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Heavy metal levels in the water and sediment Samples of Dire and Aba-Samuel reservoirs,Ethiopia

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A thesis submitted to the Joint MSc. Program of Addis Ababa University and Bahir-Dar University in partial fulfillment of the requirements for the Degree of Master of Science in Biology (Aquatic Ecosystems and Environmental Management-AEEM)

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May, 2019
Addis Ababa, Ethiopia

ACKNOWLEDGMENTS

First of all, I owe it all to almighty GOD for sparing my life and for his guidance and direction in carrying out this study. I acknowledge, with deep gratitude and appreciation, the inspiration, encouragement, valuable time, hosting and guidance given to me by my advisors Dr. Tadesse Fetahi (Coordinator of AEEM) and Dr. Demeke Kifle for their valuable comments and suggestions during the course of this work. I am really indebted to Prof. Abebe Getahun and Prof. Seyoum Mengistou for their critical comments and provided articles which help me to strength my proposal in particular and this thesis in general.

In addition, I want to express my deepest gratitude to Lecturers of AAU, NFLARC (Sebeta) and BDU who thought me the course during the study period. I would like to express my sincere gratitude to all the PhD members of Department of Zoological Sciences of Addis Ababa University (Mr. Abinet Woldesenbet, Mr.Alamrew Eyayu, Mr. Tarekegn Wondmagegn, W/ro Seble Bancha, Mr.Assefa Wosne, Mr.Tewedros Abate, W/ro Birehan Mohammed, Mr.Yirga Enawugaw, Mr.Solomon Wagaw, and Mr.Yadesa Chebsa**)** for their professional guidance. I also wish to express my gratitude to the staff of Bless Agri-foods Complex Laboratory Service P.L.C. and Horticoop Ethiopia P.L.C. for allowing me to use their Laboratory instruments for digestion and analysis of the samples respectively, Addis Ababa University through the Biology Department for giving me the opportunity to conduct my thesis.

My heartfelt thank goes to Austrian Development Cooperation (ADC) for financing the whole master's program study. Special appreciation goes to my classmates (Teklewoyni Assayehegn, Million Tesfaye, Habtamu Getnet, Helnata Tilahun, Birkti Miesho). Miss Badhatu Rata and Miss Fatuma Mohemmed also acknowledge for their encouragement. My special thanks go to Mr. kassahun Tessema, Who guided me during fieldwork, my colleagues Mr. Awol Assefa and Dr. Bikila Warkineh for their professional guidance and help and my families for their patience during the research period. Above all everything accomplished by the will of God!!!

"The fear of the LORD is the beginning of wisdom, and knowledge of the Holy One understand."

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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
APHA	American Public Health Association
ATSDR	Agency for Toxic Substances and Disease Registry
CCME	Canadian Council of Ministers for Environment
CSQGs	Consensus-Sediment Quality Guidelines
DCA	Detrended Correspondence Analysis
DWAF	Department of Water Affairs and Forestry
EEPA	Ethiopian Environmental Protection Agency
ESMAP	Energy Sector Management Assistance Program
GOI	Government of India
GON	Government of the Netherlands
HDPE	High-Density Poly-ethylene
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
ISQG	Interim Sediment Quality Guidelines
MPL	Maximum Permissible Limit
NOAA	National Oceanic and Atmospheric Administration
NRCC	National Research Council Canada
PEC	Probable Effect Concentration
PTEs	Potential Toxic Elements
RDA	Redendency analysis
SQGLs	Sediment Quality Guidelines
TEC	Threshold Effect Concentration
UNICEF	United Nations International Children’s Emergency Fund
USEPA	United State Environmental Protection Agency

ABSTRACT

Dire is among the main sources of drinking water supply for Addis Ababa city while Aba-Samuel Reservoir is a multi-purpose reservoir for the nearby residents. However, the ever-intensifying anthropogenic activities in the catchment have increased the potential pollutants of these reservoirs. Of all the contaminants, heavy metals are non-degradable, can bio-magnify along the food chain and are probably toxic to humans and aquatic biota. Therefore, there is a need for continuous monitoring of the pollution levels in the reservoirs as the assessment provides evidence-based data to protect public health. The concentrations of selected heavy metals in water and sediment samples were collected and determined from three sites in each reservoir (Inlet; Site1-S1, Center; Site2-S2 and Outlet; Site3-S3) for three (3) consecutive months (April to June 2018). Physicochemical parameters (DO, temperature, EC, and pH) were measured at the established three sampling sites using portable Multimeter, while turbidometer was used to measure turbidity. The collected water and bottom sediment samples were analyzed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) for selected heavy metals (Cu, Zn, Mn, Cr, Cd, Hg, Pb, and As). The data generated from the present study were statistically analyzed using Analysis of Variance (ANOVA). Physicochemical parameters except for temperature in Aba-Samuel Reservoir varied spatially although the differences in their levels among sampling sites were not significant ($p>0.05$). Among the physicochemical parameters measured in the field, only turbidity surpassed the acceptable limit set for drinking water by different organizations. The mean concentrations of heavy metals in bottom sediments (mg Kg^{-1}) were higher than those in subsurface water samples (mg L^{-1}). The highest concentrations of all metals measured in water and sediment samples were recorded for Mn in both Dire (0.236±0.014, 1098.90 ± 13.25) and Aba-Samuel (0.504±0.023, 1198.39± 6.85) reservoirs, respectively. Mean concentrations of all metals except Mn in water samples of Dire Reservoir were not significantly different among sampling sites ($P>0.05$), while the reverse was true for those of Aba-Samuel Reservoir. Some heavy metals in sediment samples of both reservoirs (e.g. Mn, Cr, and Pb) showed significant variations ($P<0.05$) among sampling sites while Zn showed spatial variations, which were not significant ($P>0.05$). The mean concentrations of heavy metals in water samples were all below the guideline values set by WHO (2008) and USEPA (2011) with the exception of Mn in both Reservoirs and Cd in Aba-Samuel Reservoir. Concentrations of Zn, Mn, Cr, and Cd in sediment samples are, however, above the respective reference values (ISQG, 2002; USEPA, 2010), while those of Pb and Cu were below the respective reference values (ISQG, 2002; USEPA, 2010) in both reservoirs. The results of the present study signify the importance of anthropogenic loading of pollutants and serve as an early signal for the need to take a timely measure to prevent further degradation of the reservoirs. Because the reservoirs are shallow and polymictic, the high concentrations of heavy metals in the sediment can lead to their increased levels in the water column thereby affecting public health and aquatic biota. Therefore, strategies of controlling point and non-point sources located all over the catchment areas should be developed to ensure better protection of the reservoirs, public health, and aquatic and terrestrial life.

***Keywords**:* Physicochemical parameters, public health, tropical reservoirs, water pollution

1. INTRODUCTION

1.1. Background and Justification

Water is one of the most important compounds that constitute the largest part of life on earth. 70.9% of the surface of our planet is covered by water (Bresine, 2007). 97% of the total water wealth is concentrated in the oceans, while ice caps comprise 2.4%. Other surface water bodies such as rivers, lakes, and ponds constitute 0.6% (Hirsch *et al*., 2006).

Aquatic ecosystems such as rivers, dams, and lakes provide a livelihood for rural populations and revenue for the region in many developing countries in Africa, including Ethiopia. They are used as a source of domestic water supply, irrigation, fishery development, hydropower generation, flood control, tourist attraction and opening up of new areas for development (Kitur, 2009). The multiple uses of these water bodies make them very important for the improvement of livelihoods of rural society (Stevenson, 2000).

Reservoirs have the potential to play an important role in fish production contributing significantly to the livelihoods of riparian communities (Adamneh Dagne and Fasil Degefu, 2007). However, the pollution of these aquatic environments has become a worldwide problem and concern in recent years because of the toxic effects of the pollutants on the aquatic organisms (Macfarlane and Burchett, 2000) and the serious health risk to humans. Uses of water for drinking, agricultural and industrial purposes are impaired due to anthropogenic and natural processes that degrade the water quality (Sanchez *et al*., 2007). Rapid population growth, urbanization, industrialization, use of fertilizers in agriculture and other human activities are some of the causes for the pollution of the freshwaters with different contaminants and resulting health related problems (Arain *et al*., 2008; Patil *et al*., 2012; Arumugam *et al*., 2013; Ellen *et al.*, 2015). The development of modern technology and rapid industrialization are among the foremost factors for environmental pollution. The environmental pollutants are spread through different channels and finally enter into the aquatic ecosystems resulting in significant impacts on living organisms living in it.

Among the various environmental pollutants of freshwater bodies, heavy metals are of particular concern due to their potential toxic effects, long biological half-life, persistence, abundance and the ease with which they can be bio-accumulated in the ecosystem and biomagnified along the trophic chain ultimately reaching the top consumer (WHO, 2000; Amoo *et al*., 2005; Censi *et al*., 2006). They have deleterious effects on both plant and animal life, in addition to the risk, they pose to human health via food supply systems (Kinyua and Pacini, 1991). These problems are getting more serious all over the world especially in developing countries. For example, drinking water contaminated with arsenic is one of the major causes of arsenic toxicity in more than 30 countries in the world (Chowdhury *et al*., 2000). Even if no sources of anthropogenic contamination exist, there is potential for natural levels of metals and other chemicals to be harmful to human health (Akoto and Adiyiah, 2007). For example; Cr (VI), Ni and Cd are carcinogenic; As and Cd are teratogenic, and the health effects of Pb include neurological impairment and malfunctioning of the central nervous system (Nadal *et al*., 2004).

Heavy metals accumulate in water, sediment, and organisms. Depending on environmental conditions, sediments act as both carrier and sources of contaminants in the aquatic environment (Shuhaimi, 2008). Sediments, which are a mixture of several components of mineral species as well as organic debris, represent an ultimate sink for heavy metals discharged into the environment (Bettinentti *et al*., 2003; Alkarkhi *et al*., 2009). Polluted sediments, in turn, can act as sources of heavy metals, imparting them into the water and debasing water quality (Zhong *et al*., 2006, Atkinson *et al*., 2007). To date, many researchers have conducted extensive surveys of heavy metal contamination of sediments (Raju *et al*., 2012). The results demonstrated that the accumulation of heavy metals has occurred in sediments of different regions. According to Anim-Gyampo *et al*. (2013), heavy metals tend to accumulate in soils and sediments after weathering processes and can be deposited in water bodies due to surface run-offs.

Sediments are ecologically important components of the aquatic habitat and play a significant role in maintaining the trophic status of any water body (Singh *et al*., 1997). Sediments are, therefore, one of the possible media for monitoring the health of aquatic ecosystems. Hence, the assessment of heavy metals in the sediment is significant to efforts made to evaluate the risk of pollution to an aquatic ecosystem.

The birth and growth of most cities in Ethiopia were associated with the development of infrastructures such as transportation routes and the establishment of industries. Addis Ababa has been the home for the majority of small and medium scale industries. Cities such as Addis Ababa may be the primary source of water pollution due to the presence of industries around the city which release pollutants to the nearby water bodies (Eshetu Gizaw *et al.*, 2004). The level of water pollution in Addis Ababa is tending to get higher with increasing human population and low economic status of the inhabitants. Being the socio-political and industrial center of the country, the capital Addis Ababa and its suburbs are severely affected by the problem of water pollution (Feven Solomon, 2007). Consequently, pollution of surface and groundwater is one of the most serious problems affecting the health of the residents. Currently, water quality degradation in Addis Ababa has become the main threat to the health of the residents especially those living in the downstream of rivers and in areas where there is a shortage of municipal water supply (Tamiru Alemayehu *et al.*, 2003). In developing countries like Ethiopia, there are no strict regulations for controlling pollutants from their sources like domestic, agricultural, and industrial activities (Solomon Sorsa *et al.,* 2015).

But, water is an important determinant of public health and failure to supply safe drinking water will cause a heavy health burden to human health. Effective monitoring and comprehensive assessment of public drinking water supply systems are, therefore, crucial to protect the wellbeing of the public and allow the implementation of a preventive approach to manage drinking water quality. The ability to properly track progress toward minimizing impacts on reservoir water quality and improving human access to safe water depends on the availability of baseline data that document trends both spatially and temporally. Therefore, assessment of reservoir water quality is necessary to reduce negative impacts on human health, irrigation and livestock quality. Heavy metal concentrations in aquatic ecosystems are usually monitored by measuring their concentrations in water, sediments and biota (Camusso *et al.*, 1995), which generally exist in low levels in water and attain considerable concentration in sediments and biota (Namminga and Wilhm, 1976).

Levels of physicochemical parameters and biological components in some of the Ethiopian inland surface waters were documented by some investigators (Yeshiemebet Major, 2006; Feven Solomon, 2007; Tadesse Fetahi *et al*., 2011; Habiba Gashaw and Seyoum Mengistu, 2012 and Yirga Kebede *et al*., 2016). In addition, high concentrations of trace metals (Cu, Zn, Pb and other related elements) from some of the Ethiopian inland surface waters were also reported by some studies (Zinabu Gebre-Mariam and Pearce, 2003; Abraha Gebrekidan *et al*.,2012; Tigist Ashagre *et al*., 2014; Aregawi Teklay and Meareg Amare ,2015; Chali Abate *et al*.,2016 and Abel Weldetinsae *et al* ., 2017).

Dire and Aba-Samuel reservoirs, the subjects of the present study, are of immense importance to the public as they have multiple uses, which include domestic use, livestock watering, small-scale irrigation and fishing (in Aba-Samuel Reservoir). For instance, the major issue in the case of Aba Samuel Reservoir is water pollution as most people living around the reservoir use the reservoir water for their daily activities (domestic purposes). Of the total households of the reservoir area, 40% use the reservoir and River water for drinking/cooking, while 70% of them use it for bathing/washing and about 93% of their animals depend on the Reservoir and River water (Feven Solomon, 2007). Despite the multiple uses of the numerous small reservoirs, there has been an urban bias regarding water quality studies in Ethiopia, which is unfortunate given that about 80% of the country's population lives in rural areas.

In pollution studies, water and sediment are often used as indicators of the level of pollution in a water body. Thus, the aim of this study was to ascertain the concentrations of selected heavy metals (Cd, Cu, Cr, Mn, Pb, As, Hg, and Zn), which are the most common Potential Toxic Elements (PTEs) (USEPA,2006) and public health concern in Dire and Aba-Samuel reservoirs. To determine the suitability of the reservoir waters for drinking water supply, the results of the present study were also compared with the maximum permissible levels set by (USEPA, 1999), (CCME,2003), (EEPA,2003) and WHO (2004;2008) for physicochemical parameters, EU (1998), WHO (2004;2008) and USEPA (2011) for heavy metals in water samples, and ISQG (2002), CSQGS of NOAA (2009), and USEPA (2010) for heavy metals in sediment samples.

1.2 Statement of the problem

The protection of the health of the rapidly increasing human population and aquatic life has necessitated the availability of water of sufficient quantity and acceptable quality. In developing countries, analysis of metals in freshwaters is very important as these water bodies serve as drinking water supply source for humans and as habitats for aquatic flora and fauna. The levels of contaminants in drinking water supply sources have thus become of particular interest because of the potential health risk posed to humans.

Dire and Aba-Samuel reservoirs seemed to be at risk of contamination by heavy metals from untreated agricultural, industrial and rural effluents. The input of wastewaters from domestic sources and agricultural runoff may eventually result in bio-accumulation of heavy metals in humans using water from Dire and Aba-Samuel reservoirs since their feeder rivers (Dire River and Akaki River, respectively) pass through populated residential areas and agricultural sites which may be the source of heavy metals like As, Mn, Cu, Hg and Zn. Clean water and sanitation are basic human needs in everyday life and becoming more urgent requirements for health protection and improvement of the living condition of people. The protection of public health requires the assessment of the water quality of the reservoirs with regard to selected heavy metals (Cd, Cu, As, Hg, Cr, Mn, Pb, and Zn).

1.3 Objectives

1.3.1 General objective

The general objective of this study was to investigate the level selected of physicochemical parameters and concentrations potential toxic heavy metals and to produce baseline data on their distribution in water and sediment of Dire and Aba-Samuel reservoirs,Ethiopia.

1.3.2 Specific objectives

I. To determine selected physicochemical water quality parameters of the reservoirs water,

II. To determine the concentrations of lead (Pb), cadmium (Cd), zinc (Zn), copper (Cu), chromium (Cr), mercury(Hg), arsenic (As) and manganese (Mn) in the reservoirs water and sediment and

III. To examine the association between the levels of physicochemical parameters in water and heavy metal concentrations in the reservoirs water and sediment.

1.4 Research questions

This research is intended to answer the following major questions.

1. What are the levels of selected physicochemical parameters (dissolved oxygen, electrical conductivity, pH and temperature) in the reservoirs water?
2. What are the concentrations of the selected heavy metals [lead (Pb), cadmium (Cd), zinc (Zn), copper (Cu), chromium (Cr), mercury (Hg), arsenic (As) and manganese (Mn)] in surface waters and sediment?
3. Is there a relationship between the levels of heavy metals in surface water and other physicochemical parameters?
4. Do the heavy metal concentrations in surface water exceed the permissible limits set by different organizations for drinking water?

1.5 Significance of the study

The two reservoirs are among the most indispensable reservoirs in the country, and hence protecting them from pollution is vital for human health. In this study, the measured levels of heavy metals were compared with the permissible levels recommended for drinking water supply. This was found necessary since the reservoirs are fed by a small tributary Rivers (Dire and Akaki Rivers respectively), which passes through agricultural and residential sites. The data that emanated from this research work has multiple benefits. The data generated are expected to be usable in efforts geared towards developing system-based approaches for the protection of Dire and Aba-Samuel reservoirs from degradation.

The findings of the study may encourage concerned bodies and farm owners to be more conscious of the issue and initiate institutions like Environmental Protection Authority, Ministry of Water, Irrigation and Electricity, Ministry of Agriculture, Ministry of health, etc. and researchers to protect these water bodies from further deterioration. Information gathered will be a contribution to the scientific literature, which can be used by other scholars with an interest in heavy metal pollution research. The results of the present study may also suggest possible solutions to the existing problems in the sector. Moreover, the output of this study may give a preliminary insight into the heavy metal contamination of the reservoirs.

1.6 Limitation of the study

Due to resource constraints including laboratory facilities required to conduct heavy metal analysis, the study was limited to heavy metal concentrations in water and sediment samples by excluding heavy metals in biological components of Dire and Aba-Samuel reservoirs. The absence of prior research on the same aspect, as well as historical data on other limnological features of the reservoirs, was also partly limiting to the present study.

2. LITERATURE REVIEW

2.1. Water pollution

Water pollution refers to any chemical, biological or physical change in water quality that harms living organisms or makes water unsuitable for desirable uses. It occurs in both (fresh and marine water bodies) and includes organic and inorganic chemicals, heavy metals, petrochemicals, and microorganisms. Water pollution may also occur in the form of thermal pollution and depletion of dissolved oxygen. It can come from single sources or from larger and dispersed sources. Point sources discharge pollutants at the specific location through drain pipes or sewer line into bodies of surface water. Non-point sources such as runoff, are diffused and intermittent and are influenced by a factor such as land use, climate, hydrology, topography, native vegetation, and geology. Rural source of nonpoint pollution is generally associated with agriculture, mining, forestry and organic matter of plant and animal origin (Botkin and Keller, 1997).

Industrialization, urbanization, agriculture (food production), and natural resources exploitation (mining and energy exploration) are basic activities associated with modern living and vibrant society (Gribble, 1994). Rapid urbanization and industrialization with improper environmental planning often lead to the discharge of industrial and sewage effluents into Rivers (Lokeshwari *et al*., 2006). A number of studies on Rivers and reservoirs indicate that poor farming practices and poor provision of sanitation facilities to the riparian communities (Mathooko, 2001; Mokaya *et al*., 2004), as well as leachate from open solid waste dumps which are usually located on edges of Rivers inflict serious water quality deterioration (Tamiru Alemayehu *et al*., 2003).

Water supply systems and drinking water inaccessibility in developing countries is a global concern that calls for immediate action. About 884 million people in the world still do not get their drinking water from approved sources, and almost all of these people are in developing regions (WHO/UNICEF, 2014). Global estimates suggest that nearly 1.5 billion people lack safe drinking water and out of this number, more than 300 million people living in rural areas of sub-Saharan Africa are being affected and least 5 million deaths per year can be attributed to waterborne diseases (Bresine, 2007).

2.2 Sources of heavy metals and sediments

The term heavy metal is a general collection term applying to the group of metals and metalloids with an atomic density greater than 5g/cm^3 (Guevara-Riba *et al.*, 2004). Metals are elements, present in chemical compounds as positive ions, or in the form of cations (+ ions) in solution. Heavy metals are produced from a variety of natural and anthropogenic sources; they are indeed intrinsic natural constituents of our environment. Heavy metals in water Reservoirs originate from both natural processes and anthropogenic sources. Agricultural soil is the most important sink for heavy metals due to soils' high metal retention capacities (Tokalioglu, 2006). Their origins may be classified into various sources including terrigenous derived from continents (weathering and erosion), biogenic derived from organism decays (skeletal parts, carbonaceous or siliceous), authigenic derived from seawater (chemical or biochemical precipitation and Fe-Mn nodules), volcanogenic, extra-terrestrial or cosmogonies, and anthropogenically derived from human activities. Relatively, anthropogenic sources are mainly from industrial processing, urban sewage and agricultural runoff (Rezaei and Sayadi, 2015). Once heavy metals and other pollutants are discharged into the water; they rapidly become associated with particulates and are incorporated in bottom sediments (Hogg and Norris, 1991).

Heavy metals are bio-accumulated and bio-transferred both by natural and anthropogenic sources. The most important sources of heavy metals in the environment are the anthropogenic activities such as mining, smelting procedures, steel and iron industry, chemical industry, traffic, agriculture as well as domestic activities (Antilén *et al*., 2006), which enter into surface and ground water, soils and ultimately to the biosphere. Conversely, metals also occur in small amounts naturally and may enter into the aquatic system through leaching of rocks, airborne dust, forest fires and vegetation (Iyaka, 2007). In addition, vegetables are also known to offer the most rapid and low-cost source of trace elements for the majority of people in developing nations (Taiga *et al.*, 2008).

Effluents containing heavy metals from industries are one of the principal sources of pollution for surface water, groundwater and soil (Szefer, 1997). In developing countries like Ethiopia, untreated or partially-treated wastewaters of industries are directly discharged to the nearby wetland and /or water bodies (Solomon Sorsa *et al.*, 2015). The concentration of metals released from industries varies from industry to industry and the raw materials used. Most factories in

Ethiopia, including textile and leather industries, have no effluent treatment plants (EEPA, 2003). The major problem associated with textile processing effluents is the presence of heavy metal ions, from the dying process or usage of metal-containing dyes (Correia, 1998).

Generally, metals are introduced into the environment by a wide range of natural and anthropogenic sources and with anthropogenic sources being either domestic or industrials. They occur naturally at levels that are considered not to have toxic effects on living organisms. The natural levels of metals are normally increased through various anthropogenic processes. Currently, anthropogenic inputs of metals were higher than the natural input and this may pose a great threat to aquatic life in particular and to whole ecosystems in general (Weiner, 2012). Sediment transport into aquatic systems resulted from agricultural activities, forestry, mining and industrial activities (Guven and Akinci, 2008).

2.3 Heavy metals in the aquatic environment and their distribution

Heavy metals are present in the environment in different forms such as in solid phase and in solution, as free ions, or absorbed to solid colloidal particles. Once in the aquatic environment, heavy metals are partitioned among various aquatic environmental compartments (water, suspended solids, sediments, and biota). Plants capable of taking large quantities of trace metals originating from the environment are said to be hyperaccumulators (Olajire and Ayodele, 2003). The metals in the aquatic environment may occur in dissolved or particulate forms. The main processes governing distribution and partition are dilution, advection, dispersion, sedimentation and adsorption/desorption. Thus, speciation into the various soluble forms is regulated by the instability constants of the various complexes and by physicochemical properties of water (pH, dissolved ions, redox potentials and temperature). However, heavy metals in water may be removed through several mechanisms including :(1) adsorption onto particulate; (2) chemical transformation into insoluble form; (3) precipitation and sedimentation (Balasubramania *et al.*, 1997).

Calmano *et al*. (1993) stated that the majority of metal contaminants partition onto particulate matter such as clay minerals, hydroxides, carbonates, organic substances (e.g. humic acids) and biological components (e.g. algae and bacteria). Heavy metals cannot be degraded but they are deposited, assimilated or incorporated in water, sediments and aquatic biota causing heavy metal pollution in water bodies (Linnik and Zubenko, 2000; Malik *et al*., 2010).

The transformation of heavy metals in aquatic environments occurs as biochemical mediated reduction, methylation, demethylation, and oxidation of single metal species. Redox reactions may also facilitate some transformations. The biochemical processes are carried out by microorganisms and algae. Heavy metals are taken up by both fauna and flora of the aquatic environment. This uptake could provoke an increase in the concentration of metals in an organism; if the excretion phase is slow, this can lead to the bioaccumulation and bio-magnification phenomenon (Sulter, 1993). Different exposure route leads to the availability of trace elements to the human body system. The main exposure root for human body system is through contact with the skin from air, water, dust, etc., inhalation via air and ingestion via food, water, and drugs (fig. 1).

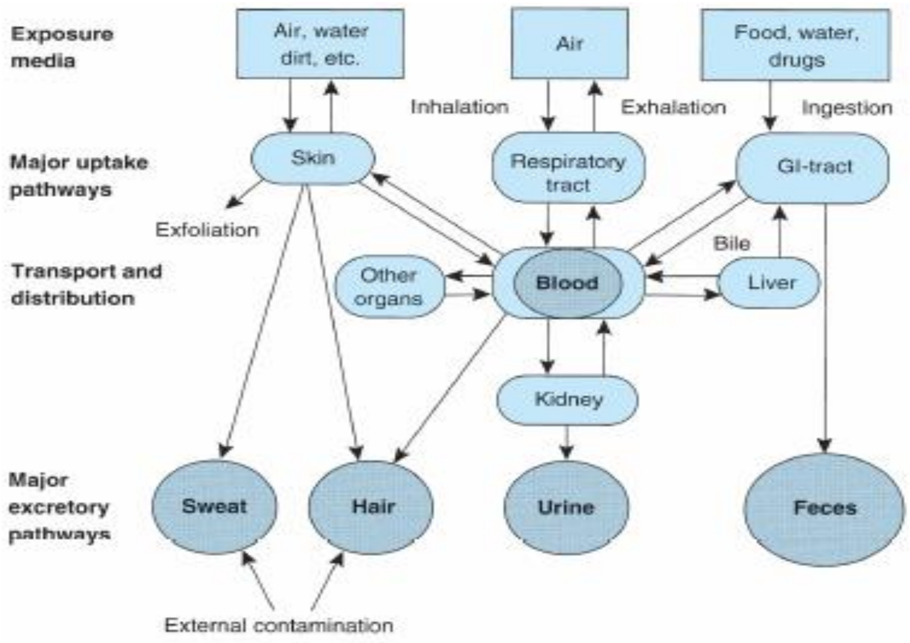


Figure 1: Metabolism after exposure to chemical elements via skin absorption, inhalation and ingestion. The arrow indicates how metals are transported in human body system (Source: Klaassen, 2007).

Tigist Ashagrie *et al*. (2015) assessed the concentration of metals (Hg, Cr, Zn Cd, and Pb) in water, sediment, and samples of the macrophyte *Schoenoplectus corymbosus* collected from six different sites of Lake Hawassa. The observed result revealed that all sampling sites had higher metals concentration in water, sediment and plant samples compared to the reference site with only Pb occurring at all sites with all the analyzed metals. Another study conducted by Zinabu Gebre-mariam and Pearce (2003) on nine Ethiopian rift-valley lakes, six Rivers (their inflows) and two industrial effluents concluded that, compared to more industrialized regions and other African lakes, the concentrations of heavy metals in Ethiopian rift-valley lakes (with the exception of the soda lakes) and their inflows were low and the water quality is relatively unimpaired with respect to heavy metals. They also recommended that pollution control measures such as proper sewage handling, careful management of grazing areas, etc., have to be taken to protect the water bodies from degradation.

2.4 Heavy metal contamination of sediments

Pollutants released to surface water from industrial and municipal discharges, atmospheric deposition and runoff from agricultural, urban and mining areas accumulate in sediments (Chukwujindu *et al.,* 2007). Like soils in the terrestrial system, sediments are the primary sink for heavy metals in the aquatic environment. The importance of sediments as a sink for a range of substances including nutrients, hydrocarbons, pesticides and heavy metals has been highlighted in many past studies (Baldwin and Howitt, 2007). Abraha Gebre-Kidan *et al*. (2012) observed that sediments play a significant role in the remobilization of contaminants in aquatic systems under favorable conditions and interactions between water and sediments. Apart from water, sediments are also responsible for the transportation of nutrients and other pollutants in the aquatic environment. Sediments capture hydrophobic chemical pollutants that enter water bodies (McCready *et al*., 2006) and slowly release the contaminant back into the water column (Chapman and Chapman 1996; McCready *et al*., 2006). Heavy metals may adsorb onto sediments or be accumulated by the benthic organisms; their bioavailability and toxicity depend upon the various forms and amount bound to the sediment matrices (Chukwujindu *et al.,* 2007). Heavy metals once adsorbed on the sediments are not freely available for aquatic organisms. Under changing environmental conditions (temperature, pH, redox potential, salinity) of the overlying water, these toxic metals are released back to the aqueous phase (Soares *et al*., 1999).

Sediments near urban areas commonly contain high levels of contaminants (Lamberson *et al*., 1992; Cook and Wells, 1996). This constitutes a major environmental problem faced by many anthropogenically impacted aquatic environments (Magalhaes *et al*., 2007). The occurrences of enhanced concentrations of heavy metals especially in sediments may also be an indication of human-induced perturbations rather than natural enrichment through geological weathering (Eja *et al.*, 2003). The contamination of sediments with heavy metals leads to a serious environmental problem (Loizidou *et al.*, 1992).

The analysis of metals in sediment is used for detection of pollutants that may be either absent or in low concentrations in the water column (Awfolu *et al*., 2005). The transport or mobility of metals from the overlying water to the sediment is dependent on a number of external environmental factors such as pH, EC, the ionic strength of the compound, anthropogenic input, the type and concentration of organic and inorganic ligands and the available surface area for adsorption caused by variation in grain size distribution (Kumar and Edward, 2009).

In addition to the physical and chemical relationships between sediments and contaminants, sediments are of fundamental importance to benthic communities in terms of providing suitable habitats for essential biological processes. Thus, sediments provide an essential link between chemical and biological processes. Akan *et al*. (2010) observed that sediments in Rivers do not only play important roles in influencing the pollution, they also record the history of their pollution. Contamination of sediments by heavy metals and other pollutants is considered by many regulatory agencies to be one of the major threats to aquatic ecosystems. Sediments are, therefore, one of the possible media in monitoring the health of aquatic ecosystems. Heavy metal distribution and bioavailability in both sediments and the overlying water column have to be considered in order to obtain a better understanding of the interactions between the organisms and their environment. Therefore, ensuring a good sediment quality is crucial to maintain a healthy aquatic ecosystem, which ensures good protection of human health and aquatic life.

Table 1: Concentration of heavy metals in sediments collected from different water bodies in mg Kg^{-1} (ND=Not Detected)

Water bodies	**Heavy metals and their concentration (mg Kg^{-1})**								
	Cr	Pb	Cd	Zn	Cu	Ni	Mn	Co	References
Lake Hashenge	86.5	3	208.0	1129	56.0	3942	71	34	Abraha Gebrekidan *et al. (*2012)
Mainefhi Reservoir, Eritrea	14.61	1.75	--	5.77	8.17	4.54	87.25	0.790	Zerabruk Tesfamariam *et al.*(2016)
Toker Reservoir, Eritrea	252.598	5.005	0.005	88.923	83.396	87.806	1455.746	33.860	Zerabruk Tesfamariam *et al.*(2016)
Ureje Reservoir	21.37	15.60	ND	200.63	100.38	-	1.85	-	Adebayo (2017)
Avsar Dam	9.41-19.9	0.64-6.35	0.34-1.23	-	18.2-38.4	19.8-39.4	-	-	Öztürk *et al.*(2009)
Lake Victoria	12.9	54.6	7.0	-	26.1	-	-	-	Kishe and Machiwa (2003)
Lake Geneva	337	620	18.4	-	727	87	-	-	Pote *et al.*(2008)

2.5 Effects of heavy metals and sediments

According to United State Environmental Protection Agency (USEPA, 2006) mercury (Hg), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) are listed as the most common Potential Toxic Elements(PTEs). The heavy metals of most environmental concern in water bodies are thus lead (Pb), chromium (Cr), arsenic (As), cadmium (Cd), copper (Cu) and zinc(Zn) (Moore *et al*., 2009). Pollution of heavy metals in the aquatic environment is a growing problem worldwide and currently, it has reached an alarming rate. Heavy metals adversely affect soil ecology, agricultural production or product quality, and surface and groundwater quality, and will ultimately harm the health of living organism through the food chain. These effects are closely related to the biological availability of heavy metals, which in turn are controlled by the metal ion speciation in the water. Heavy metals are among the most harmful water pollutants due to their non-biodegradability, long biological half-life and their potential to accumulate in aquatic ecosystems (Arian *et al*., 2008; Benzer *et al.*, 2013).

One of the severest environmental accidents in the history is the ‘Itai-Itai disease’ that started since 1912 in Japan and was named by local residents as a disease incurring severe pains felt in the spine and joints attributed to cadmium poisoning by local mining companies (Rajappa *et al*., 2010; Kaji, 2015). Although some heavy metals such as Fe, Mn, Co, Cu, and Zn are essential micronutrients for aquatic fauna and flora, they may be dangerous at high levels (Nadal *et al*., 2004; Ochieng *et al*., 2007). Heavy metals including both essential and non-essential elements have a particular significance in ecotoxicology since they are highly persistent and all have the potential to be toxic to living organisms (Storelli *et al*., 2005). Kleiman *et al*. (2008) showed that liver-related diseases were started 1980, but recently it becomes the most severe disease in northern Ethiopia (Shire area) and about 270 peoples and more have been died since then. Males and females have been equally affected and children aged between 7 and 15 appear to be most susceptible. By now the rate of disease is elevated and many of the local people have been worrying about the spreading of this liver-related disease.

Contamination with heavy metals particularly the non-essential elements may have distressing effects on the ecological balance of the recipient aquatic environment harboring diverse organisms. This has particular significance in ecotoxicology since heavy metals are highly persistent and have the potential to bioaccumulate and biomagnify in food chains and become toxic to living organisms at higher trophic levels in nature. The presence of heavy metals in the water may have a profound effect on the microalgae which constitute the main food source for bivalve mollusks in all their growth stages, zooplankton (rotifers, copepods, and brine shrimps) and for larval stages of some crustacean and fish species (Mandour *et al*., 2011). It is reported that Cd caused enzyme inhibition in erythrocytes, gills, livers, and kidneys (Bektas *et al*., 2008). Chronic diseases (Liver Cirrhosis, Renal Failure, Chronic Anemia and Hair Loss) occur due to the pollution of drinking water with heavy metals such as Cu, Cd, Ni, Cr and Pb (Wang *et al.*, 2010). Renal failure occurs when drinking water is polluted with Cd and Pb; liver cirrhosis due to pollution with Cu and molybdenum; hair loss due to pollution with Cr and Ni; and chronic anemia due to pollution with Cd and Cu (Johri *et al*., 2010). Heavy metal toxicity represents a rare, yet clinically-significant medical condition, which if overlooked or inadequately treated, results in significant morbidity and mortality (Jan *et al*., 2011). Heavy metals can directly influence behavior by influencing neurotransmitter production and utilization, impairing mental and neurological function, and altering numerous metabolic body processes (Nava-Ruize *et al.*, 2013).

Sedimentation is widely acknowledged as a major cause of degradation to the ecological condition of rivers (Hynes, 1970; Wood and Armitage, 1997). It is a major problem that shortens the lifespan of municipal water supplies, irrigation, and hydropower generation dams. The input of excess sediment into water has been recognized as a potential threat to the well-being of aquatic organisms and reduces its productivity (Chapmann, 1988). The detrimental impact of sediment and associated pollutants on water quality were extensively studied for many water bodies (Rickson, 2014).

The effects of sediments on receiving water ecosystems are complex and multi-dimensional and further compounded by the fact that sediment flux is a natural and vital process for aquatic systems. Sediment stress results from a change in sediment load originating from within the watershed, ultimately compromising the ecological integrity of the aquatic environment (Lloyd *et al*., 1987). The transport of sediments into surface waters has both physical and chemical consequences for water quality and aquatic ecosystem health including a reduction in the amount of available sunlight, thereby limiting the production of algae and macrophytes and degradation of fish habitat as spawning gravel becomes filled with fine particles. In many cases, toxic substances can be absorbed by sediment particles and then transported to other areas. Studying the quantity, quality, and characteristics of sediments in the stream help scientists and engineers to determine the sources and evaluate the impact of the pollutants on the aquatic environment. Recognizing the role of suspended sediment (SS) in the transportation of major elements from land to rivers is necessary (Chau, 2006).

Generally, epidemiological and toxicological studies have demonstrated that a strong relationship between the prevalence of several diseases in humans, particularly cardiovascular diseases, kidney disorders, and various forms of cancer and the presence of many metals such as cadmium, mercury, and lead (Nadal *et al*., 2004). Therefore, water quality requirement for a particular use plays an important role in the management of water resources and in turn forms an integral part of water quality management (Parsons and Tredoux, 1995).

2.6 Selected heavy metals under study

2.6.1 Copper

Copper is an essential constituent of living systems (Rand and Petrocelli, 1988; Nicholas *et al*., 1998). It is one of the world's most widely used metals. Although the concentration of copper is usually low in nature, it occurs in adequate quantities for growth in all aquatic environments. It is required for bone formation, maintenance of myelin within the nervous system, synthesis of hemoglobin, and as a component of key metalloenzymes, plus it forms and as an important part of cytochrome oxidase and assorted other enzymes involved in the redox reactions in the cells of animals. Although copper is important, it is toxic when concentrations exceed that of natural concentrations (< 0.05 µmol L^{-1}) (Pelgorm *et al*., 1995; Stouthart *et al*., 1996).

It originates from copper-bearing ores including sulfides, arsenates, chlorides, and carbonates as well as anthropogenic sources such as industry, mining, plating operations, usage of copper salts to control aquatic vegetation or influxes of copper containing fertilizers (Nussery, 1998). It can exist in an aquatic environment in three forms namely soluble, colloidal and particulate. Copper occurs in metalloproteins such as hemocyanin, an oxygen carrier in mollusks and arthropods, cytochrome oxidases and plastocyanin (Hughes, 1975). Copper ions (Cu^{2+}) are toxic to most life forms, 0.5 ppm being lethal to many algae species (O'Dell and Campell, 1971).

The toxicity of copper in aquatic organisms is largely attributable to Cu^{2+} that forms complexes with other ions (Nussey, 1998). Organic and inorganic substances can easily complex the cupric form of copper, which is the most common speciation of this metal and it is then adsorbed on to particulate matter. Therefore, the free ion is rarely found except in pure acidic soft water. Excess of copper in the human body is toxic and causes hypertension and produces pathological changes in brain tissues. Excessive ingestion of copper is responsible for the specific disease of the bone (Krishnamurthy and Pushpa, 1995). High doses may also cause anemia, liver and kidney damage, stomach and intestinal irritation (Tirkey *et al*., 2012). Copper-toxic effects in fish include; change biochemistry, anatomy, physiology, and behavior. It damages the gill and cause mucous to gather on the gill area (Figueiredo-Fernandes *et al*., 2007).

2.6.2 Lead

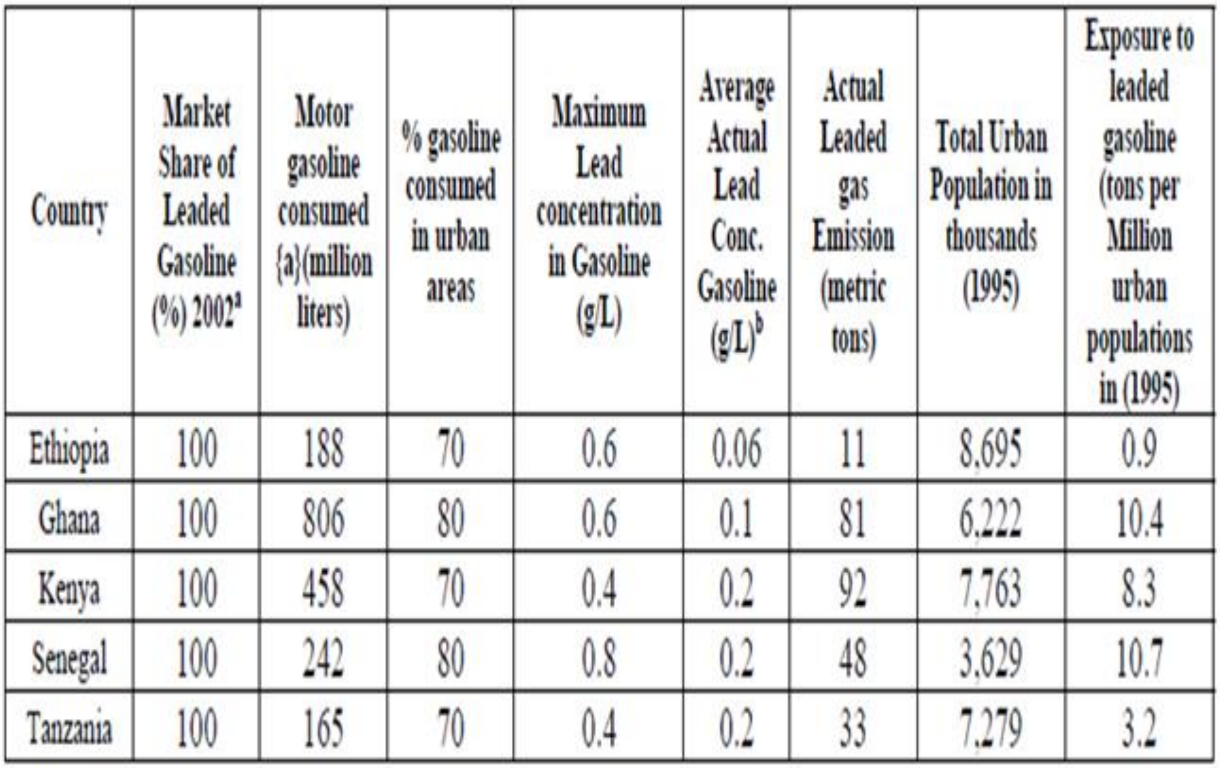
Lead (Pd) in the environment arises from both natural and anthropogenic sources. It is a natural constituent of air, water, and biosphere (Alala, 1981). Lead is an undesirable trace metal less abundantly found in earth's crust. It is extensively used and is one of the most widespread metals in the environment largely due to human activities (Tarr and Miessler, 1999). The major sources of lead in the environment are automobile exhaust, industrial wastewater, wastewater sludge and pesticides (Balba *et al*., 1991).

Lead is toxic and a major hazard to human and animals. Lead has two quite distinct toxic effects on human beings, physiological and neurological. Acute lead toxicity is initially characterized by damaging gill epithelium and ultimately suffocation. Two types of structural alterations of gill, defense/compensatory responses and direct deleterious effects were observed in chronic lead exposed fish (Parashar and Banerjee, 1999). The necrosis and desquamation of gill epithelium, as well as lamellar curling and aneurisms, were the direct deleterious effects reported in chronic lead exposed *Clarias gariepinus.* The characteristic symptoms of chronic lead toxicity include changes in the blood parameters with severe damage to erythrocytes and leucocytes and damage in the nervous system (El-Badawi, 2005). Lead deplete major antioxidants in the cell, especially thiol-containing antioxidants and enzymes that can cause significant increases in reactive oxygen species (ROS) production, followed by a situation known as oxidative stress leading to various dysfunctions in lipids, proteins, and DNA (Ercal, 2001). High levels of exposure may result in biochemical effects in humans, which in turn cause problems in the synthesis of hemoglobin, harmful effects on the kidneys, gastrointestinal tract, joints, and reproductive system, and acute or chronic damage to the nervous system (Tirkey *et al*., 2012). Lead is a systemic agent affecting the brain (Tver, 1981). The toxicity of lead is based on the fact that it is a potent enzyme inhibitor because it binds sulphydryl (SH) groups.

Lead accumulates in the bones and soft tissues, particularly in the brain, resulting in its reduced functioning (Alala, 1981; Rand and Petrocelli, 1988). The main targets of lead toxicity are the hematopoietic and nervous systems. Several of the enzymes involved in the synthesis of heme are sensitive to inhibition by lead. Even at low levels of exposure, children may show hyperactivity, decreased attention span, mental deficiencies, and impaired vision.

Low levels of Pb pollution could cause some adverse effects on fish health and reproduction (Delistraty and Stone, 2007) and also cause pathological changes in tissue and organs (Rubio *et al*., 1991) and impair the embryonic and larval development of fish species. Several effects of lead toxicity have been reported on the exposure of fish to lead. These include (1) behavioral deficits in fish within a day of exposure to sublethal concentration (2) a deficit in metabolism and survival (3) decreasing in growth rate and development (4) a deficit in behavior and learning (5) increased mucus formation in fish and (6) the level at 50 µg/g in the diet are associated with reproductive effects in some carnivorous fish (Eisler, 1997).

Table 2: Estimate of relative Lead Exposure in Selected African Countries (Source: ESMAP, 2003)



Country	Market Share of Leaded Gasoline (%) 2002[a]	Motor gasoline consumed {a}(million liters)	% gasoline consumed in urban areas	Maximum Lead concentration in Gasoline (g/L)	Average Actual Lead Conc. Gasoline (g/L)[b]	Actual Leaded gas Emission (metric tons)	Total Urban Population in thousands (1995)	Exposure to leaded gasoline (tons per Million urban populations in (1995)
Ethiopia	100	188	70	0.6	0.06	11	8,695	0.9
Ghana	100	806	80	0.6	0.1	81	6,222	10.4
Kenya	100	458	70	0.4	0.2	92	7,763	8.3
Senegal	100	242	80	0.8	0.2	48	3,629	10.7
Tanzania	100	165	70	0.4	0.2	33	7,279	3.2

[a] Market share and fuel consumption data are for 2002 but for Kenya is 1995 data.

[b] Lead content for Ghana is average actual for 2001/02 (Jan 01–May 02); for Tanzania, Senegal, and Kenya lead content is assumed.

2.6.3 Zinc

Zinc is the second most abundant trace element after Fe and is an essential trace element and micronutrient in living organisms, found almost in every cell and being involved in the nucleic acid synthesis and occurs in many enzymes (Sfakianakis *et al*., 2015). It is involved in more complicated functions, such as the immune system, neurotransmission and cell signaling (Celik and Oehlenschlager, 2004) and physiological and metabolic process in living organisms (Amundsen *et al*., 1997; Rajappa *et al.*, 2010). It is found in virtually all food and potable water in the form of salts or organic complexes (WHO, 2011). It may occur in water as a free cation as soluble zinc complexes or can be adsorbed on the suspended matter.

Zinc is a very common environmental contaminate and usually outranks all other metals and it is commonly found in association with lead and cadmium (Finkelman, 2005). Zinc shows fairly low concentration in surface water due to its restricted mobility from the place of rock weathering or from the natural sources (BIS, 1998). It is also necessary for a healthy immune system, cell division and synthesis of protein and collagen which is great for wound healing and healthy skin. However, a higher amount of it can cause anemia, pancreas damage and lower levels of a high density of lipoprotein cholesterol (Finkelman, 2005).

Zinc toxicity is modified by water chemical factors including dissolved oxygen concentration, hardness, pH and temperature of the water (Nussey, 1998) and can also be changed through other heavy metals compounds and alkaline earth metals. High temperature tends to increase zinc toxicity, while the increase in water hardness, alkalinity, and organic chelators can reduce its acute lethality and low dissolved oxygen content in water increases the toxicity of zinc (Chapman, 1978). Zinc may be toxic to aquatic organisms but the degree of toxicity varies greatly, depending on water quality characteristics as well as species being considered (Datar and Vashishtha, 1990). The permissible limit of zinc in water is 3 mg L^{-1} (WHO, 2008). Drinking water containing high levels of zinc can lead to stomach cramps, nausea, and vomiting. Other clinical signs of Zn toxicity have been reported as diarrhea, bloody urine, liver failure, kidney failure and anemia (Duruibe *et al*., 2007).

2.6.4 Chromium

Chromium is an essential micronutrient for animals and plants. It is considered as a relative biological and pollution significance element (Rajappa *et al.*, 2010). Generally, the natural content of chromium in drinking water is very low ranging from 0.01 to 0.05 mg L^{-1} except for regions with substantial chromium deposits (Wedepohl, 1978). It is an essential nutrient metal (Cr^{3+}), necessary for the metabolism of carbohydrates (Farag *et al.*, 2015). Elevated concentration can result from industrial and mining processes (Datar and Vashishtha, 1990). Poor treatment of these effluents can lead to the presence of Cr (VI) in the surrounding water bodies, where it is commonly found at potentially harmful levels to fish and other aquatic organisms (Li *et al.*, 2011; Pacheco *et al.*, 2013; Abel W/tinsae *et al.*, 2017). Chromium occurs in several oxidation states in the environment ranging from Cr^{2+} to Cr^{6+} (Rodríguez *et al.*, 2009).

The most commonly occurring forms of Cr are trivalent- Cr^{3+} and hexavalent- Cr^{6+} with both states being toxic to animals, humans, and plants (Mohanty and Kumar, 2013). In surface waters, depending on physicochemical characteristics, the most stable forms of chromium are the oxidation states trivalent Cr (III) or ($Cr^{3+)}$ and the hexavalent Cr (VI) or (Cr^{6+}). Hexavalent chromium (Cr^{6+}) is considered to be toxic (i.e. carcinogenic) because of its powerful oxidative potential and ability to cross cell membranes. In India, the chromium level in underground water has been witnessed to be more than 12 mg L^{-1} and 550-1,500 ppm/L.

Among the health effects brought about by the exposure to chromium VI include lung cancer, malignant neoplasia, chromium dermatitis and skin ulcers (Rand and Petrocelli, 1988). Perforations and ulcerations of the nasal septum and bronchial asthma have also been reported. In one of the studies, a fourfold increase in childhood leukemia was attributed to the possible consumption of water with chromium VI levels above standard recommended value (Rand and Petrocelli, 1988). The prevalence of chromium in drinking water above 5mg L^{-1} results in bleeding of the gastrointestinal tract, cancer of the respiratory tract, ulcers of the skin and mucous membrane (Rajappa *et al.*, 2010).

2.6.5 Cadmium

Cadmium is a naturally occurring non-essential trace element and its' tendency to bioaccumulate in living organisms often in hazardous levels, raises environmental concern (Kalman *et al.*, 2010). Cadmium production, consumption, and emissions to the environment have increased dramatically during the 20th century, due to its industrial use (batteries, electroplating, plastic stabilizers, pigment), and consequently lead to contamination of aquatic habitats. As a non-degradable cumulative pollutant, Cd is considered capable of altering aquatic trophic levels for centuries.

The main sources of cadmium are industrial activities as the metal widely used in electroplating, pigments, plastic, stabilizes and battery industries. Cadmium is used industrially as an anti-friction agent, as a rust inhibitor, in plastic manufacturing, like an orange coloring agent in enamels and in paints and in alkaline batteries (Purves, 1977).

Cadmium is widely known to be a highly toxic non-essential heavy metal and does not have a role in the biological process in living organisms. It is a natural element in the earth crust and usually found as a mineral with other elements. All soils, rocks, coal, and mineral fertilizers have some cadmium in them. Cadmium is highly toxic and responsible for several causes of poisoning through food. Small quantities of cadmium cause adverse changes in the arteries of the human kidney. Cadmium even in low concentration is quite toxic to human health (Mohan *et al*., 1998). It is bio persistent and once absorbed by an organism, remains resident for many years (over decades for humans) although it is eventually excreted (Tirkey *et al*., 2012). High exposure leads to obstructive lung disease and can even cause lung cancer. Cadmium produces bone defects in humans and animals (Tirkey *et al*., 2012).

2.6.6 Manganese

The element manganese (Mn) is present in over 100 common salts and mineral complexes that are widely distributed in rocks, in soils and on the floors of lakes and oceans (Finkelman, 2005). These Mn minerals include sulfides, oxides, carbonates, silicates, phosphates, arsenates, tungstates, and borates; however, the most important Mn mineral is the native black manganese oxide, pyrolusite (MnO_2). Mn is used for the production of ferromanganese steels, electrolytic manganese dioxide for use in batteries, alloys, catalysts, antiknock agents, pigments, dryers, wood preservatives, and coating welding rods. It is also used as an oxidant for cleaning, bleaching, and disinfection (as potassium permanganate) and as an ingredient in various products (WHO, 2011).

Manganese is an essential micronutrient present in all living organisms, as it functions as a cofactor for many enzyme activities (Suresh *et al*., 1999). It is necessary for the formation of connective tissues and bone, growth, carbohydrate and lip metabolism, embryonic development of the inner ear, and reproductive function (WHO, 2011 and DWAF, 1996). Mn is a metal with low toxicity but has a considerable biological significance and seems to accumulate in fish (Kumar *et al*., 2011). According to Krishna *et al*. (2014), high Mn concentration interferes with the central nervous system of vertebrates; hence a matter of concern as the consumption of Mn contaminated fish could result to health risks to the consumers. The high concentration of Mn causes liver cirrhosis and also produces a poisoning called Manganese or Parkinson disease (Kumar *et al*., 2011). It is more prevalent in groundwater supplies owing to the reducing conditions that exist underground. Manganese is an essential element in humans and animals. It is regarded as one of the least toxic elements; toxicity in humans is usually the result of chronic inhalation of high concentrations of manganese in dust from industrial sources. At levels exceeding 0.15 mg L^{-1}, manganese stains plumbing fixtures and laundry and causes undesirable tastes in beverages. It may lead to the accumulation of microbial growths in the distribution system that could give rise to taste, odor, and turbidity problems in the distributed water (WHO, 2011 and DWAF, 1996).

Table 3: Summary of selected heavy metals, their sources and their potential health effects (Source: EPA, 2005)

Heavy metals	**Major sources**	**Potential Health Effects**
Arsenic (As)	Use of arsenical pesticides, natural mineral deposits or inappropriate disposal of arsenical chemicals	Gastrointestinal, skin and nerve damage, cancer. Arsenicosis Disease
Cadmium (Cd)	Industrial activities, Cadmium fungicides, cadmium-based enamel and cadmium pigments, in nickel-cadmium dry cell batteries, phosphate fertilizers, and coal.	Gastrointestinal, kidney and lung damage
Chromium (Cr^{+6})	Textile, leather and leather products	Lung and skin damage, cancer
Lead (Pb)	Paper & paper products, automobile exhaust, industrial activity and pesticides	Nervous and immune system and kidney damage embryo/fetotoxic
Mercury (Hg)	Agriculture, industrial, -pulp and paper industries, -pharmaceuticals, chlorine and caustic soda production industry	Acrodynia or pink disease Minamata disease
Manganese (Mn)	Ferromanganese steels, electrolytic manganese dioxide	Manganese or Parkinson disease
Copper (Cu)	Industry, mining, usage of copper salts or fertilizer	Insomnia disease Wilson disease
Zinc (Zn)	Zinc fertilizers, sewage sludge, and mining.	Anemia, the effect on the digestive system and lower levels of the high density of lipoprotein cholesterol.

Table 4: Concentration of heavy metals from different water bodies in (**mg L^{-1}**)

Water bodies	Heavy metals and their concentration (mg L^{-1})									
	Cr	**Pb**	**Cd**	**Zn**	**Cu**	**Ni**	**Mn**	**As**	**Co**	**References**
Tendaho Reservoir	0.15	0.26	<MDL	2.51	0.53	0.96	0.86	-	1.23	Wondimagegne Asefa and Tarekegn Breranu (2015)
Lake Chamo	-	-	-	0.21	0.5	-	-	-	-	Belay Tafa and Eshete Assefa (2014)
Mainefhi Reservoir	0.028	-	0.004	0.016	0.004	0.011	0.065	-	-	Zerabruk Tesfamariam *et al*. (2016)
Toker Reservoir	0.017	-	0.001	0.016	0.011	0.007	0.096	-	-	Zerabruk Tesfamariam *et al*. (2016)
Ureje Reservoir	0.02	ND	0.03	0.04	0.03	-	0.06	-	-	Adebayo (2017)
Lake Beseka	ND	0.631	0.054	-	-	-	0.075	0.059	-	Fuad Abduro and Gelaneh W/michael (2016)
Avsar Dam	0.001-0.012	0.0003-0.019	0.0001-0.0012	-	0.01-0.02	0.0004-0.012	-	-	-	Öztürk *et al*. (2009)

Lake Hashenge	0.0034	0.0033	0.0087	0.9375	0.0021	0.0023	0.02	-	0.0035	Abraha Gebrekidan *et al.* (2012)
Lake Hayq	-	0.086	BDL	0.156	0.825	-	-	-	-	Aregawi Teklay and Meareg Amare (2015)
Assela River water	0.09	0.05	0.009	0.1	-	0.36	-	-	0.09	Chali Abate *et al*. (2016)
Assela Tap water	0.097	0.04	0.005	0.07	-	0.037	-	-	0.03	Chali Abate *et al*. (2016)
Siberian Pond	0.002	0.002	<0.001	-	0.002	0.002	-	-	-	Gladyshev *et al.* (2001)

3. MATERIALS AND METHODS

3.1. Description of the study areas

Dire and Aba-Samuel reservoirs , situated about 40 km in northeastern and 37 km in the southwestern parts, respectively, of Addis Ababa, the capital city of Ethiopia (Fig. 2). Some geographic and morphometric features of both reservoirs and their catchment areas are summarized in Table 5.

Table 5: Some morphometric and geographic features of Dire and Aba-Samuel Reservoirs and their catchments

Features	Reservoirs and reported values		Sources
	Dire Reservoir	**Aba-Samuel Reservoir**	
Latitude	09°10’ 35.7”N	9°156’N	Present study
Longitude	38°55’10.4”E	38°94’E	
Altitude (m a.s.l)	2548	2044	
Area (Km^2)	-	117	Feven Solomon (2007), Abraham Hailemelekot (2009), and Getu Sima (2011).
Maximum depth (m)	-	-	
Mean depth (m)	-	-	
Volume (m^3)	19×10^3	37.10 X 10^6	
Catch. Area (Km^2)	77.7	1341	
Catch. altitude (m a.s.l)	2000- 3028	3200-3391	

Dire Reservoir, which was constructed in 1999 E.C. It has an elevation of 2548 m a.s.l, a height of 46 m, water holding a capacity of 19Mm^3 and fed is by Dire River (Getu Sima, 2011). It is situated at north-west of the Legedadi catchment area and covers an area of 77.7 Km^2. The reservoir has one known small tributary, namely Dire River that feeds the reservoir from the northeast direction. There is an outflow from this reservoir to Legedadi Reservoir. There are no macrophytes in the littoral region of the reservoir and the reservoir does not support any fish (preliminary study and field observation).

Aba-Samuel Reservoir, which was constructed in the 1930s on the Akaki River by Italian occupants to supply Addis Ababa with electric power, is fed by Little and Big Akaki Rivers (Hamere Yohannes and Eyasu Elias, 2017). It has an elevation of 2044 m a.s.l and water holding capacity of 37.10 Mm^3 (Feven Solomon, 2007). Municipal and industrial effluents are discharged into this reservoir (Eshetu Gizaw *et al.*, 2004, Hamere Yohannes and Eyasu Elias, 2017). Akaki River consists of two main branches, the confluence of which is at Aba-Samuel Reservoir. The western branch of the river, the Little Akaki, arises from the north-west of Addis Ababa on the flanks of Wechacha Mountain and flows for 40 km before it reaches the reservoir. The eastern branch of the river, the Big Akaki, originates from north-east of Addis Ababa and flows into the Aba-Samuel Reservoir after 53 km flow (Hamere Yohannes and Eyasu Elias, 2017). According to the information obtained from Akaki Wereda agricultural office, African Catfish (*Clarias gariepinus*) and Nile tilapia (*Oreochromis niloticus)* were common fish species in the reservoir during the 1970s.

3.2 Meteorological and hydrological characteristics

The catchment area of Dire Reservoir is typical peri-urban highland with mixed crop-livestock farming systems (rain-fed crop production and a strong livestock component in farming). Much of the natural vegetation in the area has been destroyed by extensive cultivation and human settlement. The natural vegetation was replaced with *Eucalyptus globulus* plantation, which covers about 1000-1200 hectar. The vegetation cover of the watershed is only 11% and hence the soil is severely eroded (Feven Solomon,2007). The reservoir is surrounded by many inhabitants whose livelihoods are predominantly rain-fed agriculture and livestock rearing. Based on the agro-climatic classification of Ethiopia, Dire reservoir watershed is characterized by Moist Dega agro-climatic Zones, with an average temperature of 15°-20°C (Israel Tessema, 2011). The soil type of the Dire Reservoir watershed is typically silty loam. The area gets about 1000-1800 mm rainfall per annum, with most of the rainfall occurring between June and September. The average monthly temperature of fifteen years also revealed that the temperature reaches its peak in January, February, and March, while its lowest level occurs in October (Lelisa Gemechu, 2011).

The Akaki River catchment, which includes the city of Addis Ababa and the Aba Samuel Reservoir area, is an extensive drainage system, which covers an area of 11,454 km^2 and has an elevation drop (towards the great East Africa rift system) of over 1000m in a space of about 30 km. In the catchment, there are mountain peaks such as Mt. Intoto; (3200 m a.s.l.) Mt. Bereh (3,228 m a.s.l.) and the Wechecha range (3,391 m a.s.l.) (Brehanu Gizaw, 2002). In the Addis Ababa city, there are different perennial and intermittent streams, which are tributaries of the Little or Big Akaki Rivers, and towards the south, almost all streams or big tributaries crossing the city in different directions join either of the rivers. The two rivers flow on either side of the Addis Ababa-Debrezeit road and end up at the artificial Aba-Samuel Reservoir. Other perennial streams in the city are Bantyiktu, Kurtume, Kebena, and Ginfile. The remaining streams are intermittent in nature. Streams are dense on the top of the mountain forming radial and dendritic drainage patterns. All the major streams of the catchment originate in its northern part and retain the name Akaki as they leave the lake passing through a gorge up to 100m deep, which extends for about 8 km before joining the Awash River. And this makes Aba Samuel Reservoir an open catchment Reservoir since Akaki River is going out of it. Aba-Samuel Reservoir is located in a relatively flat area and all the streams and rivers that flow from Addis Ababa and surrounding highlands empty into the area. The reservoir expands during the rainy season and shrinks during the dry season. Ethiopia has five climatic zones and the study area is located within Weynadega or midlands zone with the altitude of 1500-2300 m a.s.l. (Deressa Temesgen *et al*., 2008).

The climatic condition and topography of the area favor the development of thick soil profiles mostly due to the physical disintegration and chemical decomposition of volcanic rocks on which it lies (Tamiru Alemayehu *et al*., 2005). The weathering products either remain in place and form residual soils or are transported and deposited to form alluvial deposits in low-lying areas. In the localities where the topography is plain to gently slope (central and southern parts) the area is covered by thick soils. The geology of Aba Samuel Reservoir is underlain by aphanitic basalt in the southeast, trachytes, rhyolites and basalt in the southwest and lacustrine clays and silts in the north (Abraham Hailemelekot, 2009, cited in Feven Solomon, 2007). In general, the types of soils, which are found in the study area, are black cotton soil, lacustrine and alluvial soils, with the black cotton soil dominating in the area. The thickness of lacustrine and alluvial silt and clay deposits in the area varies between 5 to 50m (Birehanu Gizaw, 2002). The vegetation in the study area consists mainly of Acacia, Eucalyptus, Fig/Shola, Tid/Junipers, Zembaba/Palm tree, and small shrubs. The *Eucalyptus* trees are mostly found in homesteads/settlement areas. The general land use pattern of the whole Akaki catchment is very diverse. Most of the upper part of the catchment is occupied by settlement, mixed land use practices and there are planted trees (*Eucalyptus*) farther up on the Intoto ridge. In the southern parts of the catchment, non-irrigated agriculture dominates. Most industries are concentrated along the Little and Big Akaki Rivers; their effluents flow easily into the two rivers and end up the reservoir under study. Around the study reservoir, the dominant land use practice is agriculture.

3.3 Selection of sampling sites

Based on their proximity to suspected anthropogenic sources, the potential exposure of the reservoirs to different sources of agro-industrial wastes, the presumed difference in the level (extent) of heavy metals and other pollutants, three representative sampling sites were selected: Site-1 (S1) for inlet, Site-2 (S2) for open water-center and Site-3 (S3) for outlet (Figure 2). Table 6 presents the specific location of sampling sites and their geographical positions.

Table 6: Sampling sites, their locations, and geographical positions

Sites name	Description	Altitude (m)
Dire inlet	Point of entry of Dire River	2546
Dire center	Center of the Reservoir	2551
Dire outlet	Around the Dam of the Reservoir	2546
Aba-Samuel inlet	Near inlet of big Akaki River	2043
Aba-Samuel center	Center of the Reservoir	2045
Aba-Samuel outlet	Near outlet of the Reservoir	2045

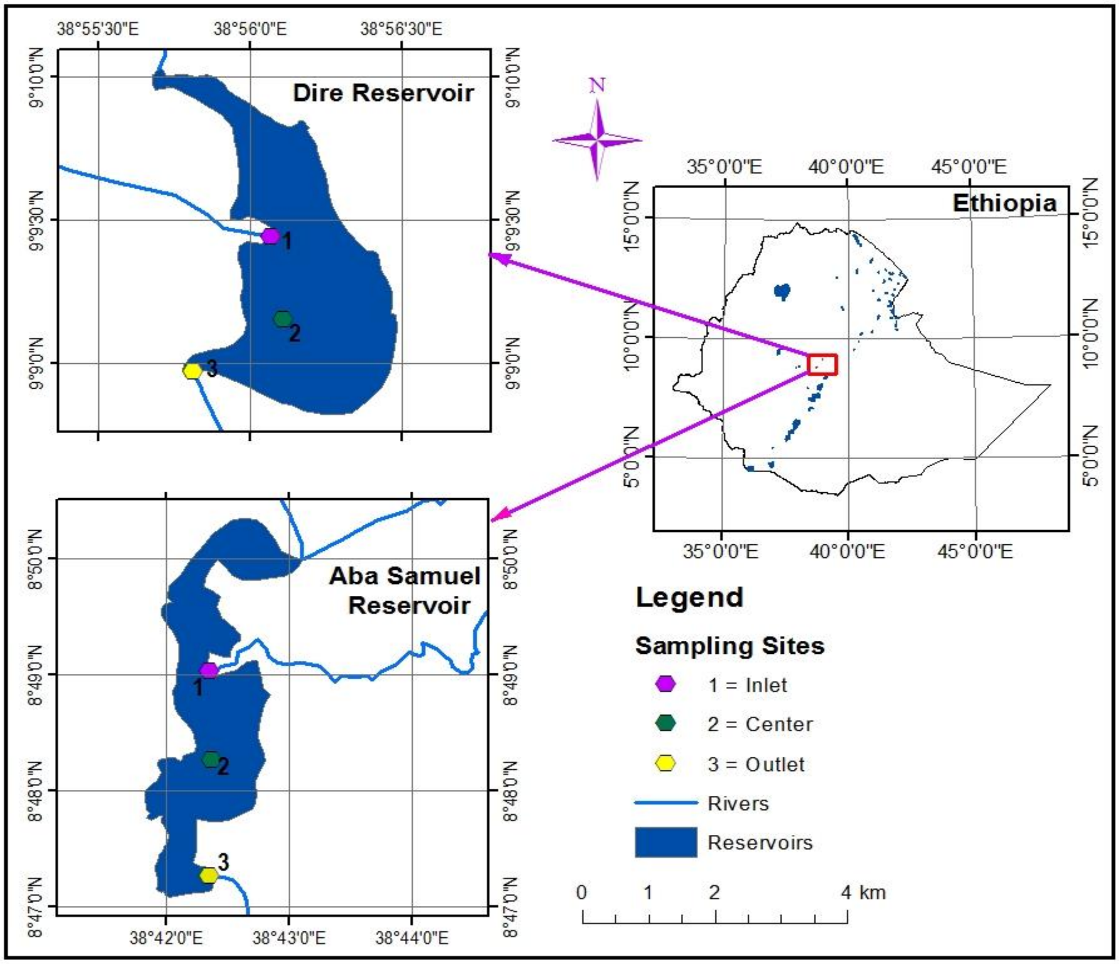


Figure 2: Map of the studied reservoirs and their respective sampling sites

3.4 Sampling protocol

Water and sediment samples were collected once in every month during April 2018 to June 2018 from two reservoirs (Dire and Aba-Samuel) at three sites viz. inlet (Site1-S1), center (Site-S2) and outlet (Site-S3)(Fig.2).

Water samples were collected from 0m,3m,5m,7m,9m,11m,and 14m depths using the graduated rope of the sampler, 2L Kemmerer water sampler was used to collect water samples between 8.30am and 16.30pm and the collected samples were well-mixed in equal proportions in a bucket to produce composite samples. One liter composite water sample from each site was taken in 1-liter polyethylene bottles. Bottles (HDPE), which were filled with 10% nitric acid (to remove metal contaminants from the bottle) and allowed to stand for 24 hours in a hot water bath and then washed and rinsed with distilled and deionized water (USEPA, 1992; 1996), were used for transporting collected samples. These bottles were thoroughly rinsed with the reservoir's water of the sampling sites three times before sample collection. The plastic bottles were corked firmly and stored in an ice box before transporting to the laboratory for analysis according to the procedures outlined in WHO (2008).

Similarly, sediment samples (300-400 g wet weight) were collected from each site using bottom sediment Grab Sampler (Ekman grab) attached to a polypropylene rope. Subsamples were taken from the central part of the grab to avoid metal contamination and kept in plastic boxes/polyethylene bags and immediately transported to the Limnology Laboratory at Addis Ababa University where they were deep-frozen (APHA, 1998). In the laboratory, sediment samples were dried in an oven for 12 hours at 90 ^{o} C. The cooled and dried sediment samples were ground using a porcelain mortar and pestle and sieved through a 1.5 mm mesh steel sieve to remove coarse materials. Later, all the samples were packed and labeled carefully and then placed at 4°C (USEPA, 1999).

All equipment used for the collection, storage, and filtration of the samples were soaked in 10 % HNO_3 for 24 hrs.in hot water bath and rinsed four times with deionized water before use (APHA, 1998) and all chemicals and reagents used were analytical grade. Freshly prepared distilled water and deionized water was used throughout the experiment for preparing standard solutions, dilution, and rinsing apparatus.

Standard methods (GOI and GON, 1999) were used for the analysis of the physicochemical parameters while APHA (1998) and USEPA (1999) were used for the determination of the studied heavy metals by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), which is the most powerful method with high selectivity, sensitivity, precision, and accuracy (Boevski and Daskalove, 2007).

3.5 *In-situ* measurement of physicochemical parameters

Dissolved oxygen, temperature, and electrical conductivity value was carried out using a multimeter probe (Model HQ40d HATCH instruments) while pH was measured using portable digital pH meter (Hanna 9024) at all sampling sites. Turbidity was estimated using a turbidimeter (Oakton T-100) and the maximum depth of the reservoir was measured with Echo test II depth sounder. Prior to measurement, the portable field instruments were calibrated using buffers of pH (pH 4.0, 7.0 and 10.0) and Potassium Chloride Solution for pH and EC, respectively. After the measurement of each water sample, the probe was rinsed with deionized water to avoid cross-contamination among different samples. The values of conductivity were corrected to 25°C using a temperature coefficient of 2.3% per degree Celsius (Talling and Talling, 1965).

3.6 Sample preparation for heavy metal analysis

100 mL unfilted water samples were preserved to pH < 2 with concentrated nitric acid (HNO_3) to minimize precipitation of metals, adsorption on the container walls and prevent the growth of algae immediately after collection (APHA, 1998).

At Bless Agri-foods complex laboratory service, 25 mL of each water sample was transferred into 50 mL acid cleaned Griffin beakers. The beaker (uncovered) was placed on hot plate at 90-95°c and 750 µL of concentrated HNO_3 was slowly added to the sample. Then the samples were evaporated to a low volume (5mL) and cooled. After cooling, another 750 µL of concentrated HNO_3 were added in to the beaker (covered) and placed on the hot plate, so gentle reflex action occurs. Heating was continued following addition of acid until the digestion was completed (indicated when digestate is light in color or does not change in appearance with continued refluxing). Then the beaker was uncovered evaporated to 3mL, removed from the hot plate and cooled. 2.5 mL of 1:1 HCl (50% distilled water and 50% HCl) was added to the beaker(covered), placed on the hot plate and refluxed for 15 minutes to dissolve any precipitate or residue resulting from evaporation. After refluxing the cover (watch glass) was removed, the beaker walls was rinsed with distilled water (which is not exceeded 25 mL). The samples were diluted with distilled water to get a total of 25 mL sample solution (APHA,1998). A blank solution was similarly prepared.

On the other hand, 0.5g of each sediment sample was weighed using electronic weighing balance (Model ATX 224) and transferred into 100 mL acid cleaned beakers. Digestion with a Micro-wave digester (LA-KITS) was done using 3 mL of 40% HF,1 mL of 30% H_2O_2 and 9 mL of 70% HNO_3 for 1 hour at 200°C. The samples were cooled and diluted with distilled water to get a total of 25 mL sample solution (APHA,1998; USEPA;1999). A blank solution was similarly prepared.

Subsequent to acidification and digestion, water and sediment samples were stored at 4°C in a refrigerator to minimize volatilization. 25 mL of both water and bottom sediment samples were taken at Horticoop Ethiopia (Horticulture) P.L.C. in Bishoftu Town for the analysis of metals Copper (Cu), Manganese (Mn), Zinc (Zn), Chromium (Cr), Lead (Pb), Arsenic (As), Mercury (Hg) and Cadmium (Cd) using ICP-OES and following the standard methods (APHA, 1998; USEPA, 1999). Finally, 25 mL of the digested water and sediment samples were filtered using Glass Fiber Filter Paper (GF/F Paper) and taken for analysis (APHA, 1998; USEPA,1999). Calibration of the instrument was carried out with a range of standard solution. After calibration, the filtered water and sediment samples were injected with autosampler from the test tube to ICP-OES instrument with peristaltic pump (APHA,1998). The samples were analyzed in triplicates, and the blank sample determinations in duplicates were also run in the same manner during the analysis. The standard series were used to draw calibration curves of intensity versus concentration of heavy metals in water and sediment samples. Afterwards, concentrations of selected heavy metals (Cu, Mn, Zn, Cr, Pb, As, Hg and Cd) in water (mg L^{-1}) and in sediments (mg Kg^{-1}) were evaluated from ICP-OES linear calibration curves using smart analyzer software.

3.7 Statistical analysis

Data collected from water and bottom sediments were analyzed using Microsoft Excel spreadsheet and SPSS (version 23). One-way ANOVA (analysis of variance) was employed to analyze the results of physicochemical and heavy metal analyses in order to know spatial variation and the water quality status of the reservoirs. Differences in concentration levels obtained for a given parameter among sampling sites were considered significant at $p < 0.05$. Sigma plot version 10 software was used for graphical presentation. Multivariate analysis using CANOCO 4.5 software package was used to show the tri-plot association between heavy metals, physicochemical parameters, and sampling sites. The relationship between the concentration of heavy metals and physicochemical variables was assessed using Redundancy Analysis (RDA). To determine the suitability of the method used in this analysis, Detrended Correspondence Analysis (DCA) was employed. According to Lepš and Šmilauer (1999), when the length of the gradient is less than 3, the heavy metals concentration show linear response to environmental variables (physicochemical parameters).Thus, RDA was employed for ordination.

4. RESULTS

4.1. Physicochemical characteristics

Table 7: Spatial variations in mean values and ranges (in parentheses) of physicochemical parameters recorded for the sampling sites of the present study on Dire and Aba- Samuel reservoirs.

	Dire Reservoir			**Aba-Samuel Reservoir**		
	Sampling Sites			Sampling Sites		
	Site1	Site2	Site3	Site1	Site2	Site3
Parameters	Mean±SE	Mean±SE	Mean±SE	Mean±SE	Mean±SE	Mean±SE
DO (mg L^{-l})	4.88±0.29 (3.79-6.14)	5.25±0. 29 (4.01-6.37)	5.11±0.42 (4.06-7.15)	3.66±0.41 (2.45-5.55)	4.18±0.55 (1.98-5.84)	4.41±0.62 (2.93-6.86)
EC (K25, μScm^{-1})	150.70±1.42 (146.72-158.60)	152.42±1.63 (146.74-159.57)	152.86±1.29 (149.17-160.18)	743.28±21.86 (656.62-800.34)	740.71±14.78 (690.38-794.67)	751.87±8.65 (720.65-782.67)
Temp.(^{o}C)	19.08±0.29 (18.20-21.00)	18.47±0.12 (18.10-19.30)	18.22±0.27 (17.50-20.30)	21.55±0.21 (21.00-22.7)	22.31±0.41 (20.90-24.80)	21.44±0.27 (20.20-22.50)
Turbidity(NTU)	223.39±65.89 (19.8-472)	284.60±86.69 (59.70-627)	258.83±56.63 (119.00-484.30	64.75±4.81 (48.5-82.8)	49.73±7.87 (19.07-73.4)	44.93±7.53 (17.11-69.4)
pH	(8.09-8.63)	(8.09-8.74)	(7.99-8.41)	(7.69-8.35)	(7.20-8.21.0)	(7.76-8.30)

Mean DO values (mg L^{-1}) of Dire Reservoir ranged from 4.88±0.29 at S1 site to 5.25±0.29 at S2 while those of Aba-Samuel Reservoir varied between 3.66±0.41 at S1 and 4.41±0.62 at S3. Electrical conductivity (K_{25}, $\mu S\ cm^{-1}$) ranged from 150.70±1.42 at S1 to 152.86±1.29 at S3 of the present study on Dire Reservoir and from 740.71±14.78 at S2 to 751.87±8.65 at S3 in Aba-Samuel Reservoir. The level of mean water temperature measured at the study sites ranged from 18.22±0.27^{o}C at S3 to 19.08±0.29 ^{o}C at S3 in Dire Reservoir and from 21.44±0.27 ^{o}C at S3 to 22.3±0.41 ^{o}C at S2 of Aba-Samuel Reservoir with the significant difference among sampling sites ($p<0.05$). The mean turbidity values (NTU) varied between 223.39±65.89 at S1 and 284.60±86.69 at S2 of Dire Reservoir and between 44.93±7.53 at S3 and 64.75±4.81 at S1 in Aba-Samuel Reservoir. The present results for pH values recorded for Dire and Aba-Samuel reservoirs did not show a considerable variation among the sampling sites. The highest pH values 8.74 and 8.35 for Dire and Aba-Samuel water samples were recorded at S2 and S1, respectively. Except for temperature, the mean values of physicochemical parameters measured in Aba-Samuel Reservoir did not show a significant difference ($p>0.05$) among sampling sites.

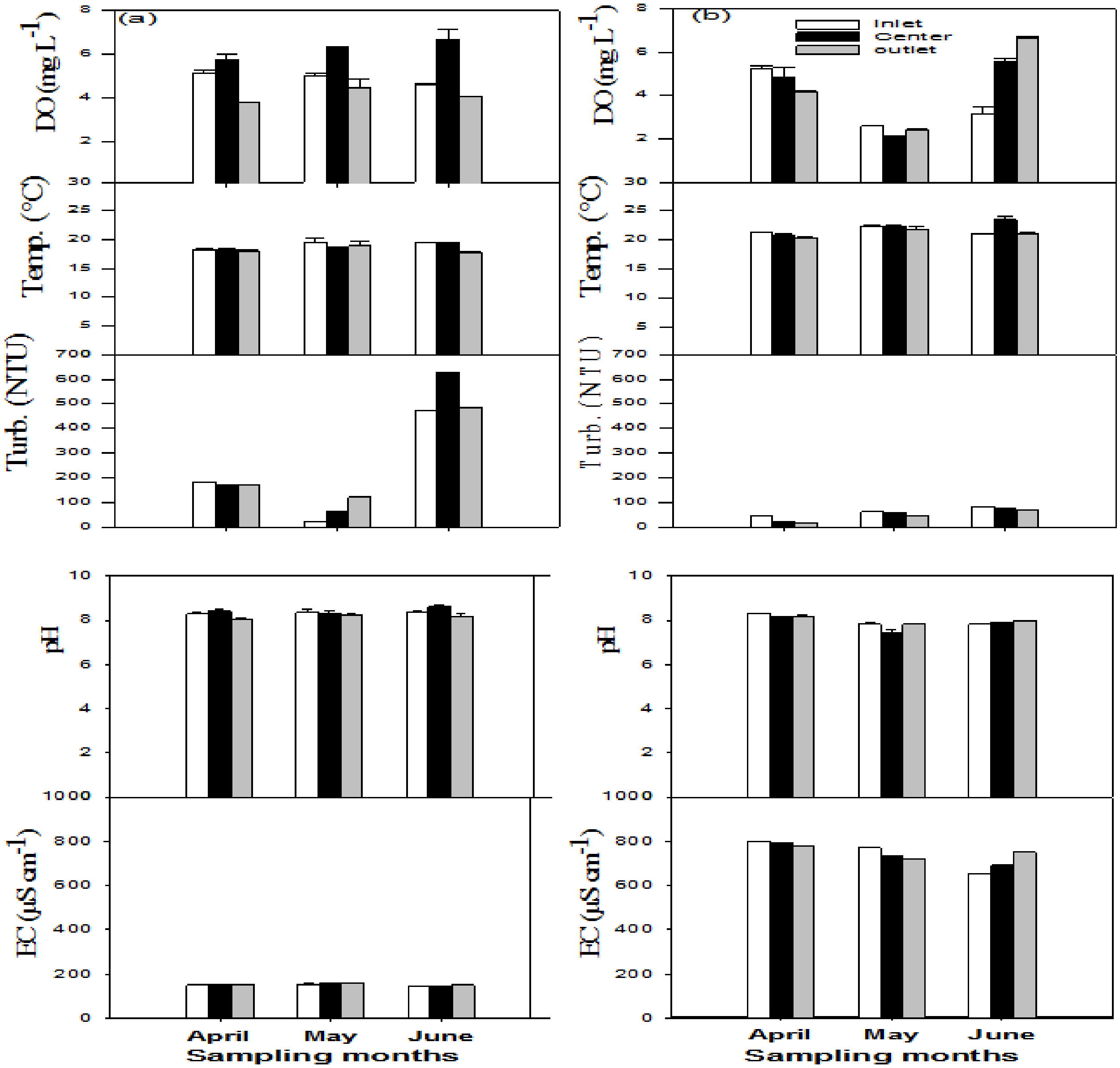


Figure 3: Mean concentrations of physicochemical parameters (a)-Dire Reservoir and (b)-Aba-Samuel Reservoir

4.2 Concentrations of heavy metals in water samples

The mean values of concentrations of all metals except Mn in water samples of Dire Reservoir were not significantly different among sampling sites ($P>0.05$), while the reverse was true for those determined in samples from Aba-Samuel Reservoir(Table 8).

In the present study, all heavy metals except Cr and Cd, which were not detected in samples from S3 of Dire Reservoir, were found at different levels of concentration (Table 8). The lowest mean concentrations of most metals were recorded for S1 in Dire Reservoir, while all metals had the lowest mean concentrations at S3 of Aba Samuel Reservoir. The mean concentrations of Mn (mg L^{-1}) ranged from 0.211 at S2 to 0.283 at S1 in Dire Reservoir, while it varied between 0.463 at S3 and 0.523 at S1 in Aba-Samuel Reservoir. Mean Cu values (mg L^{-1}) did not show variations among sampling sites in Dire Reservoir while they varied from 0.003±0.001 at S3 to 0.005±0.000 at S1 in Aba-Samuel Reservoir. Zn (mg L^{-1}) ranged from 0.005±0.002 at S2 to 0.013±0.002 at S1 and S3 of the present study on Dire Reservoir and from 0.021±0.001at S1 to 0.038±0.004 at S3 in Aba-Samuel Reservoir. The distribution of Cr and Cd (mg L^{-1}) was nearly the same among sampling sites. The mean Hg values (mg L^{-1}) varied between 0.001±0.000 at S1 and 0.004±0.000 at S3 of Dire Reservoir and between 0.003±0.000 at S3 and 0.005±0.001 at S2 in Aba-Samuel Reservoir. The mean Pb values (mg L^{-1}) varied between 0.005±0.000 at S1 and 0.016±0.002 at S3 of Dire Reservoir and 0.005±0.000at S3 to 0.009±0.000 at S1 in Aba-Samuel Reservoir. The mean As values (mg L^{-1}) varied between 0.006±0.000 at S1 and 0.008±0.000 at S3 of Dire Reservoir and from 0.006±0.000 at S3 to 0.008±0.001 at S1 in Aba-Samuel Reservoir.

Table 8: Mean spatial variations of heavy metal concentrations in water recorded for the sampling sites of the present study on Dire and Aba-Samuel Reservoirs (ND=Not Detected)

Parameters (mg L^{-1})	**Dire Reservoir**			**Aba-Samuel Reservoir**		
	Sampling Sites			Sampling Sites		
	Site1	Site2	Site3	Site1	Site2	Site3
	Mean±SE	Mean±SE	Mean±SE	Mean±SE	Mean±SE	Mean±SE
Cu	0.002±0.002	0.002±0.000	0.002±0.000	0.005±0.000	0.004±0.001	0.003±0.001
Zn	0.013±0.002	0.005±0.002	0.013±0.001	0.021±0.001	0.027±0.004	0.038±0.004
Mn	0.283±0.019	0.211±0.018	0.213±0.027	0.523±0.028	0.527±0.055	0.463±0.029
Cr	0.003±0.001	0.003±0.001	ND	0.008±0.000	0.007±0.000	0.005±0.000
Cd	0.003±0.003	0.003±0.002	ND	0.007±0.000	0.007±0.001	0.004±0.001
Hg	0.001±0.000	0.002±0.001	0.004±0.000	0.004±0.000	0.005±0.001	0.003±0.000
Pb	0.005±0.000	0.009±0.001	0.016±0.002	0.009±0.000	0.006±0.000	0.005±0.000
As	0.006±0.000	0.007±0.000	0.008±0.000	0.008±0.000	0.007±0.000	0.006±0.000

4.3 Concentrations of heavy metals in sediment samples

The concentrations of heavy metals analyzed in sediment samples collected from the reservoirs varied widely (Table 9). The concentrations of Mn, Cr, Hg and Pb showed significant variation ($P<0.05$) among sampling sites, while those of Cu, Cd and As exhibited spatial variations, which were not statistically significant ($P>0.05$) in Dire Reservoir. The variations among sampling sites in the concentrations of Mn, Pb, Cu, Cr, Cd and As were significant ($P<0.05$) although those of Hg and Zn were not significant ($P>0.05$) in Aba-Samuel Reservoir.

During the study period, all the analyzed heavy metals were detected in the sediment samples collected from all study sites in both Reservoirs. Concentrations (mg kg^{-1}) of Mn, Zn, Cr, Pb, Cu, As, Hg and Cd ranged from 1022.99 to 1218.05, 153.92 to 185.58, 45.80 to 47.03, 29.54 to 31.50, 24.50 to 27.28, 19.40 to 20.27, 18.83 to 22.43 and 2.69 to 2.97, respectively. Mn had the highest concentrations (mg kg^{-1}) of all analyzed metals, with its mean values ranging from to 1022.99 at S3 to1144.08 at S1 of Dire Reservoir and from 1163.01 at S3 to 1214.11at S3 of Aba-

Samuel Reservoir. In contrast, Cd exhibited the lowest levels (mg kg^{-1}) of all metals in both reservoirs with its mean values ranging from 2.69 at S1 to 2.79 at S2 and from 2.72 at S3 to 2.97 at S1 of Dire & Aba-Samuel reservoirs, respectively.

Table 9: Mean spatial variations of heavy metal concentrations in sediment (mg Kg^{-1}) recorded for the sampling sites of the present study on Dire and Aba-Samuel Reservoirs

Parameters (mg Kg^{-1})	**Dire Reservoir**			**Aba-Samuel Reservoir**		
	Sampling Sites			**Sampling Sites**		
	Site1	Site2	Site3	Site1	Site2	Site3
	Mean±SE	Mean±SE	Mean±SE	Mean±SE	Mean±SE	Mean±SE
Cu	24.50±0.51	25.02±0.38	24.61± 0.15	27.28±0.08	27.20±0.07	26.80±0.20
Zn	153.92±2.32	162.93±4.05	159.28±1.01	185.58±3.42	180.88±4.23	174.96±4.00
Mn	1144.08±11.51	1129.64±21.56	1022.99±4.62	1218.05±3.91	1214.11±4.52	1163.01±13.66
Cr	45.80±0.19	46.54±0.07	47.03±0.23	46.78±0.04	46.64±0.07	45.87±0.26
Cd	2.69±0.10	2.79±0.07	2.74±0.06	2.97±0.00	2.88±0.03	2.72±0.07
Hg	21.69±0.17	20.67±0.79	18.83±0.90	22.43±0.05	22.37±0.07	22.32±0.08
Pb	29.54±0.13	30.07±0.10	31.50±0.12	29.99±0.02	29.81±0.10	29.54±0.12
As	19.53±0.12	19.40±0.13	19.45±0.05	20.27±0.04	20.20±0.05	19.82±0.20

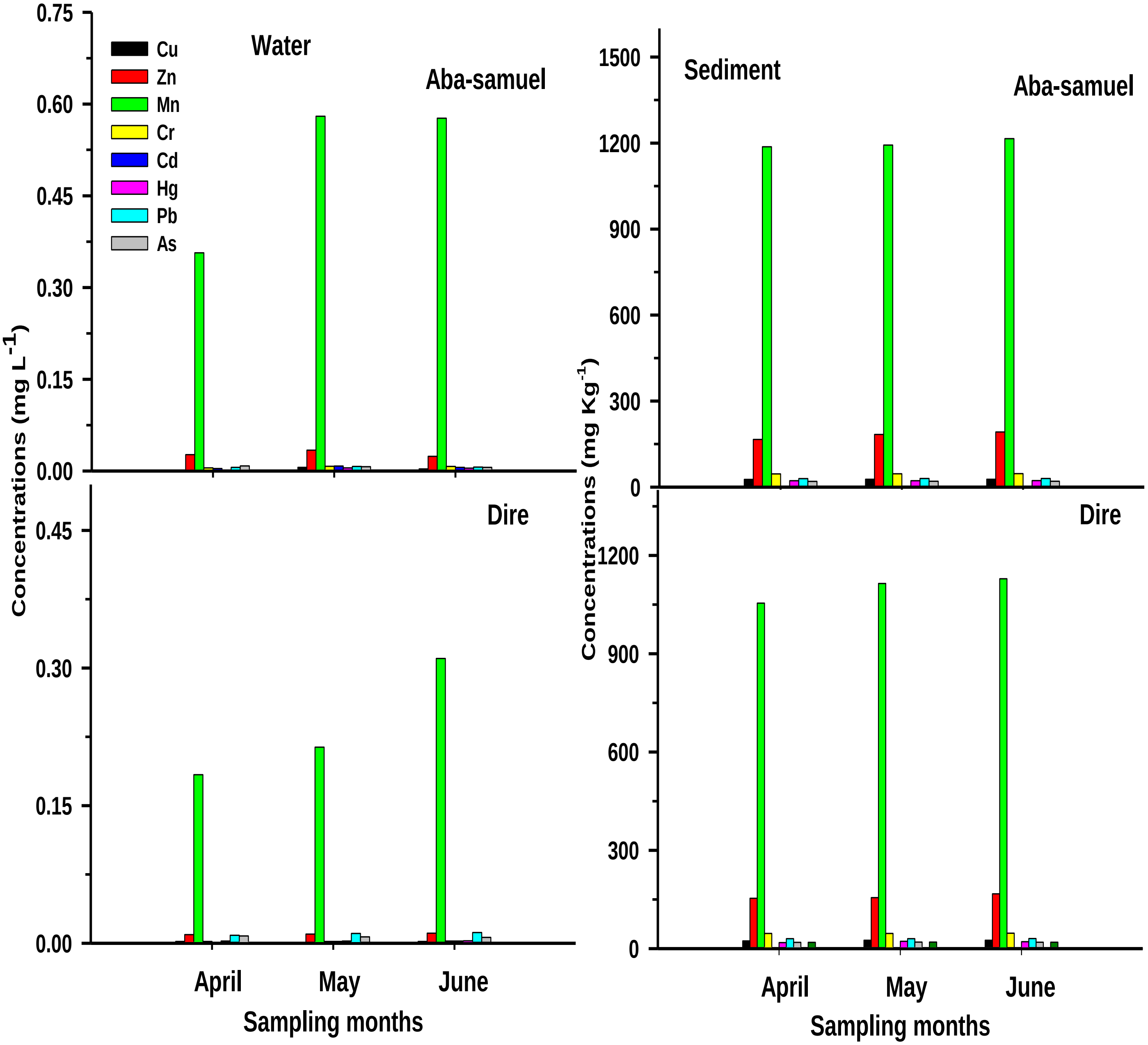


Figure 4: Temporal variations in the concentrations of metals measured in water and sediment samples collected from Dire and Aba-Samuel reservoirs

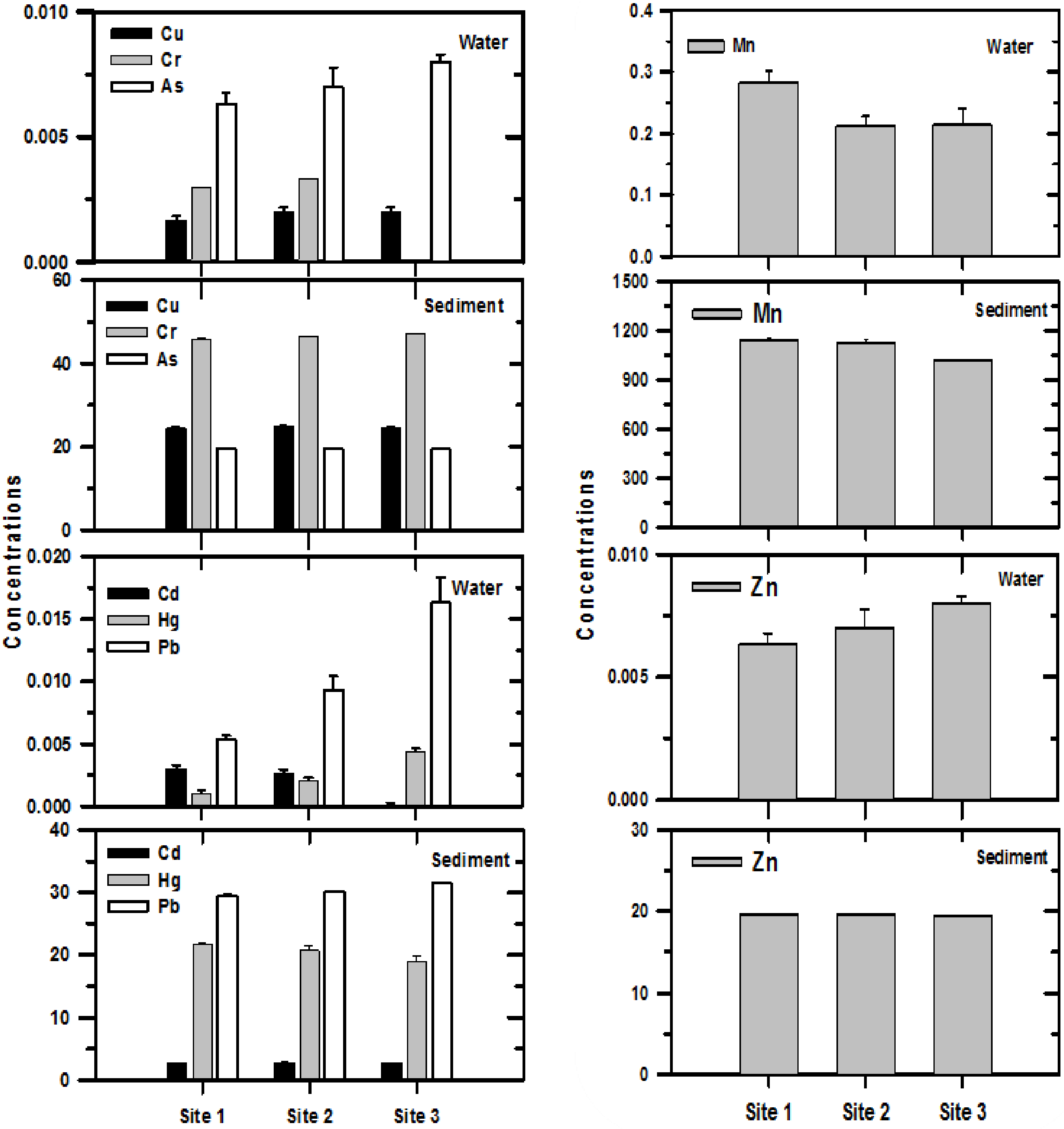


Figure 5: Spatial variations in the concentrations of metals measured in water and sediment samples collected from Dire Reservoir

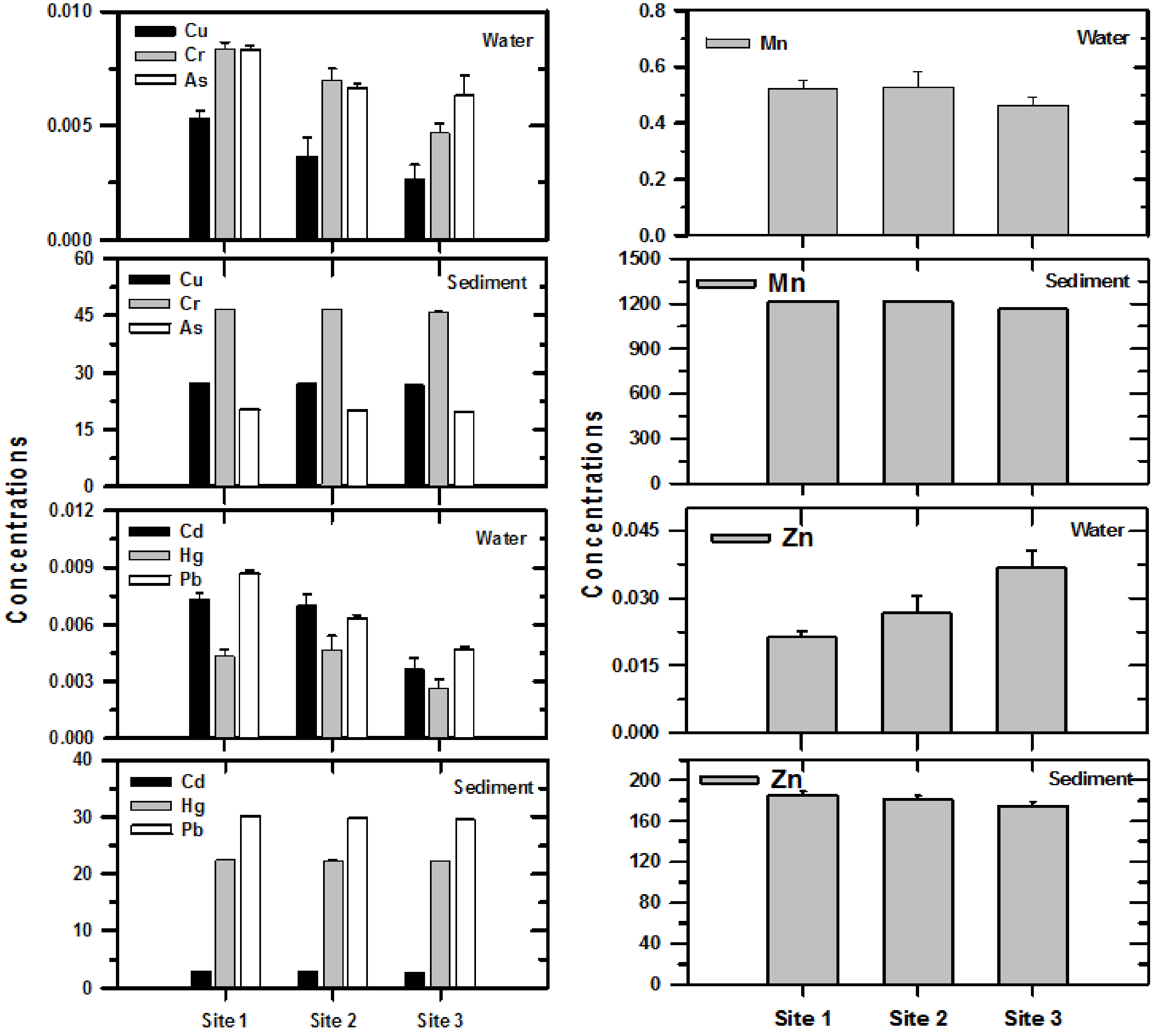


Figure 6: Spatial variations in the concentrations of metals measured in water and sediment samples collected from Aba-Samuel Reservoir

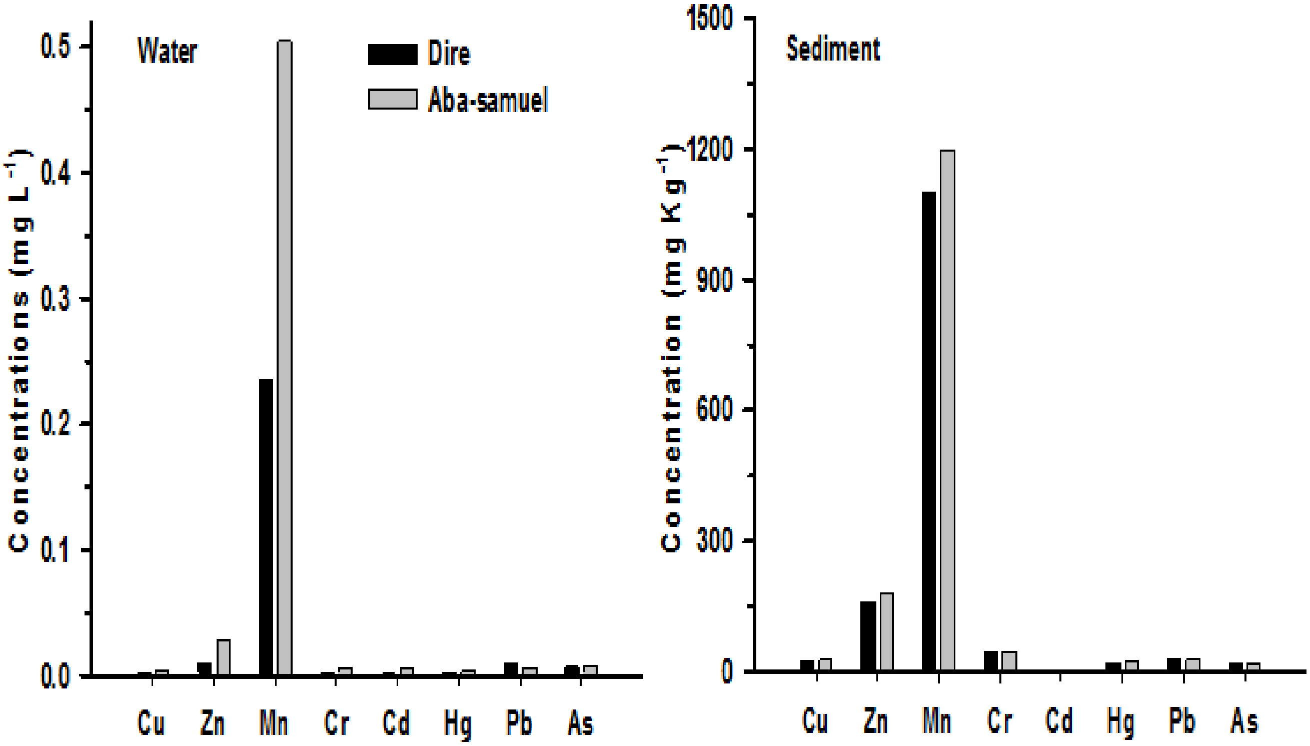


Figure 7: Mean concentrations of heavy metals in water and sediment samples of Dire and Aba-Samuel reservoirs

4.4 Multivariate analysis of the relationship between physicochemical water quality parameters

The influence of major environmental parameters on the concentration of heavy metals was analyzed using the multivariate method-RDA ordination. The physicochemical parameters temperature, DO, conductivity and turbidity were selected as main parameters that may affect the concentration of heavy metals based on the assessment of variance inflation factor (VIF<20).These physicochemical parameters affect the solubility, mobility and distribution of the selected heavy metals.

Table 10: Summary statistics of Redundancy Analysis (RDA) for the relationship between heavy metals and other physicochemical parameters [(PC) =Physicochemical parameters, (W) =Water and (S) =Sediment].

	Dire Reservoir								**Aba-Samuel Reservoir**							
	PC vs Heavy metals (W)				PC vs heavy metals (S)				PC vs heavy metals (W)				PC vs Heavy metals (S)			
Axes	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Eigen values	0.970	0.030	0	0	0.995	0.005	0	0	0.989	0.011	0	0	0.996	0.004	0	0
Heavy metals and PC correlations:	1	1	0	0	1	1	0	0	1	1	0	0	1	1	0	0
Cumulative % variance heavy metals data	97	100	0	0	99.5	100	0	0	98.9	100	0	0	99.6	100	0	0
Cumulative % Variance Heavy metals and PC relation:	97	100	0	0	99.5	100	0	0	98.9	100	0	0	99.6	100	0	0
Sum of all Eigen values	1.000				1.000				1.000				1.000			
Sum of all canonical	1.000				1.000				1.000				1.000			

The relationship between the concentrations of heavy metals and levels of physicochemical variables are shown in the ordination tri-plot (Fig.8 and 9).

In Dire Reservoir, the first Axis of the RDA ordination diagram displayed positive values for most of the heavy metals (Fig. 8a and Fig. 8b). The concentration of heavy metals from the water (Cu, Hg, Pb, and As) was positively correlated with the levels of EC at S3 (Fig.8a) while those of Zn, Cd, Cr and Pb from the sediment was positively correlated with turbidity, DO and EC (Fig.8b).

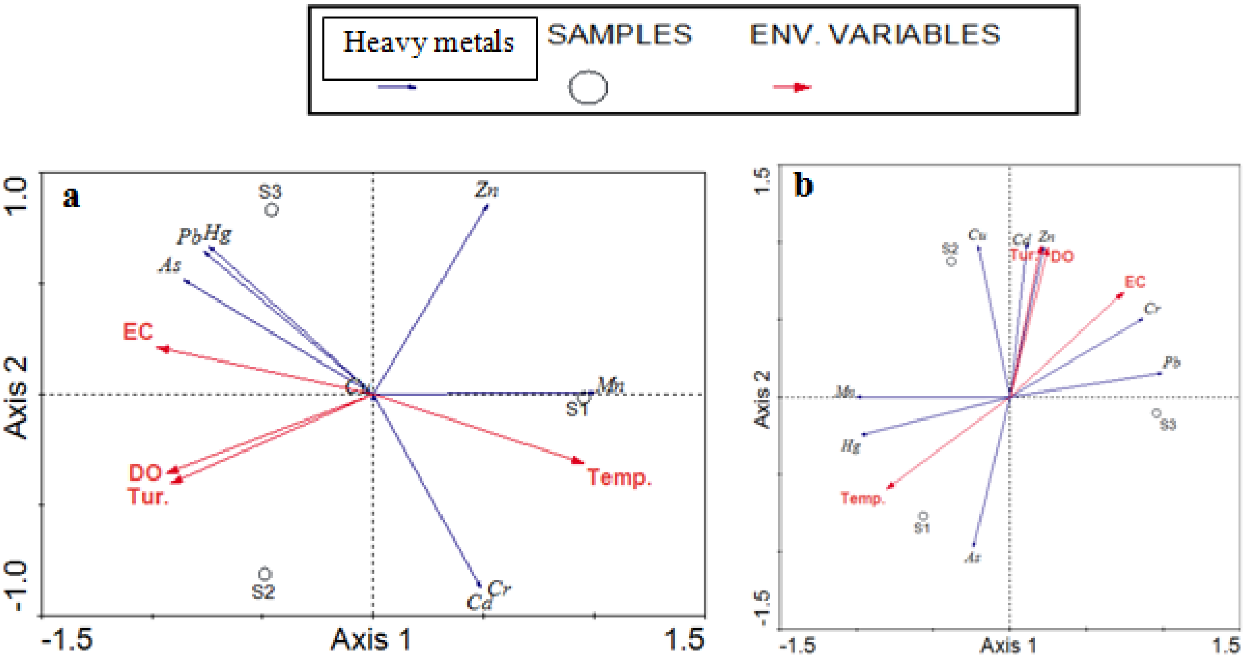


Figure 8: Tri-plot of Redundancy Analysis (RDA) of the relationship among heavy metals, physicochemical parameters and sampling sites in Dire Reservoir; **(a)-** physicochemical parameters vs. heavy metals in water and **(b)-**physicochemical parameters vs. heavy metals in sediment. Circles indicate sampling sites, DO=dissolved oxygen, Turb. =Turbidity, Temp. =Temperature and EC=Electrical conductivity.

In Aba-Samuel Reservoir, the second Axis of the RDA ordination diagram showed negative values for all of the heavy metals except Zn (Fig. 9a), while both Axis one and Axis two displayed negative values for all of the heavy metals except Mn (Fig.9b). The concentration of the heavy metals from water (Pb, As, Cu, Cr, and Cd) was positively correlated with turbidity at S1 (Fig.9a), while all heavy metals from sediment were positively correlated with turbidity at S1 (Fig.9b) and that majority of heavy metals are concentrated at S1 (inlet) of the reservoir (Fig. 9).

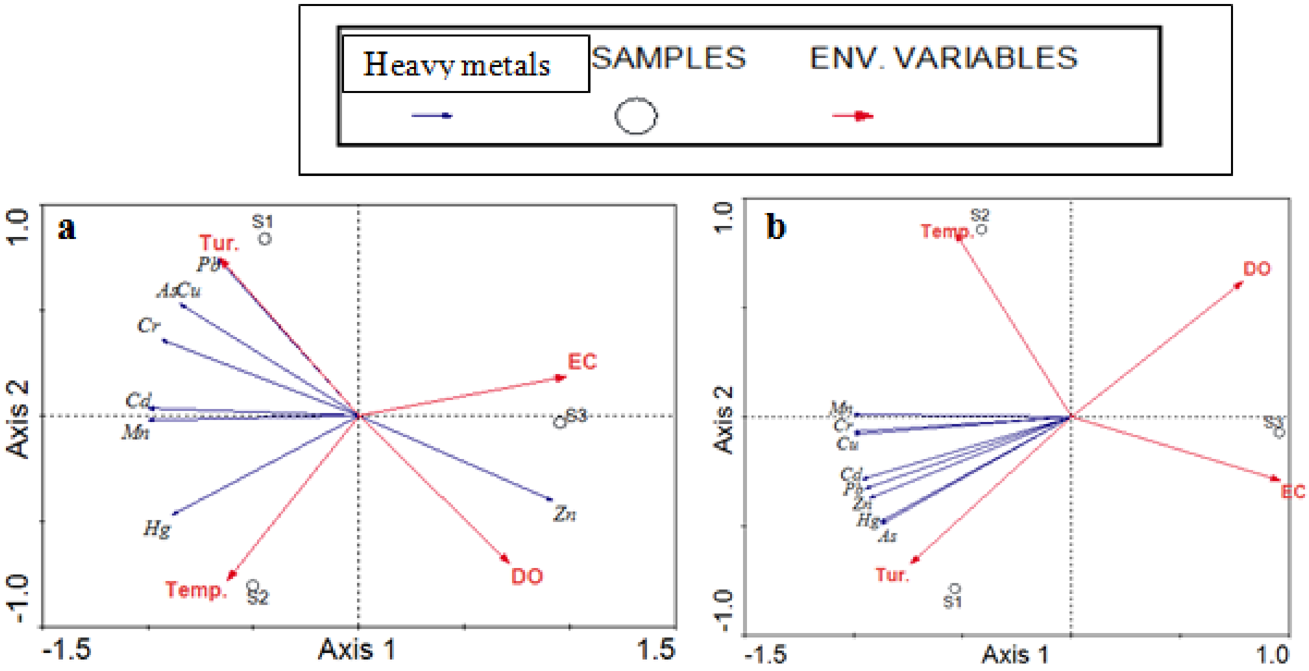


Figure 9: Tri-plot of Redundancy Analysis (RDA) of the relationship among heavy metals, physicochemical parameters and sampling sites in Aba-Samuel Reservoir; **(a)**-physicochemical parameters vs. heavy metals in water and **(b)**-physicochemical parameters vs. heavy metals in sediment. Circles indicate sampling sites, DO=dissolved oxygen, Turb. =Turbidity, Temp. =Temperature and EC=Electrical conductivity.

5. DISCUSSION

5.1. Physicochemical characteristics

Physicochemical parameters reveal information about the status of a water body at the time of sampling. Moreover, physicochemical measurements may show changes in time and space (temporal and spatial variations). In this study, levels of most of the physicochemical parameters measured in the field did not show a significant difference among the sampling sites. This may be attributable to exposed to the wind and the shallowness of the study sites result in frequent mixing. Karpisack *et al*. (2001) reported that complete mixing is frequent in lakes with a maximum depth of less than about 15-30 m. Thus, both Dire and Aba-Samuel reservoirs, with most parts shallower than 20 m and with nearly complete exposure to wind action, cannot be expected to a significant difference among the sampling sites. Furthermore, It was restricted for only three months (April, May, and June), which are minor and major rainy periods.

Table 11: Mean concentrations of physicochemical parameters (except pH) of water samples from Dire Reservoir (DRPC.) and Aba-Samuel Reservoir (ASRPC.) in comparison with the guideline values of USEPA, EEPA and WHO for drinking water

Reservoirs	DO (mg L^{-1})	EC(µS cm^{-1})	pH	Temp.(^{O}C)	Turb.(NTU)
DRPC.	5.08±0.19	151.99±0.83	7.99 - 8.74	18.59±0.15	255.61±39.61
ASRPC.	4.08±0.21	745.29±6.25	7.20 -8.35	21.67±0.14	53.14±2.91
USEPA (1999)	4.5-7.5	1500	6.5-8.5	-	-
CCME[a](2003)	5.5-9.5	-	5.0-9.5	15	-
EEPA(2003)	-	400	6.5-8.5	40	<5
WHO(2004)	-	400	6.5-9.2	-	<5
WHO(2008)	-	250	NGL**	-	NGL[a]

CCME[a]: Canadian Council of Ministers for Environment.

** NGL: No Guideline, because it occurs in drinking-water at concentrations well below those at which toxic effects may occur,

NGL[a] : No Guideline value but desirable if less than 5 NTU.

The higher DO value, particularly at S2, in Dire Reservoir may be due to its higher photosynthetic production (Helnata Tilahun, 2019), and continuous mixing (Assefa Wosnie and Ayalew Wondie, 2014), which in turn gives higher value of dissolved oxygen while the lowest DO concentration in S1 of Dire and Aba-Samuel reservoirs could be due to its oxidative consumption and higher organic matter (Feven Solomon, 2007). The lowest dissolved oxygen recorded in Aba-Samuel Reservoir might be due to the relatively high temperature and EC (Qureshimatva *et al*., 2015) and the discharge of untreated effluents from industrial activities (East Africa Metal Industry, Star soap and detergent industry, EL Hamic plastic factory, etc.) and domestic wastes into Akaki Rivers and the associated microbial activity/decomposition (Feven Solomon, 2007). The recorded values of DO concentration in the present study were usually higher at the surface of both reservoirs.

At all sites of Dire Reservoir, DO values (3.79 and 7.15) (Table 7) were within the range of USEPA's (1999) guideline values set for drinking water, while some of those recorded for sites of Aba-Samuel Reservoir (1.98 and 6.86 mg L^{-1}) (Table 7) fell out of the desirable range of DO (4.5-7.5) for drinking water set by USEPA(1999) (Table 11). DO is, however, below the permissible limits according to CCME (2003) (Table 11) in both reservoirs.

The DO concentrations in the surface water of both reservoirs were generally considerably lower than those reported for other Ethiopian lakes; Lake Kilole (9.3-13 mg L^{-1};Rediat Abate, 2008) and although they are still comparable to those reported relatively recently for Belbela Reservoir (2.5-7.9 mg L^{-1}; Feyisa Girma ,2011),Lake Hawassa (5.70-7.60 mg L^{-1}; Tigist Ashagre *et al*., 2014) and Angereb Reservoir (similar purpose reservoir in Gondar) (6.13-7.18; Assefa Mengesha *et al*., 2013).

Generally, the mean DO (mg L^{-1}) concentrations recorded for both study reservoirs were lower than the guideline values considered to suit the adaptability of aquatic life (USEPA, 1999) (early life stages =6 mg L^{-1}, other life stages=5.5 mg L^{-1}). When DO concentration is below 5 mg L^{-1}, aerobic living organisms become under stress and approaching hypoxia and anoxic condition occurs (2.5-3 mg L^{-1}), a massive death resulted (<1 mg L^{-1}) (Tadesse Fetahi *et al*., 2011).

According to Zinabu Gebre-Mariam and pearce (2003), conductivity is a very good predictor of both the total concentrations of cations and salinity in most Ethiopian water bodies. The higher EC value obtained for the Aba-Samuel Reservoir may be due to the recurring flow of municipal, industrial and agro-industrial wastes into the reservoir via the Akaki River (Feven Solomon, 2007).

The highest and mean EC values recorded for Dire Reservoir was lower than the guideline values recommended for potable water by USEPA (1999;1500 µS cm^{-1}), EEPA (2003; 400 µS cm^{-1}) and WHO (2004 ;400 µS cm^{-1} and 2008; 250µS cm^{-1}). However, the mean value obtained for Aba-Samuel Reservoir was greater than the recommended values except standards set by USEPA (1999; 1500 µS cm^{-1}). This may be associated to phenomena of mineralization or weathering of sediments, and largely due to discharge of industrial and domestic wastes and chemicals from nearby agricultural farms through runoff (Samuel Melaku *et al*., 2007).

The mean EC value in Aba-Samuel Reservoir is closer to the results obtained by Feven Solomon (2007; 658 µS cm^{-1}) for the same reservoir, Demeke Kifle (1985; 846 µS cm^{-1}) for Lake Hawassa, Adamneh Dagne (2004;519 µS cm^{-1}) for Lake Ziway, Aregawi Teklay and Meareg Amare (2015; 912 µS cm^{-1}) for Lake Hayq and Tigist Ashagre *et al*. (2014; 756.67 µS cm^{-1}) for Lake Hawassa. In addition, all the EC values recorded for both reservoirs are much lower than the values (between 2,500 and 10,000 µS cm^{-1}), which are not recommended for irrigation except for very salt tolerant crops cultivated with special management techniques (Yenkie *et al*., 2010).

Drinking water with a pH between 6.5 to 8.5 is generally considered as an optimum pH. The relatively higher pH in Dire Reservoir was likely due to increased rates of carbondioxide removal by algal photosynthesis (Adamneh Dagne, 2004). All the pH values observed in both reservoirs, with the exception of those recorded for S1 and S2 of Dire Reservoir, were within the desirable ranges of pH for drinking water set by USEPA (1999), CCME (2003), EEPA (2003) and WHO (2004) . The pH levels observed at S1 and S2 of Dire Reservoir were slightly higher than the permissible level for drinking water specified by USEPA (1999) and EEPA (2003) (Table 11). In all cases, the pH values of both reservoirs implied alkaline condition in both reservoirs, which may be associated with agro-industrial activities carried out in the surrounding areas of the reservoirs.

The pH values recorded for these reservoirs in the present study are closer to those observed previously by Feven Solomon (2007; 6.91-7.3) for Aba-Samuel Reservoir, Tigist Ashagrie *et al.*(2014; 7.7-9.52) for Lake Hawassa, Eyasu Shumbulo (2004;9.3-9.4) for Lake Chamo and Belay Tafa and Eshete Assefa (2014;8.66) for Lake Chamo. On the other hand, the pH values of Dire and Aba-Samuel reservoirs were generally lower than those recorded for the nearby crater Lakes, Bishoftu (9.2; Talling and Talling,1965), and Babogaya (8.84-9.09, Yeshiemebet Major,2006), and Lakes Hayq (8.83; Aregawi Teklay and Meareg Amare, 2015),Ziway (9;Adamneh Dagne, 2004), and Hawassa (8.78; Elizabeth Kebede *et al.*, 1994). These may reveal that there is a notable increment and decomposition of the organic matter load of the reservoirs from the catchment areas. (i.e. when decomposition occurs , carbon dioxide results and this tends to lower pH). Helnata Tilahun (2019) and Bedhatu Reta (2019) determined the high concentrations of Total Suspended Solids (TSS) on Dire and Aba-Samuel reservoir respectively.

The levels of temperature recorded for Dire and Aba-Samuel reservoirs (Table11) were above the maximum permissible limit set by the Canadian Council of Ministers for Environment (CCME, 2003) for community water used as aesthetic object although they were still lower than that set by EEPA (2003) for drinking water(Table 11). The surface water temperatures of the reservoirs were generally lower than those reported for other Ethiopian Rift Valley lakes including Lakes Hawassa (23.8-28.4°C; Demeke Kifle,1985), Chamo (27.30-29.90°C; Belay Tafa and Eshete Assefa ,2014), Lakes Chamo (26-30 ^{0}C; Eyasu Shumbulo, 2004) Hawassa (22.50-29.0°C; Tigist Ashagre *et al.*, 2014), Hayq (26.46°C; Aregawi Teklay and Meareg Amare, 2015) and Legedadi Reservoir (22.2-23.9°C; Adane Sirage, 2006) although they are still comparable to those recorded for Lakes Kilole (17.5-26°C; Rediat Abate,2008), Babogaya (20.5-28.4°C;Yeshiemebet Major, 2006), Ziway (21-24°C; Adamneh Dagne, 2004 ;18.5-27.5°C; Girma Tilahun,1988), Abijata and Langano (18-27°C; Elizabeth Kebede *et al.*, 1994), Kilole (18.5-24°C; Elizabeth Kebede *et al.*, 1994) and Belbela Reservoir (18.50-24.1°C; Feyisa Girma,2011). The recorded relatively lower values of surface water temperature of the study reservoirs may be partly attributable to the differences in altitude as the reservoirs of the present study are located at higher altitudes (>2000 m a.s.l).

Phytoplankton, other microscopic organisms, clay, silt and organic matter make a water body turbid (Das and Shrivastaba, 2003). High turbidity signify presence of large amount of suspended solids (Verma *et al*., 2012), which may suggest high rate of siltation that results in decreased depth of the water body. The mean turbidity values recorded for both reservoirs are greater than 5 NTUs (Nephelometric Turbidity Units), which is the maximum desirable limit for drinking water (Table 11) (WHO, 2004; 2008) and EEPA (2003). The high turbidity of the reservoirs may have resulted from contamination of the water bodies with wastewater, and soil erosion associated with the poor farming practices, which result in large quantities of top soil ending up in the rivers after heavy rains (Eshetu Gizaw *et al.*, 2004; Getu Sima, 2011; Hamere Yohannes and Eyasu Elias, 2017). Therefore, turbidity is among the main water quality concerns for Dire and Aba-Samuel reservoirs making their water unsuitable for direct domestic use since it will cause diseases. USEPA (1999) stated that turbidity gives shelter to pathogen from disinfection and lead to high risk of gastrointestinal illness.

The turbidity (NTU) values of the present study are generally comparable to those previously reported by Adane Sirage (2006) for Legedadi Reservoir (42-590), while they are still much higher than those recorded for Geffersa Reservoir (7.2-189; Nigatu Ebisa, 2010), Belbela Reservoir (67-103 ; Feyisa Girma, 2011), Lake Hayq (22.75; Aregawi Teklay and Meareg Amare, 2015) and that recorded by Yirga Kebede *et al.* (2016) at Abay Mouth (27.5 NTU). The mean turbidity value (NTU) of Dire Reservoir (255.61±39.61) was about five times that recorded for Aba-Samuel Reservoir (53.14±2.91). This may probably be due to the influx of much more particulate materials from the catchment through runoff, the fairly high total suspended solids (Helnata Tilahun,2019) and the resuspension of inorganic (silt and clay) and organic particles by the frequent wind-generated mixing (shallowness and greater exposure to wind).

5.2 The concentration of heavy metals in water samples

The occurrence of lowest mean concentrations of most metals at S1 of Dire Reservoir (Table 8) was attributable to dilution effects associated with it shallowness and relatively small area. Dilution masks the local concentration effects of the low and chronic exposure of the metals, by quickly reducing the concentration levels in the water (Zinabu Gebre-Mariam and Pearce, 2003) while at S3 of Aba Samuel Reservoir (Table 8) might be the adsorption of those metals at the bottom sediments. It is proved that a lower pH increases the competition between metals and hydrogen ions for binding sites. A decrease in pH may also dissolve metals-carbonate complexes, releasing metal ions into the water column (Osmond *et al*., 1995). During the sampling period of this study, in all the sites pH of the water measured to be alkaline (Table 7). These pH conditions were not favorable for the solubility of the metals; it was not expected to find high amounts of heavy metals in water samples. This in turn, decreases the toxicity effects of the metals. For example, the reduction in water temperature and pH can increase the toxicity of copper (Nussey, 1998). The chemical speciation of copper strongly depends on the pH of water (Stouthart *et al*., 1996). Copper, in water, is particulate at high pH (alkaline) and is thus not toxic, while at low pH (acidic), it is mobile, soluble and toxic (Nussey, 1998). This may be a factor for low recorded values of copper during the study period. Relatively, the concentration of Pb in Dire Reservoir at S3 were higher than Aba-Samuel Reservoir. This might be the resuspention of heavy metals from the bottom sediment to the water column after wind mixing actions.

The existence of two or more metals in a given location might be due to the chemical affinity between them (Tigist Ashagre *et al*., 2014). In accordance with our results, the pair Cr/Cd showed strong positive correlation (r=0.92; Dire Reservoir and r=0.91; Aba-Samuel Reservoir), implying that they have similar sources, chemical features, and reactivity (Nirmal *et al*., 2008). Moreover, higher metal concentration at those sites might be related to the higher correlation between those metals and physicochemical parameters (e.g. pair Zn/Temp.). The higher values of those physicochemical parameters contribute to the higher concentrations of metals as suggested by Okafor and Opuene (2006) and Igbinosa and Okoh (2009).

Table 12: Mean concentrations of heavy metals in the water (mg L^{-1}) samples of Dire and Aba-Samuel reservoirs in comparison with the guideline values set by EU (1998), WHO (2004;2008) and USEPA (2011) guidelines (DR Wat. = Dire Reservoir water; ASR Wat. = Aba-Samuel Reservoir water).

Reservoirs	Cu	Zn	Mn	Cr	Cd	Hg	Pb	As
DR. Wat.	0.002± 0.000	0.010± 0.001	0.236± 0.014	0.002± 0.000	0.002± 0.000	0.002± 0.000	0.010± 0.001	0.007± 0.000
ASR. Wat.	0.004± 0.000	0.028± 0.002	0.504± 0.023	0.007± 0.000	0.006± 0.000	0.004± 0.000	0.007± 0.000	0.007± 0.000
EU(1998)	2	NM	0.05	0.05	0.005	-	0.01	0.01
WHO(2004)	2	3	-	-	0.003	0.001	0.01	0.01
WHO(2008)	0.5	3	0.1	0.05	0.003	0.1	0.01	0.05
USEPA(2011)	1.3	5	0.1	0.1	0.005	-	0.015	0.01

The mean concentrations of heavy metals determined in water samples (Table 12) are all below the guideline values set by WHO (2008) and USEPA (2011) with the exception of Mn in both Reservoirs and Cd in Aba-Samuel Reservoir, which are slightly higher. The higher concentrations of Mn detected at both reservoirs might have been the result of the non-point source of pollution, especially the surface run-off from nearby agricultural fields that use fertilizers and pesticides and its abundance in over 100 common salts and mineral complexes that are widely distributed in rocks, in soils and on the floors of lakes and oceans (Finkelman, 2005). Especially, the higher concentration of manganese (Mn) in Aba-Samuel Reservoir (0.504 mg L^{-1}) could be the presence of metal production factories (E.g. Kality metal products) around Akaki Kality sub city, which dispose its waste in to Akaki Rivers which in turn get into Aba-Samuel Reservoir. So, Mn could be source of health problem in the near future as the level of the metal is showing an increasing trend in comparison with previous data.

The concentrations of Cd in Aba-Samuel Reservoir also deviate the guideline values set by WHO (2008) and USEPA (2011) (Table 12) implying that there could be a cause of health problem if necessary precautions are not exercised while using this water for household purpose. However, this value is lower than maximum permissible level for livestock drinking, which is 1 mg L^{-1} (Samuel Melaku *et al.*, 2003). The higher concentration of Cd, whose level is highly dependent on the pH of the medium, in Aba-Samuel Reservoir (Table 12) may have resulted from contamination of the reservoir from different sources (plastic manufacturing, as coloring in paints production, use of cadmium fungicides, and phosphates fertilizers (Fulkerson *et al*., 1973). High concentration of cadmium occurs at neutral and alkaline pH (NRCC, 1979). The use of cadmium containing agricultural chemicals including fertilizers, and pesticides might have also contributed to the contamination of the reservoir water (ATSDR, 2003). It is proved that absorption of cadmium from the gastrointestinal tract is increased if there is a deficiency in calcium (Ca) and iron (Fe) implying that nutrient deficient peoples are more susceptible for Cd exposure (NRCC, 1979). It also disrupt the normal functioning of plant enzymes because of its affinity for binding to sites containing sulfhydryl groups and causes reduced plant growth (Nicholas *et al.*, 1998).

The relatively high concentration of Cr in Aba-Samuel Reservoir than Dire Reservoir could be due to the closeness of the reservoir to the tannery industries (ELICO Awash Tannery and Batu Leather), which use Cr containing compounds for tanning and Big and Little Akaki Rivers as their waste disposal systems. All these heavy metals may cause acute or chronic health problems on aquatic organisms including human beings and resulted potential health effects (Table 3) after a long-time exposure if appropriate measures are not taken.

The mean concentrations of Cr, Pb, Cu and Zn (mg L^{-1}) (Table 12) in water samples from Dire and Aba-Samuel reservoirs were lower than those reported in the studies conducted by Wondimagegn Assefa and Tarekegn Beranu (2015, 0.15,0.26,0.53 and 2.51 respectively) in Tendaho Reservoir. However, only the concentrations Cd in both reservoirs was above those recorded for Tendaho Reservoir.

The concentrations of Cu, Pb, Cr and Cd (mg L^{-1}) in the water samples from Dire and Aba-Samuel reservoirs are close compared to those reported by Abraha Gebrekidan *et al*. (2012) for Lake Hashengie. However, the concentrations of Mn (mg L^{-1}) in both Reservoirs were above those recorded value for Lake Ashengie, while the concentrations of Zn (mg L^{-1}) are lower than those of Lake Hashenge concentration level.

The mean levels of Pb (mg L^{-1}) recorded for Dire Reservoir (0.01) and Aba-Samuel Reservoir (0.007) are closer to those reported previously for Lake Hashengie (0.0033 mg L^{-1}; Abraha Gebrekidan *et al*., 2012), Lake Mahrulu, Iran (0.005 mg L^{-1}; Moore *et al.*, 2009) and Lake Baringo, Kenya (0.043 mg L^{-1}; Ochieng *et al*., 2007) and lower than that of Tendaho Reservoir (0.26 mg L^{-1}; Wondimagegne Assefa and Tarekegn Beranu, 2015) and Lake Hayq (0.086 mg L^{-1}; Aregawi Teklay and Meareg Amare, 2015).

The concentrations of copper and Zinc (mg L^{-1}) measured during the study period are below those recorded in the study on Lake Chamo conducted by Belay Tafa and Eshete Assefa, 2014 with the exception of the concentration of Zn in Aba-Samuel Reservoir, which is slightly higher. The concentrations of Cd, Cr, Cu, Mn and Zn (mg L^{-1}) are closer to the results obtained by Zerabruk Tesfamariam *et al.* (2016) in Eritrean drinking water reservoirs (Table 4). The concentrations of Zn, Pb, Cr and Cd (mg L^{-1}) are broadly similar to those reported by Chali Abate *et al*. (2016) for a drinking water supply source of Assela town (Table 4). This is might be due to similar location of the reservoirs and the presence of potential sources (origins) of these metals.

Moreover, the few data available on Mn content of Aba Samuel Reservoir includes that of Yesihak Worku *et al*. (1999) and Tamiru Alemayehu *et al*. (2005) which are 0.1 and 0.204 mg L^{-1} both of which are far below the current result. The higher result from this study may be due to increasing input from upstream to the tributaries of the Reservoir (Little and Big Akaki Rivers) and the restoration of the Reservoir from the infestation by water hyacinth (*Eichhornia crassipes*), which is a fast growing and highly efficient aquatic plant for the absorption of heavy metals from the surrounding environment (Daniel Wolde-Michael, 2009). Daniel Wolde-Michael (2009) proved that the efficiency of water hyacinth for the removal of Cr from aqueous solution and the growth of the plant was inhibited due to Cr toxicity above 15.34 mg L^{-1} Cr concentration in water solution. He recommended that the ability of plants to stay healthy and therefore continue to grow is an important factor in the choice of plants for wastewater treatment and concluded that the application of water hyacinth for Cr removal will be sustainable if the concentration of Cr in wastewater not exceeding approximately 15.34 mg L^{-1}.

Similar findings reported by (Tigist Ashagre *et al*., 2014; Solomon Sorsa *et al.*, 2015) in Lake Hawassa and Birkti Miesho (2019) in Koka Reservoir also recorded higher concentrations of heavy metals in macrophytes and water hyacinth than in water. Mekonnen Bekele (2008) also investigated that the level of trace metals in the water hyacinth is generally many folds higher than the level of the metals found dissolved in water. He found out that metals in the roots of the plants were 1.5 to 7 times higher than those in the shoots. This higher content of metals in roots of the plants suggests that the major route of metals in to these aquatic plants is direct up take of dissolved species of the metal from the water via their roots rather than the other paths of the metals in plants tissues. Higher level of the toxicant metals in the roots means water is the major source of these metals. So it is logical to conclude that the pollution of Aba Samuel Reservoir water might be by these toxic heavy metals is mainly because of the water pollution of the tributaries of the reservoir (Little and Big Akaki Rivers) rather than direct atmospheric deposition. Actually it takes additional task to identify what particular source (alloctnous and authoctnous) release these metals in to the major tributaries of this lake (Little and Big Akaki Rivers).

Table 13: Comparison of permissible limits for heavy metals in drinking water set by some countries with the results of the present study (NM= Not Mentioned)

Standard of drinking water in some countries and in current study (mg L^{-1})							
Heavy Metals	Malaysia ESDMHM (2000)	Iran Sanayi *et al.*(2009)	Australia ANZECC and ARMCANZ (2000)	India BIS(2012)	New Zealand NMH(1995)	Studied Reservoirs	
						Dire	**Aba-Samuel**
Cu	-	-	-	-	-	0.002	0.004
Zn	3	NM	3	5	1.5	0.01	0.028
Mn	-	-	-	-	-	0.236	0.504
Cr	0.05	0.05	0.05	0.05	0.05	0.002	0.007
Cd	0.003	0.01	0.002	0.01	0.04	0.002	0.006
Hg	-	-	-	-	-	0.002	0.004
Pb	0.05	0.05	0.01	0.1	0.1	0.01	0.007
As	-	-	-	-	-	0.007	0.007

The level of Zn in Dire Reservoir (0.01 mg L^{-1}) and Aba-Samuel Reservoir (0.028mg L^{-1}) of the current study are much lower than the concentrations of Malaysia (3 mg L^{-1}), Australia (3 mg L^{-1}), India (5 mg L^{-1}) and New Zealand (1.5 mg L^{-1}). The level of Cr in Dire Reservoir (0.002 mg L^{-1}) and Aba-Samuel Reservoir (0.007mg L^{-1}) of the current study are below the permissible concentrations set for drinking water (0.05 mg L^{-1}) by Malaysia, Iran, Australia, India and New Zealand. The level of Pb in Dire Reservoir (0.01 mg L^{-1}) and Aba-Samuel Reservoir (0.007 mg L^{-1}) in current study are below the permissible concentrations set by Malaysia (0.05 mg L^{-1}), Iran (0.05 mg L^{-1}) India (0.1 mg L^{-1}) and New Zealand (0.1 mg L^{-1}). The concentration of Cd in Dire Reservoir water samples (0.002 mg L^{-1}) are below the guideline values set by Malaysia (0.003 mg L^{-1}), Iran (0.01 mg L^{-1}), India (0.01 mg L^{-1}) and New Zealand (0.04 mg L^{-1}), whereas that of

Cd in Aba-Samuel Reservoir (0.006 mg L^{-1}) during the current study is above the permissible limit of Malaysia (0.003 mg L^{-1}).

In this regard, the highest mean value of cadmium detected in Aba-Samuel Reservoir could be partly accounted for by the closeness of the reservoir to the different industries (plastic manufacturing) and whose effluents may pollute the water system and the location of the reservoir in the proximity of the highway where cadmium from car batteries could leak into the water system. It also released in cadmium fungicides, in nickel-cadmium dry cell batteries and phosphates fertilizers (Fulkerson *et al*., 1973; Purvers, 1977). It deviates not only the guideline values set by WHO (2008) and USEPA (2011) but also Malaysia (2000) (Table 13) and could may induce kidney dysfunction, skeletal damage, and reproductive deficiency, may be carcinogenic, teratogenic, genotoxic, and can cause damage to the central nervous system and produce psychological disorder (Akoto *et al.,* 2014). It can also replace zinc biochemically, interferes with enzymes and causes high blood pressure and kidney damage (Rajappa *et al*., 2010).

In general, chronic exposure to heavy metals in drinking water at concentrations above the USEPA maximum contaminant levels have been reported to cause systemic health effects in human (US EPA, 2010a). These health effects may include damage to the kidney, liver, nervous and skeletal systems, gastrointestinal distress, and mental retardation in children and abortion in pregnant women (WHO, 2003; WHO, 2004a; WHO, 2004b).

5.3. The concentration of heavy metals in sediment samples

Determination of metal elements in reservoir sediment during the study period revealed that all the analyzed heavy metals were present. Among the studied metals, Mn, Zn and Cr had the highest values at all sampling sites. This may be attributed to the fact that Mn and Zn are the most abundant elements in the earth's crust as the study on Nile sediment (Siegel *et al*., 1994) has shown. The concentration levels of Hg and Cd were low as compared to those of Zn and Cr.

The concentrations of metals in bottom sediments (mg kg^{-1}) varied widely. The mean concentration of heavy metals in sediment samples of Dire Reservoir were in the order Mn> Zn >Cr>Pb>Cu>Hg>As>Cd. Similarly, the concentration of heavy metals in sediment samples of Aba-Samuel Reservoir were ranked as Mn> Zn >Cr>Pb >Cu>Hg>As>Cd. This sequence agrees with the findings of Siegel *et al*. (1994) and Ramdan (2003) in Lake Manzala, Egypt. The low levels of Hg, As and Cd might be due to formation of complexes with organic compounds because of the high formation constants of organic metal compounds, which make them rather stable in the environment (Zhou *et al.*, 1998).

Table 14: Mean concentrations of heavy metals in the sediment samples (mg Kg^{-1}) of Dire and Aba-Samuel reservoirs in comparison with the guideline values of CSQGS of NOAA (2009), ISQG (2002) and USEPA (2010).

Reservoirs	**Cu**	**Zn**	**Mn**	**Cr**	**Cd**	**Hg**	**Pb**	**As**
DR.Sed.	24.71±0.21	158.71±1.69	1098.9±13	46.46±0.14	2.74±0.04	20.39±0.45	30.37±0.17	19.46±0.06
ASR. Sed.	27.09±0.08	180.48±2.23	1198.39±60	46.43±0.12	2.86±0.03	22.37±0.04	29.78±0.06	20.10±0.08
ISQG (2002)	35.7	123.0	460.0	37.3	0.6	-	35	-
USEPA (2010)	31.6	121	-	43.4	0.99	-	35.8	-
LEL*	16	-	-	26	0.6	-	31	-
TEC*	31.6	121.0	460	43.3	0.99	-	35.8	-
PEC*	149.0	459.0	1100	111.0	4.90	-	128.0	-
SEL*	110.0	-	-	110.0	10	-	250.0	-

DR. Sed. = Dire Reservoir sediment; ASR. Sed. = Aba-Samuel Reservoir sediment;

LEL=Lowest Effect Level; TEC = Threshold Effect Concentration;

PEC = Probable Effect Concentration and SEL= Serious Effect Level.

*LEL, TEC, PEC and SEL Source are National Oceanic and Atmospheric Administration (NOAA, 2009).

The results showed that the concentrations of Zn, Mn, Cr and Cd in sediment samples are above the standards of (ISQG, 2002; USEPA, 2010), while the concentrations of Pb and Cu in both reservoirs are below the respective reference values of ISQG (2002) and USEPA (2010). The concentration levels in the sediments of both Reservoirs were also compared with the consensus-sediment quality guidelines (CSQGs) of NOAA (2009) to assess their status because heavy metals in sediments can be secondary sources of pollution to the reservoirs water once environmental conditions are changed (Chen *et al.* 1996). CSQGs include a lowest effect level (LEL), a threshold effect concentration (TEC) and a probable effect concentration (PEC) and a serious effect level (SEL) (Table 14). Concentration of the contaminant in sediment below TEC means adverse biological effects are unlikely to occur (USEPA, 2000). Conversely, adverse biological effects are likely to occur if contaminant is above PEC level (Smith *et al.*, 1996). MacDonald *et al.* (2000) noted that most of the TEC provide an accurate basis for predicting the absence of sediment toxicity, and most of the PECs, provide an accurate basis for predicting sediment toxicity.

In this study, the mean concentrations of Zn, Mn, and Cr and Cd in the sediment samples of Dire and Aba-Samuel reservoirs are higher than the proposed TECs, indicating that there may be a potential harmful effect and a predictor for the presence of metal toxicity associated with these metals. On the other hand, the mean concentration values of heavy metals in sediment samples of both reservoirs, with the exception of the slightly higher concentration of Mn in Aba-Samuel Reservoir, are all lower than the proposed PECs guideline values implying that only Mn is likely to cause adverse effects on the aquatic organisms. In addition, in both Reservoirs the mean value of Pb greater than the proposed LELs, indicating that there may be causes result an adverse alteration of morphology of an organism while concentrations of Cu, Cr, Cd and Pb higher than the suggested SELs, representing that there may be effect on physiology of an organism after a long exposure (Akan *et al*., 2010).

The mean concentration values of Pb and Mn are greater than the results obtained by Abraha Gebrekidan *et al.* (2012) in Lake Hashenge, while those of Cr, Cd, Cu and Zn are lower than those reported by the same investigators for Lake Hashenge (Table 1). The concentrations of Mn, Zn, Cr, Pb and Cu are greater than those recorded by Zerabruk Tesfamariam *et al*. (2016) in Mainefhi Reservoir, Eritrea, while concentrations Cr, Cu and Mn are low compared to the same investigators observed in Toker Reservoir, Eritrea (Table1). The concentrations of Cr, Pb and Cu are greater than those measured by Adebayo (2017), Öztürk *et al*. (2009), and Kishe and Machiwa (2003) in Ureje Reservoir, Avsar Dam and Lake Victoria, respectively (Table 1) although they are still lower than the results obtained by Pote *et al*. (2008) in Lake Geneva.

Anthropogenic pollution of the Dire Reservoir area is also unlikely as there are no industries (e.g. leather and metal production factories) and not much transport or traffic related activities around Dire Reservoir (Getu Sima, 2011). In contrary, anthropogenic pollution of the Aba-Samuel Reservoir area is likely to occur as there are industries (e.g. tannery, textile, plastic, metal etc. production industries) and much transport or traffic related activities (Feven Solomon, 2007). The concentrations of Mn in both water and sediment samples of both reservoirs were highest compared to those of other trace metals.

The total concentration of metals in both reservoirs followed the order of metals in sediment>metals in water, which agrees with the findings of Tigist Ashagre *et al*. (2014). This is due to adsorption capacity of heavy metals onto sediments and the phenomenon of chemisorption, a process, which enables metals to form strong chemical complexes with the organic material present in the wastewater (USEPA, 1999). In addition, adsorption of cations by organic matter present in the sediment layers, and their interaction with organic matter in aqueous phase lead to their sedimentation thereby resulting in high concentrations in the sediments (Kumar and Edward, 2009). These metals are only released after their maximum absorption limits have been exceeded; hence higher concentrations of the metals in the bottom sediments compared to the subsurface water samples (Adebayo *et al*., 2017). In most cases, majority of heavy metals are associated with sampling sites experiencing high suspended particulate matter and can, therefore, be considered as indicators of turbidity of the reservoirs.

6. CONCLUSIONS

The results of this study have provided information on the level of pollution of the reservoirs based on physicochemical parameters including heavy metals. Among the physicochemical parameters measured in this study, turbidity, whose levels in both study reservoirs is higher than the maximum permissible limit set for drinking water (%NTU), is among the main water quality concerns for reservoirs making their water unsuitable for direct domestic use. DO values recorded in the present study were generally within the range of USEPA's (1999) guideline values set for drinking water, some of the levels observed at sites of Aba-Samuel Reservoir, which seem to reflect the level of organic pollution, are worrying as they obviously create stressful conditions, which are potentially lethal, to aerobic aquatic life.

All heavy metals except Cadmium (Cd) and Chromium (Cr) at S3 of Dire Reservoir were detectable in water samples of both Dire and Aba-Samuel reservoirs. The highest heavy metal concentration was found for manganese and zinc was the heavy metal with the second highest concentration in both reservoirs. The total concentration of metals in water samples of both reservoirs followed the order of concentration in the sediment. The mean concentrations of heavy metals in the water samples were all below the guideline values set by international organizations, with the exception of Mn in both reservoirs and Cd in Aba-Samuel Reservoir, which are slightly higher.

Determination of metals in sediment samples collected from the reservoirs revealed that all the analyzed heavy metals were present at concentrations much higher than those measured in the water samples. The concentrations of Zn, Mn, Cr, and Cd were higher than the (ISQGs, 2002; USEPA, 2010) guidelines while Pb and Cu were lower than those standards.The mean concentrations of the heavy metals in sediment samples from Dire and Aba-Samuel reservoirs were in the order of Mn > Zn > Cr> Pb > Cu > Hg > As > Cd. The results of the statistical analysis revealed the strong associations of water temperature, DO, turbidity and EC and heavy metal concentrations suggesting the potential influence of the former on the distribution and levels of the later.

Generally speaking, the differences in the levels of physicochemical parameters including heavy metals between those measured in the present study and those reported previously are attributable to the differences in the location of sampling points and their proximity to the industrial sites. Moreover, the difference in the sampling period may have also contributed to the observed discrepancy in the results obtained as the present study was carried out only during the months of the minor and major rainy periods (April, May and June), which may have resulted in the dilution of the concentrations of metals. The present results also seem to suggest that Aba-Samuel Reservoir is slightly more polluted than Dire Reservoir. This may be explained by the higher anthropogenic disturbance occurring in its catchment areas.

7. RECOMMENDATIONS

- Possible measures should be taken to control point and nonpoint sources of pollution including the inflowing rivers to prevent from further degradation of these drinking water reservoirs.
- Pollution control measures such as proper sewage handling, careful management of grazing areas, etc., have to be taken to protect the water bodies from degradation
- Reservoirshore protection by macrophytes and constructed wetlands should be considered as a means to reduce heavy metal concentration (especially for the reduction of Mn and Zn concentrations).
- Additional research on metals in biota (fish, plankton, and macrophyte species) should be done to determine their bioaccumulation factors (BAFs) and translocation ability (TLA) since water samples only indicate the situation at the time of sampling, while concentrations in the organism are the result of past as well as current pollution levels.
- Further research for heavy metals exposures of residents should be assessed near Aba-Samuel Reservoir and Akaki Rivers.
- Coordinated work of policymakers, scientists and local community is vital in the development of strategies of conservation of the water resources.
- Year round study should be conducted to understand spatial and temporal variations of the studied parameters.

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