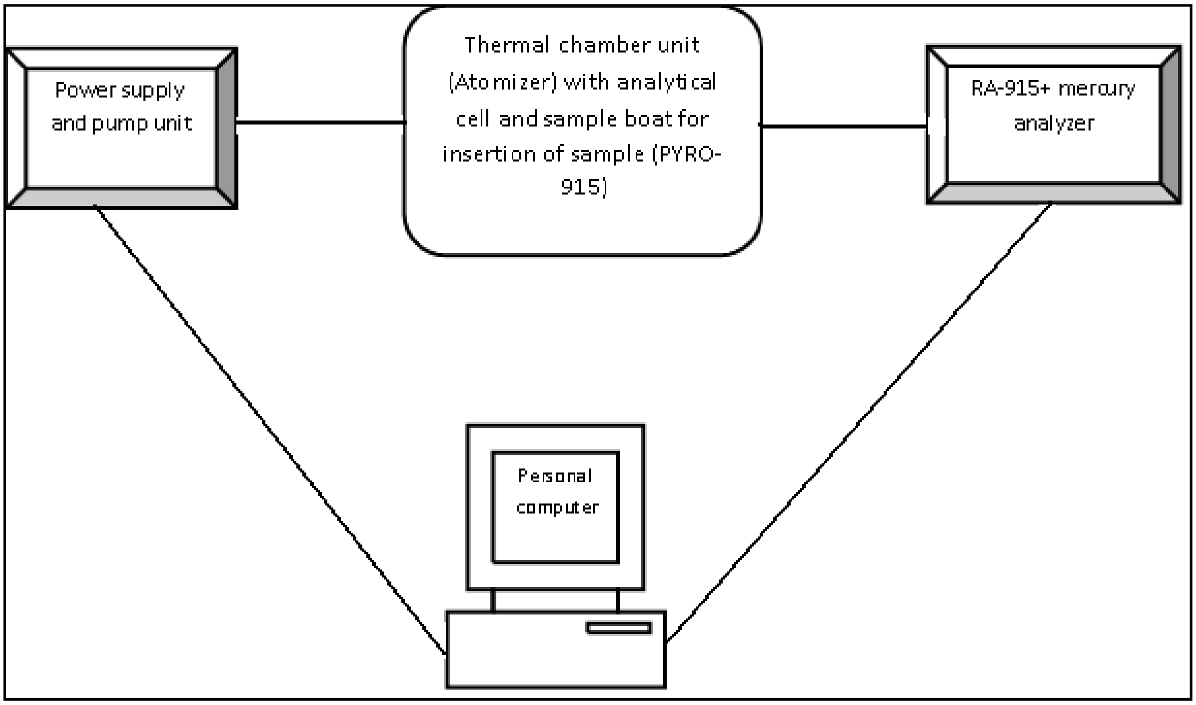

Figure 9. A schematic diagram of the experimental set-up of the RA-915+ analyzer with PYRO-915+ attachment.

Mercury content in the sample was determined from the integrated analytical signal with due account of the preset calibration coefficient using CRM 7002 mercury sample. The calibration curve was plotted as the mass of CRM (mg) versus peak area (arbitrarily unit) using a CRM of Tibetan soil.

3.7.6. The GC-MS

The PAHs in the purified extract were determined using an Agilent 7890A series gas chromatograph (GC). The GC used splitless mode (split ratio of 127 to 1[3]) and interfaced to an Agilent 5975C series inert mass selective detector (MSD) with triple-axis detector (TAD). Separation of the compounds was achieved using a fused silica capillary column (DB-5 MS, 30 m x 0.25 mm i.d. x 0.25 µm film thickness; J&W Scientific, USA). The various instrumental parameters are listed in Table 6.

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[3] For PAHs analysis, we used the split vent flow of 100 mL/min and the column flow of 0.78829 mL/min. Therefore the split ratio would be calculated as: Split ratio = [Split vent flow/column flow] = [(100 mL/min)/(0.78829 mL/min)] = 127. Therefore, for an injection of 1 µ L (1000 nL), the actual amount entering the column would be 1/127 of 1000 nL or 8 nL. The effect of split injection is thus to decrease the sample size from 1 µ L to 8 nL.

Table 6. Instrument operating conditions of GC-MS for the determination of PAHs in sediment samples of Akaki River, Lake Awassa and Lake Ziway, Ethiopia.

Parameters	**Description**
Analytical column	DB-5 MS fused silica capillary column (30 m x 0.25 mm i.d. x 0.25 µm film thickness; J&W Scientific, USA)
Mobile phase	He
Column flow, mL/min	0.788
Split ratio	127 to 1
Oven temperature programming	Start at 60 °C and hold for 2 min at this temperature, ramp from 60 °C to 160 °C at 15 °C/min and hold for 9 min at this temperature, ramp from 160 °C to 260 °C at 5 °C/min and hold for 3 min at this temperature, and then ramp from 260 °C to 300 °C at 5 °C/min and hold for 1.67 min at this temperature with a total oven temperature run time to be 50.34 min
Temperature for sample inlet (maximum), MSD transfer line heater, ion source and quadrupole mass analyzer, °C	325, 310, 230 and 150, respectively
Detector	MSD operated in electronic impact mode at 70 eV
Acquisition mode	Identification in scan mode and quantification in selected ion monitoring (SIM) mode
Ions selected for each PAH, m/z (The underlined Q_{Ions} were used for quantification.)	naphthalene (128, 127, 129, 102), acenaphthylene (152, 151, 76, 150), fluorene (166, 165, 167, 182), phenanthrene (178, 176, 179, 76), anthracene (178, 176, 179, 89), fluoranthene (202, 200, 203, 187), pyrene (202, 203, 101, 200), chrysene (228, 226, 229, 113), benzo[*a*]anthracene (228, 226, 229, 114), benzo[*k*]fluoranthene (252, 250, 253, 126), benzo[*b*]fluorantene (252, 253, 250, 126), benzo[*a*]pyrene (252, 253, 250, 126), indeno[1,2,3-*cd*]pyrene (276, 277, 274, 136) and benzo[*ghi*]perylene (276, 137, 138, 274)

3.8. Preparation of Standards

For F-AAS, a series of working standard solutions of metals (0, 1, 2, 5 and 10 mg/L for Cr; 0, 2.5, 5, 10 and 20 mg/L for Mn; and 0, 10, 50, 100 and 200 mg/L for Fe) were prepared by appropriate dilution with deionized water of the 1000 mg/L metal stock solutions. For ICP-MS and ICP-OES, series of 1, 5, 10, 20 and 40 ng/mL (1, 5, 10, 20, 40, 100 and 500 µg/mL for Mn, Fe and Zn) of mixed standards containing V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Sn, Hg and Pb were prepared from the 1000 mg/L metal stock solution were prepared in presence of 50 µL of 10-µg/mL intermediate mixed internal standard (Ga, In and Tl) and 0.5 mL of conc. HNO_3 and diluted to the mark using deionized water. Standard blanks were prepared in a similar way.

3.9. Quality Assurance

Analysis of the set of samples was accompanied by a procedural blank except LIBS, which were carried throughout the entire analytical procedure in a manner identical to the samples. For validation of the F-AAS method, the SRM 8704 was used for quality control purposes so as to monitor the accuracy of the measurements. The BCR 320R, SRM 1643e, SRM 2709a, and SRM 2587 were used for ICP-OES, ICP-MS and/or mercury analyzer. For calibrating the mercury analyzer, CRM 7002 was used. The analytical accuracy of the method was checked by analyzing the CRMs while the precision of measurement was assessed by performing replicate measurements after being treated in similar manner to the samples.

For GC-MS, the SRM 1944 was analyzed for quality assurance checks. Instrumental calibrations were checked by injection of the continuing calibration solution of 0.5 µg/mL concentration. The GC-MS calibration was verified after running at most every ten samples.

3.10. Identification and Quantification

For potentially toxic element quantification, analysis was performed using external calibration and internal standardization (for ICP-MS) using multi-elements standard solutions for generating the calibration curves. The plots of the changes of instrumental response with changing concentration of analyte (calibration curves) create linear relationship. Moreover, background correction was done for ICP-OES so as to get the best results. Analyte determinations were carried out under optimized conditions for the introduction of aqueous solutions. The instrument was conditioned for about half an hour and optimized daily. The ICP-MS was optimized daily by monitoring the signals obtained using a multi-elemental solution containing a 10 μg/L SMART tune solution for mass calibration that contained Ba, Be, Ce, Co, In, Mg, Pb, Rh and U. The daily performance was checked based on the recommended optimization values for ICP-MS performance. Three independent replicates of each sample were measured and the concentrations were determined as the average of the replicate inputs.

The identification of the PAHs in the sediment samples was confirmed by the retention time and abundance of confirmation ions in the authentic PAHs standards. The US EPA 14 priority PAHs were quantified based on at least seven-point calibration curve for individual compounds. The automated library searching was performed using the NIST Mass Spectral Database. In this study, the concentrations of PAHs are expressed on a dry-mass basis.

3.11. Statistical Packages used in Data Analysis

Statistical analysis of data were carried out with the use of SPSS v16.0 for Windows statistical program (SPSS 16.0.0 for windows, SPSS Inc., Polar Engineering and Consulting 2007), Microcal™Origin version 6.0 (Microcal Software, Inc. USA) and OriginPro 8 SRO v8.0725 (B725) (OriginLab Corporation, USA). Ternary plot and Pearson’s correlation matrix at 95% confidence interval were used. To construct the dendrogram for PAH source identification, R version 3.0.2. (The R Foundation for Statistical Computing, R Core Team, Austria 2013) was used.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1. Introduction

In this chapter, results obtained using the various techniques are discussed. Based on international guidelines, the levels of pollution of the sampling areas with respect to the potentially toxic elements and PAHs in sediment, plant and water samples are presented. This chapter has five major sections: (*i*) assessment of the levels of potentially toxic elements in sediment using LIBS; (*ii*) distribution of mercury in the sediments of selected freshwater bodies of Ethiopia; (*iii*) potentially toxic elements in selected freshwater bodies of Ethiopia; (*iv*) assessment of potentially toxic elements in Swiss chard and sediment of Akaki River, Lake Awassa and Lake Ziway, Ethiopia; and (*v*) distribution of PAHs in sediments of Akaki River, Lake, Awassa and Lake Ziway.

4.2. Assessment of the Levels of Potentially Toxic Elements in Sediment Using LIBS

4.2.1. Optimization of experimental conditions

In order to enhance the sensitivity of the LIBS for analyzing sediment samples, important experimental parameters such as laser pulse energy, gate delay time, gate width and gain level were investigated (Table 3). The spectrometer requires periodic internal calibration using a mercury-argon lamp, since the spectral position shifts due to variations in laboratory conditions (Mohamed 2008). Additionally, to obtain improved results, metal emission lines with no or minimal interference, which may arise due to the sample matrix, and maximum signal intensities were selected. The NIST atomic spectral database (Ralchenko *et al*. 2011) was also used to identify all the spectral lines recorded for analytes using the LIBS system. The most intense wavelength for each element was selected to study the effect of different experimental parameters. Accordingly, the selected wavelengths for Cr, Mn and Fe were 425.43 nm, 403.076 nm and 404.58 nm, respectively. In this work, Mn and Fe were used for the optimization of the instrument since both elements were expected to occur at higher concentration and subsequently quantified along with Cr.

In the early stages of plasma radiance, an intense continuum emission, known as Bremsstrahlung[4], resulted. After an appropriate delay, the plasma cooled to the point where atomic and ionic emissions could be observed. Hence, the optimization of the delay time was fundamental and chosen according to the maximum LIBS signal intensity for each element present in the samples.

The delay time with respect to the laser pulse had to be optimized to reduce the undesirable effect of the continuum radiation. A typical plot of the dependence of LIBS signal intensity at the selected wavelengths on delay time, are presented in Figure 10.

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[4] Bremsstrahlung is from the German word bremsen (to break) and strahlung (radiation), thus “breaking radiation” or “deceleration radiation”. It is essentially electromagnetic radiation that is produced by the acceleration and collision of charged particles with other charged particles such as atomic nuclei. Here the laser plasma ignition could be expected to be observed at approximately 10 ns then Bremsstrahlung radiation between 1 to 2 µs and finally line spectra emission at approximately 100 µs.

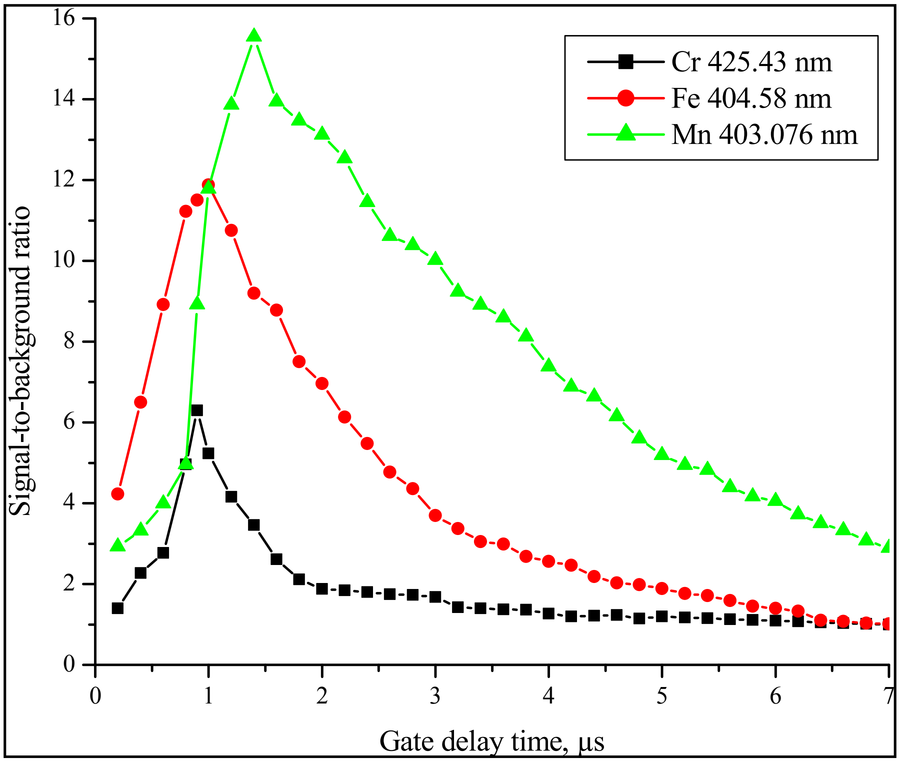


Figure 10. Dependence of LIBS signal intensity on gate delay time for Cr, Fe and Mn in sediment samples.

It is clear from the figure (Figure 10) that the maximum LIBS signals are recorded at 0.9 µs, 1.4 µs and 1.0 µs for Cr, Mn and Fe, respectively, where maximum signal-to-background ratios were observed.

Emission spectra at different laser energies were recorded at a constant gate width to study its effect on the line emission intensity. The best signal-to-background ratio of analyte lines in sediment sample was obtained at a laser pulse energy of 53.5 mJ (Figure 11).

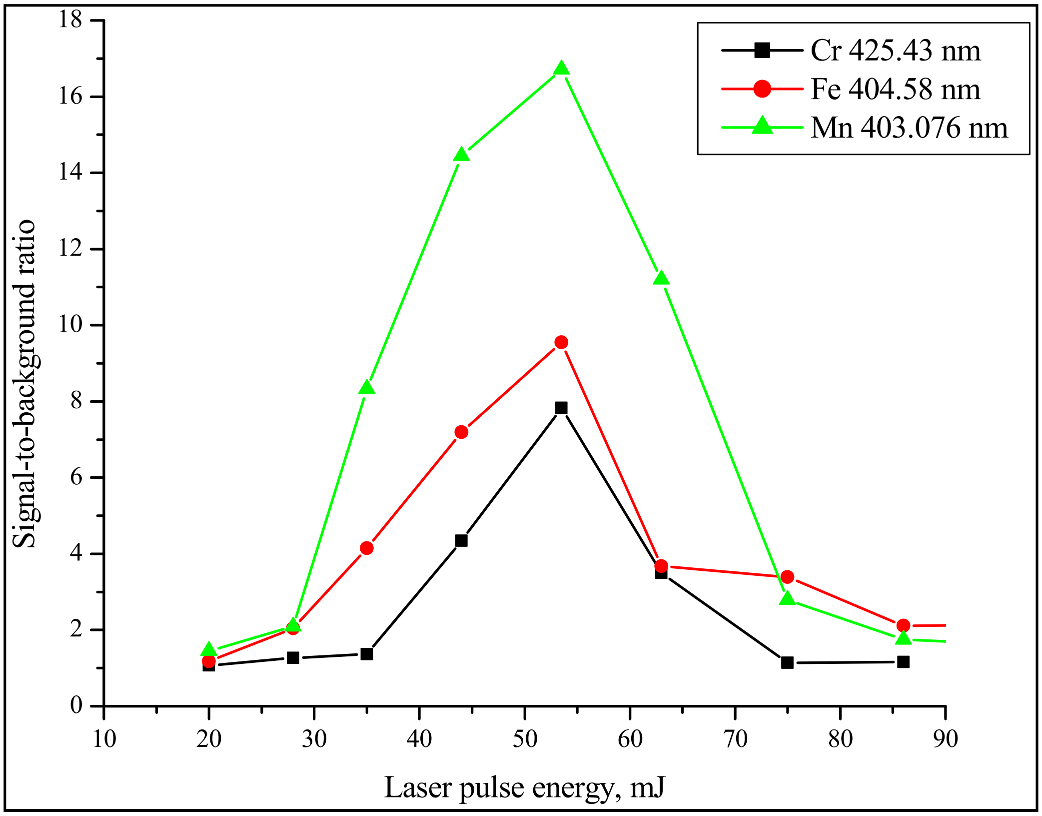
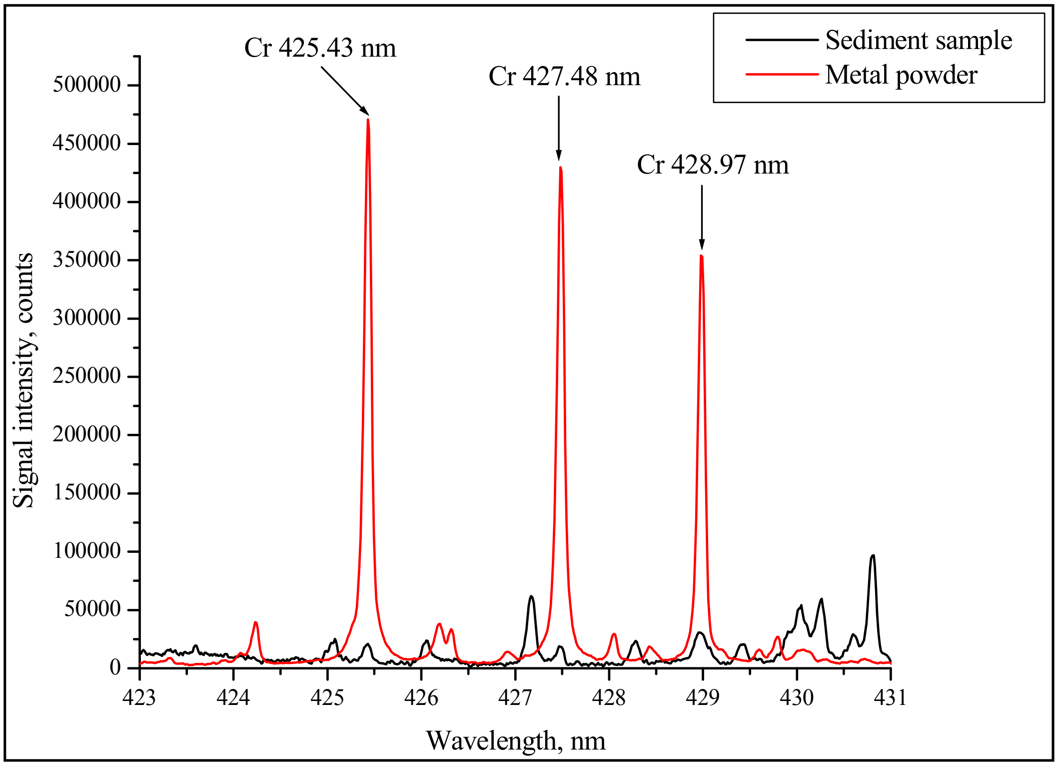


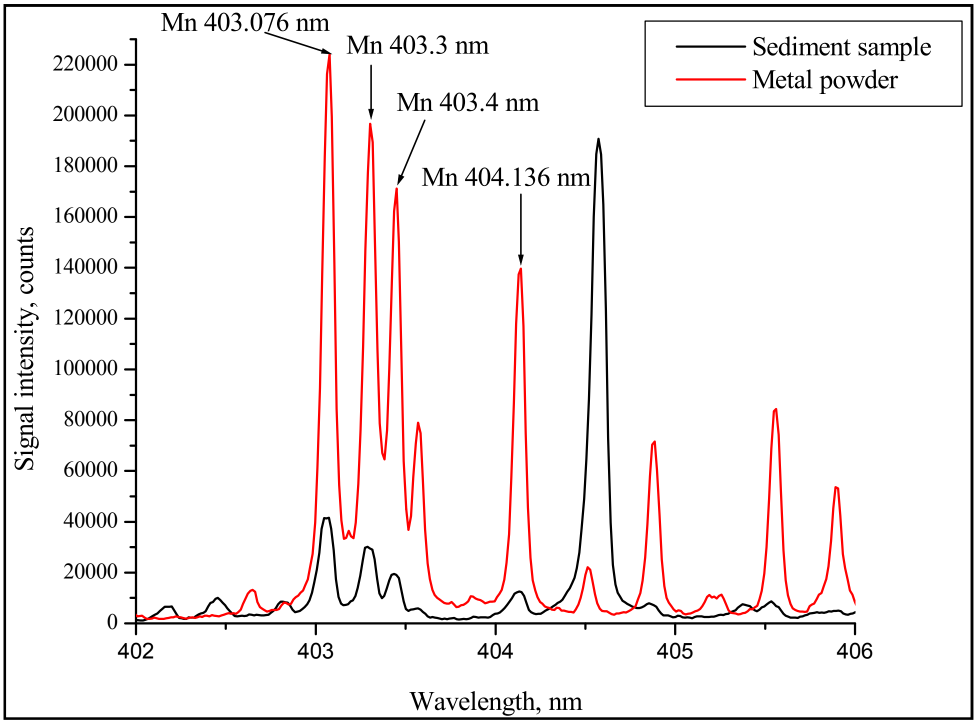
Figure 11. Effect of variation of laser pulse energy on the signal-to-background ratio of Cr, Fe and Mn lines of sediment samples.

The laser energy of 53.5 mJ was selected for subsequent analysis in all cases (Table 3). The binding materials also play an important role in efficiently coupling the laser energy to the sample, ablating a measurable quantity of mass, and reducing fractionation and deviation between measurements (Lal *et al*. 2004). Hence boric acid was used as binding material.

4.2.2. Spectral analysis

The spectra of Cr, Mn and Fe metal powder standard and sediment samples are presented in Figures 12.


Sediment sample
Metal powder
Cr 425.43 nm
Cr 427.48 nm
Cr 428.97 nm
Signal intensity, counts
0
50000
100000
150000
200000
250000
300000
350000
400000
450000
500000
423
424
425
426
427
428
429
430
431
Wavelength, nm


Sediment sample
Metal powder
Mn 403.076 nm
Mn 403.3 nm
Mn 403.4 nm
Mn 404.136 nm
Signal intensity, counts
0
20000
40000
60000
80000
100000
120000
140000
160000
180000
200000
220000
402
403
404
405
406
Wavelength, nm

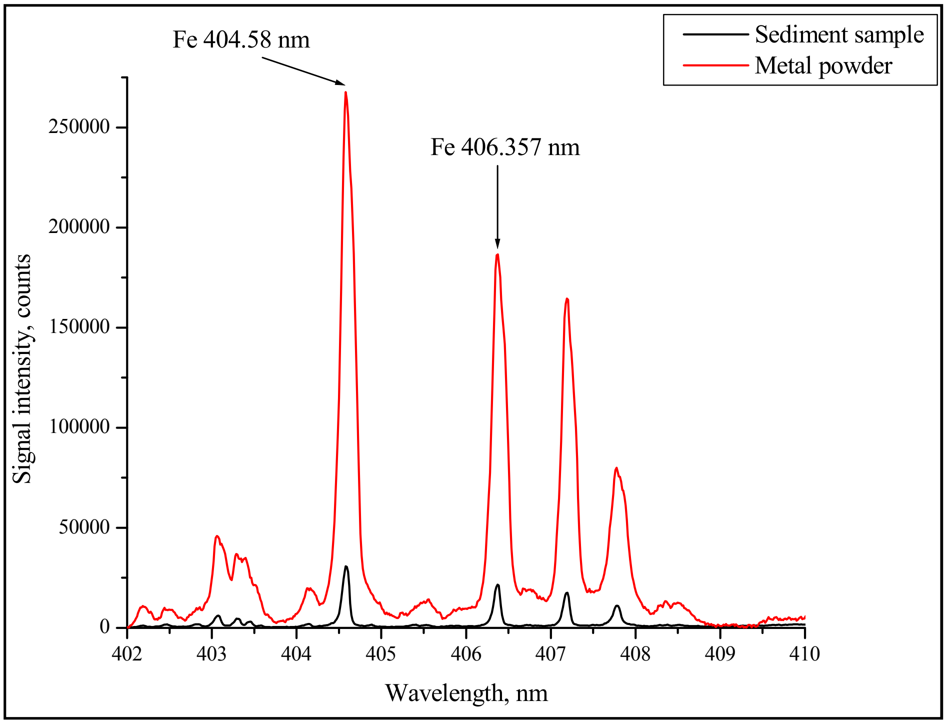


Figure 12. The LIBS spectra of Cr, Mn and Fe in a sediment sample and the spectra of metal powders with the strong emission lines labeled.

In the figure (Figure 12), the spectra of metal powder were overlaid on to the spectra recorded for sediment samples to identify the prominent emission lines of the analytes. Additional lines due to the presence of other elements exist in the selected wavelength region; however, for this study, the best lines of the elements of interest are indicated.

There are three strong emission lines of Cr at 425.43 nm, 427.48 nm and 428.97 nm; four strong emission lines of Mn at 403.076 nm, 403.3 nm, 403.4 nm and 404.136 nm; and two strong emission lines of Fe at 404.58 nm and 406.357 nm (Ralchenko *et al*. 2011). From Figure 12, it can be extracted that the emission line at 425.4 nm, 403.076 nm and 404.58 nm exhibited strong intensities (with relatively minimal interference) for Cr, Mn and Fe, respectively, and therefore were selected for this study.

4.2.3. The calibration curves

For the quantification of potentially toxic elements in sediment samples, CRMs were employed for construction of the calibration curves. The calculations were based on the peak height measurements at the selected wavelengths of 425.43 nm, 403.076 nm and 404.58 nm, for Cr, Mn and Fe, respectively. The linear regression coefficient (R) values for all the calibration curves were greater than 0.998, suggesting strong linear relationship between the LIBS signal and the concentration of analytes. Therefore, the calibration relations were used for the determination of analyte in the samples. The R values for all calibration curves of analytes using F-AAS were greater than 0.999, and therefore used for quantification.

4.2.4. The LODs of LIBS method

The LOD of LIBS for each element was calculated based on the International Union of Pure and Applied Chemistry (IUPAC) convention (Le Drogoff *et al*. 2001; Sabsabi *et al*. 2005; Mohamed 2008; Dell'Aglio *et al*. 2011). Accordingly, the equation: LOD = $3b/S$, was used, where b is the standard deviation of the background and S is the calibration sensitivity (S = slope of the calibration curve). The calculated LODs for Cr, Mn and Fe were 0.043 mg/g, 0.039 mg/g and 0.079 mg/g, respectively. The LODs obtained for Mn in sediment samples (0.039 mg/g) is almost an order better than that reported in the literature for the same element (Lazic *et al*. 2001) which indicates the better performance of our method as compared to the latter. There were no other studies that reported the LODs for Mn, and also for Cr and Fe.

4.2.5. The LODs of F-AAS method

For F-AAS analysis, the LODs of the selected potentially toxic elements in the sediment samples were determined by analyzing the blanks based on three times the standard deviation of the average of ten individual prepared blank solutions. The LODs values obtained for Cr, Fe and Mn were 0.120 µg/g, 0.510 µg/g and 0.250 µg/g, respectively, are comparatively better than obtained in LIBS method.

4.2.6. Quality control for LIBS method

The RSDs of the two methods, LIBS and F-AAS, were determined using triplicate measurements. The maximum RSD values of 20% and 5% were obtained in LIBS and F-AAS measurements, respectively. It can be concluded that the F-AAS method gives 100 times higher LOD values as compared with the LIBS method. The relatively higher RSD value in LIBS measurements may be attributed to the combination of various factors including the variation in the amount of vaporized mass from shot-to-shot, deviation in laser energy and also changes in the distance between the focal plane and the sample surface (Rossbach and Zeiller 2003; Trevizan *et al*. 2008,2009).

Further, since CRMS were used for constructing calibration curves for LIBS, the accuracy of the technique could not be verified using the CRMS. Rather the accuracy of the LIBS technique was compared with that of the F-AAS method using t-test at the 95% level of confidence. The calculated *p*-values were 0.46, 0.37 and 0.002 for Mn, Cr and Fe, respectively, from which it can be concluded that the two methods show some similarity in some cases (but not strongly correlated) for Mn and Cr, while were significantly different for Fe.

4.2.7. Accuracy of F-AAS method

The Buffalo River Sediment RM® 8704 was used for quality control purposes so as to monitor the accuracy of the F-AAS measurements. The results obtained are presented in Table 7, and demonstrate that the determined results are in good agreement with the certified values.

Table 7. Quality control result (mean ± SD, in mg/kg) for F-AAS using RM® 8704.

Element	**F-AAS reading**	**Certified value**	**% Agreement**
Cr	111 ± 3.8	122 ± 3.8	91.0
Mn	526 ± 21	544 ± 21	96.6
Fe	3.74 ± 1.5	3.97 ± 1.0	94.1

4.2.8. Elemental analysis of sediment samples

Sediment sample spectra were recorded under identical experimental conditions to those used for the metal powder and CRMs. The selected potentially toxic elements present in the sediment samples were identified and the corresponding concentrations are listed in Table 8.

Table 8. Concentration of potentially toxic elements (mean ± SD, in μg/g) in sediment samples of Akaki River using LIBS and F-AAS.

Sample site name	Cr		Fe		Mn	
	LIBS	**F-AAS**	**LIBS**	**F-AAS**	**LIBS**	**F-AAS**
AA Biheretsigie	59.6 ± 12	116 ± 6.2	37100 ± 2680	52400 ± 913	895 ± 27	1880 ± 101
AA Bulbula	72.4 ± 1.0	137 ± 5.2	63900 ± 3720	64000 ±1110	1700 ± 227	1640 ± 15
AA Gefersa	110 ± 8.4	85.7 ± 4.0	40700 ± 655	71000 ± 612	1990 ± 254	2050 ± 43
AA Kebena	116 ± 3.5	170 ± 2.3	42100 ± 3770	53300 ± 586	1860 ± 297	1880 ± 32
AA Kera	138 ± 17	147 ± 7.8	69500 ± 10500	76200 ± 1340	1910 ± 214	1830 ± 43
AA Kidanemihret	181 ± 36	181 ± 3.1	26900 ± 775	49000 ± 570	1290 ± 190	1240 ± 26
AA Melkaqurani	82.2 ± 1.0	60.7 ± 3.0	58400 ± 2510	65100 ± 3260	**3640 ± 727**	**4460 ± 223**
AA TAR Alert	517 ± 84	591 ± 20	53400 ± 4810	73000 ± 880	2030 ± 343	1970 ± 35
AA TAR and Kidanemihret	238 ± 48	182 ± 2.9	52900 ± 2690	69200 ± 1240	1960 ± 144	2010 ± 42
AA TAR and Melkaqurani	199 ± 10	209 ± 5.8	61200 ± 8410	75000 ± 2230	1870 ± 89	2850 ± 142
AA TAR before Kidanemihret	190 ± 9.6	366 ± 6.6	**71800 ± 10000**	72000 ± 433	2480 ± 306	2500 ± 62
AA TAR before Melkaqurani	**707 ± 72**[5]	1080 ± 9.3	40600 ± 4260	65600 ± 1360	1590 ± 135	1520 ± 15
AA TAR Kalti	385 ± 59	481 ± 14	58700 ± 5460	74900 ± 2110	2070 ± 238	2230 ± 54
AA TAR Kolfe	638 ± 66	**1370 ± 14**	56600 ± 3990	**83300 ± 1160**	2030 ± 353	2010 ± 26

Net line intensities were calculated by subtracting the background intensities from the signal intensities prior to the determination of the concentrations of the selected elements. The concentrations of the elements obtained using LIBS varied between 0.060 and 0.707 mg/g for Cr, 0.895 and 3.64 mg/g for Mn, and, 26.9 and 71.8 mg/g for Fe, while F-AAS results varied between 0.061 and 1.37 mg/g for Cr, 1.24 and 4.46 mg/g for Mn and, 49.0 and 83.3 mg/g for Fe. The mean concentrations of the metals obtained using LIBS were: Cr: 0.259 mg/g; Mn: 1.95 mg/g; and Fe: 52.4 mg/g, while the results obtained using F-AAS were: Cr: 0.369 mg/g; Mn:

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[5] The maximum values for the specific element from the totality of the sampling areas.

2.15 mg/g; and Fe: 67.4 mg/g as summarized in Table 9. Therefore, it can be concluded that the LIBS technique leads to underestimation of the obtained values as compared to the F-AAS technique.

Table 9. Summary of the results obtained for the composition of potentially toxic elements in sediment using LIBS and F-AAS.

Parameters	**Element**					
	Cr		**Fe**		**Mn**	
	LIBS	**F-AAS**	**LIBS**	**F-AAS**	**LIBS**	**F-AAS**
Selected wavelength, nm	425.43	357.9	404.58	248.3	403.076	279.5
LOD, µg/g	42.9	0.120	79.0	0.510	38.9	0.250
R for calibration graph	0.9981	1	0.9997	0.9997	0.9989	0.9999
Minimum concentration, µg/g	59.6	60.7	26900	49000	895	1240
Maximum concentration, µg/g	707	1370	71800	83300	3640	4460
Average concentration, µg/g	259	369	52400	67400	1950	2150
Maximum RSD values	≤ 20%	≤ 5%	≤ 20%	≤ 5%	≤ 20%	≤ 5%

In general, area wise comparison shows that areas where less number of industries (such as Biheretsigie and Gefersa) have the lowest concentrations the potentially toxic elements, while areas with large number of industries (such as AA TAR Kolfe and AA Melkaqurani) have the highest concentrations of the selected metals. The high levels of the potentially toxic elements are therefore attributed to an increase in anthropogenic activities around the areas. Melaku *et al.* (2005a) determined selected potentially toxic elements, including Cr and Mn, in sediment samples collected from TAR by ICP-MS. They reported values ranged from 0.061–16.3 mg/g and 1.20–6.48 mg/g, for Cr and Mn, respectively. The values obtained in this work are reported in the literature are comparable.

4.2.9. Assessment of sediment contamination based on SQGs

Numerical SQGs have been used to identify contaminants of concern in aquatic ecosystem (MacDonald *et al*. 2000). Sediments could be classified as non-polluted, moderately polluted and heavily polluted, based on SQGs specified by the United States Environmental Protection Agency (US EPA) (US EPA 1992; Long *et al*. 1995; Perin *et al*. 1997; Bakan and Ozkoc 2007; Harikumar *et al*. 2009; Nasir and Harikumar 2011). There are no SQG values for Mn and Fe. As can be seen from the results, with reference to SQGs (Table 10), Akaki River is heavily polluted by Cr.

Table 10. Concentration of potentially toxic elements in the sediment in comparison with SQGs.

Element mg/kg	**Mean LIBS**	**Mean F-AAS**	**SQG non-polluted**	**SQG moderately polluted**	**SQG heavily polluted**
Cr	259	369	< 25	25-75	> 75

4.3. Distribution of Mercury in the Sediments of some Freshwater Bodies of Ethiopia

4.3.1. Precision, accuracy and LOD

The validity of the method was proven by the agreement between the measured and certified concentrations of mercury in CRMs of sediments and soils (Table 11). Discrepancies between concurrent measurements did not exceed 5% at the 95% confidence level for different sample masses. The RSD did not exceed 11% (Table 11).

Table 11. Concentrations of Hg in CRMs of sediments and soils (mean ± SD, in µg/kg).

Certified Reference Material	**Average concentration**	**Certified value**	**Recovery, %**
Standard Reference Material 2587	275 ± 7.1	290.0 ± 9.0	94.7
Standard Reference Material 2709a	856 ± 67	900.0 ± 200	95.1
Certified Reference Material 320R	848 ± 63	850.0 ± 90	99.7
Certified Reference Material 7002	92.2 ± 5.4	90.0 ± 12	102

Due to the absence of samples of sediment without mercury, which could have been used as blanks, the LOD for mercury in sediment samples was calculated from the equation of the calibration curve (Miller and Miller 2005). Consequently, masses ranging from 8 to 23 mg of a CRM of Tibetan soil with estimated mercury concentration of 18 µg/kg was used. The calibration curve was plotted as the mass of CRM (mg) versus peak area (arbitrarily unit). The calibration curve is shown in Figure 13.

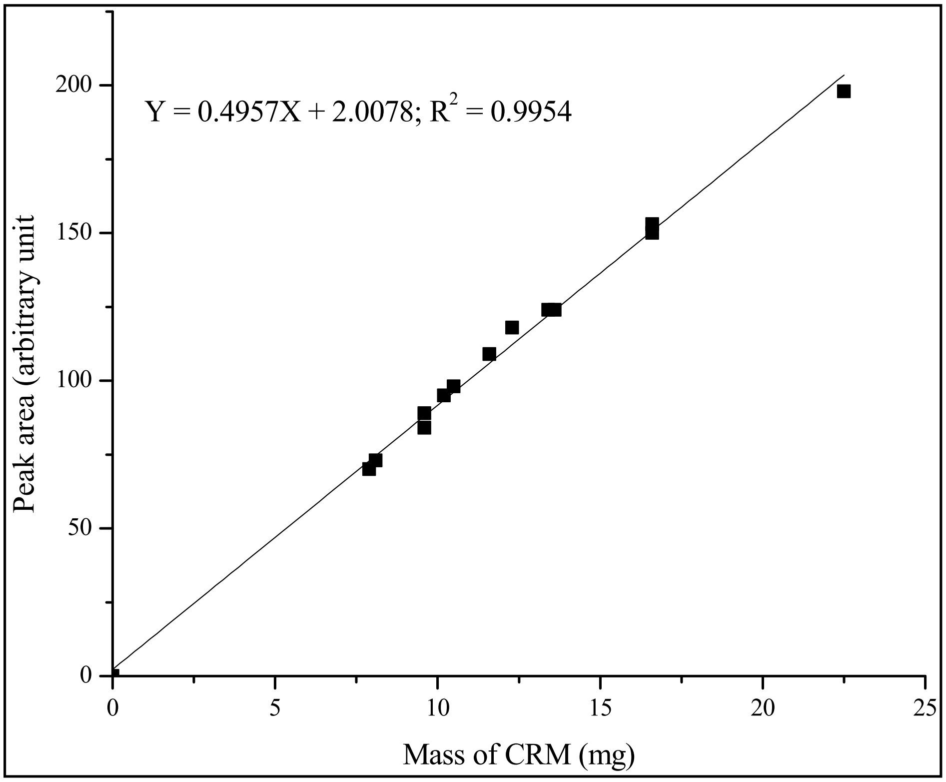

Figure 13. Calibration curve for Hg constructed using different masses of CRM of Tibetan soil (NCS DC 78302).

From the calibration curve, the minimum absolute mass of Hg that can be detected was found to be 13 pg of Hg. The typical mass of soil sample used for this analysis was 250 mg; the LOD in concentration unit was 0.05 µg/kg. Grobecker and Detcheva (2006) reported a LOD of 2.4 µg/kg using CRMs of different origin and using a solid sampling with a specially designed furnace and Zeeman atomic absorption spectrometry. Even if Grobecker and Detcheva (2006) used Zeeman atomic absorption spectrometry similar to the one used by the current method of ours, the difference could arise from the one-step temperature programming making incomplete combustion of Hg and also the usage of laboratory specially designed furnace (Ni-Cr alloy) in the former technique.

The present method is more sensitive than using F-AAS (0.7 µg/kg (Frazier *et al*. 2000)), CV-AAS (1 µg/kg (Tomiyasu *et al*. 2000), 1.5 µg/kg (Ullrich *et al*. 2007), and 5 mg/kg (Cossa and Gobeil 2000)), FI-CV-AAS (0.7 mg/kg (Desy *et al*. 2000)), CV-AFS (5 µg/kg (Berto *et al*. 2006)), and fluorescence spectrometry (0.075 µg/kg (Kainz *et al*. 2003)), but less sensitive than ICP-MS (1 ng/kg (Thompson-Roberts and Pick 2000)).

4.3.2. Mercury in sediment samples

The concentrations of total mercury in the sediment samples are summarized in Table 12.

Table 12. Concentrations of Hg (mean ± SD, in ng/g) in sediment samples of Akaki River, Lake Awassa and Lake Ziway, Ethiopia using elemental mercury analyzer.

Sample area name	**Average concentration, µg/kg**
AA Biheretsigie	10.5 ± 0.7
AA Bulbula	13 ± 1.0
AA Entoto	26.3 ± 1.1
AA Gefersa	16.5 ± 0.7
AA Kebena	81.5 ± 3.5
AA Kera	29.0 ± 1.0
AA Kidanemihret before TAR	**110 ± 6.4**[6]
AA Melkaqurani before TAR	3.90 ± 0.6
AA TAR Alert	47.5 ± 4.9
AA TAR before Kidanemihret	16.0 ± 0.1
AA TAR before Melkaqurani	38.0 ± 2.8
AA TAR Kaliti	24.0 ± 1.5
AA TAR Kolfe	13.5 ± 0.7
AA TAR with Kidanemihret	74.5 ± 2.1
AA TAR with Melkaqurani	14.0 ± 1.2
AA TlAR at KK Textile Factory	4.20 ± 0.10
AA TlAR with TAR at Aba Samuel	24.3 ± 2.1
Awassa Amoragedel	26.0 ± 1.3
Awassa Asamaber	12.3 ± 0.2
Awassa Buko	17.0 ± 1.2
Awassa Deset	16.0 ± 0.02
Awassa Fidelserawit	16.5 ± 0.7
Awassa Kerisa	67.0 ± 1.5
Awassa Mezinagna	35.5 ± 0.7
Awassa Muate	7.07 ± 0.1
Awassa Samijersa	7.70 ± 0.6
Awassa Shewaber	20.0 ± 2.8
Awassa Tikurwuha	45.5 ± 0.7
Awassa Wondotika	14.0 ± 1.3
Ziway Bochesa	33.0 ± 1.4
Ziway Debresina	40.5 ± 2.1
Ziway Gabriel	84.0 ± 2.8
Ziway Gelila	**110 ± 5.7**
Ziway Korekonch	22.5 ± 0.7
Ziway Mezinagna	16.5 ± 0.7
Ziway Sedeicha	43.5 ± 0.7
Ziway Shalo	30.0 ± 2.8
Ziway Wameicha	36.5 ± 0.7
Ziway Wofdeset	24.0 ± 2.8

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[6] The maximum values for the specific element from the totality of the sampling areas.

As can be seen from the table, the concentration ranges are between 3.9 to 110 µg/kg for Akaki River, 12 to 67 µg/kg for Lake Awassa, and 17 to 110 µg/kg for Lake Ziway. When compared to Lake Awassa, Lake Ziway had a higher concentration of mercury. The average values for the areas are 24 µg/kg for Lake Awassa, 32 µg/kg for Akaki River, and 44 µg/kg for Lake Ziway.

As to our knowledge there is no other work done for mercury in sediment in the area under investigation, therefore, the data obtained in this study could be used as a baseline for future studies. In addition, Ethiopia does not have the guidelines for mercury concentration in sediment samples and thus, the results are compared with the international guidelines. The total mercury concentration in all the samples is below the maximum allowed limit in US EPA guideline, which is 200 µg/kg for sediment (US EPA 2000a,b). The obtained results are also within the range for mercury concentrations in sediments of aquatic systems reported by Di Leonardo *et al.* (2006), ranged between 10 µg/kg and $5x10^5$ µg/kg. Camargo (2002) suggested that values of mercury lower than 100 µg/kg may be related to natural (unpolluted) areas, while values higher than 1000 µg/kg are generally found in contaminated areas. Hence, the sources of mercury in the present study areas can be related to natural, rather than anthropogenic origin.

Comparing the measured mercury concentrations to the US EPA regulations (Ligero *et al.* 2002) may be employed to assess the extent of anthropogenic pollution in the investigated sediments. According to the US EPA regulation, sediments with mercury concentrations below 300 µg/kg are considered not polluted. This was the case for the analyzed sediments (Table 12). However, mercury is known for its biomagnification[7] and bioconcentration[8], which are functions of age, species and trophic position in the food web (Watras and Bloom 1992; Weiner and Shields 2000;

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[7] Biomagnification occurs when a higher level predator eats a lower level organism and ingests the substance with it.

[8] Bioconcentration occurs when the material is absorbed from water, and the intake is less than the output.

Williams *et al*. 2011) and also metabolized slowly (Burrini and Cagnini 1997). Because mercury is distributed globally and its release from one country has the potential to be a component of deposition in another, it is critical to have knowledge of the amount released from natural and anthropogenic sources as well as the potential for transport, deposition and recycling. This knowledge can be used to formulate regulatory actions for reducing the impact of mercury on health and the environment.

4.4. Potentially Toxic Elements in Freshwater Bodies of Ethiopia

4.4.1. Internal standardization[9] and analytical performances of ICP-MS

For monitoring the concentrations of potentially toxic elements in the water samples using ICP-MS, careful selection of the isotopes of the given element is critical. When the element of interest had more than one isotope, the masses of at least two were monitored and the isotope with lower interference and higher abundance was selected. Accordingly, the following isotopes were used for the final analysis: ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{68}Zn, ^{82}Se, ^{107}Ag, ^{114}Cd, ^{120}Sn, ^{202}Hg and ^{208}Pb.

In ICP-MS, internal standardization is used to correct for instrumental instability and/or signal drift and non-spectral interferences, consequently for obtaining better accuracy and precision. Moreover, if analyte elements are spread over a wide range of atomic masses, one internal standard will not suffice, but several carefully selected internal standards must be used (Vandecasteele *et al*. 1988; Vanhaecke *et al*. 1992; Shinohara *et al*. 1998, Sartoros and Salin 1999; Oconnor *et al*. 2003; Wang *et al*. 2003; Ataro *et al*. 2008; Finley-Jones *et al*. 2008; Finely-Jones and Holcombe 2009). Evidently, the internal standard(s) should be chosen based on the closeness in mass number and ionization potential to that of the analyte of interest (Ataro *et al*. 2008; Finley-Jones *et al*. 2008; Finely-Jones and Holcombe 2009). Accordingly, multi-element internal standards, containing Ga for V, Cr, Mn, Fe, Co, Ni, Cu, Zn and Se; In for Ag, Cd and Sn; and Tl for Hg and Pb were used.

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[9] Internal standardization is the normalization of all data to a non-analyte isotope present in the same or known concentrations in all samples and standards. Ideally, internal standards should be un-interfered, mono-isotopic species.

All analytes were quantified using linear calibration functions established from the analysis of a blank and a series of standard solutions with typical correlation coefficients > 0.999 for all analytes. Instrument calibration was checked periodically with standards containing the analytes of interest at 10 and/or 20 µg/L (mg/L for Fe and Zn) and results within ± 10% of the nominal value were considered.

4.4.2. The LOD of potentially toxic elements in water samples using ICP-MS

The LODs of the selected potentially toxic elements in the water samples were determined by analyzing blanks based on three times the standard deviation of the average of ten individual prepared blank solutions (Table 13).

Table 13. Summary of the LODs and analytical quality as determined using SRM 1643e for the analyzed elements using a ELAN DRC-e ICP-MS instrument in the presence of Ga, In and Tl multi-element internal standards.

Analyte	**LOD (µg/L)**	**Concentration in µg/L**	
		Measured	**Certified**
V	0.015	43.1 ± 0.69	37.9 ± 0.59
Cr	0.416	22.3 ± 0.28	20.4 ± 0.24
Mn	0.017	40.7 ± 2.1	39.0 ± 0.45
Fe	0.045[a]	94.0 ± 2.1	98.1 ± 1.4
Co	0.109	30.0 ± 0.47	27.1 ± 0.32
Ni	0.035	66.5 ± 0.58	62.4 ± 0.69
Cu	0.186	24.0 ± 0.48	22.8 ± 0.31
Zn	0.005[a]	76.1 ± 3	78.5 ± 2.2
Se	0.937	11.1 ± 0.14	12.0 ± 0.14
Ag	0.294	0.92 ± 0.08	1.06 ± 0.08
Cd	0.012	4.67 ± 0.02	6.57 ± 0.07
Sn	0.038	-	NA
Hg	0.289	-	NA
Pb	0.136	20.7 ± 0.22	19.6 ± 0.21

[a]The LODs for Fe and Zn are in mg L^{-1}; NA - data not available.

The calculated LOD indicated that all the analyzed elements had good or acceptable LODs. The obtained LODs for V, Cr, Ni, Se, Cd and Hg are better and, for Mn and Cu are comparable with those reported for the same elements in Italian tap water by Cidu *et al*. (2011).

4.4.3. Analytical quality

Trace element concentrations determined in SRM 1643e for the analyzed elements with the exception of Hg and Sn were used to validate the method. Reproducibility has been estimated by calculating the RSD; relative differences between the measured concentration and the certified concentration for specific elements are reported as percent error ($\%Error = 100 \times (C_M - C_C)/C_C$, where C_M and C_C are measured and certified concentrations, respectively). Results on the analytical quality are reported in Table 13. The precision of the entire analytical procedure for each element was estimated by calculating the RSD and in all cases it was found to be in a range of ± 10%.

4.4.4. Concentration of potentially toxic elements in water samples using ICP-MS

Total elemental concentrations of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Ag, Cd, Sn, Hg and Pb in water samples were determined simultaneously using ICP-MS. Table 14 shows the analytical results (mean ± standard deviation) for the water samples from Akaki River, Lake Awassa and Lake Ziway.

Table 14. Potentially toxic elements concentrations (mean ± SD, in µg/L) in water samples of Akaki River, Lake Awassa and Lake Ziway by ICP-MS.

Area	**V**	**Cr**	**Mn**	**Fe**	**Co**
AA Biheretsigie	4.50 ± 0.29	1.95 ± 0.09	1110 ± 97	269 ± 23	0.78 ± 0.01
AA Bulbula	2.75 ± 0.20	1.67 ± 0.16	661 ± 27	255 ± 14	0.93 ± 0.03
AA Entoto	3.64 ± 0.35	1.49 ± 0.02	125 ± 11	468 ± 30	1.4 ± 0.12
AA Gefersa	1.07 ± 0.03	< 0.416	2.94 ± 0.11	131 ± 12	0.43 ± 0.47
AA Kebena	0.92 ± 0.04	0.88 ± 0.04	1460 ± 68	447 ± 35	0.44 ± 0.04
AA Kera	2.90 ± 0.12	0.97 ± 0.09	734 ± 36	194 ± 8	0.55 ± 0.04
AA Kidanemihret before TAR	3.05 ± 0.20	1.23 ± 0.22	965 ± 76	335 ± 24	0.80 ± 0.02
AA Melkaqurani before TAR	0.93 ± 0.13	0.78 ± 0.16	1.05 ± 0.07	49.0 ± 4.2	0.38 ± 0.03
AA TAR Alert	4.67 ± 0.34	3.26 ± 0.13	750 ± 35	126 ± 12	**1.99 ± 0.13**
AA TAR before Kidanemihret	3.79 ± 0.27	2.10 ± 0.06	251 ± 22	< 0.045	1.02 ± 0.03
AA TAR before Melkaqurani	1.84 ± 0.18	5.99 ± 0.31	**1580 ± 135**	111 ± 5.0	0.96 ± 0.01
AA TAR Kaliti	5.14 ± 0.44	**83.0 ± 8.1**	1070 ± 99	291 ± 16	0.80 ± 0.03
AA TAR Kolfe	3.75 ± 0.18	46.2 ± 3.2	1210 ± 101	202 ± 14	1.27 ± 0.02
AA TAR with Kidanemihret	3.32 ± 0.23	2.72 ± 0.40	1210 ± 3	361 ± 21	1.17 ± 0.01
AA TAR with Melkaqurani	3.80 ± 0.14	7.04 ± 0.16	545 ± 33	196 ± 11	1.37 ± 0.02
AA TlAR at KK Textile Factory	1.22 ± 0.10	1.63 ± 0.02	638 ± 30	531 ± 40	2.00 ± 0.02
AA TlAR with TAR at Aba Samuel	1.30 ± 0.20	2.37 ± 0.06	1160 ± 10	330 ± 70	6.67 ± 0.08
Awassa Amoragedel	1.67 ± 0.14	2.42 ± 0.43	33.6 ± 2.2	272 ± 19	< 0.109
Awassa Asamaber	7.30 ± 0.08	3.86 ± 0.06	190 ± 20	37 ± 1.1	< 0.109
Awassa Buko	4.13 ± 0.14	1.11 ± 0.24	11.3 ± 0.9	176 ± 1.4	< 0.109
Awassa Deset	3.97 ± 0.21	1.95 ± 0.78	19.0 ± 1.3	154 ± 5.0	< 0.109
Awassa Fidelserawit	4.85 ± 0.35	4.84 ± 0.78	23.6 ± 1.4	162 ± 7.8	< 0.109
Awassa Kerisa	2.73 ± 0.23	2.29 ± 0.46	12.1 ± 0.9	176 ± 13	< 0.109
Awassa Mezinagna	3.26 ± 0.30	2.95 ± 0.52	14.8 ± 0.9	139 ± 11	< 0.109
Awassa Muate	5.83 ± 0.39	3.57 ± 0.05	3.57 ± 0.1	87 ± 1.1	< 0.109
Awassa Samijersa	5.59 ± 0.36	3.05 ± 0.05	3.05 ± 0.1	34 ± 1.1	< 0.109
Awassa Shewaber	2.67 ± 0.21	2.21 ± 0.10	21.4 ± 1.2	59.3 ± 4.0	< 0.109
Awassa Tikurwuha	2.93 ± 0.28	1.34 ± 0.38	14.1 ± 0.6	94.0 ± 8.5	< 0.109
Awassa Wondotika	3.91 ± 0.33	4.64 ± 0.79	15.7 ± 1.0	143 ± 13	< 0.109
Ziway Bochesa	15.3 ± 1.3	2.09 ± 0.13	19.8 ± 1.2	1254 ± 71	0.38 ± 0.09
Ziway Debresina	18.7 ± 1.8	3.74 ± 0.37	32.7 ± 2.0	**1760 ± 121**	0.54 ± 0.05
Ziway Gabriel	11.1 ± 0.71	3.37 ± 0.23	17.6 ± 1.1	1080 ± 57	0.231 ± 0.03
Ziway Gelila	16.6 ± 1.3	4.63 ± 0.73	27.0 ± 1.6	1380 ± 69	0.55 ± 0.17
Ziway Korekonch	9.82 ± 0.69	2.12 ± 0.28	7.59 ± 0.34	331 ± 8	< 0.109
Ziway Mezinagna	9.88 ± 0.76	3.78 ± 0.24	17.3 ± 1.0	769 ± 48	0.31 ± 0.04
Ziway Sher	17.8 ± 1.28	7.11 ± 1.96	31.0 ± 1.5	1690 ± 81	0.47 ± 0.00
Ziway Shalo	11.9 ± 0.56	2.11 ± 0.07	17.8 ± 0.7	890 ± 21	0.35 ± 0.02
Ziway Wameicha	17.6 ± 0.94	3.02 ± 0.29	28.2 ± 1.0	1410 ± 54	0.40 ± 0.03
Ziway Wofdeset	**18.8 ± 1.7**[10]	6.98 ± 0.65	32.4 ± 2.0	1680 ± 120	0.90 ± 0 .01

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[10] The maximum values for the specific element from the totality of the sampling areas.

Continued ...

Area	**Ni**	**Cu**	**Zn**	**Se**	**Ag**
AA Biheretsigie	6.28 ± 0.19	1.59 ± 0.17	14.3 ± 1.2	< 0.937	< 0.294
AA Bulbula	3.91 ± 0.19	2.67 ± 0.04	16.3 ± 0.6	< 0.937	< 0.294
AA Entoto	1.18 ± 0.05	1.70 ± 0.16	13.7 ± 1.1	0.253 ± 0.013	< 0.294
AA Gefersa	2.68 ± 0.29	1.10 ± 0.06	5.50 ± 0.71	< 0.937	0.33 ± 0.01
AA Kebena	3.40 ± 0.09	0.77 ± 0.08	11.7 ± 0.6	< 0.937	< 0.294
AA Kera	8.84 ± 0.12	2.45 ± 0.23	14.7 ± 0.6	1.09 ± 0.03	< 0.294
AA Kidanemihret before TAR	9.20 ± 0.37	2.23 ± 0.12	12.3 ± 1.2	1.07 ± 0.08	< 0.294
AA Melkaqurani before TAR	4.67 ± 0.21	1.43 ± 0.05	11.0 ± 0.9	< 0.937	0.92 ± 0.01
AA TAR Alert	7.29 ± 0.66	4.66 ± 0.22	17.5 ± 0.7	< 0.937	0.67 ± 0.07
AA TAR before Kidanemihret	6.25 ± 0.20	1.73 ± 0.16	11.5 ± 0.7	< 0.937	0.61 ± 0.03
AA TAR before Melkaqurani	3.86 ± 0.12	1.48 ± 0.08	13.7 ± 0.6	< 0.937	1.09 ± 0.11
AA TAR Kaliti	8.33 ± 0.39	2.36 ± 0.22	13.5 ± 0.7	< 0.937	< 0.294
AA TAR Kolfe	5.45 ± 0.11	3.41 ± 0.31	16.0 ± 1.0	1.01 ± 0.08	0.31 ± 0.01
AA TAR with Kidanemihret	**12.8 ± 0.76**	2.58 ± 0.12	18.7 ± 1.5	1.21 ± 0.11	0.85 ± 0.02
AA TAR with Melkaqurani	6.60 ± 0.37	3.18 ± 0.19	15.7 ± 0.6	< 0.937	0.46 ± 0.03
AA TlAR at KK Textile Factory	9.15 ± 0.10	2.81 ± 0.05	13.6 ± 1.2	1.12 ± 0.03	< 0.294
AA TlAR with TAR at Aba Samuel	14.6 ± 0.2	1.94 ± 0.05	13.9 ± 1.3	1.43 ± 0.03	< 0.294
Awassa Amoragedel	2.59 ± 0.16	3.36 ± 0.29	38.7 ± 1.5	1.19 ± 0.02	**1.50 ± 0.18**
Awassa Asamaber	13.6 ± 0.1	2.47± 0.31	9.0 ± 0.6	1.13 ± 0.12	< 0.294
Awassa Buko	1.20 ± 0.05	2.78 ± 0.08	8.67 ± 0.6	1.18 ± 0.01	0.71 ± 0.08
Awassa Deset	1.56 ± 0.12	2.84 ± 0.15	10.7 ± 0.6	1.12 ± 0.06	< 0.294
Awassa Fidelserawit	3.38 ± 0.03	4.28 ± 0.40	13.3 ± 0.6	1.03 ± 0.02	0.50 ± 0.07
Awassa Kerisa	2.81 ± 0.21	1.92 ± 0.36	18.7 ± 1.2	1.20 ± 0.05	0.81 ± 0.04
Awassa Mezinagna	1.14 ± 0.10	2.71 ± 0.39	11.7 ± 0.6	1.24 ± 0.01	< 0.294
Awassa Muate	2.07 ± 0.19	2.03 ± 0.50	11.7 ± 0.6	1.12 ± 0.03	< 0.294
Awassa Samijersa	1.67 ± 0.16	2.25 ± 0.52	9.8 ± 0.6	1.17 ± 0.03	0.41 ± 0.08
Awassa Shewaber	0.43 ± 0.04	1.68 ± 0.10	7.67 ± 0.6	1.16 ± 0.02	< 0.294
Awassa Tikurwuha	1.12 ± 0.02	2.27 ± 0.04	7.00 ± 0.9	< 0.937	< 0.294
Awassa Wondotika	1.04 ± 0.05	3.10 ± 0.17	6.00 ± 0.9	1.65 ± 0.14	< 0.294
Ziway Bochesa	4.58 ± 0.31	3.92 ± 0.18	21.7 ± 0.6	1.50 ± 0.03	< 0.294
Ziway Debresina	4.47 ± 0.09	6.10 ± 0.48	59.0 ± 3.0	**1.96 ± 0.04**	< 0.294
Ziway Gabriel	6.00 ± 0.17	3.31 ± 0.22	34.3 ± 1.2	1.17 ± 0.09	< 0.294
Ziway Gelila	10.9 ± 0.4	5.70 ± 0.34	42.3 ± 2.1	1.88 ± 0.12	< 0.294
Ziway Korekonch	3.52 ± 0.19	4.74 ± 0.23	29.7 ± 0.6	1.14 ± 0.04	< 0.294
Ziway Mezinagna	7.97 ± 0.70	4.40 ± 0.35	**300 ± 11**	0.99 ± 0.04	< 0.294
Ziway Sher	4.69 ± 0.37	5.73 ± 0.08	48.7 ± 1.5	1.79 ± 0.14	0.51 ± 0.04
Ziway Shalo	7.30 ± 0.17	5.96 ± 0.04	82.7 ± 2.3	1.35 ± 0.07	< 0.294
Ziway Wameicha	5.43 ± 0.32	5.23 ± 0.41	34.3 ± 0.6	1.48 ± 0.13	< 0.294
Ziway Wofdeset	3.78 ± 0.85	**12.4 ± 0.6**	272 ± 12	1.72 ± 0.04	< 0.294

Continued ...

Area	**Cd**	**Sn**	**Hg**	**Pb**
AA Biheretsigie	0.151 ± 0.01	0.376 ± 0.02	< 0.289	2.07 ± 0.03
AA Bulbula	0.114 ± 0.01	0.197 ± 0.01	< 0.289	1.42 ± 0.03
AA Entoto	0.272 ± 0.02	0.354 ± 0.03	< 0.289	1.76 ± 0.05
AA Gefersa	0.050 ± 0.01	0.177 ± 0.01	< 0.289	1.18 ± 0.07
AA Kebena	0.107 ± 0.01	0.132 ± 0.01	< 0.289	0.953 ± 0.03
AA Kera	0.127 ± 0.003	0.187 ± 0.001	< 0.289	2.40 ± 0.02
AA Kidanemihret before TAR	0.478 ± 0.03	0.406 ± 0.01	< 0.289	2.80 ± 0.14
AA Melkaqurani before TAR	0.247 ± 0.01	0.584 ± 0.002	< 0.289	6.24 ± 0.03
AA TAR Alert	0.195 ± 0.02	0.622 ± 0.02	< 0.289	5.50 ± 0.32
AA TAR before Kidanemihret	0.462 ± 0.01	0.448 ± 0.02	< 0.289	2.43 ± 0.11
AA TAR before Melkaqurani	0.244 ± 0.01	0.208 ± 0.001	< 0.289	1.78 ± 0.03
AA TAR Kaliti	0.161 ± 0.01	0.237 ± 0.02	< 0.289	2.52 ± 0.19
AA TAR Kolfe	0.437 ± 0.06	0.311 ± 0.03	< 0.289	4.17 ± 0.12
AA TAR with Kidanemihret	0.243 ± 0.02	0.398 ± 0.02	< 0.289	3.94 ± 0.22
AA TAR with Melkaqurani	0.278 ± 0.01	0.649 ± 0.03	< 0.289	4.38 ± 0.02
AA TlAR at KK Textile Factory	0.355 ± 0.016	0.344 ± 0.005	< 0.289	3.26 ± 0.17
AA TlAR with TAR at Aba Samuel	0.216 ± 0.002	0.346 ± 0.006	< 0.289	2.27 ± 0.20
Awassa Amoragedel	0.193 ± 0.01	0.767 ± 0.03	< 0.289	2.22 ± 0.12
Awassa Asamaber	0.414 ± 0.02	0.374 ± 0.01	< 0.289	< 0.136
Awassa Buko	0.129 ± 0.01	0.428 ± 0.02	< 0.289	1.63 ± 0.01
Awassa Deset	0.359 ± 0.02	0.747 ± 0.01	< 0.289	2.99 ± 0.13
Awassa Fidelserawit	0.447 ± 0.01	0.743 ± 0.02	< 0.289	3.26 ± 0.07
Awassa Kerisa	0.093 ± 0.003	0.874 ± 0.03	< 0.289	3.45 ± 0.18
Awassa Mezinagna	< 0.012	0.495 ± 0.02	< 0.289	0.445 ± 0.03
Awassa Muate	0.117 ± 0.05	0.312 ± 0.01	< 0.289	< 0.136
Awassa Samijersa	0.370 ± 0.006	0.318 ± 0.01	< 0.289	2.92 ± 0.25
Awassa Shewaber	< 0.012	0.187 ± 0.01	< 0.289	0.198 ± 0.01
Awassa Tikurwuha	0.393 ± 0.01	0.444 ± 0.02	< 0.289	2.01 ± 0.07
Awassa Wondotika	0.135 ± 0.002	0.381 ± 0.01	< 0.289	0.514 ± 0.02
Ziway Bochesa	0.013 ± 0.001	0.469 ± 0.04	< 0.289	2.22 ± 0.07
Ziway Debresina	0.279 ± 0.01	2.14 ± 0.08	< 0.289	2.61 ± 0.05
Ziway Gabriel	0.175 ± 0.01	1.25 ± 0.02	< 0.289	1.44 ± 0.12
Ziway Gelila	0.248 ± 0.01	0.620 ± 0.06	< 0.289	1.82 ± 0.17
Ziway Korekonch	**0.633 ± 0.02**	1.14 ± 0.05	< 0.289	1.20 ± 0.10
Ziway Mezinagna	0.126 ± 0.01	0.907 ± 0.03	< 0.289	1.36 ± 0.08
Ziway Sher	0.227 ± 0.01	**4.76 ± 0.12**	< 0.289	1.51 ± 0.11
Ziway Shalo	0.302 ± 0.02	0.512 ± 0.03	< 0.289	5.18 ± 0.16
Ziway Wameicha	0.197 ± 0.01	0.496 ± 0.04	< 0.289	1.77 ± 0.05
Ziway Wofdeset	0.282 ± 0.03	0.792 ± 0.13	< 0.289	**7.18 ± 0.16**

It has been noted that the concentration of Cr, Mn, Co, Ni, Ag, Hg and Pb were generally highest in Akaki River, while V, Fe, Cu, Zn, Se, Cd and Sn were highest in Lake Ziway. For all elements, the lowest concentrations were observed in Lake Awassa. The possible reason in case of Akaki River could be the inappropriate and uncontrolled use of the river for the disposal of domestic and factory wastes, while for Lake Ziway the various small- and large-scale farming may have caused the pollution. The presence of high concentrations of Mn and Fe in the water might have contributed in the changed color of the water (besides due to the occurrence of algae, suspended matters and water weeds) in the areas (Davies 1996).

When compared to the maximum concentration of trace elements for drinking water quality in the Ethiopian section of the East African Rift Valley as reported by Reimann *et al*. (2003), both Lake Awassa and Lake Ziway (both are part of Ethiopian section of East African Rift Valley) have lower maximum concentration of all the analyzed elements, with the exception of Ag. Regarding TAR, the values obtained in this study are lower than those reported by Weldegebriel *et al*. (2012), which may be attributed to the difference in the sample locations.

4.4.5. Comparison of the concentration of potentially toxic elements in water with international guidelines for drinking and irrigation water

The average results of the concentration of potentially toxic elements in water of Akaki River, Lake Awassa and Lake Ziway were compared with the drinking water guideline values set by European Commission (EC) Council Directive (EC 1998) and World Health Organization, WHO (2011). It was also compared to the guidelines of international water quality for agriculture set by the Food and Agricultural Organization, FAO (Ayers and Westcot 1994) (Table 15).

Table 15. Summary of average concentration of potentially toxic elements (mean ± SD, in µg/L) in water samples of Akaki River, Lake Awassa and Lake Ziway, Ethiopia determined by ICP-MS compared to international guidelines.

Area	**V**	**Cr**	**Mn**	**Fe**	**Co**
Average all	6.66 ± 0.49	6.68 ± 0.69	361 ± 23	503 ± 28	0.516 ± 0.04
Average Akai River	3.03 ± 0.20	11.3 ± 0.94	824 ± 52	212 ± 15	0.921 ± 0.06
Average Awassa	3.35 ± 0.24	2.64 ± 0.50	18.4 ± 1.2	153 ± 10	< 0.038
Average Ziway	14.7 ± 1.1	3.90 ± 0.50	23.1 ± 1.3	1224 ± 65	0.413 ± 0.04
EC Directive[11]	-	50	50	-	-
WHO Guidelines[12]	-	50[13,14]	400[15]	-	-
RMC for irrigation water[16]	100	100	200	5000	50
Area	**Ni**	**Cu**	**Zn**	**Se**	**Ag**
Average all	4.95 ± 0.26	3.46 ± 0.21	37.6 ± 1.5	0.882 ± 0.04	0.281 ± 0.02
Average AA	6.40 ± 0.29	2.26 ± 0.15	13.7 ± 0.75	0.313 ± 0.02	0.375 ± 0.02
Average Awassa	1.70 ± 0.09	2.77 ± 0.22	13.6 ± 0.62	1.08 ± 0.04	0.392 ± 0.04
Average Ziway	5.87 ± 0.36	5.76 ± 0.30	92.5 ± 3.5	1.50 ± 0.07	0.051 ± 0.01
EC Directive	20	2000	-	10	-
WHO Guidelines	70	2000	-	10	-
RMC for irrigation water	200	200	2000	20	-
Area	**Cd**	**Sn**	**Hg**	**Pb**	
Average all	0.228 ± 0.01	0.699 ± 0.03	< 0.289	2.57 ± 0.09	
Average AA	0.235 ± 0.02	0.352 ± 0.02	< 0.289	2.99 ± 0.10	
Average Awassa	0.194 ± 0.01	0.563 ± 0.02	< 0.289	1.86 ± 0.07	
Average Ziway	0.248 ± 0.01	1.31 ± 0.06	< 0.289	2.63 ± 0.11	
EC Directive	5	-	0.1	10	
WHO Guidelines	3	-	0.6[17]	10	
RMC for irrigation water	10	-	-	5000	

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[11] European Commission Directives 1998.

[12] World Health Organization 2011.

[13] Provisional guideline value, as there is evidence of hazard, but the available information on health effect is limited.

[14] Total Cr.

[15] Concentrations of the substance at or below the health-based guideline value may affect the appearance, taste or odor of the water, leading to consumer complaints.

[16] Ayers and Westcot 1994 (RMC – Recommended maximum concentration) – the guidelines of international water quality for agriculture set by FAO.

[17] Inorganic Hg.

The concentration of V was present in the range of 0.920–18.8 µg/L in the analyzed water samples. For V, no detrimental health effects from drinking water have been reported by an international organization (EC 1998; WHO 2011). The obtained values are less than the international guidelines value for irrigation water, 100 µg/L (Ayers and Westcot 1994).

Total Cr concentrations in the analyzed water samples found to be < 0.416–83.0 µg/L, where for all, except TAR at Kaliti, the concentration are within the desirable limit of Cr specified as 50 µg/L for drinking water (EC 1998; WHO 2011). The highest value for TAR at Kaliti area could be due to the presence of tannery factories, which dispose of their effluents directly and/or indirectly into the river. The values obtained in most of the areas are less than the Norwegian recommended value (< 10 µg/L) and maximum acceptable value (< 50 µg/L), and the uncontaminated background concentration of a standard from the Netherlands (20 µg/L) (Banks *et al*. 1995). The obtained values are also less than the international guidelines value for irrigation water of 100 µg/L (Ayers and Westcot 1994).

The concentrations of Mn in the analyzed samples were found to range from 1.05–1580 µg/L. The desirable limit is specified as 50, 500 and 400 µg/L for drinking water by EC (1998) and WHO (2011), respectively. The values obtained for Lake Awassa and Lake Ziway are less than the Norwegian recommended value (< 50 µg/L) while Akaki River values are higher than even the Norwegian maximum acceptable value (< 100 µg/L) (Banks *et al*. 1995). The obtained values in some areas are also higher than the international guidelines value for irrigation water, 200 µg/L (Ayers and Westcot 1994). Therefore, urgent actions by the concerned government authorities are highly recommended.

The concentration of iron is found in natural freshwaters at levels ranging from 500 to 50000 µg/L (Davies 1996). The samples analyzed contained Fe in the range of <0.045–1760 µg/L, which is much lower than natural freshwater values. It may also be present in drinking water as a result of the use of Fe coagulants or the corrosion of steel and cast Fe pipes during water distribution. No guideline value for Fe in drinking water is proposed by the WHO or EC due to the reason that Fe. In addition, since the taste and appearance of water are affected by concentrations below the health-based value (EC 1998; WHO 2011). There is usually no noticeable taste at Fe concentrations < 300 mg/L, although turbidity and color may develop (WHO 2011; Abdul *et al*. 2012). The values obtained in this analysis are much lower than the Norwegian recommended value (< 100 mg/L) (Banks *et al*. 1995). The obtained values are also less than the international guidelines value for irrigation water of 5 mg/L (Ayers and Westcot 1994).

The concentration of Co in the analyzed water samples was found to be < 0.109–1.99 µg/L. The EC (1998) and WHO (2011) have not established guidelines for Co in drinking water probably due to the assumption that the concentration of Co in the drinking water was significantly low (Abdul *et al*. 2012). The value obtained in this analysis is much less than the uncontaminated background concentration (20 µg/L) of a standard from the Netherlands (Banks *et al*. 1995). The obtained concentrations are also less than the international guideline values for irrigation water of 50 µg/L (Ayers and Westcot 1994).

The concentration of Ni in water samples ranged from 0.432–12.8 µg/L, which implies that all of the samples being contained Ni at levels the permissible limit. The maximum recommended value for Ni in drinking water is 20 and 70 µg/L given by EC (1998) and WHO (2011), respectively. The values obtained in this analysis are less than the uncontaminated background concentration of a standard from the Netherlands (20 µg/L) (Banks *et al*. 1995). The obtained values are also much lower than the international guideline values for irrigation water, 200 µg/L (Ayers and Westcot 1994).

The concentrations of Cu in water samples ranged from 0.765–12.4 µg/L. The desirable limit of Cu in drinking water is 2 mg/L, above that Cu also imparts color and causes an undesirable bitter taste to water (EC 1998; WHO 2011). The values obtained in this work are much lower than both Norwegian recommended value (< 100 µg/L), and maximum acceptable value (300 µg/L), and lower than the uncontaminated background concentration of a standard from the Netherlands (20 µg/L) (Banks *et al*. 1995). The obtained values are also less than the international guideline values for irrigation water of 200 µg/L (Ayers and Westcot 1994).

In the analyzed water samples, Zn was present at levels ranging from 5.50–300 µg/L and hence below the Ethiopian guideline. No health-based guideline values have been proposed for Zn in drinking water (EC 1998; WHO 2011). The values obtained in this analysis are less than the Norwegian recommended maximum value (300 µg/L) (Banks *et al*. 1995). The obtained values are also less than the international guideline values for irrigation water of 2 mg/L (Ayers and Westcot 1994).

The concentrations of Se in the water samples ranged from <0.937–1.96 µg/L. The levels of Se in drinking water vary greatly in different geographical areas but the international guideline value for drinking water is 10 µg/L (EC 1998; WHO 2011). Hence, all the samples are within the permissible limit. The obtained values are also lower than the international guideline value of 20 µg/L for irrigation water (Ayers and Westcot 1994).

The concentration of Ag was found in the range of < 0.294–1.50 µg/L. There is no adequate data with which to derive a health-based guideline value for Ag in drinking and irrigation water (Ayers and Westcot 1994; EC 1998; WHO 2011).

The concentration of Cd in the study areas ranged from < 0.012–0.633 µg/L, which is well below the recommended maximum permissible limit for Cd in drinking water of 3 µg/L (WHO 2011) and 5 µg/L (EC 1998), the Norwegian recommended value (< 1 µg/L) and maximum accepted value (5 µg/L), and the uncontaminated background concentration of a standard from the Netherlands (1 µg/L) (Banks *et al*. 1995). The obtained values are also less than the international guideline values for irrigation water of 10 µg/L (Ayers and Westcot 1994).

The concentration of Sn in the study area was found in the range of 0.132–4.76 µg/L. For the general population, drinking water is not a significant source of Sn. However, there is an increased use of Sn in solder, which may be used in domestic plumbing, and a corrosion inhibitor. Therefore, the presence of Sn in drinking-water does not represent a hazard to human health (EC 1998; WHO 2011).

The concentration of Hg in all water samples were below the LOD (0.289 µg/L). The recommended guideline values for Hg are 0.1 and 0.6 µg/L for drinking water as given by the EC (1998) and WHO (2011), respectively, and hence the obtained values are within the permissible limit.

The concentrations of Pb in water samples ranged from <0.136–7.18 µg/L. The permissible limit of Pb concentration in drinking water is 10 µg/L (EC 1998; WHO 2011). For all of the samples, the concentrations were within the permissible limit. The concentrations obtained in this analysis are less than the Norwegian maximum acceptable value (20 μg/L) and the uncontaminated background concentration of a standard from the Netherlands (20 μg/L) (Banks *et al*. 1995). The obtained values are also well within the international guideline values for irrigation water of 5 mg/L (Ayers and Westcot 1994).

The results from the different areas (Addis Ababa – AR, Lake Awassa and Lake Ziway) are compared using one-way ANOVA. The results indicate that the means of the three areas are not significantly different for the elements Cr, Ag, Cd and Pb, however, for the remaining elements, the means of the three studied areas are significantly different.

4.5. Assessment of Potentially Toxic Elements in Swiss chard and Sediment of Akaki River, Lake Awassa and Lake Ziway, Ethiopia

4.5.1. Leaching methods and microwave-assisted digestion

Since the sample introduction system for the ICP-MS and ICP-OES require liquid samples, the sediment and plants samples were digested prior to analysis. For this purpose, digestion with 3:1:1:1, v/v, $HCl:HNO_3:HF:H_3BO_3$ was found to be suitable for determining the "total-recoverable" potentially toxic elements in sediments, while microwave-assisted acid solubilization proved to be the most suitable method for the digestion of complex matrices, *i.e.*, sediments containing oxides, clay, silicates and organic substances (Bettinelli *et al*. 2000; Melaku *et al*. 2005a,b; Wilson *et al*. 2006; Gaudino *et al*. 2007; Esen and Balci 2008).

For plant samples an acid/oxidant mixture of 4:1 v/v, $HNO_3:H_2O_2$ was effective for the complete digestion (Itanna 2002; Margui *et al*. 2005; Oleszczuk *et al*. 2007; Bakkali *et al*. 2009; Kula *et al*. 2011; Marin *et al*. 2011). Here H_2O_2 is added in order to enhance the destruction of the organic matter.

4.5.2. Calibration curves and limit of detection

The calibration curves showed linearity ($r > 0.997$) of the detector response for the quantified elements. For the calculation of the LODs for ICP-MS and ICP-OES, ten separate blank solutions were analyzed. Due to the absence of samples of sediment without Hg, which could have been used as blanks, the LOD for Hg in sediment samples was calculated from the equation of the calibration curve (Mekonnen *et al*. 2012a). The calibration curve and LODs of the selected elements are summarized in Table 16.

Table 16. The LODs and calibration curve equations for the quantification of potentially toxic elements in plant and sediment samples using ICP-MS, ICP-OES and elemental mercury analyzer.

Element	**Calibration equation**	**Correlation coefficient (R) value**	**LOD for**	
			Sediment	**Plant**
V	Y = 13821X + 25488	0.99970	0.404	0.039
Cr	Y = 12221X + 14419	0.99952	0.829	0.729
Mn*	Y = 2518X – 2810	0.99961	0.343	0.039
Fe*	Y = 955X – 2051	0.99993	0.589	0.289
Co	Y = 14534X + 6780	0.99972	0.201	0.205
Ni	Y = 3151X + 2213	0.99941	0.079	0.683
Cu	Y = 7130X + 29824	0.99746	0.668	0.695
Zn*	Y = 47658X – 85914	0.99996	0.639	0.585
As	Y = 1306X + 1274	0.99928	0.161	0.013
Se	Y = 214X + 121	0.99944	0.951	0.941
Ag	Y = 12760X + 22273	0.99866	0.779	0.294
Cd	Y = 3493X + 2230	0.99938	0.027	0.014
Sn	Y = 832X + 2955	0.99935	0.316	0.03
Hg	Y = 0.4957X + 2.0078	0.99769	0.050	0.050
Pb	Y = 20196X + 11595	0.99953	0.152	0.225

*The unit for the LOD is in µg/mL while for the other elements is in ng/mL.

4.5.3. Analytical performance

The efficiency of the developed digestion procedure was evaluated for different CRMs and is reported as percent recovery. The obtained recoveries ranged from 87.2% (Se) – 103% (Zn), and 85.6% (Zn) – 109% (Mn) for sediment and plant samples, respectively. The percent error recovery of the method for most of elements is ±10, showing satisfactory recovery and then applicability of the developed method (Table 17).

Table 17. Recovery test for potentially toxic elements (mean ± SD, in mg/kg, n = 3) in CRMs measured using ICP-MS, ICP-OES and RA-915+ mercury analyzer.

Reference Material No.	V		Cr		Mn	
	Measured (% Recovery*)	Certified	Measured (% Recovery)	Certified	Measured (% Recovery)	Certified
320R	42.6 ± 1.9 (91.7)	46.5 ± 2.8	53.4 ± 0.1 (90.5)	59 ± 4	852 ± 9 (93.6)	910 ± 50
2709a	100 ± 0.2 (91.1)	110 ± 11	115 ± 10 (88.8)	130 ± 9	524 ± 15 (99.1)	529 ± 18
8704	84.3 ± 2.0 (89.2)	94.6 ± 4.0	101 ± 2 (90.0)	122 ± 4	545 ± 19 (100)	544 ± 21
1515	0.23 ± 0.03 (89.2)	0.26 ± 0.03	0.26 ± 0.06 (86.7)	0.3a	57 ± 0.4 (109)	54 ± 3
73348	2.1 ± 0.1 (87.4)	2.4 ± 0.3	2.2 ± 0.2 (97.2)	2.3 ± 0.3	52 ± 4 (90.2)	58 ± 6
	Fe		**Co**		**Ni**	
320R	24900 ± 380 (96.9)	25700 ± 1300	8.9 ± 0.2 (91.4)	9.7 ± 0.6	25.1 ± 1.2 (92.7)	27.1 ± 2.2
2709a	30100 ± 330 (89.4)	33600 ± 700	11.8 ± 0.6 (92.5)	12.8 ± 0.2	79.8 ± 2.5 (93.8)	85 ± 2
8704	36300 ± 1100 (91.4)	39700 ± 1000	13.3 ± 0.06 (98.1)	13.6 ± 0.43	39.5 ± 4.1 (92.2)	42.9 ± 3.7
1515	73 ± 2 (88.0)	83 ± 5	0.08 ± 0.1 (88.9)	0.09a	0.83 ± 0.15 (91.2)	0.91 ± 0.12
73348	967 ± 8 (94.8)	1020 ± 67	0.38 ± 0.03 (96.7)	0.39 ± 0.05	1.6 ± 0.0 (96.8)	1.7 ± 0.4
	Cu		**Zn**		**As**	
320R	42.3 ± 1.8 (91.4)	46.3 ± 2.9	325 ± 5 (102)	319 ± 20	19.6 ± 0.52 (90.5)	21.7 ± 2.0
2709a	30.6 ± 3.0 (90.3)	33.9 ± 0.5	106 ± 4 (103)	103 ± 4	9.62 ± 0.72 (91.6)	10.5 ± 0.3
8704	-	NA**	422 ± 3 (103)	408 ± 15	15.9 ± 0.1 (93.2)	17a
1515	5.21 ± 0.64 (92.4)	5.64 ± 0.24	10.7 ± 0.2 (85.6)	12.5 ± 0.3	0.034 ± 0.009 (89.5)	0.038 ± 0.007
73348	4.9 ± 0.1 (94.1)	5.2 ± 0.5	19.0 ± 0.2 (92.4)	20.6 ± 2.2	0.87 ± 0.08 (91.2)	0.95 ± 0.12
	Se		**Ag**		**Cd**	
320R	0.84 ± 0.05 (87.5)	0.96 ± 0.18a	-	NA	2.43 ± 0.19 (92.1)	2.64 ± 0.18
2709a	1.31 ± 0.18 (87.2)	1.5a	-	NA	0.354 ± 0.012 (92.7)	0.371 ± 0.002
8704	-	NA	-	NA	2.75 ± 0.40 (93.6)	2.94 ± 0.29
1515	0.048 ± 0.004 (95.1)	0.050 ± 0.009	-	NA	0.013 ± 0.002 (97.8)	0.013 ± 0.002
73348	0.176 ± 0.015 (95.6)	0.184 ± 0.013	0.259 ± 0.019 (96)	0.027 ± 0.006	0.12 ± 0.01 (88.4)	0.14 ± 0.06
	Sn		**Hg**		**Pb**	
320R	9.1 ± 0.0 (97.3)	9.4 ± 1.7[a]	0.79 ± 0.02 (93.1)	0.85 ± 0.09	81.5 ± 3 (95.8)	85 ± 5
2709a	-	NA	0.79 ± 0.01 (88.2)	0.9 ± 0.2	17.1 ± 0.1 (99.1)	17.3 ± 0.1
8704	-	NA	-	NA	152 ± 0.17 (101)	150 ± 17
1515	< 0.030	< 0.2[a]	0.045 ± 0.002 (103.4)	0.044 ± 0.004	0.450 ± 0.020 (95.8)	0.470 ± 0.024
73348	-	NA	-	NA	6.5 ± 0.6 (91.7)	7.1 ± 1.1

[a] Information concentration/Information value/Indicative value); *numbers in the parentheses are recovery values; **NA - data not available.

4.5.4. Analysis of sediment and Swiss chard samples for potentially toxic elements, and comparison with national and international guidelines

4.5.4.1.1. Elemental determination in the sample

The microwave digested aqueous samples were applied to determine the levels of potentially toxic elements in sediment and vegetable samples, while Hg was directly determined in sediment and vegetable samples. Each type of sample was analyzed in triplicate. The concentrations of the fifteen selected potentially toxic elements in sediment and plant samples from Akaki River, Lake Awassa and Lake Ziway are summarized in Table 18 and 19, respectively.

Table 18. Potentially toxic element concentrations (mean ± SD, in µg/kg (mg/kg for Mn, Fe and Zn)) in sediment samples of Akaki River, Lake Awassa and Lake Ziway, Ethiopia.

Area	**V**	**Cr**	**Mn**	**Fe**
AA Biheretsigie	13600 ± 250	31200 ± 1200	1600 ± 1	68300 ± 780
AA Bulbula	< 0.404	< 0.829	8600 ± 480	130000 ± 170
AA Entoto	17100 ± 840	24800 ± 760	4630 ± 350	123000 ± 2400
AA Gefersa	37100 ± 2060	45200 ± 2800	3780 ± 260	127000 ± 3850
AA Kebena	32100 ± 870	36500 ± 2000	2680 ± 15	105000 ± 4850
AA Kera	13900 ± 370	61600 ± 621	4450 ± 53	60700 ± 3190
AA Kidanemihret before TAR	8010 ± 240	28700 ± 400	5000 ± 91	114000 ± 8700
AA Melkaqurani before TAR	14900 ± 1350	17800 ± 210	6630 ± 450	121000 ± 5050
AA TAR Alert	13700 ± 480	32500 ± 760	6510 ± 610	**142000 ± 13800**
AA TAR before Kidanemihret	11800 ± 140	68700 ± 870	3320 ± 12	90700 ± 1390
AA TAR before Melkaqurani	17100 ± 320	35700 ± 1870	7740 ± 340	132000 ± 410
AA TAR Kaliti	18300 ± 260	32700 ± 2200	4290 ± 400	88700 ± 220
AA TAR Kolfe	20900 ± 450	**84300 ± 3100**	2560 ± 80	97100 ± 8130
AA TAR with Kidanemihret	7930 ± 500	18800 ± 320	5390 ± 490	109000 ± 1250
AA TAR with Melkaqurani	15900 ± 430	40100 ± 2100	5800 ± 6	114000 ± 4430
AA TlAR at KK Textile Factory	7250 ± 210	17100 ± 850	5270 ± 79	91200 ± 3320
AA TlAR with TAR at Aba Samuel	21600 ± 1600	20900 ± 370	2750 ± 7	85100 ± 580
Awassa Amoragedel	25500 ± 1290	74300 ± 7430	58300 ± 2950	2400 ± 86
Awassa Asamaber	12400 ± 540	5990 ± 299	43800 ± 426	2130 ± 3
Awassa Buko	16800 ± 248	44200 ± 757	39400 ± 510	1640 ± 15
Awassa Deset	18000 ± 323	30300 ± 1920	46800 ± 805	2320 ± 13
Awassa Fidelserawit	23900 ± 919	26200 ± 371	45500 ± 962	1550 ± 141
Awassa Kerisa	18000 ± 962	16600 ± 487	40700 ± 2710	2150 ± 149
Awassa Mezinagna	53400 ± 1601	19300 ± 673	6040 ± 162	1800 ± 26
Awassa Muate	38800 ± 3610	62000 ± 4980	52800 ± 324	2150 ± 152
Awassa Samijersa	34600 ± 1530	31900 ± 1814	44900 ± 807	2150 ± 65
Awassa Shewaber	32200 ± 1460	17500 ± 574	47800 ± 1320	1650 ± 1
Awassa Tikurwuha	75200 ± 5360	29000 ± 655	41000 ± 91	1380 ± 2
Awassa Wondotika	3350 ± 108	36200 ± 436	47400 ± 1930	2250 ± 97
Ziway Bochesa	53400 ± 2010	25600 ± 694	57000 ± 380	1830 ± 43
Ziway Debresina	65100 ± 3380	42400 ± 792	46700 ± 183	1680 ± 16
Ziway Gabriel	79300 ± 1500	40800 ± 1650	44800 ± 105	1070 ± 3
Ziway Gelila	62100 ± 2510	52500 ± 4820	**83500 ± 720**	855 ± 8
Ziway Korekonch	59500 ± 4540	63400 ± 1643	49820 ± 706	1570 ± 18
Ziway Mezinagna	61100 ± 1540	53400 ± 5620	55700 ± 1840	2290 ± 201
Ziway Sher	**99800 ± 2650**[18]	49700 ± 1990	54700 ± 1140	2000 ± 16
Ziway Shalo	76600 ± 5280	23800 ± 164	60200 ± 1680	1320 ± 49
Ziway Wameicha	62600 ± 2160	52300 ± 1790	76900 ± 3840	1680 ± 92
Ziway Wofdeset	95000 ± 2070	43800 ± 1590	70700 ± 711	1780 ± 46

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[18] The maximum values for the specific element from the totality of the sampling areas.

Continued…

Area	**Co**	**Ni**	**Cu**	**Zn**
AA Biheretsigie	3120 ± 37	12500 ± 390	8990 ± 730	410 ± 8
AA Bulbula	51.7 ± 0.83	< 0.079	< 0.668	250 ± 17
AA Entoto	6080 ± 130	15000 ± 540	3920 ± 350	240 ± 3
AA Gefersa	11500 ± 750	10700 ± 140	15100 ± 790	190 ± 1
AA Kebena	9100 ± 410	17000 ± 310	9610 ± 280	250 ± 6
AA Kera	5760 ± 530	42800 ± 480	20700 ± 240	**670 ± 45**
AA Kidanemihret before TAR	5650 ± 85	12200 ± 150	9300 ± 170	410 ± 2
AA Melkaqurani before TAR	9150 ± 250	10900 ± 220	2570 ± 130	190 ± 0
AA TAR Alert	6710 ± 140	12500 ± 390	2030 ± 30	220 ± 16
AA TAR before Kidanemihret	4680 ± 80	11100 ± 140	4990 ± 440	310 ± 4
AA TAR before Melkaqurani	8160 ± 180	16000 ± 390	19800 ± 590	230 ± 3
AA TAR Kaliti	9280 ± 98	14400 ± 40	4720 ± 150	260 ± 15
AA TAR Kolfe	7650 ± 250	15700 ± 220	14100 ± 630	330 ± 1
AA TAR with Kidanemihret	5190 ± 390	11100 ± 290	210 ± 20	200 ± 4
AA TAR with Melkaqurani	8240 ± 290	14400 ± 800	3720 ± 230	210 ± 10
AA TlAR at KK Textile Factory	4860 ± 130	10800 ± 770	< 0.668	170 ± 9
AA TlAR with TAR at Aba Samuel	4560 ± 180	10800 ± 570	4260 ± 61	190 ± 4
Awassa Amoragedel	6160 ± 39	44900 ± 565	1710 ± 158	236 ± 2
Awassa Asamaber	871 ± 11	7010 ± 30	4990 ± 311	349 ± 2
Awassa Buko	410 ± 7	2800 ± 158	6110 ± 107	253 ± 2
Awassa Deset	343 ± 12	10000 ± 105	7240 ± 689	418 ± 6
Awassa Fidelserawit	2810 ± 63	2880 ± 84	39700 ± 818	215 ± 14
Awassa Kerisa	2273 ± 47	4350 ± 168	59000 ± 2060	338 ± 20
Awassa Mezinagna	7790 ± 190	6860 ± 423	33600 ± 977	225 ± 4
Awassa Muate	3310 ± 141	48800 ± 857	28600 ± 656	349 ± 3
Awassa Samijersa	1930 ± 18	7310 ± 232	29800 ± 377	343 ± 8
Awassa Shewaber	6850 ± 70	7147 ± 436	52600 ± 1250	264 ± 8
Awassa Tikurwuha	3400 ± 75	16918 ± 384	86700 ± 976	250 ± 1
Awassa Wondotika	326 ± 27	11800 ± 172	22800 ± 272	395 ± 11
Ziway Bochesa	4260 ± 58	7510 ± 407	70200 ± 1610	201 ± 3
Ziway Debresina	9910 ± 468	18400 ± 423	47600 ± 1280	210 ± 0
Ziway Gabriel	5520 ± 120	14100 ± 778	59200 ± 1760	139 ± 0
Ziway Gelila	37800 ± 1120	**68000 ± 4480**	92900 ± 1260	107 ± 0
Ziway Korekonch	16800 ± 1040	27600 ± 1130	76000 ± 1880	171 ± 1
Ziway Mezinagna	13800 ± 488	32600 ± 3250	108700 ± 2420	243 ± 3
Ziway Sher	14600 ± 1250	28000 ± 261	**126900 ± 4260**	156 ± 9
Ziway Shalo	31100 ± 2780	41000 ± 2490	97000 ± 2840	166 ± 4
Ziway Wameicha	60300 ± 2120	46800 ± 1780	105000 ± 2710	140 ± 4
Ziway Wofdeset	**74600 ± 3040**	60700 ± 1090	96000 ± 1600	120 ± 3

Continued…

Area	**As**	**Se**	**Ag**	**Cd**
AA Biheretsigie	< 0.161	85.5 ± 1.4	7200 ± 390	500 ± 6
AA Bulbula	< 0.161	46.8 ± 0.4	4830 ± 140	1260 ± 82
AA Entoto	< 0.161	82.7 ± 7.1	3300 ± 220	170 ± 15
AA Gefersa	< 0.161	36.9 ± 0.7	2540 ± 50	115 ± 3
AA Kebena	< 0.161	78.2 ± 0.3	4100 ± 73	180 ± 7
AA Kera	< 0.161	52.8 ± 0.5	3350 ± 37	1230 ± 97
AA Kidanemihret before TAR	< 0.161	88.2 ± 1.1	2580 ± 220	< 0.007
AA Melkaqurani before TAR	< 0.161	85.7 ± 1.5	3540 ± 65	220 ± 6
AA TAR Alert	< 0.161	95.8 ± 2.5	1950 ± 37	150 ± 3
AA TAR before Kidanemihret	< 0.161	49.8 ± 0.2	2590 ± 50	200 ± 16
AA TAR before Melkaqurani	< 0.161	62.6 ± 1.4	2410 ± 110	150 ± 6
AA TAR Kaliti	< 0.161	57.0 ± 1.0	4150 ± 140	220 ± 6
AA TAR Kolfe	< 0.161	40.0 ± 0.4	2590 ± 140	430 ± 35
AA TAR with Kidanemihret	< 0.161	52.1 ± 1.1	1660 ± 17	120 ± 1
AA TAR with Melkaqurani	< 0.161	65.3 ± 0.4	3030 ± 54	160 ± 8
AA TlAR at KK Textile Factory	< 0.161	58.2 ± 0.6	2290 ± 65	220 ± 11
AA TlAR with TAR at Aba Samuel	< 0.161	60.4 ± 0.8	2590 ± 150	110 ± 4
Awassa Amoragedel	< 0.161	49.2 ± 0.3	4330 ± 99	1200 ± 15
Awassa Asamaber	< 0.161	49.9 ± 0.4	8390 ± 697	574 ± 48
Awassa Buko	< 0.161	42.4 ± 0.4	6690 ± 33	279 ± 4
Awassa Deset	< 0.161	82.7 ± 7.1	15600 ± 357	807 ± 29
Awassa Fidelserawit	< 0.161	46.9 ± 1.4	8040 ± 173	460 ± 12
Awassa Kerisa	< 0.161	90.7 ± 0.6	11500 ± 424	736 ± 2
Awassa Mezinagna	< 0.161	54.8 ± 0.7	5700 ± 247	498 ± 20
Awassa Muate	< 0.161	53.4 ± 1.4	13000 ± 99	1230 ± 42
Awassa Samijersa	< 0.161	48.2 ± 1.4	16300 ± 387	749 ± 66
Awassa Shewaber	< 0.161	50.0 ± 1.3	15000 ± 419	884 ± 31
Awassa Tikurwuha	< 0.161	51.2 ± 1.1	17800 ± 1286	531 ± 40
Awassa Wondotika	< 0.161	92.3 ± 2.1	11400 ± 994	870 ± 24
Ziway Bochesa	< 0.161	61.9 ± 5.1	17300 ± 265	377 ± 5
Ziway Debresina	< 0.161	53.7 ± 0.9	21200 ± 474	1010 ± 52
Ziway Gabriel	< 0.161	66.6 ± 0.5	28600 ± 2690	394 ± 8
Ziway Gelila	< 0.161	58.8 ± 0.8	22700 ± 1900	557 ± 31
Ziway Korekonch	< 0.161	72.9 ± 1.9	39000 ± 435	668 ± 40
Ziway Mezinagna	< 0.161	49.5 ± 0.4	**59100 ± 851**	**8872 ± 116**
Ziway Sher	< 0.161	49.6 ± 1.0	49100 ± 897	344 ± 6
Ziway Shalo	< 0.161	52.4 ± 1.4	39000 ± 2410	486 ± 14
Ziway Wameicha	< 0.161	56.4 ± 1.6	30800 ± 927	3230 ± 34
Ziway Wofdeset	< 0.161	**123 ± 2**	30400 ± 624	275 ± 4

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Area	**Sn**	**Hg**	**Pb**
AA Biheretsigie	1270 ± 71	67.3 ± 4.0	10600 ± 250
AA Bulbula	6150 ± 77	13.0 ± 1.0	73700 ± 1300
AA Entoto	6320 ± 98	26.3 ± 1.1	45000 ± 410
AA Gefersa	3760 ± 320	17.0 ± 0.0	33600 ± 700
AA Kebena	5970 ± 100	34.3 ± 2.5	43100 ± 1000
AA Kera	1600 ± 69	29.0 ± 1.0	35900 ± 750
AA Kidanemihret before TAR	2990 ± 75	18.0 ± 1.0	20000 ± 450
AA Melkaqurani before TAR	4220 ± 65	12.3 ± 1.2	**75400 ± 800**
AA TAR Alert	4280 ± 110	12.0 ± 1.0	55300 ± 730
AA TAR before Kidanemihret	4310 ± 6	45.0 ± 1.7	67300 ± 1800
AA TAR before Melkaqurani	7850 ± 87	10.0 ± 0.9	28800 ± 1000
AA TAR Kaliti	5010 ± 170	9.50 ± 0.87	18500 ± 400
AA TAR Kolfe	4930 ± 120	32.0 ± 1.0	40700 ± 1800
AA TAR with Kidanemihret	3520 ± 130	7.80 ± 0.70	29000 ± 400
AA TAR with Melkaqurani	3220 ± 43	12.7 ± 1.2	4850 ± 77
AA TlAR at KK Textile Factory	2880 ± 210	4.20 ± 0.10	24900 ± 690
AA TlAR with TAR at Aba Samuel	4170 ± 240	24.3 ± 2.1	43400 ± 1890
Awassa Amoragedel	4970 ± 224	16.0 ± 0.2	37300 ± 1040
Awassa Asamaber	9710 ± 852	12.3 ± 0.2	44200 ± 2760
Awassa Buko	7450 ± 9	2.07 ± 0.06	38800 ± 478
Awassa Deset	**17400 ± 807**	3.17 ± 0.06	56600 ± 1280
Awassa Fidelserawit	6760 ± 73	8.43 ± 0.59	32800 ± 2490
Awassa Kerisa	11300 ± 232	12.3 ± 0.6	39900 ± 1240
Awassa Mezinagna	4690 ± 177	**92.7 ± 5.7**	24400 ± 665
Awassa Muate	11600 ± 149	7.07 ± 0.14	66500 ± 5610
Awassa Samijersa	11500 ± 251	7.70 ± 0.62	32200 ± 640
Awassa Shewaber	11800 ± 135	11.7 ± 0.6	37100 ± 1420
Awassa Tikurwuha	6980 ± 487	42.7 ± 1.1	33500 ± 106
Awassa Wondotika	10700 ± 247	5.00 ± 0.09	36000 ± 2850
Ziway Bochesa	6170 ± 458	19.7 ± 1.2	31800 ± 1180
Ziway Debresina	5320 ± 56	72.7 ± 2.1	35700 ± 2930
Ziway Gabriel	4010 ± 181	59.3 ± 1.2	15800 ± 187
Ziway Gelila	1690 ± 33	38.0 ± 1.0	33200 ± 1580
Ziway Korekonch	5570 ± 87	32.7 ± 0.6	30600 ± 524
Ziway Mezinagna	11700 ± 782	26.3 ± 0.6	31500 ± 435
Ziway Sher	4380 ± 57	32.3 ± 3.1	21600 ± 1350
Ziway Shalo	3940 ± 124	31.0 ± 1.7	16300 ± 994
Ziway Wameicha	2430 ± 89	34.3 ± 0.6	10100 ± 367
Ziway Wofdeset	526 ± 6	52.3 ± 1.5	18900 ± 243

Table 19. Potentially toxic elements concentrations (mean ± SD, in µg/kg (mg/kg for Mn, Fe and Zn, dry mass)) in leaves and stems of Swiss chard samples irrigated with Akaki River, Ethiopia as determined by ICP-OES, ICP-MS and with a mercury analyzer.

Area	**V**		**Cr**		**Mn**	
	Leaf	**Stem**	**Leaf**	**Stem**	**Leaf**	**Stem**
AA Bulbula	1800 ± 35	400 ± 32	1440 ± 24	390 ± 13	94.1 ± 6.6	27.2 ± 0.04
AA Kebena	580 ± 20	400 ± 6	2420 ± 224	470 ± 40	150 ± 11	**160 ± 2**
AA Kera	430 ± 6	310 ± 4	1170 ± 115	730 ± 63	32.9 ± 1.1	56.1 ± 4.6
AA TAR before Kidanemihret	670 ± 27	430 ± 40	**9960 ± 886**	**1050 ± 76**	**330 ± 0.4**	45.7 ± 2.5
AA TAR Kolfe	**2030 ± 24**[19]	**530 ± 14**	4790 ± 58	380 ± 5	140 ± 5	120 ± 9
AA TAR with Kidanemihret	1470 ± 65	300 ± 28	4970 ± 350	1000 ± 27	230 ± 12	27.3 ± 0.44
Area	**Fe**		**Co**		**Ni**	
AA Bulbula	1400 ± 95	130 ± 3	380 ± 6	53.6 ± 0.9	750 ± 31	130 ± 2
AA Kebena	460 ± 10	460 ± 7	180 ± 3	85.3 ± 1.2	1140 ± 44	260 ± 21
AA Kera	370 ± 33	230 ± 1	130 ± 2	50.9 ± 1.0	850 ± 38	80 ± 2
AA TAR before Kidanemihret	**2700 ± 101**	320 ± 23	190 ± 3	110 ± 2	680 ± 38	680 ± 28
AA TAR Kolfe	600 ± 1	**670 ± 12**	**530 ± 6**	**220 ± 2**	1250 ± 24	150 ± 2
AA TAR with Kidanemihret	1630 ± 43	170 ± 4	300 ± 6	130 ± 2	**2770 ± 55**	**1610 ± 42**
Area	**Cu**		**Zn**		**As**	
AA Bulbula	9010 ± 530	2890 ± 39	60.2 ± 1.7	88.0 ± 2.6	210 ± 6	130 ± 2
AA Kebena	7120 ± 81	1860 ± 62	150 ± 1	38.0 ± 0.8	130 ± 5	120 ± 1
AA Kera	**24600 ± 270**	**7930 ± 280**	41.6 ± 1.8	34.9 ± 0.8	110 ± 2	140 ± 3
AA TAR before Kidanemihret	5290 ± 93	6170 ± 440	**160 ± 2.18**	68.0 ± 2.6	140 ± 6	140 ± 2
AA TAR Kolfe	6430 ± 110	2510 ± 56	73.7 ± 2.7	**180 ± 5**	250 ± 11	**160 ± 6**
AA TAR with Kidanemihret	6910 ± 500	5680 ± 67	34.5 ± 2.5	47.4 ± 1.1	**590 ± 49**	130 ± 11
Area	**Se**		**Ag**		**Cd**	
AA Bulbula	**370 ± 14**	**250 ± 7**	< 0.294	< 0.294	< 0.014	< 0.014
AA Kebena	28.1 ± 2.6	180 ± 7	< 0.294	< 0.294	< 0.014	< 0.014
AA Kera	160 ± 5	280 ± 7	< 0.294	< 0.294	< 0.014	< 0.014
AA TAR before Kidanemihret	26.9 ± 1.5	210 ± 5	< 0.294	< 0.294	< 0.014	< 0.014
AA TAR Kolfe	220 ± 6	58.9 ± 3.3	< 0.294	< 0.294	< 0.014	< 0.014
AA TAR with Kidanemihret	16.7 ± 0.7	71.2 ± 5.1	< 0.294	< 0.294	< 0.014	< 0.014
Area	**Sn**		**Hg**		**Pb**	
AA Bulbula	30100 ± 960	50300 ± 1160	**68.3 ± 4.9**	5.80 ± 0.07	**860 ± 10**	140 ± 9
AA Kebena	43200 ± 1000	32200 ± 1000	36.0 ± 3.0	**42.0 ± 3.0**	360 ± 8	230 ± 11
AA Kera	35800 ± 990	48300 ± 1100	61.5 ± 0.6	5.83 ± 0.12	840 ± 12	160 ± 9
AA TAR before Kidanemihret	5240 ± 63	36200 ± 1000	51.3 ± 0.9	30.3 ± 2.5	850 ± 10	360 ± 32
AA TAR Kolfe	**52600 ± 1200**	**51400 ± 1100**	37.0 ± 1.7	38.7 ± 1.2	850 ± 21	290 ± 8
AA TAR with Kidanemihret	43500 ± 1100	17900 ± 770	24.7 ± 0.5	11.6 ± 0.2	440 ± 27	**380 ± 13**

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[19] The maximum values for the specific element from the totality of the sampling areas.

4.5.4.1.2. Comparison of the concentrations of potentially toxic elements with national and/or international guidelines

The average concentrations (μg/g) of the potentially toxic elements in the sediment samples from the Akaki River, Lake Awassa and Lake Ziway are depicted in Figure 14.

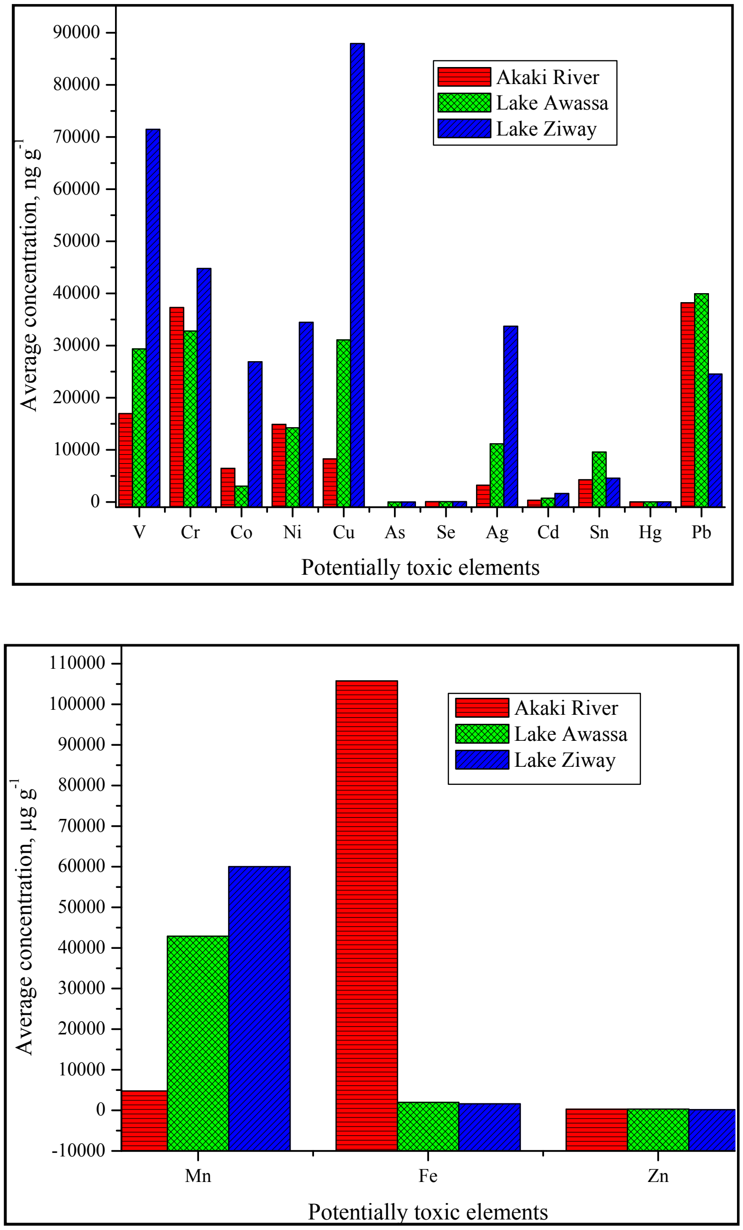

Figure 14. Elemental average concentrations (in μg/kg (mg/kg for Mn, Fe and Zn, dry mass)) of potentially toxic elements in sediments of Akaki River, Lake Awassa and Lake Ziway.

Moreover, the area-wise sum of the average concentrations of potentially toxic elements in sediment samples for the sampling sites of each area are illustrated in Figures 15-17.

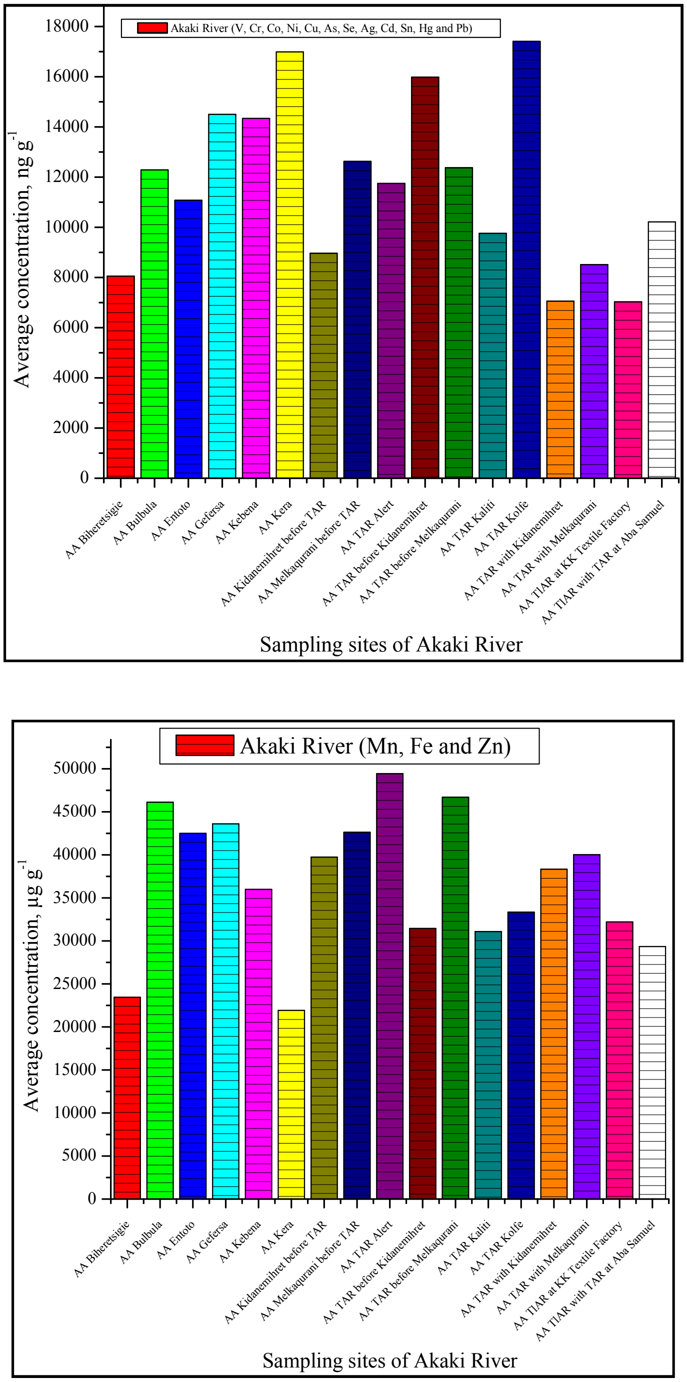

Figure 15. Area-wise sum of the average concentrations (in µg/kg (mg/kg for Mn, Fe and Zn, dry mass)) of potentially toxic elements in sediments of Akaki River.

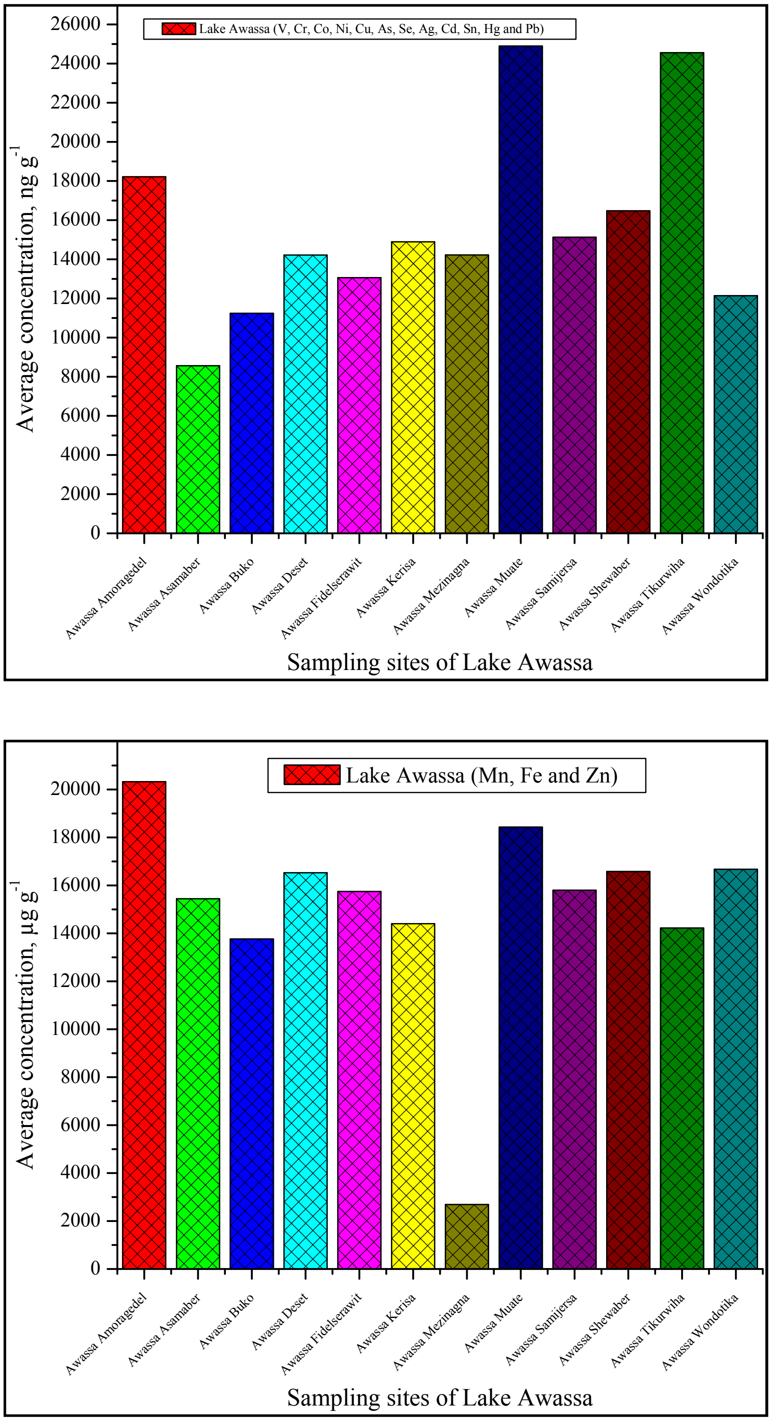

Figure 16. Area-wise sum of the average concentrations (in µg/kg (mg/kg for Mn, Fe and Zn, dry mass)) of potentially toxic elements in sediments of Lake Awassa.

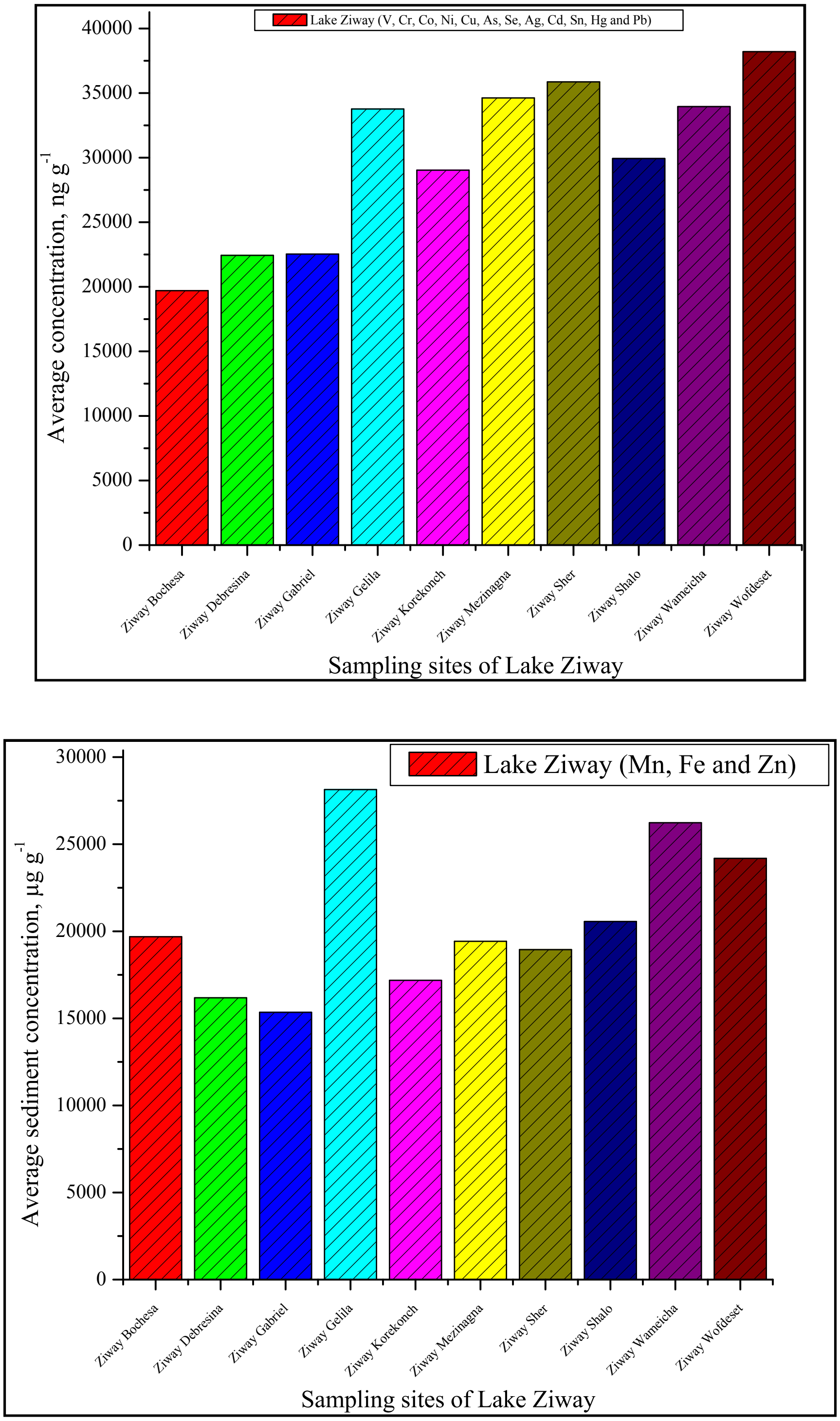

Figure 17. Area-wise sum of the average concentrations (in µg/kg (mg/kg for Mn, Fe and Zn, dry mass)) of potentially toxic elements in sediments of Lake Ziway.

For Akaki River, the minimum and maximum elemental loads were obtained in AA Biheretsigie and AA TAR Kolfe, respectively. Based on the elemental concentrations, the pattern in sediment is: As << Hg < Se < Cd < Ag < Sn < Co < Cu < Ni < V < Cr < Pb < Zn < Mn < Fe. The minimum concentration is observed for the known toxic elements (such as As, Hg and Cd) while the highest concentration is observed for Zn, Mn and Fe.

For the vegetable samples from Akaki River, based on the elemental concentrations the pattern in leaf is: Ag ≈ Cd << Hg < Se < As < Co < Pb < V < Ni < Cr < Cu < Sn < Zn < Mn < Fe, whereas for stem: Ag ≈ Cd << Hg < Co < As < Se < Pb < V < Ni < Cr < Cu < Sn < Mn < Zn < Fe. Similar result was observed in the works of Itanna (1998a; 2002) and Weldegebriel *et al*. (2012) done on selected metals in leafy vegetables (Swiss chard) grown in Addis Ababa, particularly Kera and Peakok (Kebena and Bulbula) farms. The pattern in leaf and stem are more or less similar, except in the cases of Co and As, and, Mn and Zn interchange their places which might be related to the specific accumulation preferences of the plant for these elements. These elements will accumulate in specific body parts of plants such as leaves and roots (Cheng, 2003; Akan *et al*. 2013).

As can be seen from the results the highest concentration of the potentially toxic elements in sediment and vegetable samples is observed for AA TAR Kolfe. Moreover, the minimum concentration is observed for the elements As, Hg and Cd while the highest concentration is observed for Zn, Mn and Fe.

Research work done so far in and around Akaki River (Addis Ababa) reported that anthropogenic effects in the area are increasing from time-to-time and accountable for increment in elemental concentration of the area. For instance, the work done by Itanna (1998b) on farmlands close to old and new industrial sites of Ethiopia indicated that Cr and Ni have reached toxic levels in the vertisols at Akaki and emphasized the tendency of other metals to reach this level, unless the situation is improved soon. Alemayehu (2001) reported that improper and continued disposal of domestic and industrial wastes in Addis Ababa represent a serious risk to the aquatic environment. The result also indicated that there are high levels of Cr and Mn in the water.

With respect to air quality, Etyemezian *et al*. (2005) showed a possible pollution in the urban and residential of the city of Addis Ababa by Pb. The study conducted by Melaku *et al*. (2005a) on sediment samples reported that the heavy metal pollution state of TAR and some of its tributaries is alarming. Itanna *et al*. (2008) reported that the total concentrations of Cr, As and Ni in two vegetable farms of Addis Ababa exceeded the normal limit and recommended regular monitoring of the soil conditions of the farms. Teju *et al*. (2012) explained that a slightly higher quantity of Pb was obtained for the roadside soils of Addis Ababa. Weldegebriel *et al*. (2012) also reported that Cd and Pb in vegetables grown in irrigated soil of Akaki River surpassed the maximum recommended levels.

When compared to the concentrations of potentially toxic elements in water, Mekonnen *et al*. (2012b) also found a gradual decrease in quality of the water in Akaki River from the recent upsurge in anthropogenic activities. They suggested that strict measures be imposed by the responsible bodies to control the levels of potentially toxic elements. The report also showed that high concentrations of Fe, Mn and Zn were present in water from Akaki River, while the lowest concentrations were observed for Ag, Cd and Hg. These results correspond to those obtained in sediment samples of the current study.

Mekonnen *et al*. (2013) showed the Akaki River was polluted with potentially toxic elements. The work done by Mekonnen *et al*. (2012a) indicated that the concentrations of Hg in sediment samples from TAR ranged from 3.9 to 110 ng/g with an average concentration of 38 ng/g. In the current study, the concentrations of Hg were found to range from 4.20 to 67.3 ng/g, with an average concentration of 22 ng/g. The lower value obtained for Hg in the current study which may be related to non-point sources in the former study. However, fortunately the concentrations of Hg are below the US EPA guideline limit of 200 ng/g for sediment (US EPA 2000a,b).

For Lake Awassa, the minimum and maximum elemental loads were obtained in Asamaber and Muate, respectively. Based on the elemental concentrations, the pattern in sediment is: As << Hg < Se < Cd < Co < Sn < Ag < Ni < V < Cu < Cr < Pb < Zn < Fe < Mn. For Lake Ziway, the minimum and maximum elemental loads were obtained in Bochesa and Wofdeset, respectively. Based on the elemental concentrations the pattern in sediment is: As << Hg < Se < Cd < Sn < Pb < Co < Ag < Ni < Cr < V < Cu < Zn < Fe < Mn. For both lakes similar pattern in elemental load is observed. In both lakes, the minimum concentration is observed for the known toxic elements (such as As, Hg and Cd) while the highest concentration is observed for Zn, Fe and Mn.

Quantitative data on the potential toxic elements in sediments from Lake Awassa and Lake Ziway are inadequate (Nigussie *et al*. 2010; Mekonnen *et al*. 2012a; Yohannes *et al*. 2013a). Nigussie *et al*. (2010) had reported highest concentrations of Mn, Zn and Cu (similar to the current study) since they easily form complexes with organic compounds because of the high formation constants of organo-metallic compounds, which make them rather stable in the environment. However, in the former study the least amount was observed for Cr in contrary to the current study. Beside the difference in time and techniques used, the reason for highest concentration of Cr in the current study could be related to the anthropogenic effects.

Mekonnen *et al*. (2012a) reported that an average concentration of Hg in sediment samples from Lake Awassa and Lake Ziway of 29 and 44 µg/kg, respectively. All the samples had concentrations of mercury well within the US EPA guideline limit of 200 µg/kg for sediments (US EPA 2000a,b).

Yohannes *et al*. (2013b) determined the concentrations of nine selected potentially toxic elements in sediments from Lake Awassa using F-AAS after HNO_3 microwave digestion. In this study, the potentially toxic elements content followed the order Zn >Ni > Pb > Cu > Cr > Co > As > Cd > Hg. There are some differences between the results reported by Yohannes *et al*. (2013b) and that obtained in our study. These differences may be attributed to the different techniques used for the sample preparation and analysis. The HNO_3 used by Yohannes *et al*. (2013b) was probably inadequate for complete digestion of the samples as compared to the one used in our study (Bettinelli *et al*. 2000; Melaku *et al*. 2005a,b; Wilson *et al*. 2006; Gaudino *et al*. 2007; Esen and Balci 2008). Moreover, in the current study, more reliable techniques (ICP-OES, ICP-MS and mercury analyzer) were used for the final quantification while Yohannes *et al*. (2013b) used F-AAS.

When comparing the two lakes, Lake Ziway has, on average higher concentration of elemental load than Lake Awassa. A similar result was observed on the contamination level of the water of both lakes where Lake Ziway has higher concentrations of potentially toxic elements than Lake Awassa (Mekonnen *et al*. 2012b).

The bivariate correlation procedure was used to compute the pair-wise association for the two lakes using SPSS software. The procedure is powerful for determining the strength and direction of the association between the two lakes. Since the Pearson correlation coefficient measures only the linear association, Spearman's rho and Kendall's tau-*b* statistics were used because they measure the rank order association between the two lakes. Moreover, they work regardless of the distributions of the variables. The statistical analysis resulted in Pearson, Kendall's and Spearman's correlation values for the two lakes of 0.789, 0.771 and 0.879, respectively, at the 0.01 level (2-tailed). The high values obtained suggest that there is a significant correlation between the two lakes, indicating similar sources of pollution for the two lakes.

4.5.5. Potentially toxic elements pollution source analysis

It is important to analyze and control the sources of pollution of potentially toxic elements in sediments, since they have been shown to threaten the health of aquatic animals and humans. Potentially toxic elements in sediments often exhibit complex interrelationships. Numerous factors control their relative abundance; e.g., the original potentially toxic elements contents of rocks and parent materials, processes of soil formation, contamination by human activities and other anthropogenic factors (Li *et al*. 2008; Yi *et al*. 2011).

Using SPSS software, Pearson correlation analysis was implemented to determine the relationship between the elements. Based on the Pearson product moment correlation coefficients, significant correlations were found between V and Co, V and Cu, Cr and Ni, Cr and Cu, Cr and Zn, Cr and Hg, Mn and Fe, Fe and Sn, Ni and Cu, Cu and Zn, Zn and Cd, Zn and Hg, Ag and Cd, and, Ag and Hg at the $p < 0.05$ and $p < 0.01$ level. High correlations between specific elements in the sediments could reflect the same or similar levels of contamination and/or release from the same or similar sources of pollution.

The analysis of paired samples correlation for the potentially toxic elements (Ag-Ag and Cd-Cd in leaves-stems are not included) in plant (leaves and stems) and sediment samples of Akaki River were also performed. The paired sample correlation showed that Fe-Fe, Co-Co, Zn-Zn, Hg-Hg and Pb-Pb (As-As in leaves-stems) in leaves-stems matrix show negative correlations while V-V, Cr-Cr, Co-Co, Ni-Ni, Cu-Cu, Se-Se and Sn-Sn shows a positive correlation which could indicate the later elements could have similar sources. Maximum permitted levels of potentially toxic elements in Swiss chard (based on average values compared with the international guidelines) were surpassed by Cr, Fe and Pb. When looking at specific sites, Zn and As in some cases, also surpassed the guideline value (Table 20). Therefore, the above elements are of greater concern in vegetable consumption.

Table 20. Average concentrations of potentially toxic elements (in mg/kg) in Swiss chard as compared with recommended maximum limit for vegetables.

Element	**Recommended maximum limit value**[*]	**Current average value in**	
		stem	**Leaf**
Cr	2.30	0.672	4.12
Mn	500	72	165
Fe	426	328	1194
Co	50.0	0.108	0.284
Ni	67.9	0.484	1.24
Cu	73.3	4.50	9.88
Zn	99.4	75.0	88.0
As	0.430	0.135	0.237
Cd	0.200	< 0.014	< 0.014
Pb	0.300	0.259	0.698

*Itanna (2002) and references cited therein; Codex Alimentarius Commission, (FAO/WHO), 2001. Food additives and contaminants. Joint FAO/WHO Food Standards Programme, ALINORM 01/12A: 1 – 289.

4.5.6. Assessment of sediment pollution using sediment contamination indices

4.5.6.1.1. Comparison with effect-based SQGs

Sediment chemistry data alone do not provide sufficient information for assessing the risks posed by sediment associated contaminants to aquatic organisms and classifying or managing contaminated sediments (Long *et al.* 1995). Interpretive tools are also required to relate sediment chemistry data to the potential for adverse biological effects to decide if sediment-associated contaminants are present at concentrations which could, potentially, harm the designated uses of the aquatic systems. Comparison of sediment with other similar works and national and/or international guidelines will give evidence for the status of the area with respect to the selected potentially toxic elements. One of the guideline used for sediments is the sediment quality guidelines (SQGs). The SQG is a chemical benchmark that is intended to define the concentration of sediment-associated contaminants that are associated with a high or a low probability of observing harmful biological effects or unacceptable levels of bioaccumulation[20].

Numerical SQGs can be used to help interpret the significance of chemical concentrations in sediments, identify contaminants of concern and prioritize areas for regulation or restoration (MacDonald *et al*. 1996,2000; Harikumar *et al*. 2009). The numerical SQGs have been empirically established based on biological exposure tests, field observations and other studies. These guidelines are useful as a screening tool and help to prioritize particular contaminants or areas of concern (Hernandez-Crespo *et al*. 2012). Sediments were classified as non-polluted, moderately polluted and heavily polluted (Perin *et al*. 1997; Harikumar *et al*. 2009).

The average concentration of potentially toxic elements in the sediments and their comparison with SQGs are summarized in Table 21.

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[20] Bioaccumulation is the term for materials that will build up in an organism to much higher levels than are found in the backgrounds. The first thing that occurs is that the material must enter the organism.

Table 21. Concentrations of potentially toxic elements (in mk/kg) in the sediment and their comparison with SQGs.

Element	This study mean for			This study range for			SQG non-polluted	SQG moderate polluted	SQG heavily polluted
	Akaki River	Lake Awassa	Lake Ziway	Akaki River	Lake Awassa	Lake Ziway			
Cr	37.3	32.8	44.8	< 0.829 – 84.3	5.99 – 74.3	23.8 – 63.4	< 25	25 – 75	> 75
Ni	14.9	14.2	34.5	< 0.079 – 42.8	2.80 – 48.8	7.51 – 68.0	< 20	20 – 50	> 50
Cu	8.26	31.1	87.9	< 0.668 – 20.7	1.71 – 86.7	47.6 – 127	< 25	25 – 50	> 50
Zn	277	303	165	166 – 669	215 – 418	107 – 243	< 90	90 – 200	> 200
Pb	38.2	39.9	24.5	4.9 – 75.4	24.4 – 66.5	10.1 – 35.7	< 40	40 – 60	> 60

From the table (Table 21) it is concluded that the sediments of Akaki River are polluted moderate to heavy rate with Cr, Zn and Pb, non-polluted to moderate rate with Ni, and non-polluted with Cu. Some sampling sites are heavily polluted with Cr, Zn and Pb, which is consistent with the previous study reported for Cr by Mekonnen *et al*. (2013). Lake Awassa is non- to moderately polluted with Cr, Ni, Cu and Pb, but highly polluted with Zn. Some of the sampling sites are heavily polluted with Cu and Pb. Lake Ziway is non- to moderately polluted with Cr and Ni, moderately to highly polluted with Cu and Zn, while non-polluted with Pb. Some of the sampling sites are heavily polluted with Ni. Unless the mechanisms for control of pollution and remediation of the lakes ecosystem are made practical, the situation could become progressively worse and adversely affect the biota living in the ecosystem. This situation could ultimately affect human life, since both lakes are sources of fish consumption throughout the country.

4.5.6.1.2. Ecotoxicological implications of contamination by potentially toxic elements

The ecotoxicological implications of potentially toxic elements contamination in sediments were determined using the "effects" data SQGs. For predicting toxicity in sediment, numerical SQGs based on effects range-low (ERL[21]) and effects range-median (ERM[22]) concentrations for 9 potentially toxic elements were identified (US EPA 1992; Long *et al*. 1995; 1998; MacDonald *et al*. 1996; Buchman 2008; Harikumar *et al*. 2009). The ERL and ERM values identify threshold concentrations that, if exceeded, are expected to produce ecological or biological effects. The ERLs were intended to represent chemical concentrations toward the low end of the effects ranges, that is, below which adverse biological effects were rarely observed. The ERMs were intended to represent concentrations toward the middle of the effects ranges and above which effects were more frequently observed.

The potential use of ERL – ERM range of SQGs are: (*i*) identification of potentially toxic chemicals in ambient sediments; (*ii*) ranking and prioritization of areas and sampling sites for further investigation; (*iii*) assessment of potential ecological hazards of contaminated sediments; (*iv*) description of the kinds of toxic effects previously associated with specific concentrations of chemicals; (*v*) quantification of the relative likelihood of toxicity over specific ranges in chemical concentrations; (*vi*) identification of the need for sediment management initiatives; and (*vii*) design of spiked-sediment bioassay experiments (US EPA 1992). The comparison of the concentrations of potentially toxic elements with ERL – ERM are shown in Table 22.

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[21] ERL is the lower 10th percentile of the effects data for each chemical was identified.
[22] ERM is the median, or 50th percentile, of the effects data was identified.

Table 22. Concentrations of potentially toxic elements (mg/kg, dry mass) in riverine and lake sediments and their comparison with ERL – ERM range for SQGs.

Element	**ERL – ERM range**	**This study range**	**Percentage of number of sampling site**		
			< ERL – ERM range	**Between ERL – ERM range**	**> ERL – ERM range**
Akaki River					
Cr	81 – 370	< LOD – 84.3	97	3	-
Ni	20.9 – 51.6	< LOD – 42.8	94	6	-
Cu	34 – 270	< LOD – 20.7	100	-	-
Zn	150 – 410	166 – 669	-	88	12
As	8.2 – 70	< LOD	100	-	-
Ag	1.0 – 3.7	1.7 – 7.1	-	76	24
Cd	1.2 – 9.6	< LOD – 1.3	88	12	-
Hg	0.15 – 0.71	0.004 – 0.067	47	53	-
Pb	46.7 – 218	4.9 – 75.4	76	24	
Lake Awassa					
Cr	81 – 370	5.99 – 74.3	100	-	-
Ni	20.9 – 51.6	2.80 – 48.8	83	17	-
Cu	34 – 270	1.71 – 86.7	100	-	-
Zn	150 – 410	166 – 669	-	92	8
As	8.2 – 70	< LOD	100	-	-
Ag	1.0 – 3.7	4.3 – 17.8	-	-	100
Cd	1.2 – 9.6	0.28 – 1.2	100	-	-
Hg	0.15 – 0.71	0.005 – 0.093	100	-	-
Pb	46.7 – 218	24.4 – 66.5	83	17	-
Lake Ziway					
Cr	81 – 370	23.8 – 63.4	100	-	-
Ni	20.9 – 51.6	7.51 – 68.0	30	50	20
Cu	34 – 270	47.6 – 127	100	-	-
Zn	150 – 410	107 – 243	40	60	-
As	8.2 – 70	< LOD	100	-	-
Ag	1.0 – 3.7	17.3 – 59.1	-	-	100
Cd	1.2 – 9.6	0.28 – 8.9	80	20	-
Hg	0.15 – 0.71	0.020 – 0.073	100	-	-
Pb	46.7 – 218	10.1 – 35.7	100	-	-

Based on the ERL – ERM range, for Akaki River (Table 22), there are some sampling sites for which the Zn and Ag levels are greater than the range, thereby predicting that the areas could be toxic to aquatic organisms with probable effects. In addition to this, the sampling sites for which the Zn, Ag, Cd, Hg and Pb are between ERL – ERM range signaling possible risk of contamination. These areas need strict policy measures so as at least to decrease the status of contamination since some of the elements are the known toxic substances for biota. While for Cr, Cu and As, since the current study ranges are less than ERL, no effects could be observed with the current situation, but strict measures should be taken to prevent an increase in level of the potentially toxic elements.

Based on ERL – ERM range, for Lake Awassa and Lake Ziway (Table 22), there are some sampling sites for Zn and all sites for Ag which are greater than the range, thereby predicting that the areas could be toxic to aquatic organisms with probable effects. In addition to this, the sampling sites for Ni, Zn and Pb are between ERL – ERM range signaling possible contamination. These areas need strict policy measures so as at least to decrease the status of contamination since some of the elements are the known toxic substances for biota. While for Cr, Cu, As, Cd and Hg for the whole sampling sites, and for Ni and Pb for most of the sampling sites, since the current study ranges are less than ERL, no effects could be observed with the current situation, but strict measures should be taken to prevent an increase in level of the potentially toxic elements.

4.6. Comparison of the Concentrations of Potentially Toxic Elements in Sediment and Water Samples

The levels of potentially toxic elements in sediment and water samples for the three sampling areas (Akaki River, Lake Awassa and Lake Ziway) are compared in Figure 18.

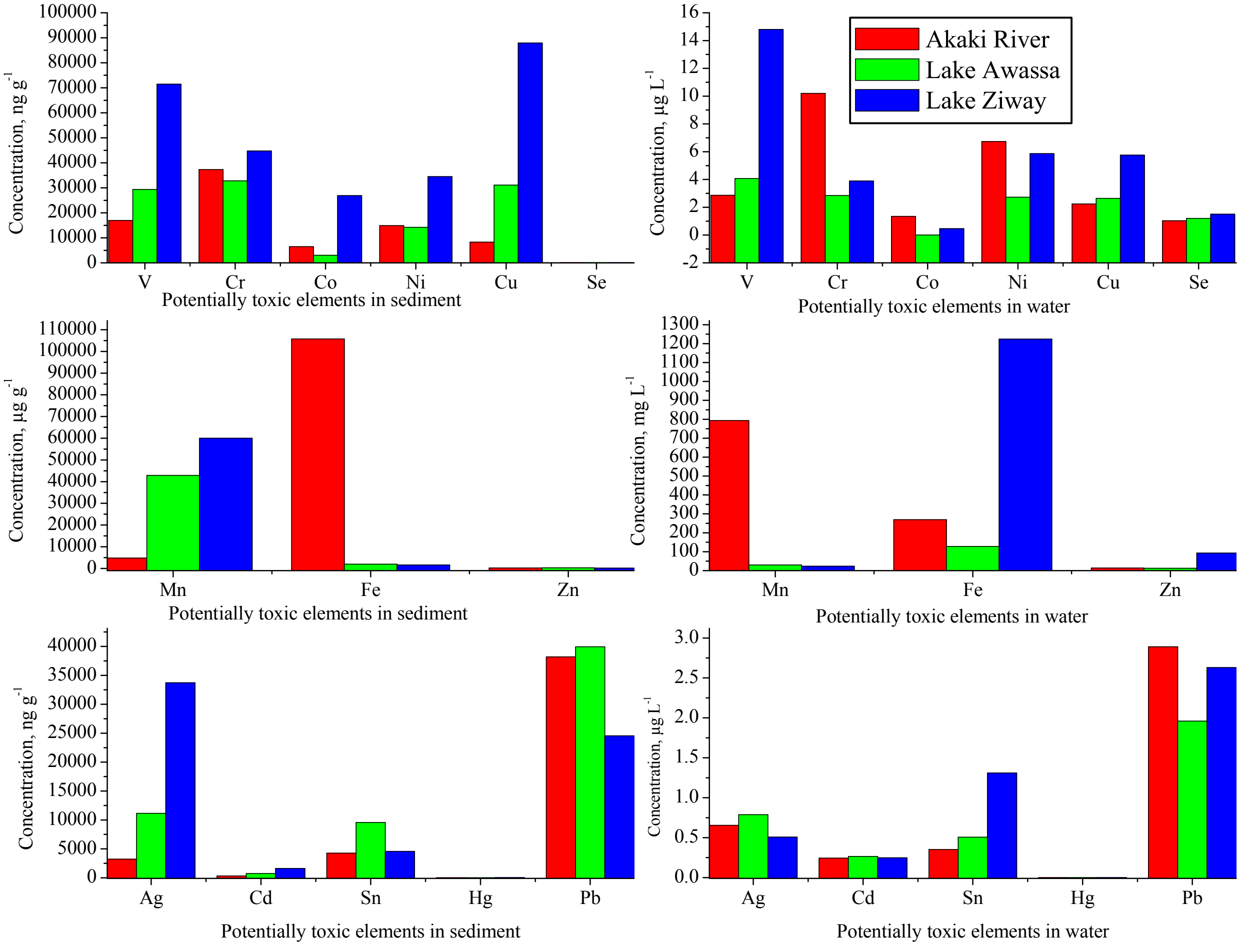

Figure 18. Sum of the average elemental concentrations of potentially toxic elements in sediments and water of Akaki River, Lake Awassa and Lake Ziway.

As can be observed from the graph, similar trends were observed for the quantified elements, which could indicate that the main source for the potentially toxic elements present in the sediment is primarily from the water. For each element and sampling area, the sum of the average elemental concentration of the sediment is much greater than that of the water. For Akaki River and Lake Awassa, the ratios of Fe in sediment and water show similar trend, however, for Lake Ziway, a different ratio is observed, even if the concentration in the sediment is much higher than the water in all cases. The discripancy in case of Lake Ziway needs further works so as to justify it.

4.7. Distribution of PAHs in Sediments of Akaki River, Lake Awassa and Lake Ziway, Ethiopia

4.7.1. The PAHs in Ethiopian context

To the best of our knowledge, no investigations have been carried out on the distribution and sources of PAHs in freshwater bodies of Ethiopia. There are a few studies on persistent organic pollutants, including those of Yohannes *et al*. (2013a,b) who investigated the levels of organochlorine pesticides (OCPs) and potentially toxic elements in fish and sediment collected from Lake Awassa, however they did not investigate the presence of PAHs. Prasse *et al*. (2012) assessed contamination and sources of metals, polychlorinated biphenyles (PCBs) and PAHs in urban soils from Addis Ababa, Ethiopia. Therefore, this study is the first study to investigate the distribution of PAHs in freshwater sediments and will serve to provide baseline data for future studies.

4.7.2. Microwave-assisted extraction

The ideal sample preparation step should be fast, relatively simple and inexpensive, allowing quantitative recovery of analytes with minimal loss or degradation, generating little or no hazardous wastes, and yield a solution that is sufficiently concentrated to allow the measurement of the analytes (Alvarez-Aviles *et al*. 2007). Critical parameters that need to be considered for microwave-assisted solvent extraction include the temperature, the irradiation time and the volume of the solvent chosen for the extraction. In order to perform a simple, fast and efficient extraction of PAHs, the volume of solvents, the microwave power and the extraction time were optimized. The literature indicates that the highest PAHs recoveries are obtained using hexane/acetone (1:1, *v:v*) as a solvent and therefore this combination was used for extraction (Shu *et al*. 2000; Villar *et al*. 2004; Li *et al*. 2006; Svoboda *et al*. 2007; Wang *et al*. 2007).

Sulfur is one of the particular interfering elements in PAHs analysis in sediment since it is soluble in organic solvents and is therefore, co-extracted with target organic compounds. Removal of sulfur is possible using different reagents, including potassium hydroxide in ethanol (Ricklund *et al*. 2008), tetrabutylammonium (TBA) hydrogen sulfate saturated with sodium sulfite (Svoboda *et al*. 2007) and activated copper (Ledgard 2007; Liang *et al*. 2007). Activated copper was therefore used for the removal of sulfur from the sediment samples. The primary surface impurities on copper are copper oxides. For this reason, the copper powder was activated using HCl in presence of heat and then washed with water, methanol and diethyl ether in that order (Ledgard 2007).

4.7.3. Method validation for PAHs

Quality control criteria were used to ensure the correct identification and quantification of the target compounds. Analysis of the set of samples was accompanied by a procedural blank and a triplicate sample, which were carried throughout the entire analytical procedure in a manner identical to the samples. Relative percent differences of triplicate samples were less than 10%. The efficiency of the MAE and the cleanup for PAHs from sediment samples and sample blanks was determined using SRM 1944. The recoveries were satisfactory, with averages recoveries ranging from 89.0% to 98.2% (Table 23).

Table 23. Certified and measured concentrations for selected PAHs in SRM 1944 for method validation.

PAHs	**Certified concentration values (mg/kg dry mass, n = 3)**	**Measured concentration (mg/kg dry mass, n = 3)**
Naphthalene	1.65 ± 0.31	1.53 ± 0.17
Acenaphthylene	Not reported	-
Fluorene*	0.85 ± 0.03	0.77 ± 0.06
Phenanthrene	5.27 ± 0.22	5.11 ± 0.16
Anthracene	1.77 ± 0.33	1.63 ± 0.19
Fluoranthene	8.92 ± 0.32	8.53 ± 0.27
Pyrene	9.70 ± 0.42	8.88 ± 0.41
Benz[*a*]anthracene	4.72 ± 0.11	4.20 ± 0.29
Chrysene	4.86 ± 0.10	4.63 ± 0.13
Benzo[*b*]fluoranthene	3.87 ± 0.42	3.73 ± 0.57
Benzo[*k*]fluoranthene	2.30 ± 0.20	2.23 ± 0.18
Benzo[*a*]pyrene	4.30 ± 0.13	4.22 ± 0.17
Indeno[1,2,3-*cd*]pyrene	2.78 ± 0.10	2.73 ± 0.15
Benzo[*ghi*]perylene	2.84 ± 0.10	2.63 ± 0.11

*This concentration is provided as a reference value.

The GC-MS instrumental calibrations were tested after running ten samples, and the calibration check was maintained within ±15% for all analytes of interest by analyzing a standard solution at 0.5 µg/mL. The LODs ranged from 1.28 ng/g (phenanthrene) to 3.92 ng/g (naphthalene) (Table 24).

Table 24. List of PAHs for analysis, correlation coefficient and LODs for SIM GC-MS mode.

PAHs	**Chemical formula**	**No. of rings**	**Retention time, min**	**R^2**	**LOD (ng/g, dm[a])**
Naphthalene	$C_{10}H_8$	2	7.869	0.994	3.92
Acenaphthalene	$C_{12}H_8$	3	10.998	0.995	1.46
Fluorene	$C_{13}H_{10}$	3	13.564	0.991	1.53
Phenanthrene	$C_{14}H_{10}$	3	20.106	0.983	1.28
Anthracene	$C_{14}H_{10}$	3	20.485	0.998	2.22
Fluoranthene	$C_{16}H_{10}$	4	27.515	0.993	2.77
Pyrene	$C_{16}H_{10}$	4	28.908	0.991	1.78
Benza[*a*]anthracene	$C_{18}H_{12}$	4	35.187	0.987	3.38
Chrysene	$C_{18}H_{12}$	4	35.007	0.978	3.38
Benzo[*b*]fluoranthene	$C_{20}H_{12}$	5	40.503	0.981	2.69
Benzo[*k*]fluoranthene	$C_{20}H_{12}$	5	40.656	0.976	2.69
Benzo[*a*]pyrene	$C_{20}H_{12}$	5	42.232	0.987	2.55
Indeno[1,2.3-*cd*]pyrene	$C_{22}H_{12}$	6	47.549	0.955	2.33
Benzo[*ghi*]perylene	$C_{22}H_{12}$	6	48.251	0.990	1.99

dm[a] – dry mass

The repeatability of at least two parameters in the gas chromatographic method, the retention time (confirming the identity of the analyte of interest) and the peak area or height (quantifying the analyte of interest), was achieved satisfactorily with the chromatographic method under the study conditions.

4.7.4. Analytical determination of PAHs

The complete resolution of the 14 US EPA priority PAHs was obtained with a careful choice of the chromatographic conditions, including the stationary phase, by carrying out a fast GC analysis on a DB-5[23] MS fused silica capillary column after MAE and cleanup step. The obtained chromatogram of 14 of the 16 US EPA PAH priority standards is presented in Figure 19.

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[23] DB-5 is (5% di-phenyl)-dimethylpolysiloxane where the dominant interaction is dispersive/induced dipole with non-polar, wide range of application and high temperature limit. Fused silica is synthetic quartz of high purity.

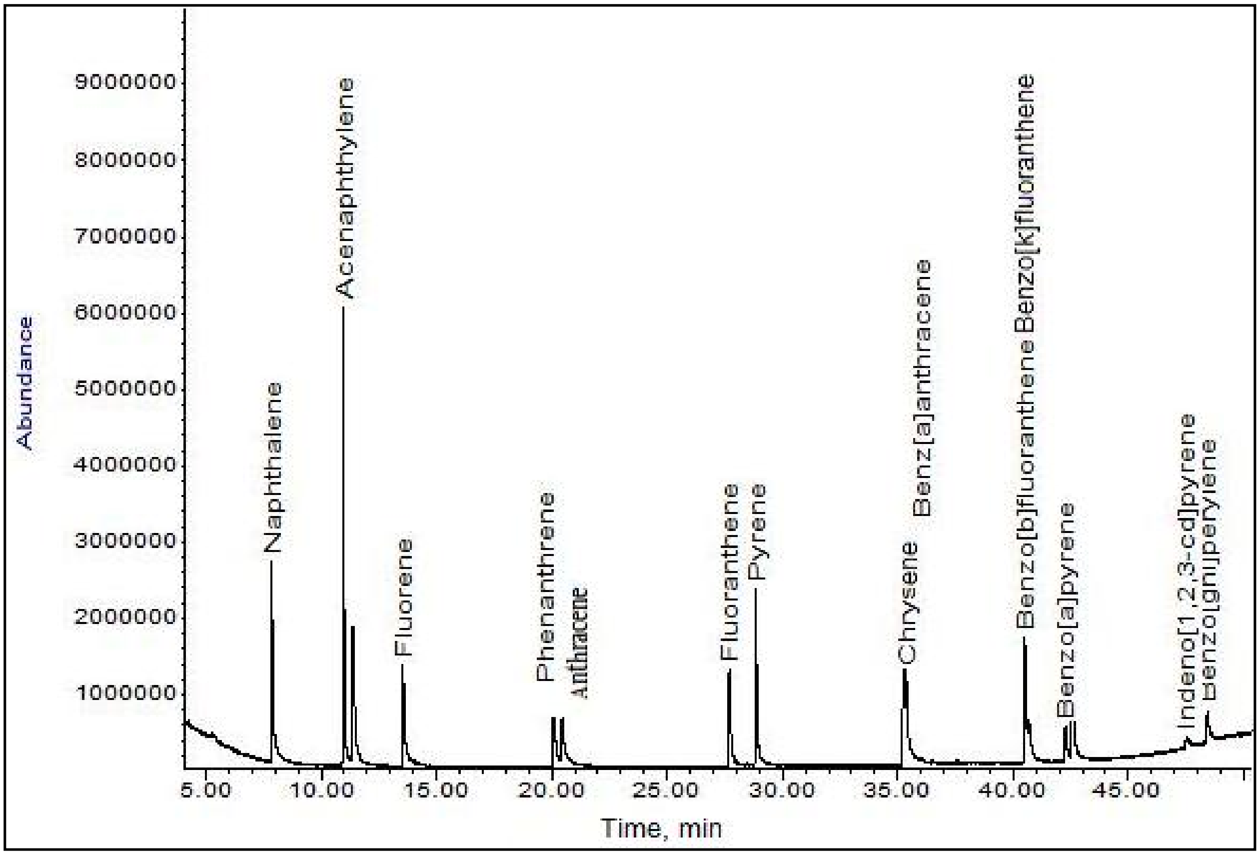
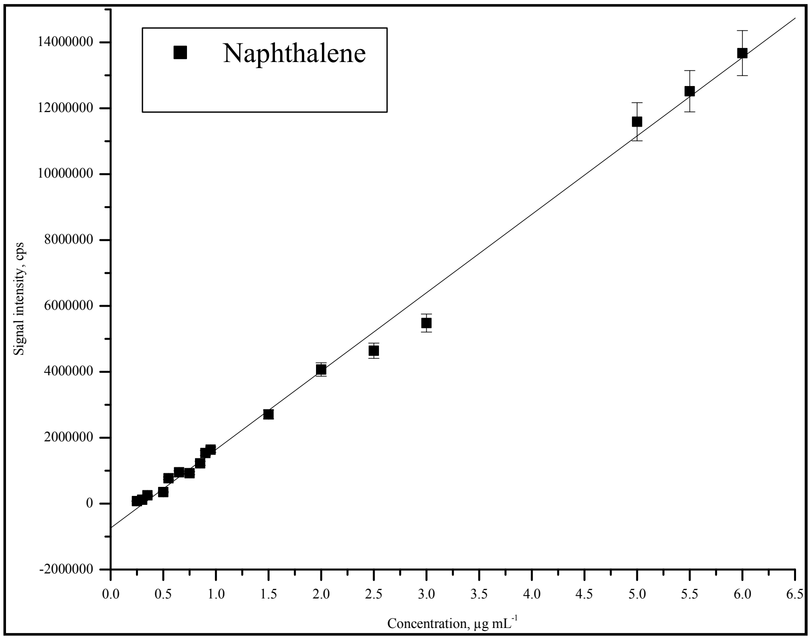


Figure 19. Chromatogram of a standard solution of the 14 quantified PAHs using DB-5 MS fused silica capillary column (30 m x 0.25 mm i.d. x 0.25 µm film thickness).

Quantification was performed using at least a seven-point calibration curve for each individual PAH. Two of these calibration curves are depicted in Figure 20. The correlation coefficients (R^2) varied from 0.955 to 0.998 (Table 24).



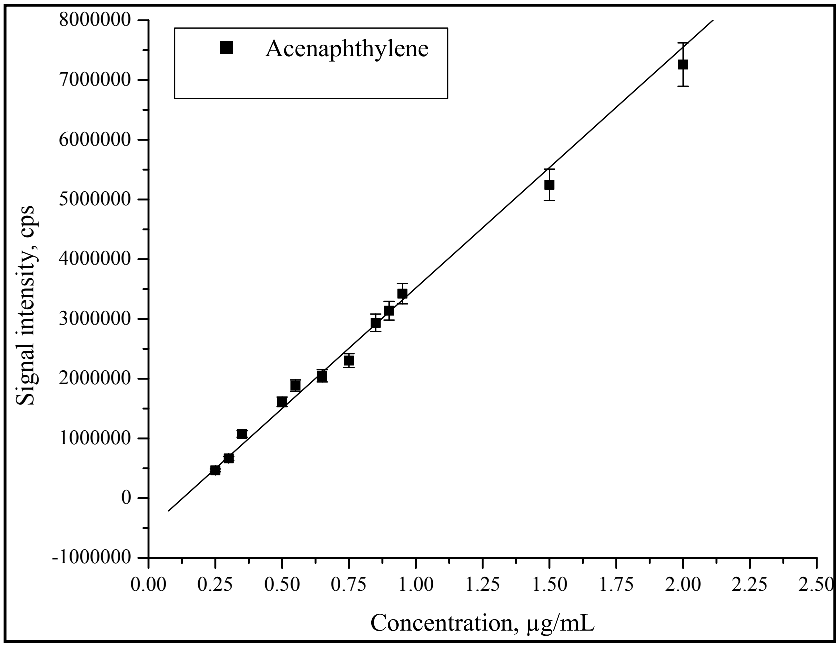


Figure 20. Selected calibration curves for PAHs (naphthalene and acenaphthylene) determination using GC-MS.

4.7.5. The PAH concentrations in sediment samples of Akaki River, Lake Awassa and Lake Ziway, Ethiopia

The total concentrations of PAHs (dry mass basis) in sediment samples of Akaki River, Lake Awassa and Lake Ziway, Ethiopia are presented in Table 25.

Table 25. The PAH concentrations (ng/g-dry mass, RSD ≤ 10%) in sediments samples of Akaki River, Lake Awassa and Lake Ziway, Ethiopia, using GC-MS after MAE.

No.	Sample Name	Naphthalene	Acenaphthylene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benz[*a*]anthracene	Chrysene	Benzo[*b*]fluoranthene	Benzo[*k*]fluoranthene	Benzo[*a*]pyrene	Indeno[*1,2,3-cd*]pyrene	Benzo[*ghi*]perylene	ΣLMW^{a}	ΣHMW^{b}	ΣPAHs^{c}
1	AA Bulbula	68.8	<1.46	<1.53	9.83	<2.22	<2.77	<1.78	<3.38	<3.38	4.91	<2.69	<2.55	4.91	4.91	78.6	14.7	93.4
2	AA Entoto	140	25.0	15.0	20.0	<2.22	<2.77	9.99	<3.38	<3.38	5.00	<2.69	5.00	<2.33	5.00	200	25.0	225
3	AA Gefersa	278	14.9	49.7	308	19.9	209	174	<3.38	<3.38	4.97	4.97	4.97	9.94	14.9	671	422	1090
4	AA Kebena	149	9.94	4.97	179	9.94	119	94.5	<3.38	<3.38	4.97	<2.69	4.97	<2.33	4.97	353	229	582
5	AA Kera	92.2	9.71	<1.53	24.3	24.3	19.4	24.3	<3.38	<3.38	4.85	4.85	<2.55	4.85	4.85	150	63.1	214
6	AA Kidanemihret before TAR	29.8	4.97	<1.53	59.6	59.6	24.8	<1.78	<3.38	<3.38	4.97	<2.69	<2.55	4.97	4.97	154	39.7	194
7	AA TAR Alert	94.7	4.99	15.0	439	259	1310	828	39.9	49.9	9.97	<2.69	4.99	15.0	4.99	813	2260	3070
8	AA TAR before Kidanemihret	19.7	<1.46	9.84	44.3	44.3	4.92	4.92	<3.38	<3.38	4.92	<2.69	<2.55	<2.33	<1.99	118	14.8	133
9	AA TAR before Melkaqurani	353	19.9	4.98	229	219	89.6	74.7	<3.38	<3.38	4.98	4.98	4.98	4.98	9.96	826	194	1020
10	AA TAR Kaliti	169	9.93	29.8	69.5	14.9	49.6	84.4	<3.38	4.96	4.96	4.96	4.96	4.96	4.96	293	164	457
11	AA Melkaqurani before TAR	94.1	<1.46	<1.53	39.6	<2.22	19.8	14.9	<3.38	<3.38	4.95	<2.69	4.95	14.9	4.95	134	64.4	198
12	AA TAR Kolfe	<3.92	5.00	145	90.0	20.0	40.0	30.0	<3.38	<3.38	5.00	<2.69	<2.55	<2.33	10.0	260	85.0	345
13	AA TAR with Kidanemihret	79.3	4.95	14.9	34.7	34.7	24.8	19.8	<3.38	4.95	4.95	<2.69	<2.55	<2.33	4.95	168	59.5	228
14	AA TlAR at KK Textile Factory	<3.92	4.98	14.9	119	4.98	4.98	<1.78	<3.38	<3.38	<2.69	<2.69	<2.55	<2.33	4.98	144	9.96	154
15	AA TlAR with TAR at Aba Samuel	<3.92	<1.46	<1.53	<1.28	<2.22	<2.77	<1.78	<3.38	<3.38	<2.69	<2.69	<2.55	<2.33	<1.99	-	-	-
16	Awassa Amoragedel	64.9	9.99	20.0	69.9	69.9	<2.77	<1.78	<3.38	5.00	5.00	5.00	<2.55	5.00	5.00	235	25.0	260
17	Awassa Asamaber	14.7	4.89	<1.53	9.78	<2.22	<2.77	<1.78	<3.38	<3.38	4.89	<2.69	4.89	<2.33	4.89	29.3	14.7	44.0
18	Awassa Buko	29.9	<1.46	<1.53	69.7	14.9	149	134	<3.38	<3.38	4.98	<2.69	<2.55	4.98	4.98	115	299	413
19	Awassa Fidelserawit	24.8	9.92	4.96	34.7	4.96	4.96	4.96	<3.38	<3.38	4.96	<2.69	<2.55	4.96	4.96	79.4	24.8	104

No.	Sample Name	Naphthalene	Acenaphthylene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benz[*a*]anthracene	Chrysene	Benzo[*b*]fluoranthene	Benzo[*k*]fluoranthene	Benzo[a]pyrene	Indeno[*1,2,3-cd*]pyrene	Benzo[*ghi*]perylene	ΣLMW[a]	ΣHMW[b]	ΣPAHs[c]
20	Awassa Kerisa	64.9	4.99	25.0	79.9	<2.22	<2.77	15.0	<3.38	<3.38	4.99	4.99	4.99	<2.33	<1.99	175	30.0	205
21	Awassa Mezinagna	<3.92	<1.46	<1.53	<1.28	<2.22	<2.77	<1.78	<3.38	<3.38	4.98	4.98	<2.55	9.95	4.98	-	24.9	24.9
22	Awassa Muate	105	5.00	9.99	20.0	5.00	69.9	40.0	<3.38	<3.38	5.00	<2.69	5.00	5.00	5.00	145	130	275
23	Awassa Samijersa	84.6	<1.46	14.9	59.7	59.7	<2.77	14.9	<3.38	<3.38	4.97	<2.69	4.97	4.97	4.97	219	34.8	254
24	Awassa Shewaber	<3.92	<1.46	<1.53	<1.28	<2.22	<2.77	<1.78	<3.38	<3.38	4.99	<2.69	<2.55	20.0	4.99	-	29.9	29.9
25	Awassa Tikurwuha	87.1	9.67	<1.53	33.9	38.7	<2.77	9.67	<3.38	<3.38	<2.69	4.84	<2.55	4.84	4.84	169	24.2	193
26	Awassa Wondotika	39.8	<1.46	<1.53	4.97	<2.22	<2.77	<1.78	<3.38	<3.38	4.97	4.97	<2.55	<2.33	<1.99	44.7	9.94	54.7
27	Ziway Bochesa	109	4.96	19.8	64.5	64.5	<2.77	14.9	<3.38	<3.38	4.96	<2.69	<2.55	9.92	4.96	263	34.7	298
28	Ziway Debresina	94.6	<1.46	<1.53	34.8	<2.22	29.9	9.95	<3.38	4.98	4.98	<2.69	4.98	<2.33	4.98	129	59.7	189
29	Ziway Gabriel	54.7	4.97	9.94	<1.28	<2.22	<2.77	4.97	<3.38	<3.38	4.97	<2.69	<2.55	<2.33	4.97	69.6	14.9	84.5
30	Ziway Gelila	65.0	5.00	15.0	25.0	25.0	<2.77	<1.78	<3.38	<3.38	5.00	<2.69	<2.55	<2.33	5.00	135	9.99	145
31	Ziway Korekonch	<3.92	<1.46	<1.53	<1.28	<2.22	<2.77	<1.78	<3.38	<3.38	4.99	<2.69	<2.55	4.99	4.99	-	15.0	15.0
32	Ziway Mezinagna	133	<1.46	24.6	14.8	88.6	14.8	<1.78	<3.38	<3.38	4.92	4.92	4.92	9.85	4.92	261	44.3	305
33	Ziway Sedeicha	71.2	4.45	13.4	35.6	40.1	<2.77	8.91	<3.38	<3.38	4.45	4.45	4.45	4.45	4.45	165	31.2	196
34	Ziway Shalo	59.5	<1.46	49.6	24.8	<2.22	4.96	<1.78	<3.38	<3.38	<2.69	4.96	4.96	<2.33	4.96	134	19.8	154
35	Ziway Wameicha	89.3	<1.46	29.8	<1.28	79.4	<2.77	4.96	<3.38	<3.38	4.96	<2.69	<2.55	<2.33	9.92	198	19.8	218
36	Ziway Wofdeset	83.7	<1.46	9.84	24.6	<2.22	9.84	9.84	<3.38	<3.38	<2.69	4.92	<2.55	<2.33	4.92	118	29.5	148
	Total PAHs	2840	178	551	2270	1200	2200	1630	39.9	69.7	158	63.8	74.0	153	183	7050	4570	11600
	%Composition	24	1.53	5	20	10	19	14	0.34	0.60	1.4	0.55	0.64	1.3	1.58	60.7	39.3	100

ΣLMW[a]: sum of naphthalene, acenaphthylene, fluorine, phenanthrene and anthracene; ΣHMW[b]: sum of fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluorantene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, , indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene; ΣPAHs[c]: sum of 14 PAHs.

The highest concentration of total PAHs was found at Akaki River from TAR Alert area; while the lowest concentration was found at Akaki River from AA TlAR with TAR at Aba Samuel area. The total content of the 14 PAHs analyzed ranges from not detected to 3,070 ng/g (average 534 ng/g) for Akaki River, 24.9 to 413 ng/g (average 169 ng/g) for Lake Awassa and 15.0 to 305 ng/g (average 175 ng/g) for Lake Ziway.

The levels of the total PAHs for the entire sampling area follow on average the order: naphthalene (24%) > phenanthrene (20%) > fluoranthene (19%) > pyrene (14%) > anthracene (10%) > fluorene (5%) > benzo[*ghi*]perylene (2%) > acenaphthylene (2%) > benzo[*b*]fluorantene (1%) > indeno[1,2,3-*cd*]pyrene (1%) > benzo[*a*]pyrene (1%) > chrysene (1%) > benzo[*k*]fluoranthene (1%) > benzo[*a*]anthracene (0.3%), the distributions are varying substantially among the different locations. Therefore, among all the 14 PAHs, naphthalene, phenanthrene and fluoranthene were predominant species (accounting 63%) while benzo[*a*]pyrene, chrysene, benzo[*k*]fluoranthene and benzo[*a*]anthracene were found at lowest amount (accounting < 2%).

Regarding PAH total concentrations for Akaki River of this study (not detected to 3,070 ng/g): Prasse *et al*. (2012) reported a range of 712 to 3,040 ng/g for Akaki River of Ethiopia in soil samples, which is comparable to the current study. With respect to the global context, in the current study obtained results are much less than those reported for Yamuna River of India (4,500 to 23,600 ng/g) (Agarwal *et al*. 2006) and riverine environments of Thailand (6 to 8,400 ng/g) (Boonyatumanond *et al*. 2006). However, the values are higher than those determined in a study of Gao-ping River of Taiwan (8 to 356 ng/g) (Doong and Lin 2004) and Aojiang River in Wenzhou of China (491 to 883 ng/g) (Li *et al*. 2010). Therefore, the obtained concentrations for the Akaki River are comparable to corresponding levels in Ethiopia, India, China and Thailand, but still one order of magnitude higher than peak concentrations in Taiwan.

Regarding PAH total concentrations in the lakes, since there is no other study done in Ethiopian context, the current study serves to provide baseline data for both lakes. When compared to other global studies of lake systems, Lake Awassa (24.9 to 413 ng/g) and Lake Ziway (15.0 to 305 ng/g) have lower total concentrations of PAHs than those obtained for Meiliang Bay in Lake Taihu of China (1,210 to 4,750 ng/g) (Qiao *et al*. 2006), Lake Baiyangdian of China (97.2 to 2,400) (Guo *et al*. 2011) and Lake Taihu of China (209 to 1,000 ng/g) (Zhang *et al*. 2012). Therefore, the obtained concentrations of the Ethiopian lakes are comparable to and even less to the corresponding levels in China.

4.7.6. Composition and source identification of PAHs

According to the number of aromatic rings, the 14 PAHs were divided into three groups, representing 2 + 3 ring PAHs, 4 ring PAHs, and 5 + 6 ring PAHs (Socclo *et al*. 2000; Doong and Lin 2004). Percentage proportions of PAH species with 2 + 3 rings (61%), with 4 ring (34%) and 5 + 6 ring (5%) were detected. Compositions and relative abundance of individual PAH in sediments are quite similar in which the 2 + 3 ring PAHs are predominant based on ternary graph or triangular plot[24] (Figure 21).

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[24] Ternary plot (triangular plot or diagram) is a way of displaying the distribution and variability of three-part compositional data where the data can be expressed in proportions or use absolute measures. The ternary display is a triangle with sides scaled from 0 to 1 (or 0 to 100%). Each side represents one of the three components. A point is plotted so that a line drawn perpendicular from the point to each leg of the triangle intersects at the component values of the point.

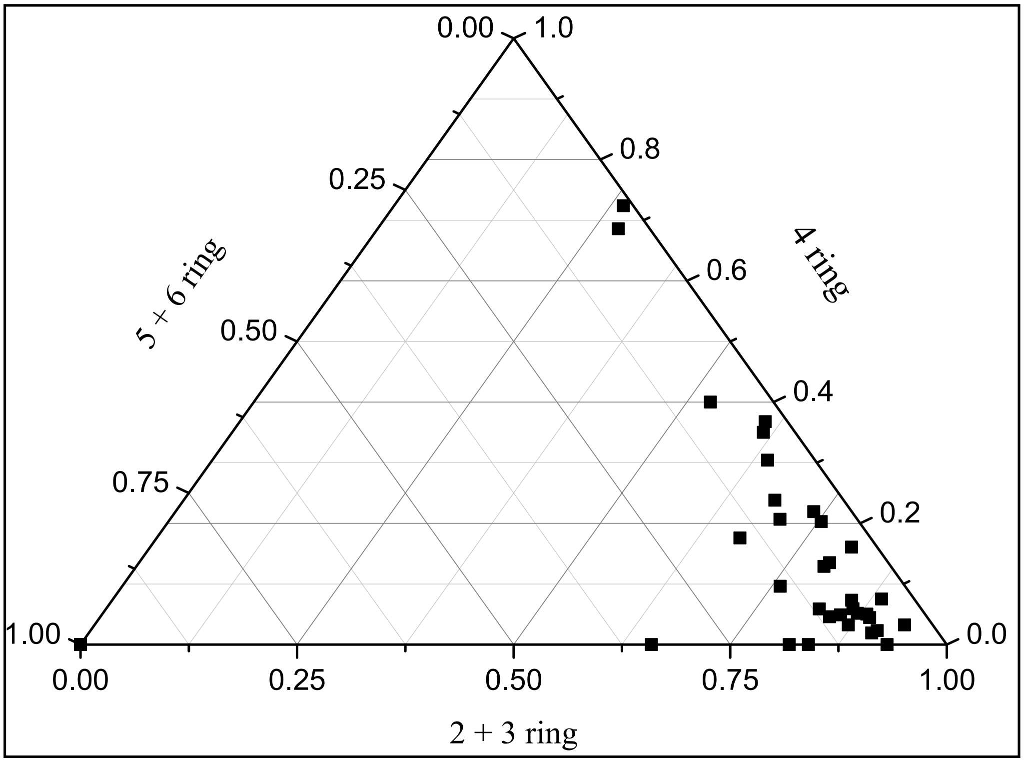

Figure 21. Triangular diagram of percentage concentrations for 14 PAHs in sediments of Akaki River, Lake Awassa and Lake Ziway, Ethiopia.

The choice of the plot in Figure 21 is to show the compositions of the systems composed on the three groups of PAH species graphically in an equilateral triangle. The choice of the origin index of PAHs was founded on the fact that petrogenic contamination is characterized by the predominance of the lower molecular weight PAHs (LMW: bi-, tri- and tetra-aromatics), while the higher molecular weight PAHs (HMW) tend to dominate in the pyrolytic PAH contamination distribution (Soclo *et al*. 2000; Doong and Lin 2004). As the lower molecular weight PAHs dominate the higher molecular weight PAHs, the ratio indicates that these three sampling area (Akaki River, Lake Awassa and Lake Ziway) emanate essentially from an identical source and are indicative of a petrogenic origin (Socclo *et al*. 2000; Doong and Lin 2004). The petrogenic PAHs may be mainly from the leakage of crude oil and refined products from urban vehicle traffic (Socclo *et al*. 2000; Doong and Lin 2004).

Moreover, the results obtained from the dendrogram[25] (Figure 22), except from Site 7 (AA TAR Alert), the sampling sites could be grouped in to three groups, where most of them possibly originate from similar sources, supporting the above explanation. The source for Site 7 could be some non-point source and needs some further work so as to identify its source.

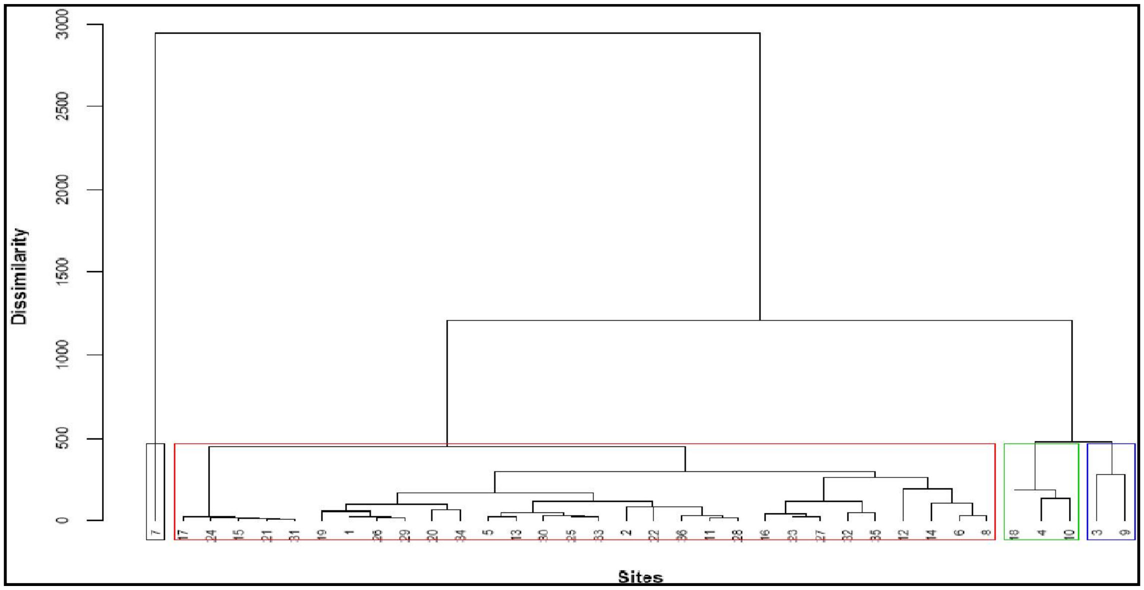

Figure 22. Dendrogram for sources of the 14 PAHs in sediments of Akaki River, Lake Awassa and Lake Ziway, Ethiopia. Note that numbering code for the sites is similar to the numbers given in Table 25.

4.7.7. Evaluation of ecotoxicological risk of PAHs using SQGs

The SQGs provide a scientifically defensible basis to evaluate the potential effects of sediment-associated contaminants on aquatic organisms. Long *et al*. (1995) noted that the correlation between impacts and chemical concentrations was fairly good for individual PAHs and total PAH and suggested effects range-low (ERL) and effects range-median (ERM) concentrations for

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[25] A dendrogram (from Greek *dendron* "tree" and *gramma* "drawing") is a tree diagram frequently used to illustrate the arrangement of the clusters produced by hierarchical clustering (a method of cluster analysis which seeks to build a hierarchy of clusters). In order to decide which clusters should be combined (for agglomerative), or where a cluster should be split (for divisive), a measure of dissimilarity between sets of observations is required. In most methods of hierarchical clustering, this is achieved by use of an appropriate metric (a measure of distance between pairs of observations), and a linkage criterion which specifies the dissimilarity of sets as a function of the pair-wise distances of observations in the sets.

sediment-sorbed contaminants. For assessing the potential effects of all contaminants determined in sediments, PAH levels in sediment were compared with effects-based on SQG values in Table 26.

Table 26. The PAH levels in sediment samples of Akaki River, Lake Awassa and Lake Ziway, Ethiopia, compared with effects-based SQG values.

Compound	**SQGs values, ng/g (dry mass)**		**This study percent incidence of effects**		
	ERL	**ERM**	**< ERL**	**ERL-ERM**	**> ERM**
Naphthalene	160	2100	92	8	-
Acenaphthylene	44	640	100	-	-
Fluorene	19	540	75	25	-
Phenanthrene	240	1500	94	6	-
Anthracene	85.3	1100	92	8	-
Fluoranthene	600	5100	97	3	-
Pyrene	665	2600	97	3	-
Benzo[*a*]anthracene	261	1600	100	-	-
Chrysene	384	2800	100	-	-
Benzo[*b*]fluoranthene	NA[a]	NA	-	-	-
Benzo[*k*]fluoranthene	NA	NA		-	-
Benzo[*a*]pyrene	430	1600	100	-	-
Indeno[1,2,3-*cd*]anthracene	NA	NA	-	-	-
Benzo[*ghi*]perylene	NA	NA	-	-	-
Total PAHs	4022	44792	100	-	-

NA[d] – Not available.

Results of this study showed that the total PAH concentrations at all sites are below the ERL. At all sampling sites, individual PAH such as acenaphthylene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluorantene, benzo[*k*]fluoranthene, benzo[*ghi*]perylene, benzo[*a*]pyrene and indeno[1,2,3-*cd*]pyrene are substantially less than their ERL, while for the whole sampling areas all individual PAH are substantially less than ERM. For individual PAH such as naphthalene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene only few sampling sites are greater than their ERL. Though, at present level the PAHs may not exert adverse biological effects, continuous follow up is recommended. Increase in PAHs over time could not be ascertained due to an absence of prior investigations. However, in future the current study could provide baseline values to determine increases in PAH concentrations as urbanization and population growth increase.

4.7.8. Sediment pollution levels with respect to PAHs

Sampling sites could be classified as "highly contaminated", if total PAH concentrations are higher than 500 ng/g, "moderately contaminated", if total PAH concentrations range from 250 ng/g to 500 ng/g, and "slightly contaminated", if total PAH concentrations are below 250 ng/g (da Silva *et al*. 2007; Maioli *et al*. 2010;2011). Our data demonstrate that these sediment samples, of which 66.7%, 22.2% and 11.1% of sampling sites, can be classified as slightly contaminated, moderately contaminated and highly contaminated, respectively. The majorities of the sediment sampling sites (32 from the 36) are classified as slightly to moderately contaminated. However, four sites (all of them from Akaki River) revealed PAH concentrations above 500 ng/g.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

In this chapter, a summary of the main findings of the study are given. Moreover, based on the research outputs, possible recommendations are forwarded to the various stakeholders (policy makers, environmentalists, non-governmental organizations, industries and government organizations which are directly and/or indirectly related to the issues raised in it). Lastly but not the least, related future research works are forwarded based on the findings and the current research gaps.

In the work the levels of potentially toxic elements and PAHs in sediment, Swiss chard and water of Akaki River, Lake Awassa and Lake Ziway, Ethiopia, were determined, employing comprehensive sample volume, effective sample pretreatment and various state-of-the-art instrumentation. The implications of the levels of potentially toxic elements and PAHs were also evaluated based on national/international guidelines.

The LIBS method was used for the determination of the concentration of Cr, Mn and Fe in sediment samples collected from Akaki River, Ethiopia. From the LIBS, results obtained for the elements varied between 0.060–0.707 mg/g for Cr, 0.895–3.64 mg/g for Mn and 26.9–71.8 mg/g for Fe, whereas the results obtained using F-AAS varied from 0.061–1.37 mg/g for Cr, 1.24–4.46 mg/g for Mn and 49.0–83.3 mg/g for Fe. There was a slight difference in the ranges of concentrations obtained by the two methods; however, F-AAS gives 100 times higher LOD values than LIBS. Moreover, the LIBS technique leads to underestimation of the obtained values as compared to the F-AAS technique. The LIBS was then subsequently employed for the determination of the levels of potentially toxic elements, since it is very simple in handling, environmentally friendly and avoids the lengthy and corrosive acid digestion route.

In the present study, for the first time, the level of mercury in sediment samples from Akaki River, Lake Awassa, and Lake Ziway, Ethiopia were determined. The LOD for determination of mercury in sediment samples was 0.05 µg/kg, with RSDs values less than 11%. All the samples had concentrations of mercury below the US EPA guideline limit of 200 µg/kg for sediment.

In addition, ICP-MS, due to the better sensitivity than LIBS, F-AAS and ICP-OES, was used for the determination of potentially toxic elements in the water samples from Akaki River, Lake Awassa and Lake Ziway, Ethiopia. The average concentration found varied in the decreasing order of Fe > Mn > Zn > Cr > V > Ni > Cu > Pb > Se > Sn > Co > Ag > Cd > Hg. Area wise comparison revealed that the concentrations are the highest in Lake Ziway and the lowest in Lake Awassa. Although at the present state the quality of most of the water bodies in this part of the country can be considered to be adequate for domestic, irrigation and related purposes, a gradual decrease in quality of the water is evident from the recent upsurge in anthropogenic activities in the sub-regions. This needs strict follow-up from the responsible authorities to control the level of potentially toxic elements in the freshwater environments of Ethiopia.

Further, ICP-OES and ICP-MS were used to determine potentially toxic elements in the sediment and vegetable samples in the freshwater bodies of Ethiopia (Akaki River, Lake Awassa and Lake Ziway). From the analysis, it was found that the sediment accumulated higher concentrations of potentially toxic elements than vegetables. The discharge of untreated effluent from industries, solid wastes and wastewater from households and institutions are assumed to be the major sources of pollution of the Akaki River flowing through the city of Addis Ababa. In addition, a significant correlation between the two lakes was found, indicating similar sources of the potentially toxic elements for the two lakes.

Based on numerical SQGs, the lakes are currently not polluted or moderately polluted with Cr and Ni, but highly polluted with Zn. Unless control and remediation mechanisms for the lake ecosystems are made practical, the situation could be deteriorate to the extent that living organisms are affected. Ultimately humans, at the pinnacle of the food chain, would also be affected. Fish from the lakes are distributed across the country. Some of the sampling sites indicated concentrations of potentially toxic elements within the ERL – ERM range, which imply possible effects on the aquatic organisms. Strict policy measures are recommended to decrease the status of contamination, since some of the elements are known to be toxic towards organisms.

Research on potentially toxic elements and PAHs in Ethiopian is sparse. In this present study, the concentrations of PAHs in the sediments of the freshwater bodies of Ethiopia (Akaki River, Lake Awassa and Lake Ziway) were determined using GC-MS. In contrast to countries, such as India, China and Thailand, relatively low concentrations were observed in the Ethiopian river and lakes. The evaluation of ecotoxicological risk indicated that all the sediment sampling sites are at lesser sediment toxicity risk according to SQGs guidelines for PAHs.

Though the concentrations of some of the potentially toxic elements, as well as those of PAHs are within the limits proposed by national and/or international guidelines, the history of their levels and therefore the influence of anthropogenic effects could not be determined, as there were no reliable data in the literature for the specified sampling areas. However, this study can be used as a baseline for further studies.

In summary, the qualities of water and sediments of the investigated aquatic system are degrading as a result of the presence of potentially toxic elements and PAHs pollution, resulting from domestic, industrial and other anthropogenic activities in the vicinities of the river and the lakes. Therefore, remediation mechanisms should be implemented and properly practiced around the rivers and lakes catchment areas.

The Federal Democratic Republic of Ethiopia (FDRE) has released three proclamations that are directly and/or indirectly related to environment and pollution (FDRE 2002a,b,c). However, based on the results obtained in this study, the proclamations seem of little or no practical value in limiting the levels of known pollutants (potentially toxic elements and PAHs) in the environment. Therefore, serious attention and combined efforts from the various stakeholders are necessary to mitigate the existing situation and to prevent the possible toxicity effects to the population, in particular, and the ecosystem as a whole.

5.2. Recommendations

The total potentially toxic elements concentration in sediments, plant and water alone is not sufficient to carry out environmental risk assessments of potentially toxic elements or for evaluating the environmental impact of potentially toxic elements emissions in a defined geographical area. It is essential to quantify and identify the chemical forms of the element in sediment in order to evaluate its impact on aquatic systems by using element speciation techniques based on sequential extraction (exchangeable fraction, the carbonate bound fraction, the Fe-Mn oxide bound fraction, the organic matter bound fraction and the residual fraction) techniques. So, future works shall focus on speciation analysis (sequential extraction).

Sediment toxicity depends not only on the concentrations of potentially toxic materials, but also on their biological availability, which is controlled by acid volatile sulfides, pH, particle size and type, organic content, re-suspension potential, and the specific form of contaminant. Therefore, besides their concentration, it will be advisable to study the above parameters so as to get precise results.

Besides the physico-chemical properties of the sediment, plant and water properties, comprehensive sediment-assessment approach which focuses on bioavailability and bioaccumulation information, clean-up strategies, ecotoxicological studies should be future areas of concern.

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ANNEX

A. Publications

Kebede Nigussie Mekonnen, Abayneh Ataro Ambushe, Bhagwan Singh Chandravanshi, Mesfin Redi Abshiro, Robert Ian McCrindle and Nikolay Panichev. Distribution of mercury in the sediments of some freshwater bodies in Ethiopia. ***Toxicological & Environmental Chemistry 2012, 94:9, 1678–1687.*** http://dx.doi.org/10.1080/02772248.2012.728602.

Kebede Nigussie Mekonnen, Abayneh Ataro Ambushe, Bhagwan Singh Chandravanshi, Mesfin Redi Abshiro and Robert Ian McCrindle. Potentially toxic elements in some freshwater bodies in Ethiopia. ***Toxicological & Environmental Chemistry 2012, 94:10, 1980–1994.*** http://dx.doi.org/10.1080/02772248.2012.744024.

Kebede Nigussie Mekonnen, Abayneh Ataro Ambushe, Bhagwan Singh Chandravanshi, Mesfin Redi Abshiro, Anton du Plessis and Robert Ian McCrindle. Assessment of the concentration of Cr, Mn and Fe in sediment using laser-induced breakdown spectroscopy. ***Bulletin of the Chemical Society of Ethiopia 2013, 27:1, 1–13.*** http://dx.doi.org/10.4314/bcse.v27i1.1.

Kebede Nigussie Mekonnen, Bhagwan Singh Chandravanshi, Mesfin Redi Abshiro, Abayneh Ataro Ambushe, Robert Ian McCrindle and Stanely Moyo· Distribution of Polycyclic Aromatic Hydrocarbons in River and Lake Sediments of Ethiopia **(ready for submission)**.

Kebede Nigussie Mekonnen, Abayneh Ataro Ambushe, Bhagwan Singh Chandravanshi, Mesfin Redi Abshiro, and Robert Ian McCrindle. Elemental concentrations of sediments from Lake Awassa and Lake Ziway, Ethiopia using ICP-MS, ICP-OES and mercury analyzer **(ready for submission)**.

Kebede Nigussie Mekonnen, Abayneh Ataro Ambushe, Bhagwan Singh Chandravanshi, Mesfin Redi Abshiro, and Robert Ian McCrindle. Assessment of potentially toxic elements in Swiss chard and sediment of Akaki River, Ethiopia **(ready for submission)**.

B. Oral Presentations

Certificate of acknowledgment for oral presentation entitled "**Assessment of levels of trace metals in sediment using Laser-Induced Breakdown Spectroscopy**" on the **4th African Laser Centre (ALC) Student** Workshop 2011, 9–13 November 2011, Zevenwacht Wine Estate, Kuils River, Western Cape, South Africa.

Oral presentation entitled "**Potentially toxic elements in some freshwater bodies in Ethiopia**" on the "**PACN Congress on Agricultural Productivity, Water and Waste"** from 26–27 November 2012, United Nations Conference Centre, Addis Ababa, Ethiopia. A book of abstract was published for the Congress.

C. Trainings

Certificate of attendance entitled "**Introduction to Practical GC-Mass Spectrometry**" at the Department of Chemistry, Addis Ababa University, Addis Ababa, Ethiopia held on 25 January 2010 – 29 January 2010, in collaboration with Royal Society of Chemistry (RSC) and Chemical Society of Ethiopia (CSE).

Course certificate entitled "**Basic Laser Safety Course**" by National Laser Centre (NLC), CSIR, held on 23rd August, 2011 in Pretoria, South Africa.

Certificate of participation by Royal Society of Chemistry (RSC) entitled "**PACN-INASP Workshop on Scientific Writing"** from 28–29 November 2012, Addis Ababa University, Addis Ababa, Ethiopia. The workshop was organized by RSC, AUTHORAID, Federation of African Society of Chemistry (FASC) and Syngenta.

Certificate of attendance entitled "**Introduction to Inductively Coupled Plasma Mass Spectrometry Training Course**" on 28 May 2013, by Separation Science, Johannesburg, South Africa.