University of Natural Resources and Life Sciences, Vienna

United Nations Educational, Scientific and Cultural Organization

Institute for Water Education in partnership with UNESCO

NUTRIENT DYNAMICS AND CONCENTRATIONS OF HEAVY METALS ALONG THE COURSE OF MEGECH RIVER, TRIBUTARY OF LAKE TANA, ETHIOPIA

Thesis submitted for the award of the title

"Master of Science"

by

Flipos Engdaw Woldeab

---

supervised by

Prof. Thomas Hein

Dr. Getachew Beneberu

This thesis is submitted in partial fulfilment of the requirements of the Joint academic degree of Master of Science in Limnology and Wetland Management

Jointly awarded by

The University of Natural Resources and Life Sciences (Boku), Vienna, Austria

the UNESCO – IHE Institute for Water Education, Delft, the Netherlands

Egerton University, Njoro, Kenya

University of Natural Resources and Life Sciences (Boku), Vienna, Austria

April 2019

Dedication

To my elder brothers TADESSE and DAGNEW Engdaw

“ኦ እግዚኦ አእርፍ ነብሳተ አግብርቲከ ገብረ ህይወት ወህንጻ ኢየሱስ”

Acknowledgment

"ንሴብሆ ለእግዚአብሔር ለዘበስብሀተ ቅዱሳን ይሴባህ"

It is a great pleasure to express my gratitude to my supervisor Prof. Thomas Hein, for his valuable suggestions, constructive comments and cooperation throughout the research work. I'm also thankful to my co-supervisor Dr. Gtachew Beneberu for his unreserved cooperation in soliciting a laboratory to work and guidance during field work. I'm also grateful to acknowledge Marye Mulugeta, Lidya Tesfaye, Marelgn, Weldearegawi and Gebremeskel for their support during sampling and laboratory work.

I would like to thank NFP (The Netherland Fellowship program) for the financial support throughout my postgraduate study. I also acknowledge the Austrian Development Corporation (ADC) for funding my research work.

I would like to express my appreciation to IPGL officers especially to Mr. Gerold, Ms. Nina, Ms. Marie and Mrs. Susanne for all your timely advice and support during the study and research work.

My deepest appreciation goes to my beloved mother Yeshhareg Admassu for the strength, love and moral support. I'm also indebted to all my sisters Tigzye, Teqush, Etalem, Seblye, and to my brothers Surye, Wubie Amanu and Terefe. All my nephews and my only niece Hulun-beanch, thank you all for the love, moral support and encouragement.

I am also thankful to all my friends, colleges and classmates for the experience we shared and the friendship we enjoyed.

Above all, I thank the almighty God and his mother saint Mary!

Abstract

Nutrient enrichment and excess heavy metal concentrations caused by anthropogenic activities are major threats of aquatic pollution in developing countries like Ethiopia. So far, there is limited information regarding concentrations of nutrients and heavy metals in the freshwater bodies of northern Ethiopian highlands. Therefore, this study aimed to assess current status and spatial distribution of nutrients and heavy metals from water, sediment and *Eichhornia crassipes* samples of Megech river located in North Gondar zone of Amahara region from November 2018 to January 2019. Sampling sites (M1-M6) were identified based on anthropogenic influence and a total of 30 water, 30 sediment and 10 *E. crassipes* samples were collected along the river. Results revealed that, mean TP, SRP, TN, NO_2-N, NO_3-N and NH_4-N concentration in the water ranged from 85.56-123.33 µg L^{-1}; 23.5-97.73 µg L^{-1}; 2.82 to 4.87 mg L^{-1}; 14.48 to 20.11 µg L^{-1}; 1.24 to 1.94 mg L^{-1} and 4.83 to 11.14 µg L^{-1}, respectively. Mean TP and TN in the water and sediment were higher than USEPA standard to cause eutrophication. Concentrations of Cu (0.11 to 0.17 mg L^{-1}), Zn (0.11 to 0.16 mg L^{-1}) and Cr (0.03-0.05 mg L^{-1}) in the water were within WHO, ECE, SA and USEPA guidelines for domestic use. In the sediment, maximum concentrations of heavy metals detected at site M2 were within the recommended SQG for aquatic systems. Higher concentrations of heavy metals in *E. crassipes* was in the stem, root and leaf parts. Generally, higher concentrations of nutrients and heavy metals were observed at sites with severs anthropogenic activity (M2). Therefore, continuous monitoring and seasonal studies with representative samples including benthic organisms and other macrophytes are needed to know the impact on downstream sections.

Key Words/phrases: Anthropogenic, *Eichhornia crassipes*, Heavy metals, Megech river, Nutrients

TABLE OF CONTENTS

Lists of figures

List of tables

List of abbreviations

APHA	American Public Health Associations
Ca	Calcium
Cd	Cadmium
Cr	Chromium
CSA	Central Statistical Agency
Cu	Copper
DWAF	Department of Water Affairs and Forester
ECA	European Commission for Environment
FAO	Food and Agriculture Organization
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
K	Potassium
LFDP	Lake Fisheries Development Program
masl	meters above sea-level
Mg	Magnesium
N	Nitrogen
NH_4	Ammonium
NO_2	Nitrite
NO_3	Nitrate
PEC	Probable Effect Concentration
Pb	Lead
PCA	Principal Component Analysis
SA	South African
SRP	Soluble Reactive Phosphorus
SQG	Sediment Quality Guideline
TEC	Threshold Effect Concentration
TN	Total nitrogen
TP	Total phosphorus
USEPA	United States Environmental Protection Authority
WHO	World Health Organization
Zn	Zink

CHAPTER 1: INTRODUCTION

1.1. Background

Water is one of the most precious gifts of nature to mankind in which the terrestrial ecosystem cannot function without it (Lawson, 2011; Kerketta *et al*., 2013). Water with good quality plays a great role on the health of humans and sustain economic growth (Sunday and Agbaji, 2012; FAO, 2017; Akale *et al*., 2018). However, contamination of aquatic systems with a wide range of pollutants such as nutrient enrichment and excess concentrations of heavy metals has become a major issue across the world (Canli *et al*., 1998; Voegborlo *et al*., 1999; Dirilgen, 2001; Kebede and Wondimu, 2004; Vutukura, 2005; Bennett *et al*., 2017). Together with natural sources, influx of unwanted pollutants in aquatic systems and their adverse environmental effects associated with, waste effluents from industries particularly discharge of toxic chemicals, high volume municipal sewage due to high population growth (Pizarro *et al*., 2010), and agricultural activities (Elisabeta *et al*., 2010) are among the major causes of water pollution (Gebremariam *et al*., 2002; Desta *et al*., 2003; Lokhande *et al*., 2011; Ogundiran and Fawole, 2018). Due to fast rate of deterioration, contamination of aquatic systems with a wide range of pollutants including nutrients and heavy metals become a matter of concern in developing countries (Dirilgen, 2001; Kebede and Wondimu, 2004; Vutukura, 2005; Bennett *et al*., 2017). Consequently, problem of getting good quality water worsens in developing countries (Kerketta *et al*., 2013; Tadesse *et al*., 2018).

Essential nutrients such as phosphorus (P), nitrogen (N) and others determine productivity of aquatic ecosystem and limit abundance and distributions of algal communities (Mulholland and Webster, 2010; Pizaro *et al*., 2010; Bouwman *et al*., 2013; Robson, 2014). Nevertheless, excess concentrations in aquatic systems will bring deterioration of water quality (Halliday *et al*., 2014; Datri *et al*., 2015), eutrophication (Carpenter, 2005; Khan and Ansari, 2005)

followed by loss of biodiversity (Rabalais, 2002), disrupt food web structure and high organic matter accumulation (Pearl *et al*., 2016; Yun and An, 2016), finally increased cost of treatment and greenhouse gas emissions (Rabalais, 2002; Carpenter, 2005; Paerl, 2006; Costa *et al*., 2018).

On the other hand, contaminations of aquatic systems with heavy metals such as cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg), zinc (Zn), cobalt (Co) and others became a major concern worldwide due to their non-biodegradable nature and adverse toxic effects from long-term low-level exposure (Dimari *et.al*., 2008; Ibrahim and Sa'id, 2010 and Kerketta *et al*., 2013; Pigłowski, 2018). In consensus, disturbance in the natural ecological balance in line with their devastating effect on both flora and fauna life make excess heavy metals concentration in aquatic environment a major concern worldwide and ranked as major polluting chemicals in both developed and developing countries (Dimari *et al*., 2008; Ibrahim and Sa'id, 2010). But their impact is more severe in developing countries due to the low rate of wastewater treatment.

It is a fact that all living organisms require different quantities of the aforementioned heavy metals for the normal functioning of the body physiology (Akele *et al*., 2016). However, excess levels of exposure will damage the organism resulting to various disorders and toxicities (Jan *et al*., 2015). In line with the above, Ackova (2018), explained the bio-accumulative nature of heavy metals in the food chain where the level of concentration increases with trophic state. Similarly, in aquatic systems compared to water and sediments, higher and stable concentrations of heavy metals would be obtained from macrophytes due to long term exposure (Kebede and Wondimu, 2004; Ackova, 2018).

Ethiopia is one of the developing countries suffering from environmental and water pollution that are caused by nutrient enrichment and excess heavy metals concentrations (Kebede & Wondimu, 2004; Desta, 2007; Beyene and Redaie, 2011; Gebremedhin *et al*., 2018). Compared

to other eastern and northern African countries, Ethiopia has 12 major river basins with the mean annual flow of 122 billion metric cube and more than 36 lakes with surface area of about 7,500 km^2 making the country water tower (Awulachew *et al*., 2007; FAO, 2015; Gebremedhin *et al*., 2018). However, various anthropogenic activities such as land use, urbanization (Lanckriet *et al*., 2017; Alemu *et al*., 2018), human settlement, development activities and other practices associated with rapid population growth (Wondimu, 2016; Goshu and Aynalem, 2017; Aghoghovwia *et al*., 2018; Gebremedhin *et al*., 2018); combined with natural factors and hydrological variations (Paerl *et al*., 2016; Lanckriet *et al*., 2017) are currently threating the water quality as well biodiversity of the system through their profound effect on nutrient enrichment and excess heavy metal concentrations (Arhonditsis *et al*., 2007).

In Ethiopia particularly in Lake Tana and its tributaries including Megech River, anthropogenic activities in settlements, industrial activities associated with some sort of production work (Wondim, 2016; Lanckriet *et al*., 2017; Gebremedhin *et al*., 2018), and agricultural chemicals applied to farmlands (Alemu *et al*., 2017; Akale *et al*., 2018) have led to widespread external nutrient levels and eutrophication. Intensifying agricultural practices with increased use of fertilizers and pesticides are being held mainly responsible for degrading the water quality of the lake (Wondie *et al*., 2007; Emama *et al*., 2010). In consensus, recent studies depicted that apart from nutrient pollution, Ethiopian inland water bodies are suffering from environmental and water pollution that are caused by heavy metals and other contaminants that exist in geology, aqueous waste effluents from farming lands, industries, household activities and hospitals (Kebede and Wondimu, 2004; Desta, 2007; Beyene and Redaie, 2011; Gebremedhin *et al*., 2018).

1.2. Problem statement and justification

There is a great deal of information on the assessment of nutrients and heavy metals from water, sediment and macrophytes of Ethiopian inland waters (Kebede and Wondimu, 2004; Desta, 2007; Beyene and Redaie, 2011; Degefaw *et al*., 2013; Akele *et al*., 2016; Dribaba *et al*, 2018; Kassegn *et al*., 2018). But, most of the above studies are conducted in the rift valley lakes and tributaries due to their location and chance for comparison (Tudorancea and Taylor, 2002; Fetahi, 2010; Wondim, 2016). Studies on Lake Tana and its tributaries mainly focus on faecal pollution, limnological and ecological studies on fish diversity, phytoplankton and macrophyte composition and chlorophyll *a* biomass (Wudneh, 1998; Berhanu *et al*., 2002; Degen *et al*., 2002; Wondie *et al*., 2007; Goraw *et al*., 2010; Anteneh *et al*., 2014; Wondim, 2016; Kassa, 2016; Gebremedhin *et al*., 2018). Apparently, most studies are restricted to one site mainly gulf of Bahir Dar and fail to consider the spatial and temporal variations at large scale.

Information on nutrient concentrations and quantifications of heavy metals from water and sediment samples of Megech River is diminutive. Discharging domestic and municipal waste without treatment, excavation, huge dam constructions, sand mining, intensive agriculture, application of detergents for car and cloth washing, bathing and animal watering are some of the common anthropogenic activities along the course of the river. As a result, the river is assumed to bring more nutrients and pollutants in to Lake Tana (Mehari *et al*., 2014; Wassie *et al*., 2014). Little has been done by the recently established Tana sub basin organization (TaSBO) on nutrient assessment at gaging stations of the river and the lake (TaSabo, 2011; Wondim, 2016). Recently, Alemu *et al*. (2017) assessed temporal variation of dissolved phosphorus only at gaging stations. Apart from that report, there is no well-organized and published work on the assessment of nutrients and heavy metals from water and sediment of Megech River along its course. Therefore, the purpose of the present study is to determine the

concentrations of nutrient and heavy metals from the water, sediment and *Eichhornia crassipes* along the course of the river.

1.3. Objectives

1.3.1. General objective

Assessing the concentrations of nutrients and selected heavy metals from water, sediment and *E. crassipes* of Megech River and littoral area of Lake Tana, Ethiopia.

1.3.2. Specific objectives

- To determine concentrations of TP, SRP, TN, NH_4-N, NO_3-N, and NO_2-N in the water of Megech River and littoral area of Lake Tana.
- To determine concentrations of TP, SRP, TN, NH_4-N and NO_3-N in the sediment of Megech River and littoral area of Lake Tana.
- To quantify concentrations of alkali (K), alkaline earth (Ca and Mg) and heavy metals (Cu, Zn, Cr, Cd, and Pb) in the water and sediment of Megech River.
- To determine concentrations of alkali (K), alkaline earth (Ca and Mg) and heavy metals (Cu, Zn, Cr, Cd, and Pb) in *E. crassipes* macrophyte at littoral area of Lake Tana.

1.4. Research questions

1. What is the current status of nutrients and heavy metals in Megech River?
2. Is there spatial variation in nutrients and heavy metals concentrations along the course of Megech River?
3. Where does high concentration of metal accumulate in the river found (water, sediment or macrophyte)?

1.5. Hypothesis

- Nutrient and heavy metal concentrations along Megech River exceeds the permissible limits of different standards (WHO, USEPA, SA and ECE) set for water quality assessments due to sever anthropogenic activity.
- Nutrient and heavy metal concentration show significant variation between study sites of Megech River as a response to different human activity and source of pollutant (e.g. domestic wastewater, industrial effluent, agriculture, animal watering and dam construction).
- Compared to water, higher concentrations of nutrients and heavy metals are found in the sediment and *E. crassipes* due to adsorption, absorption, and less soluble forms.

1.6. Significance of the study

The present study will fill the study gap on nutrient and heavy metal analysis from water, sediment and *E. crassipes* of Megech River and littoral area of Lake Tana by providing clear and first-hand information. It also benefits policy makers, hydrologists, fishery officers in the legislation and implementation of watershed management system as well in prevention of water pollution. In addition, the study will recommend possible immediate measures to be taken to reduce high nutrient and heavy metal contaminations from both point and non-point sources.

CHAPTER 2: LITERATURE REVIEW

2.1. Nutrient enrichment in aquatic systems

Atmospheric deposition, weathering of rocks, leaching from diffuse sources such as fertilizers, soil particles and manure are some of the most common ways that nitrogen and phosphorus can enter in to the aquatic system (Rabalais, 2002; Carpenter, 2005; Marti *et al*., 2006; Pizarro *et al.,* 2010; Inamdar *et al.,* 2015). Understanding the elemental cycles and transformations of nutrients especially N and P is essential in knowing ecosystem biogeochemistry (Marti *et al*., 2006). Growth, availability and productivity of most aquatic organisms depend on the concentrations and stoichiometry of essential nutrients (Pizarro *et al*., 2010; Bouwman *et al*., 2013). Apart from their natural distribution in the geology and catchment of aquatic ecosystems, point and non-point sources of pollutants related with sewage (Carpenter, 2005; Marti *et al*., 2006), industrial discharges, change in land use, runoff from agriculture (Rabalais, 2002; Elisabeta *et al*., 2010; Kassa, 2016), construction sites and urban areas increased loadings in to rivers and lakes which finally result enrichment of nutrients in water (Carpenter, 2005; Hauer and Lamberti, 2007; Pizarro *et al*., 2010). Different forms of nutrients from terrestrial catchment enter in to aquatic systems through runoffs which is highly dependent on biogeochemical, hydrological and ecological process (Karl and Bjorkman, 2002; Moss, 2010; Marti *et al.*, 2006; Inamdar *et al*., 2015). Level of oxygen concentration, nature of the inorganic matrix or minerals of the environment including sediment and microbial communities present in the system highly influence nutrient cycling in aquatic ecosystems (Dahm, 1998; Baldwin and Mitchell, 2000; Bouwman *et al*., 2013).

2.1.1. Nitrogen in aquatic systems

Although there are variations in quantity and transformations based on environmental scenarios and associated oxidation states, N in aquatic ecosystem can exists as dissolved organic (DON), particulate organic (PON) and dissolved inorganic nitrogen (DIN); where the latter includes

nitrite (NO_2^-), nitrate (NO_3^-), and ammonium (NH_4^+) (Rabalais, 2002; Durand *et al*., 2011; Inamdar *et al*., 2015; Rachel and Deborah, 2015). The above-mentioned forms of N show variation in dominance either due to depth, enrichment gradient, oxygen concentration, decomposition rate, temperature and salinity of the water. Among the different forms of N that can be derived from terrestrial environment and enter in to the water through inflow, NO_2^-, NO_3^- and NH_4^+ are relatively important forms which can be used by autotrophic organisms (Rabalais, 2002; Inamdar *et al*., 2015).

Nitrogen enters both lotic and lentic freshwater ecosystems through point and non-point sources (Marti *et al*., 2006; Strokal *et al*., 2016). However, presence of several intermediate compounds and different oxidation states make N cycle relatively complex in aquatic systems (Inamdar *et al*., 2015). Through fixation, atmospheric N is converted to NH_4^+ which is most usable form of N by plants as nutrient followed by nitrification that is conversion of NH_4^+ to NO_3^-. The above-mentioned process in aquatic systems is highly dependent on concentrations of dissolved oxygen (DO) which determine the redox potential of the element (Baldwin and Mitchell, 2000). Therefore, denitrification will take place during low DO conditions (Strokal *et al*., 2016). On the other way, amount of NH_4^+ in aquatic ecosystem can be improved either through ammonification that take place through decomposition of N rich compounds or direct addition from excreta of aquatic organisms including zooplankton, fish and others. Conversely, away from the atmospheric fixing, N delivered from agriculture, sewage, wastewater, industrial effluent and others mainly comes as NO_3^- and transported to adjacent water (Pizarro *et al.*, 2010; Inamdar *et al.*, 2015). Depending on the controlling factors in the pathway the cycle, flux and accumulation of NO_3^- continues (Carpenter, 2005; Marti *et al*., 2006).

In lotic ecosystems, hydrological conditions have inevitable impact in bringing allochthonous organic matter and accelerating rate of decomposition to produce NH_4^+ (Durand *et al*., 2011).

Due to the presence of high DO in rivers as well as large amount of NH_4^+ derived from waste water and sewage, fast rate of nitrification occurs in the system (Pretty *et al*., 2006; Strokal *et al*., 2016). In contrast, sporadic rate of denitrification takes place in the river water column, if the concentration of DO fall below 1 mg L^{-1}. This may be either due to inflow of wastewater effluent or presence of fine sediment deposit at the surface (Sarneel *et al*., 2010; Durand *et al*., 2011).

On the other hand, lentic ecosystems provide more residence time for the water to stay and larger surface area for exchange of atmospheric nutrients. The finding of Carpenter (2005), depicted that lake type and population dynamics located at different zones of the lake are the key factors that determine the dynamics and cycling of N in lake ecosystem. For instance, both organic (derived from decomposition) and inorganic N (taken by aquatic plants) dominate shallow lakes (Rabalais, 2002). Form and distribution of N throughout the depth profile of lakes depend on the trophic level and DO (Baldwin and Mitchell, 2000; Carpenter, 2005). In oligotrophic lakes, low concentration of DO reduce the transformation of NH_4^+ to NO_3^- (Pretty *et al*., 2006). Therefore, NH_4^+ almost remains the same from epilimnion to hypolimnion while NO_3^- slightly increase at the hypolimnion due to reduced DO. Less NH_4^+ and high NO_3^- dominate the epilimnion of eutrophic lakes due to high oxygen production by algae that enhance rate of nitrification (Sarneel *et al*., 2010).

2.1.2. Phosphorus in aquatic systems

It is difficult to differentiate all the different categories of P from water. Several authors depicted PO_4^- (orthophosphate) as the major and abundant form of P recorded during analysis in aquatic ecosystem (Karl and Bjorkman, 2002; Lampert and Sommer, 2007; Gerhardt *et al*., 2010; Moss, 2010). In contrast to N, P in water can occur either being bound to plant and animal tissue, sewage, waste and food residues or being precipitated in the sediment with different

metals such as iron (Fe^{3+}), aluminium (Al^{3+}), and calcium (Ca^{2+}) in large amount to form insoluble complexes (Niirnber, 1994; Baldwin and Mitchell, 2000; Gerhardt *et al*., 2010).

The different categories of P recorded in limnological studies includes available P for use by phytoplankton called soluble reactive phosphorus (SRP) which consists of the free ions and many unstable P compounds (Carpenter, 2005). Total dissolved phosphorus (TDP) consists of dissolved organic as well as the colloidal P which contribute to SRP and finally the total phosphorus (TP), which consists of both the dissolved and the particulate forms (Lampert and Sommer, 2007; Gerhardt *et al*., 2010).

Compared with other nutrients, its presence in a very small amount makes P growth limiting factor for algal communities and other aquatic macrophytes (Carpenter, 2005; Hou *et al*., 2013; Robson, 2014). Therefore, uptake by algae, bacteria and adsorption by sediment are major internal sink of SRP though the cycle continues when there is release of SRP by decomposition and anoxic reduction of metals such as Fe^{3+}, Al^{3+} and Ca^{2+} (Niirnberg, 1994; Baldwin and Mitchell, 2000; Gerhardt *et al*., 2010). The findings of many researchers revealed that rapid P cycle in the sediment water interphase of aquatic systems has less ecological impact, if the growth of organisms and transfer of P depends on net uptake (Niirnberg, 1994; Baldwin and Mitchell, 2000; Karl and Bjorkman, 2002; Carpenter, 2005). Apart from the anthropogenic and allochthonous sources of P, autochthonous supplies from animal excretion and bacterial decomposition of the non-reactive forms play a significant role (Strokal *et al*., 2016).

In lentic ecosystems, algal communities' growth and abundance, zooplankton grazing, depth, redox potential and DO concentrations are some of the major factors that control P cycle in the water (Carpenter, 2005). Uptake by phytoplankton and sedimentation results reduced SRP in the epilimnion. Consequently, concentration of SRP in the hypolimnion rise and precipitate with different cations depend on DO (Lampert and Sommer, 2007; Gerhardt *et al*., 2010).

During fall P rich water from the hypolimnion will mix with mixing epilimnion which will increase P concentration and redistribution in the surface (Carpenter, 2005;).

Phosphorus moves in to sediments through adsorption on clay particles or together with sinking organisms. Lampert and Sommer (2007) described, the final fate of P in the sediment water interphase highly depends on redox condition, sediment characteristics such as particle size and organic content in the hypolimnion. Concentration of P at the sediment water interphase zone is higher than the open water (Gerhardt *et al*., 2010). When the sediment water is oxidized, cations such as Ca^{2+}, Al^{3+}, Fe^{3+} in the sediment occur in their oxidized form which can bind with P (adsorption) to form an insoluble precipitate (Niirnberg, 1994; Gerhardt *et al*., 2010). However, if the cations are reduced under anoxic conditions, it will form soluble complex which can release (desorption) P in to the water (Baldwin and Mitchell, 2000; Gerhardt *et al*., 2010).

2.1.3. Nutrient enrichment in Ethiopian inland waters

In Ethiopian context particularly in Lake Tana catchment, unbalanced environmental protection and development interventions, high population growth, urbanization, irrigation based intensive agriculture are among the major problems to the inland water systems (Goshu and Aynalem, 2017). Alemu *et al*. (2017) assessed the temporal variations of dissolved phosphorus from Lake Tana tributaries and reported a DP value of 0.32 mg L^{-1}. The study also explained the gradual decline in concentration of DP from upstream to downstream. Kassa (2016) assessed nutrient dynamics and macrophyte ecology in the littoral area of Lake Tana and reported a TP, SRP and NO3-N values of 0.57, 0.23 and 1.09 mg L^{-1}, respectively. The finding added to explain gradual nutrient enrichment in the littoral area of Lake Tana compared with previous reports of Wondie *et al.* (2007). The study suggested non-point sources derived from agricultural runoff as major contributors. In addition, both partially treated and untreated

waste effluent discharges to the nearby water bodies from different households, small and macro industries make the anthropogenic effects sever (Kassa, 2016). Gebremedhin *et al*. (2018), depicted agricultural runoffs, bathing, washing using detergents, excavations, sand mining, and animal defecations while watering as major contributors to the recent nutrient enrichment in the vicinity. According to Akale *et al*. (2018), excess applications of fertilizers on farms due to the need for food production has increased NO_3-N concentrations in some springs of Northern Ethiopian highlands. Tibebe *et al*. (2018), also explained the effects of anthropogenic activities and industrial effluents in recent nutrient enrichment of Lake Ziway.

2.2. Heavy metals

Heavy metals, also known as trace metals are groups of metals and metalloids having high specific weight and greater density which is > 4 kg/m^3 than water (Appenroth, 2010; Yahaya *et al*., 2010; Saha and Paul, 2016; Ackova, 2018; Pigłowski, 2018). Some heavy metals such as Cu, Zn, Fe and Ni are essential as micronutrient for the physiological functioning of plant and animal life despite their deficiency or surplus could cause several disorders. In contrast, Akele *et al*. (2016) depicted that, there is no known physiological importance reported for other heavy metals, including Hg, Pb, Cd, and Cr. Therefore, ingestion at low concentrations or above permissible limits are detrimental to health because of their toxicity and resistance to degradation (Saha and Paul, 2016; Gebreyohannes and Gebrekidan, 2018; Showqi *et al*., 2018).

Apart from natural (weathering of rock, soil and atmospheric) sources, mainly heavy metals are introduced and distributed into the environment via anthropogenic sources such as urban and agricultural runoff, sewage and industrial effluent, mining, smelting, production and use of compounds and materials containing metals, burning of fossil fuels and waste dumping (El-Sayed *et al*., 2011; Saha and Paul, 2016; Gebreyohannes and Gebrekidan, 2018; Kassegn *et al*., 2018; Showqi *et al.*, 2018). Further, leaching and oxidation taking place at different strata

of soil and sediment cause heavy metals to be released from geology to the nearby environment. Similar to other nutrients and pollutants, heavy metals enter aquatic ecosystem through runoff (Saha and Paul, 2016; Yan *et al.*, 2018). Förstner and Wittmann, (1983) and Fernández-Luqueño *et al*. (2013), pointed out some of the manufacturing processes that release heavy metals during production and processing activities. Cadmium enters into aquatic systems through phosphate containing fertilizers, insecticides, batteries, industrial discharge from metal-finishing industries and photography (Saha and paul, 2016). Effluents from construction works, brewery, wiring, mining, motor industries and algal controlling additives are common sources for Cu (Olowu *et al*., 2012; Mulugeta and Gashaw, 2017). Zinc enter water bodies from mining and metallurgical process, burning of coal, effluents of paper and pulp industries (Kassegn *et al*., 2018). Waste effluents from petroleum refining industries, nonferrous metalworks, chlorine and inorganic chemicals release Pb to the environment. Most common sources of Cr include burning of fossil fuels, plastic manufacturing, electroplating of metals and extensive use in the leather and tannery industries (Gautam *et al*., 2015; Akele *et al*., 2016; Tadesse *et al*., 2018).

2.2.1. Heavy metal pollution in aquatic ecosystem

Various research findings make known that contamination of surface and ground water with heavy metals are caused by both natural and anthropogenic sources where the latter lay over in the past decades and has posed a significant effect in developing countries due to poor waste treatment practices (Saha and Paul, 2016; Bhuyana *et al*., 2017). Within the water column, variation in concentrations of heavy metals is evident as extremely high concentration is found in the sediment, macrophyte and fish samples than in water due to adsorption and heavy mass (Kebede and Wondimu, 2004; Bhuyana *et al*., 2017).

Heavy metals and their compounds get in to the body of organisms through inhaled gas, dust fume, food, drinking water and skin or mechanical contact. In higher organisms such as fishes

the concentrations of heavy metals can be accumulated either through bioaccumulation where the organism absorbs the metals or takes them in; gradually, the concentrations become higher than the source; or through biomagnification where the metals are transferred through food chain and the top predator or the climax community will end having higher concentration of heavy metals (Arnot and Gobas, 2006; El-Sayed *et al*., 2011; Zhang *et al*., 2018).

In Ethiopia, untreated industrial effluents are major sources of pollution to inland water bodies. For example, the finding of Dsikowitzky *et al*. (2012) depicted, high concentration of some heavy metals from Tikur wuha River which is influenced by Hawassa textile factory. According to the finding, Cd concentration was found 60 times higher than the permissible limit by standards while Pb and As were within the range of the standard from Lake Koka and Hawassa. Similarly, Gebreyohannes and Gebrekidan (2018) assessed the effects of small metal work industries on Elalla River of the northern Ethiopia. They reported, higher concentrations of heavy metals including Cr and Cd above FAO standards. Conversely, Muhammd (2018) compared concentrations of heavy metals from treated and untreated waste effluents of BGI brewery, textile and tannery industries from Kombolcha city. The findings reported higher concentrations of heavy metals in the untreated effluent than treated one. However, the level of concentration varies among the industries. Highest values of Pb were found in the effluent from the brewery and textile industry while highest Cr levels were found in the effluent from the tannery.

2.2.2. Heavy metals in aquatic sediments

The non-degradable nature of heavy metals makes them a permanent addition to aquatic systems. Consequently, higher concentrations can be found in the body of organisms and sediment (Kassegn *et al*., 2018). According to the reports of Akele *et al*. (2016), Dribaba *et al*. (2018) and Kassegn *et al*. (2018), assessment of heavy metals from sediment provide an insight

on the long-term pollution state of the aquatic system and the catchment. Furthermore, it is important to understand mobility of pollutants between water and sediment. Usually, open water systems such as rivers and lakes are more vulnerable to heavy metal contamination caused by anthropogenic activities (Melaku *et al*., 2005; Decena *et al*., 2018). However, low solubility of metals together with the organic matter and mineral content of sediments facilitate adsorption process (Dribaba *et al*., 2018). In line with the above Akele *et al*. (2016), described sediments as ready sink for pollutants including heavy metals where concentrations vary based on the amount of input. Moreover, variation on the availability of pollutants depend on the strength of the association between sediment compounds and metals. For example, heavy metals that bound to clay and sand particles are much more available than heavy metals bound to sulphides and iron oxides (Kelderman and Osman, 2007; Akele *et al*., 2016). Physico-chemical parameters of the water such as pH and redox potentials also highly influence the proportions of metal concentrations within the system either by reshuffling of metals bound to carbonates or mobilizing from sediment to water or vice versa (Kelderman and Osman, 2007).

The non-degradable nature of heavy metals in aquatic systems may result in a gradual accumulation within the sediment and tissue of organisms (Orosun *et al*., 2016; Dribaba *et al*., 2018; Rajeshkumar and Li, 2018; Zhang *et al*., 2018). Generally, fates of heavy metals entering aquatic system can be geo-accumulation, bioaccumulation or biomagnification. In addition, alteration of heavy metals accumulated in the sediment into different complexes by biological activity may be hazardous to organisms (Dribaba *et al*., 2018).

2.2.3. Heavy metals in aquatic macrophytes (*Eichhornia crassipes*)

Water hyacinth, *Eichhornia crassipes* is widely infested and submerged aquatic macrophyte with fast growth rate that exhaust nutrients by affecting surrounding environment (Gichuki *et al*., 2012). Some of the environmental and ecological impacts of water hyacinth include competition for nutrient with algal communities, suppressing other species growing in the

vicinity, fishing, blockage of channels, increased evapo-transpiration resulting in water loss and resistance to unfavourable conditions (Gichuki *et al*., 2012; Ndimele, 2012; Ebro *et al*., 2017; Ndimele, 2012). Littoral regions of Lake Tana have been seriously affected by the infestations of *E. crassipes* in the past ten years causing various economic and ecological problems. (Anteneh *et al*., 2014; Admas *et al*., 2017; Ebro *et al*., 2017).

The macrophyte has vibrant growth rate in extremely contaminated wastewater with high content of nutrients and heavy metals (So *et al*., 2003; Jafari, 2010). Water hyacinth absorbs metallic pollutants such as Pb, Cd, Ni, Zn, Cr and Cu by roots and accumulates either in the leave, stem or other aerial parts. Shao and Chang (2004) observed high metal absorbing and translocating capability of the macrophyte with metal binding sites. It has also a good phytoremediation potential for metallic pollutants including Cr, Pb, Hg, and Cd. both in waste treatment pond and wetlands. Jones *et al*. (2018), reported the good potential (47% for Zn, 22% for Mn, and 23% As) of water hyacinth in heavy metal removal. Conversely, Okunowo and Ogunkanmi (2010), indicated phytoremediation potential of the macrophyte with removal efficiency of 13.52 mg kg^{-1}. Kabeer *et al*. (2013), also disclosed significant metal removal capacity of the macrophyte where higher concentrations were recorded from root, stem and leaf.

CHAPTER 3: MATERIALS AND METHODS

3.1. Description of study area

Megech River is one of the major tributaries of Lake Tana located in the northern part of Ethiopia between 12°43'40"N - 37°23'53"E and 12˚14N -37˚18'E with an altitude range of 1848 to 2942 m.a.s.l (Figure 1). The river originates near the Semien Mountains National Park at an altitude of about 3500 to 4000 m.a.s.l. and has a length of about 80 to 90 km with total surface catchment cover of 513 km^2 (Abebe and Kebede, 2017; Alemu *et al*., 2017). Annual rain falls of the area ranges between 896 mm to 1592 mm with monthly maximum temperature range of 21 to 27˚C and minimum range of 10-13˚C. The climate of the region is 'tropical highland monsoon' with a single rainy season between June and September. During the rainy season, width of the river ranges on average about 10-15 m and 1.5-2.50 m deep. The river flows through Dembya plain until it joins Lake Tana (Awulachew *et al*., 2009; Anteneh *et al*., 2014; Abebe and Kebede, 2017).

Lake Tana is the largest lake of Ethiopia located in the North West part between 12°10'North and 37°23'East with an altitude of 1800 (Figure 1). Total surface area of the lake is about 3,050 km^2 with maximum and mean depths of 14m and 8m, respectively (Setegn *et al*., 2008; Wondim, 2016; Gebremedhin *et al*., 2018). Though there are 40 different rivers that drain in to Lake Tana, Gilgel Abbay, Ribb, Gumara and Megech Rivers are the four major tributaries of the lake that fed about 95 % of the water. Recent studies on the hydrological modelling of the lake revealed that mean annual inflow into the lake was 158 m^3s^{-1} which is 4,986 Mm^3y^{-1} and outflow from the lake was estimated to be 119 m^3s^{-1} or 3,753 Mm^3y^{-1} (Setegn *et al*., 2008). Currently, Lake Tana is facing multiple challenges to continue as an ecosystem. These includes siltation, improper waste discharge and habitat destruction. Moreover, the recent water hyacinth infestation becomes a major problem for sustainable existence and fish stock decline of the lake (Goshu and Aynalem, 2017; Gebremedhin *et al*., 2018).

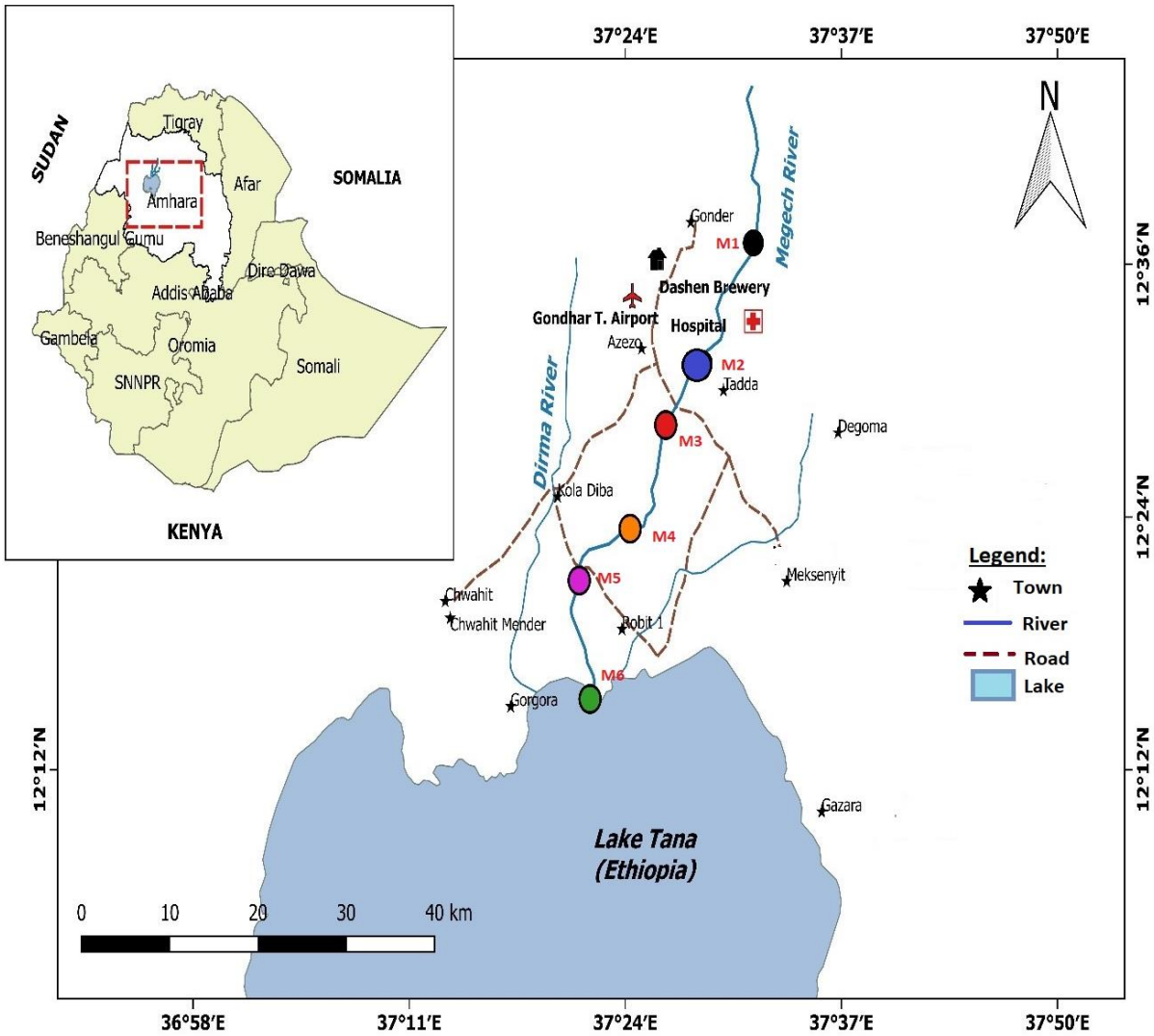


Figure 1. Map of Megech River including sampling sits

3.2. Study design

The study was a field investigation where water and sediment samples were collected from six different sampling sites along the course of the river. Sampling sites were identified based on their closeness to human interference (anthropogenic activity) and pollution potentials of the area. The first sampling site M1 was in the upstream area before the river cross Gondar city at Angereb. Second sampling site M2 was next to Gondar city after the waste from the city enters the river and third sampling site M3 was at Tseda town after the irrigation dam construction works. Fourth and fifth sampling site M4 and M5 were at Sufankera and Robit area where there

is intensive agriculture of Dembya wereda. The last sampling site M6 was at Achera; the littoral region of Lake Tana which is dominated by water hyacinth. In addition to water and sediment samples, water hyacinth samples for heavy metal analysis were collected from M6.

Table 1. Sampling sites and descriptions of activities during sampling in Megech River.

Location	Site code	Activities	Remark
Angereb	M1	Mountainous, small vegetable irrigation farms	Relatively less human interference.
Megech	M2	Residence, sewage inflows from Angereb and other tributaries, municipal sewage, dam construction, high excavation, sand mining, water abstraction, car washing	Relatively high human interference, More sandy soil and red soil from mountain excavation for dam construction
Tseda	M3	Small irrigation farm, municipal waste from Tseda	Bathing and swimming
Sufankera	M4	Intensive agriculture, animal watering, bathing and washing clothes, irrigation, water abstraction, sand mining	Small tributaries join the river, runoff
Robit	M5	Intensive agriculture, animal watering, bathing and swimming, Irrigation, farming close to the bank	Muddy bottom, runoff due to rain
Achera	M6	Huge water hyacinth infestation, farming close to the shore, animal watering and grazing, few fishing activities	Relatively clear water, small tributaries

3.3.Sampling and measurements

i. Water sampling for nutrient and heavy metal analysis

In-situ physico-chemical parameters of water such as temperature (Temp), pH, dissolved oxygen (DO), electrical conductivity (EC) and turbidity (Tur) were measured using multi meter probe (HQ40d, model 10115) in triplicate prior to collecting water and sediment samples.

A total of 30 water samples were collected 5 times every 10 days from 15th November 2018 to 7th January 2019. During sampling, replicate water samples were collected across the width of the river, 10 -20 cm depth from the surface, 30 cm from left and right bank and at a distance of 50 cm interval on each sampling site.

All collected replicate water samples were homogenized in a single container to have one composite sample. The composite water samples were filtered through 0.47 μm GFF using 300 ml vacuum hand filter and collected in a pre-cleaned (using 10% H_2SO_4, rinsed with distilled water) plastic bottles for SRP, NO_3-N, NO_2-N, NH_4-N; for heavy metal (Cu, Zn, Cr, Cd and Pb) and for alkali and alkaline earth metals (Ca, Mg, and K) analysis whereas unfiltered water samples were collected for TP and TN. Both the filtered and the unfiltered water samples were kept in a cool box till transported to Bahir Dar University Blue Nile research laboratory.

ii. Sediment sampling for nutrient and heavy metal analysis

A total of 30 fine sediment samples of about 500 g each were collected from six sampling sites with the help of stainless-steel trowel. Five replicates were taken from the same sampling site at a distance of 1 m. Impurities including plastics, big stones, plant parts, and others were separated. All the collected sediment samples were immediately wrapped with plastic bags and stored in a cool box until transported to Bahir Dar University Blue Nile research laboratory.

iii. Macrophyte sampling

A total of 10 different *E. crassipes* macrophyte samples were collected once (on 15th November 2018) from site M6 which is shores of Lake Tana where Megech River drains into. The collected macrophyte were sorted into leaf, stem and root parts using stainless surgical blade. The different parts were quickly wrapped with polyethylene plastic bags and kept in a cool box till transported to Bahir Dar University Blue Nile research laboratory.

3.4. Laboratory analysis design

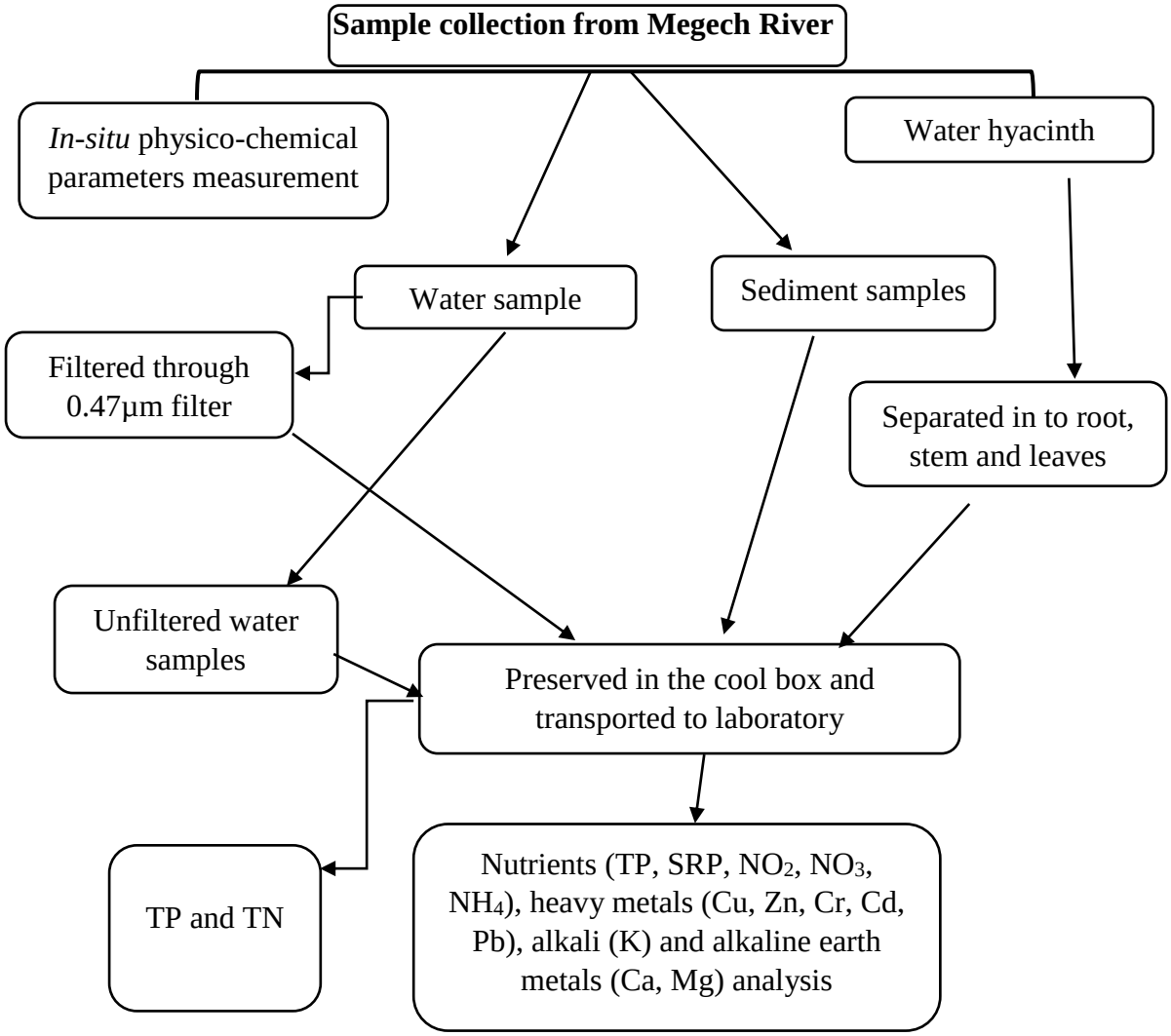


Figure 2. Summary of sampling and laboratory analysis for nutrients and heavy metals from water, sediment and *E. crassipes* of Megech River.

3.4.1. Laboratory analysis

Collected water samples were transferred to washed bottles. For the chemical analysis of nutrients (TP, SRP, TN, NO_3, NO_2 and NH_4), heavy metals (Cu, Zn, Cr, Cd, and Pb), alkali (K) and alkaline earth metals (Ca and Mg) from water, sediment and macrophyte samples, the standard methods outlined by American public health association (APHA,1999) were adopted.

a. Soluble reactive phosphorous (SRP) from water samples

Soluble reactive phosphorus (SRP) was determined using the ascorbic acid method following the standard procedure (APHA,1999). 25 ml of filtered water sample was mixed with 2.5ml of mix reagent made from ammonium molybdate, sulphuric acid, ascorbic acid and potassium antimony tartrate in 2:5:2:1 ratio. Then, after 15 minutes of incubation absorbance was measured by Jenway 6405 UV spectrophotometer at 885nm.

b. Soluble reactive phosphorus (SRP) from sediment samples

Soluble reactive phosphorus from sediment samples were extracted by adding 50 ml of NH_4Cl to 3 g of sediment sample in a vessel. The contents were closed and left on a shaker for 16 hrs. The extracts were centrifuged for 15 min at 3000 rpm. SRP was analysed according to the methods followed for water; 2.5ml of mix reagent was added to 25ml of the supernatant then absorbance was measured at 885nm (APHA, 1999).

c. Total Phosphorous (TP) from water samples

Total phosphorus was analysed through digestion of unfiltered water sample and reducing the different forms of phosphorus present in the water into the free ortho-phosphate form (SRP). In the persulfate digestion process, 1 ml of $K_2S_2O_8$ was added to 25ml of unfiltered water sample and digested for 90 minutes at about 120 °C. after cooling, the evaporated water was replaced by distilled water to make the end volume 25 ml. The digestate then transferred to another tube and analysed by the ascorbic acid method mentioned above (APHA, 1999).

d. Total phosphorous from sediment samples

Total phosphorous from sediment sample were extracted by adding 150 ml of 0.5 M H_2SO_4 to previously dried and powdered 3 g of sediment. The content was digested in Kjeldahl digester for 30 minutes at 400 °C. After cooling, the contents were adjusted to 50 ml using distilled

water and centrifuged for 15 min at 3000 rpm. Absorbance was measured at 885 nm according to the protocol for SRP.

e. Nitrite-Nitrogen (NO_2-N) from water

The nitrite-nitrogen determination was carried out using the reaction between Sulfanilamid and N-Naphthyl-(1)-ethylendiamin-dihydrochlorid. To 25 ml of the filtered sample, 1 ml of Sulfanilamid solution was added. After 2-8 minutes, 1 ml of N-Naphthyl-(1)-ethylendiamin-dihydrochlorid solution was added to this mixture and gently mixed. The solution was left for 10 minutes and absorbance was measured at a wavelength of 543 nm (APHA, 1999).

f. Total Nitrogen (TN) from water

Total nitrogen from unfiltered water sample was determined by carrying out persulphate digestion method to convert the nitrogen forms into the nitrate as stated in APHA, (1999). To 25ml of unfiltered water sample, 5 mL $K_2S_2O_8$ solution was added followed by covering of each flask with cotton plug and aluminium foil. Contents were digested in Kjeldahl digester for 1 hour at 110 °C. After cooling, contents were transferred to 50 mL volumetric flasks and mixed by adding 1 M HCl. Absorbance was measured at 220 and 275 nm (APHA,1999).

$$\text{TN (NO3)} = \text{Absorbance220} - (2 \times \text{Absorbance 275})$$

g. Nitrate (NO_3-N) from water samples

Nitrate-nitrogen was determined using sodium-salicylate method where 1 ml of sodium salicylate was added to 20 ml of filtered water sample in an evaporation bottle. The contents were placed in an oven at 95°C until it was dried. The resulting residue was dissolved by 1 ml of concentrated H_2SO_4 followed by adding 40 ml of distilled water. Finally, 7 ml of potassium-sodium hydroxide-tartrate solution was added, and the absorbance was measured using Jenway 6405 UV spectrophotometer at a wavelength of 420 nm.

h. Nitrate-nitrogen (NO_3-N) from sediment samples

3 g of fresh sediment sample was extracted using 100 ml of 0.5 M K_2SO_4. After shaking the contents for 1 hour, it was filtered through 0.47µm filter paper. To 20 ml of extracted sample, 1 ml of salicylic acid was added and mixed. After 30 minutes, 10 ml 4 M sodium hydroxide was added. Absorbance was measured after 1 hour at 420 nm (Okalebo *et al*., 2002).

$$\mathrm{NO3-N\ (mg\ /g)} = \frac{(C-B)\times V\times D}{W}$$

Where; C = concentration of NO_3^--N in the extracted solution, B = concentration of NO_3^--N in the blank, V = total volume of the extract; D= dilution factor, W = weight of sediment

i. Total Nitrogen (TN) from sediment

Total nitrogen in sediment samples was determined using Kjeldahl digestion method. 25 ml of digestion mixture (made from salicylic acid and sulphuric acid-selenium mixture) was added into the digestion tube containing 3 g of sediment sample. The contents were digested in Kjeldahl digester for 1 hour at 110 °C. after cooling, 3 ml of H_2O_2 were added and heated at 330 °C until it became colourless. The final volume was adjusted to 50 ml with distilled water. the digestate then transferred into another tube and analysed by salicylate method for NO_3-N.

j. Ammonium-nitrogen (NH_4-N) from water

2.5 ml of sodium salicylate solution was added to 25 ml of filtered water sample followed immediately by the addition of 2.5 ml of hypochlorid solution. The mixture was then placed in a water bath at a temperature of 25 °C in the dark for 90 minutes. Absorbance was then measured at a wavelength of 655 nm (APHA, 1999).

k. Ammonium-nitrogen (NH_4-N) from Sediment

For extraction, 100 ml of 0.5 M K_2SO_4 was added to 3 g of fresh sediment sample and transferred into a plastic bottle. The content was placed on a shaker for 1 hour and filtered through 0.47µm filter paper. 2.5 ml of mix reagent A (which is made from sodium salicylate, sodium citrate, sodium tartrate and sodium nitroprusside) was added to the 25 ml of extract. After 15 minutes the content was well mixed using vortex followed by addition of 2.5 ml of mix reagent B (which is made from sodium hydroxide and sodium hypochlorite). The content was mixed and stand for 1-hour. Absorbance was measured using Jenway 6405 UV spectrophotometer at 655nm.

$$\mathrm{NH4-N\ (\mu g\ /g)} = \frac{(C-B)\times V\times D}{W}$$

Where; C = concentration of NH_4^--N in the extracted solution, B = concentration of NH_4^--N in the blank, V = total volume of the extract; D= dilution factor, W = weight of sediment

3.4.2. Heavy metals and cation analysis

a. Sample digestion

For the digestion of water, sediment and macrophyte samples, optimization of the analytical standards (APHA, 1996; APHA, 1999) and literature materials (Assefa and Berhanu, 2015, Gebreyohannes and Gebrekidan, 2018) were used. During optimization process, volume of chemical mixture ratio, clearness of the solution and time were considered (Appendix 2).

b., Alkali, alkaline earth and heavy metals from water sample

Analysis of alkali, alkaline earth and heavy metals from filtered water samples were analysed following aqueous sample digestion procedures where, 100 ml of well mixed sample was transferred to 250 ml conical flask. The contents were digested by adding 3.0 ml HNO_3 (70%) for 1 hour at 120 °C; the content was cooled for 5 min and additional 3 ml HNO_3 was added.

Digestion continued for 40 minutes at 180 °C. After 5 min of cooling, 10 ml 1:1HCl was added and digested for 20 min at 240 °C. After digestion was completed, the remaining digestate (about 20 ml) was cooled. The end volume of the digestate was adjusted to 50 ml and filtered using 0.45 μm Whatman prior to analysis (APHA, 1999; Assefa and Berhanu, 2015). Concentrations of heavy metals was analysed by Getaneh Dessalegn using Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS, model NOVA300) at Amahara design soil chemistry and water quality laboratory.

c. Alkali, alkaline earth and heavy metals from Sediment

Based on the above optimization, relatively fine sediment (silt) samples were collected from bottom surface of the river and littoral area of Lake Tana using a stainless-steel trowel. Heavy metal analysis from sediment samples was carried out by digesting 1 g of dried and sieved sediment in 100 ml Erlenmeyer flask using 6.0 ml of HNO_3 and 2 mL $HClO_4$. The resulting mixture was heated for 105 min at 180 °C in fuming hood. Contents were cooled for 5 min and 3 ml of H_2O_2 was added and heated for 10 min at 240 °C. The digestate produced was dissolved in 10 ml of 30% HNO_3 and filtered through Whatman filter paper (0.45 μm). Finally, heavy metals were analysed after the end volume of the remaining digestate was adjusted to 50 ml (APHA, 1996; Assefa and Berhanu, 2015) and then analysed by Getaneh Dessalegn using GFAAS (model NOVA300) at Amahara design soil chemistry and water quality laboratory.

d. Alkali, alkaline earth and heavy metals from *E. crassipes*

Different parts of the macrophyte were oven dried and powdered using mortar and pestle. The powdered macrophyte samples of about 1.0 g (leaf, stem and root) were placed in a 100 ml round bottom flask and digested by adding 6 ml nitric acid (HNO_3), and 4 ml 30% H_2O_2 following the optimal digestion procedure (APHA, 1999; Gebreyohannes and Gebrekidan,

2018). Heavy metals were then analysed from respective digestates by Getaneh Dessalegn using GFAAS at Amahara design soil chemistry and water quality laboratory.

3.5. Method validation

a. Instrumental working conditions

To assure and control the quality of data, instrumental working conditions were adjusted to the maximum sensitivity as mentioned by the manufacturer. Calibration curves were plotted using standard solutions (Appendix 1). Blanks were prepared in each digestion procedure by adding the acids used in to the sample to see the level of trace metals in the acid. All reagents used for analysis were analytical grade reagents. Moreover, materials and glassware's used for the analysis were acid washed and rinsed with deionized water.

b. Method Detection Limit (MDL)

Method detection limits (MDL) were determined by treating optimized selected mixture chemical of ($HNO_3/H_2O_2/HClO_4$) with distilled water (instead of sample) and similar method were applied as the sample digestion.

c. Recovery

Method validation of the digestion procedure was determined through spiking experiment where a solution with known concentration was added to the sample. A known solution of 200 µL of 0.724 mg L^{-1} Cu, 200 µL of 1.122 Zn, 200 µL of 0.56 mg L^{-1} Cr, 200 µL of 0.214 mg L^{-1} Cd, 200 µL of 0.082 mg L^{-1} Pb, 200 µL of 1.152 mg L^{-1} K, 200 µL of 1.214 mg L^{-1} of Ca and 200 µL of 0.866 mg L^{-1} of Mg analytes were added to the flask containing the sample. Percent of recovery was calculated after digesting both spiked and non-spiked samples following same procedure (Appendix 3).

$$Recovery(\%) = \frac{(Spiked\ sample\ Conc. - Unspiked\ sample\ conc.)}{Known\ conc.} \times 100$$

3.6. Data analysis

The data recorded from both field and laboratory analysis was summarised using descriptive statistics such as mean and standard deviation. After the data was checked for normality using Shapiro-Wilk test, both parametric and non-parametric ANOVA was computed to compare the spatial variation in physico-chemical, nutrient and concentrations of heavy metals. Principal component analysis (PCA) was performed to identify the most important variable to describe the spatial variation between variable measured at site. MS excel was used to organize and the data and analysis was done using SPSS (IBM. Ver. 21.0) software.

CHAPTER 4: RESULTS

4.1. Physico-chemical parameters

The overall assessment of physico-chemical water quality parameters (Table 2) showed spatial variations from site to site. Mean surface water temperature ranged from 16.18 °C at site M1 to 24.88 °C at M6. pH of the river was slightly alkaline ranging from 8.38 to 8.70 at M1 and M3, respectively. There was a slight decline in the concentrations of DO from upstream to downstream where the highest was at M1 and the lowest at M6. Electrical conductivity showed a significant difference ($p < 0.05$) among the sites. The Kruskal-Wallis non-parametric ANOVA showed that M1 and M6 significantly differ from M2. Turbidity showed a wide range of values along the course of the river where the maximum was at site M5 (570.00 NTU) which is eleven times higher than M6 (52.66 NTU) and six times higher than M1 (89.20 NTU). The second highest turbidity was noted at site M3. There were statistically significant spatial and temporal differences ($p < 0.05$) in turbidity of Megech River.

Table 2. Physico-chemical water quality parameters of Megech River at different sampling sites (Mean ± SD; n = 5; Temp = temperature, DO = dissolved oxygen, EC = electrical conductivity, Tur = turbidity).

Site	Temp (˚C)	pH	DO (mg L^{-1})	EC (µS/cm)	Tur (NTU)
M1	16.86 ± 0.36*	8.38 ± 0.01	9.88 ± 0.12*	421.80 ± 2.28*	89.20 ± 4.33*
M2	19.42 ± 0.72	8.43 ± 0.01	7.78 ± 0.41	658.40 ± 8.65*	223.20 ± 8.98
M3	22.62 ± 0.18	8.70 ± 0.02	8.29 ± 0.04	431.60 ± 1.95	419.96 ± 3.77*
M4	23.06 ± 0.15*	8.63 ± 0.02	7.88 ± 0.16	438.60 ± 1.14	416.00 ± 14.4
M5	21.86 ± 0.42	8.51 ± 0.01	7.69 ± 0.07	462.4 ± 0.55*	575.00 ± 10.22*
M6	24.88 ± 0.29*	8.28 ± 0.07	7.45 ± 0.47*	148.72 ± 0.35*	52.66 ± 4.90*

* $p < 0.05$

4.2. Nutrient concentration in the water samples

Concentrations of nutrients analyzed from water samples of Megech River are given in Table 3. The maximum TP concentration was at M4 and the minimum at M1. Site M2 (97.73 µg L^{-1}) had the highest SRP concentration and M6 (23.5 µg L^{-1}) had the lowest. Mean values for TN, NO_2-N, NO_3-N and NH_4-N ranged from 2.82 to 4.87 mg L^{-1}; 14.48 to 20.11 µg L^{-1}; 1.24 to 1.94 mg L^{-1} and 4.83 to 11.14 µg L^{-1}, respectively along the course of the river. There were statistically significant differences in concentrations of TP between sites, Kruskal-Wallis non-parametric ANOVA ($p < 0.05$) indicated M3 and M4 were different from M1. SRP differed between M2 and M6 ($p < 0.05$).

Table 3. Concentrations of nutrients in the water samples along the course of Megech River (Mean ± SD, n = 5; TP = total phosphorus, SRP = soluble reactive phosphorus, TN = Total nitrogen)

Site	TP(µg/l)	SRP(µg/l)	TN (mg/l)	NO_2^-(µg/l)	NO_3^-(mg/l)	NH_4(µg/l)
M1	85.56 ± 5.39*	32.25 ± 4.95*	4.39 ± 0.46	19.59 ± 1.77*	1.94 ± 0.12*	11.14±0.40
M2	114.22 ± 4.54	97.73 ± 7.93*	4.87 ± 0.78*	20.11 ± 1.32*	1.76 ± 0.32	6.74 ± 0.51
M3	122.22 ± 8.85*	47.75 ± 2.40	3.55 ± 0.35	15.07 ± 0.71	1.45 ± 0.19	6.94 ± 0.34
M4	123.33 ± 11.79*	41.00 ± 1.63	3.68 ± 0.28	15.07 ± 2.24	1.42 ± 0.10	5.69 ± 0.31
M5	108.22 ± 5.36	51.25 ± 1.98	2.82 ± 0.50*	14.48 ± 0.42*	1.25 ± 0.08*	5.09 ± 0.33
M6	111.11 ± 10.26	23.50 ± 1.63*	3.06 ± 0.24*	14.63 ± 0.59*	1.24 ± 0.03*	4.83 ± 0.27

* $p < 0.05$

4.3. Nutrient concentrations in the sediment samples

Analysis of nutrients in the sediment samples (Table 4) showed that, highest concentrations of TP (581.67 µg g^{-1}) was recorded at site M5 and the lowest at M4 (375.67 µg g^{-1}). Mean maximum and minimum SRP ranged from 208.17 to 333.5 µg g^{-1} at site M3 and M2, respectively. Concentrations of TN and its derivatives (NO_3-N and NH_4-N) in the sediment showed very low variability. There were statisticaly significant ($p < 0.05$) spatial variation in TP and SRP concentrations in the sediment between sites, site M1 and M3 were different from M5 ($p = 0.038$) also M2 and M5 were different from M4 ($p = 0.014$). TN and NH_4-N in the sediment of Megech River did not showed significant variation ($p > 0.05$) between sites.

Table 4. Concentrations of nutrients in sediment samples along the course of Megech River (Mean ± SD, n = 5; TP = total phosphorus, SRP = soluble reactive phosphorus, TN = Total nitrogen).

Site	TP (µg/g)	SRP (µg/g)	TN (mg/g)	NO_3-N (mg/g)	NH_4-N (µg/g)
M1	391.17 ± 8.81*	311.67 ± 9.50*	8.01 ± 1.23	5.54 ± 0.06	34.21 ± 4.87
M2	467.00 ± 14.77*	333.50 ± 12.92*	6.07 ± 1.68	5.58 ± 0.18	42.06 ± 5.86
M3	394.00 ± 6.73*	208.17 ± 11.57*	6.21± 1.66	5.87 ± 0.10	37.18 ± 3.75
M4	375.67 ± 13.35*	256.83 ± 11.06	6.26 ± 1.57	5.87 ± 0.05	35.58 ± 5.57
M5	581.67 ± 16.03*	261.67 ± 15.14	6.51 ± 0.47	5.88 ± 0.03	36.95 ± 3.69
M6	408.33 ± 13.18	237.83 ± 9.35*	6.15 ± 1.39	5.81 ± 0.06	36.65 ± 3.66

* $p < 0.05$

4.4. Alkali and alkaline earth metals from water and sediment samples

Concentrations of alkali (K) and alkaline earth (Ca and Mg) metals from water and sediment samples are given in Table 5. The highest value for Ca (84.80 mg L^{-1}) was at site M2 and the lowest at M1 (63.73 mg L^{-1}). Concentration of Mg ranged from 36.90 to 64.07 mg L^{-1} at site M6 and M3, accordingly. Mean concentration range of K (27.33 to 42.07 mg L^{-1}) was above the maximum permissible limits of WHO for drinking water (Table 6). Compared to water, higher concentrations were measured in the sediment samples. There was statistically significant difference ($p < 0.05$) between sediment samples for the content of Ca and Mg. However, change in the distribution of K was nonsignificant. The order of concentration of alkali and alkaline earth metals in the water and sediment of Megech River followed same trend Ca > Mg > K.

4.5. Heavy metals concentrations in the water and sediment samples

Among the five trace metals assessed at different sampling sites, concentrations of Cu (0.11 to 0.17 mg L^{-1}) and Zn (0.11 to 0.16 mg L^{-1}) in the water did not show significant difference ($p > 0.05$) between sites and remained below the maximum permissible limits of WHO, USEPA, ECE and SA standards for drinking, irrigation and animal watering. Concentrations of Cr and Cd at site M5 and M6, Pb at site M5 were not detected in the water sample (Table 7). Although there was no appreciable amount Cd and Pb detected at any of the different sampling sites, they remained above all standards for drinking water when detected (Table 6). The increasing order of heavy metals in the water was Cu ≈ Zn > Pb >Cr > Cd.

Heavy metals in the sediment ranged from 8.02 to 12.68 mg kg^{-1} for Cu, 3.74 to 6.06 mg kg^{-1} for Zn, 1.34 to 2.56 mg kg^{-1} for Cr, 0.68 to 1.24 mg kg^{-1} for Cd and 1.02 to 1.82 mg kg^{-1} for Pb. Almost maximum concentrations of all heavy metals analysed from sediment samples were measured at site M2 and the minimum at site M3 (Table 7). There was statistically significant

difference ($p < 0.05$, Kruskal-Wallis test) between M2 and M3 of trace metals. Order of heavy metals in the sediment was Cu > Zn > Cr > Pb > Cd.

Table 5. Concentrations of alkali and earth alkaline metals in water (mg L^{-1}), sediment (mg kg^{-1}) and *E. crassipes* (mg kg^{-1}) along the course of Megech River and littoral area of Lake Tana (Mean ± SD; n = 5 for water and sediment; n =10 for *E. crassipes;* Ca = calcium; Mg = magnesium; K = potassium).

	Site	Ca	Mg	K
Water	M1	63.73 ± 7.11*	48.53 ± 3.50	42.07 ± 3.91*
	M2	84.80 ± 4.83*	50.93 ±2.47	41.03 ±1.39
	M3	84.20 ± 1.73*	64.07 ± 2.64*	29.93 ± 0.47
	M4	65.43 ± 4.25	41.13 ± 1.40	27.33 ±1.75*
	M5	68.77 ± 3.27	46.10 ± 3.65	36.30 ± 3.05
	M6	66.47 ± 7.66	36.90 ± 3.39*	30.37 ±4.28
Sediment	M1	396.87 ± 7.80	210.3 ± 12.30*	79.61 ± 4.76
	M2	378.90 ± 11.22*	191.8 ± 11.79	78.20 ± 11.18
	M3	394.45 ± 7.18	208.58 ± 8.63	72.48 ± 6.92
	M4	420.40 ±7.37*	209.96 ±10.62	84.13 ± 7.00
	M5	402.90 ± 7.48	204.94 ±6.95	77.41 ± 4.87
	M6	370.52 ± 7.19*	182.46 ± 9.73*	79.51 ± 5.99
E. crassipes	Leaf	464.8 ± 4.19*	253.87 ± 5.20*	114.69 ± 3.90*
	Stem	570.63 ± 8.09*	385.37 ± 1.26*	158.69 ± 3.62*
	Root	297.47 ± 4.46*	189.4 ± 4.20*	66.36 ± 2.58**

* $p < 0.05$

Table 6. Mean concentrations (mg L^{-1}) of metals in water samples of Megech River and international standard values.

		Drinking water				Irrigation	livestock watering
Metal	**Current study**	**WHO**	**USEPA**	**ECE**	**South A.**	**South A.**	**South A.**
Cu	0.14	2	1.3	2	1.0	0.2	5
Zn	0.13	3	5	5	3	1.0	20
Cr	0.03	0.05	0.1	0.05	0.05	NA	1.0
Cd	0.02	0.003	0.005	0.005	0.005	0.01	0.01
Pb	0.04	0.01	0.015	0.01	0.01	0.2	0.1
K	34.51	1.5	NA	NA	NA	NA	NA
Ca	72.23	75	NA	NA	NA	NA	NA
Mg	47.94	NA	NA	NA	NA	NA	NA

DWAF, 1996; ECE, 1998; USEPA, 2011; WHO, 2011

N.A. = Not available; *Value below all standards* *Value above all standards*

Table 7. Concentrations of heavy metals from water, sediment and *E. crassipes* of Megech River and littoral area of Lake Tana (Mean ± SD; n = 5 for water and sediment; n =10 for *E. crassipes;* Cu = copper; Zn = zinc; Cr = chromium; Cd = cadmium; Pb = lead).

	Site	Cu	Zn	Cr	Cd	Pb
Water (mg L^{-1})	M1	0.15 ± 0.01	0.16 ± 0.03	0.03 ± 0.01	ND	0.04 ± 0.01
	M2	0.11 ± 0.02	0.15 ± 0.03	0.05 ± 0.01	0.04 ±0.01	0.04 ±0.01
	M3	0.13 ± 0.03	0.13 ± 0.01	0.04 ± 0.01	0.04 ± 0.01	0.04 ±0.01
	M4	0.17 ± 0.01	0.13 ± 0.02	ND	ND	0.03 ±0.01
	M5	0.12 ± 0.02	0.11 ± 0.0	0.05 ± 0.02	0.03 ± 0.01	ND
	M6	0.13 ± 0.03	0.11 ± 0.02	ND	ND	0.06 ±0.02
Sediment (mg kg^{-1})	M1	10.24 ± 1.27	4.58 ± 0.55	1.78 ± 0.25	0.78 ± 0.24	1.22 ±0.26
	M2	12.68 ± 1.09	6.06 ± 0.52	2.56 ± 0.41	1.24 ± 0.11	1.82 ± 0.23*
	M3	8.02 ± 1.29	3.74 ± 0.49	1.34 ± 0.23	0.68 ± 0.15	1.02 ± 0.19*
	M4	11.50 ± 1.25	5.38 ± 0.56	2.22 ± 0.26	1.12 ± 0.15	1.66 ±0.22
	M5	11.38 ± 1.10	5.42 ± 0.56	2.06 ± 0.30	1.06 ± 0.15	1.48 ± 0.29
	M6	9.76 ± 1.49	4.36 ± 0.77	1.82 ± 0.26	0.90 ± 0.16	1.38 ± 0.24
E. crassipes (mg kg^{-1})	Leaf	12.57 ± 1.90*	5.23 ± 0.45	1.17 ± 0.12	0.77 ± 0.15	1.01 ±0.02
	Stem	17.67 ± 1.06*	7.78 ± 0.65	1.30 ± 0.20	0.80 ± 0.10	1.00 ± 0.06
	Root	15.20 ± 0.95	6.57 ± 0.67	1.05 ± 0.04	0.73 ± 0.06	0.95 ± 0.04

* $p < 0.05$; *ND =Not detected*

4.6. Heavy metals content and distribution in *E. crassipes*

Concentrations of alkali, alkaline earth and heavy metals from different parts leaf, stem and root of *E. crassipes* samples collected from the littoral region of Lake tana (site M6) are given in table 5 and 7. Alkali (K) and earth alkaline (Ca and Mg) showed statistically significant differences ($p < 0.05$; Tukey test) between stem, root and leaf parts. The order of abundance of Ca, Mg and K was stem > leaf > root. Except for Cr (1.17 mg kg^{-1}) and Pb (1.01 mg kg^{-1}), higher concentrations of heavy metals analysed were observed in the stem followed by the root and leaf of the macrophyte (Figure 3). There was no significant difference ($p > 0.05$) in the distributions of Cd, Cr and Pb between macrophyte parts. Compared to water samples, significantly higher concentrations of heavy metals were measured in the sediment and macrophyte samples (sediment > *E. crassipes* > water).

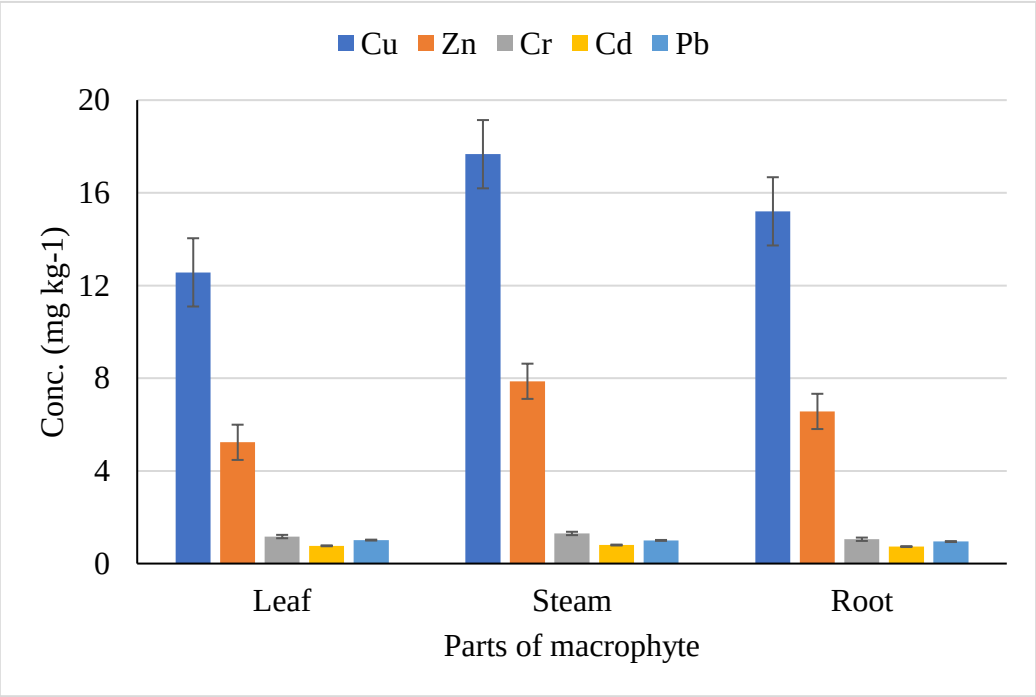


Figure 3. Concentrations of Heavy metals from different parts of *E. crassipes* (N= 10).

4.7. Principal Component Analysis

Principal component analysis was computed by combining all the physico-chemical parameters, nutrients, heavy metals, alkali and alkaline earth metals from both water and sediment samples. The output of PCA showed that, the first two components explained about 47.31 % of the total variation (PC1 = 26.26 and PC2 = 21.05%). The score plot of the combined PC indicated separate clustering's of site M1 and M2 while others were overlapping for the first two components (Figure 4). The combined loading plot (Figure 5) depicted that, PCA separated site M1 and M2 from other sites owing to higher values of SRP-s, K-w, temperature and EC which had higher loading factors on the first axis (Table 8). The second component PC2 was mainly explained by some environmental variables and nutrients from water (DO, turbidity, NH_4-w, TP-w). Eigenvalues, proportions of variance, and loadings for the PC are given in table 8 and figure 5.

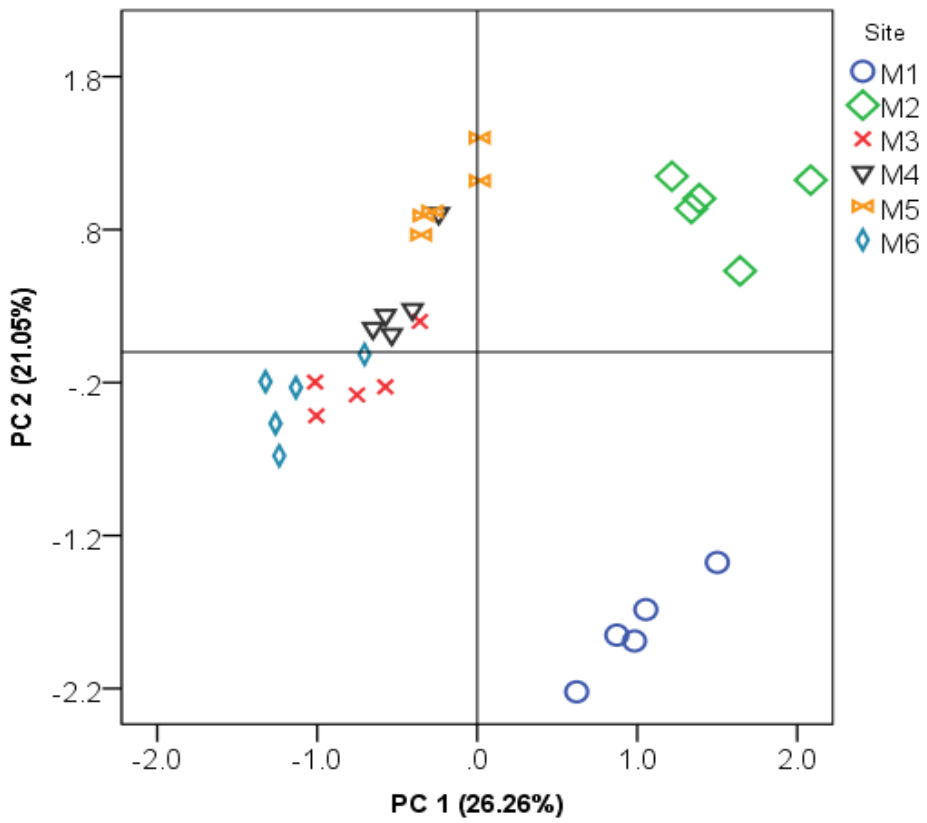


Figure 4. Score plot of PCA for all parameters measured from water and sediment samples of Megech River

Table 8. Contribution (loadings) of variables to the Principal component

Variable	PC 1	PC2
Eigenvalue	10.092	7.463
Variance	26.26	21.05
Cumulative variance	26.26	47.31
Temp	**-0.853**	0.392
DO	0.109	**-0.793**
EC	**0.740**	0.406
Tur	-0.147	**0.651**
TP-w	-0.276	**0.592**
SRP-w	**0.746**	0.341
NO_2-w	**0.843**	-0.509
NH_4-w	0.293	**-0.745**
K-w	**0.859**	-0.100
NO_3-s	0.360	**0.716**
SRP-s	**0.888**	-0.023

Bold = parameters with high loadings

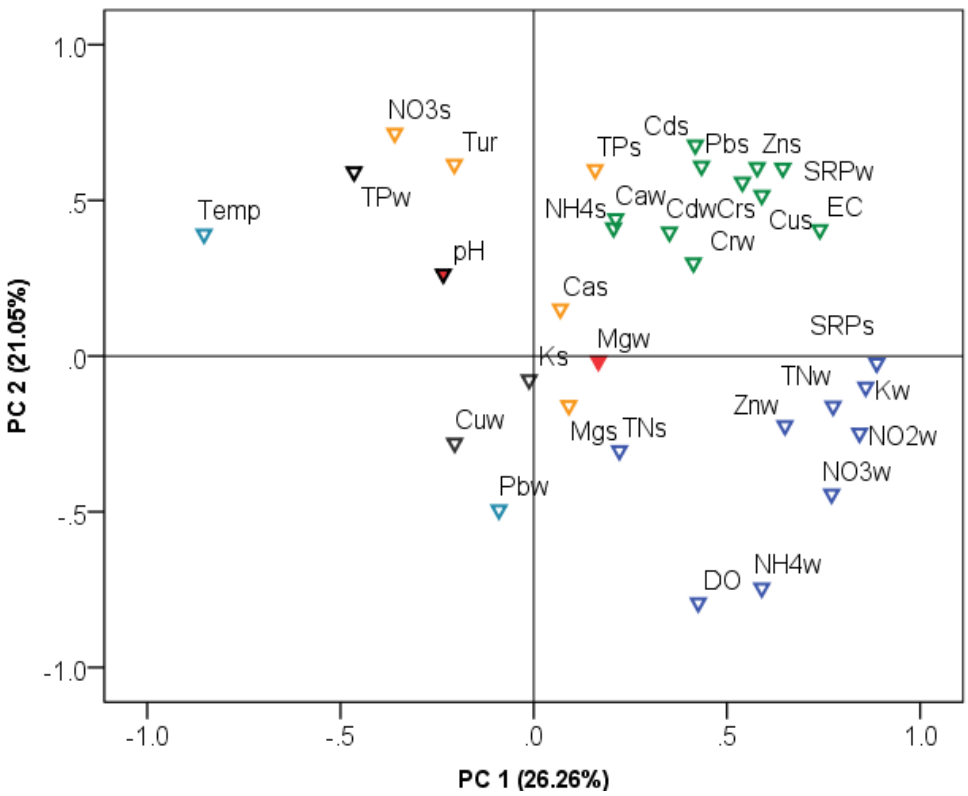


Figure 5. PCA loading plot indicating ordination of all parameters from water and sediment samples of Megech River.

By considering parameters measured only from water samples, about 60 % of variation was explained by PC1 (36.31%) and PC2 (24.59%) indicating a distinct clustering of sites (Figure 6). According to the loading plot (Figure 7), the highest contribution towards PC 1 was by Temp, NO_2-N, NO_3-N and K-w with the loading values of -0.93, 0.87, 0.87 and 0.83, respectively; and for PC2 was by Tur (0.75), Ca-w (0.72) and SRP-w (0.7).

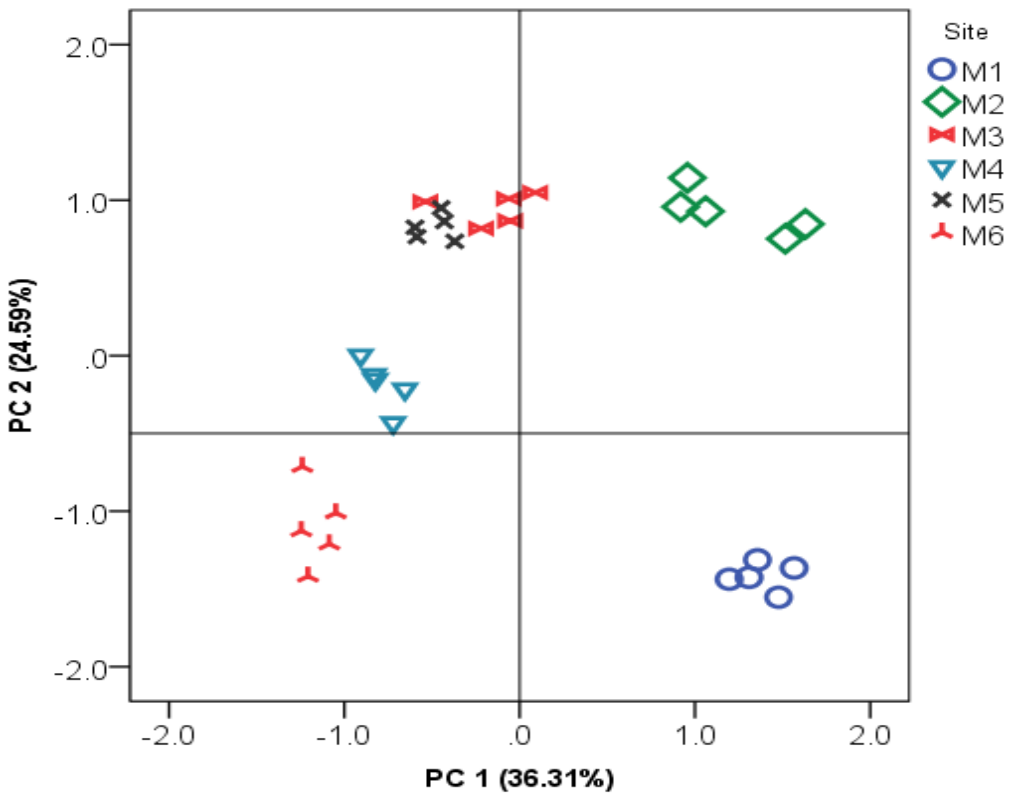


Figure 6. Score plot of PCA for all parameters measured from water samples of Megech River.

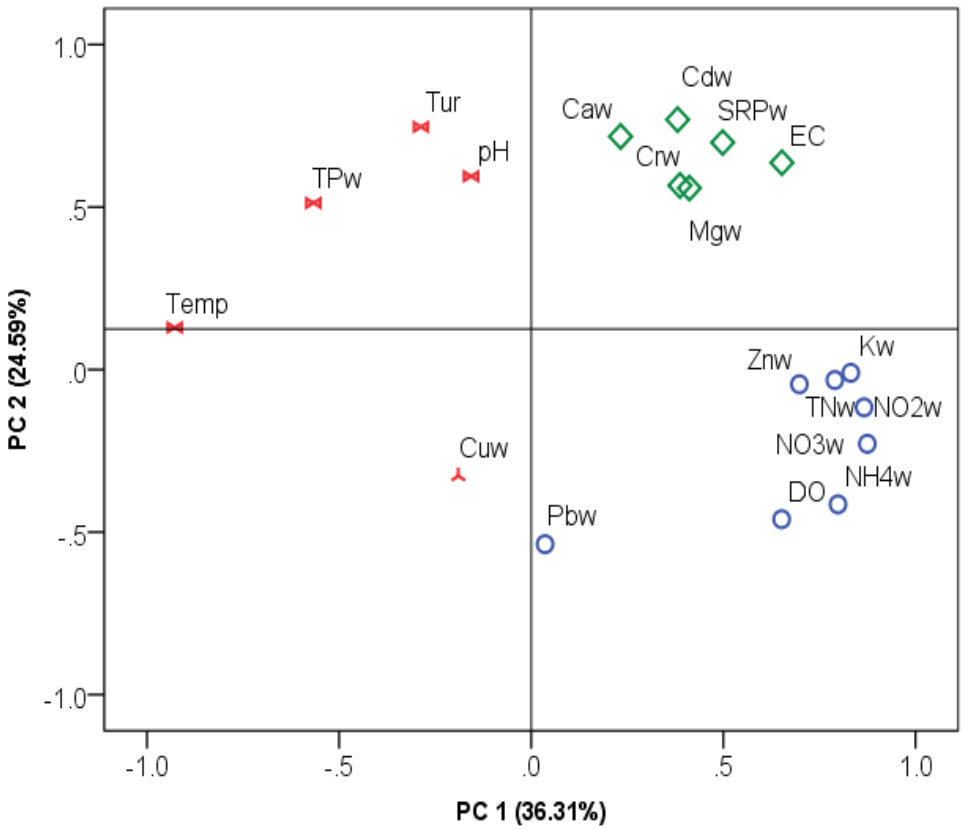


Figure 7. PCA loading plot indicating ordination of all parameters from water samples of Megech River.

CHAPTER 5: DISCUSSION

5.1. Physico-chemical parameters

Change in physico-chemical parameters of water such as temperature, DO and pH has the potential to influence biogeochemical activities, sorption, precipitation and solubility of nutrients and metals in the water column (Li *et al*., 2013; Akele *et al*., 2016; Wondimu, 2016). In our study, the high temperature observed at site M6 was within the normal environmental temperature range of 21-27 ˚C (Abebe and Kebede, 2017). The observed spatial variability was due to the difference in sampling time and canopy cover by vegetation.

The slightly alkaline pH range of 8.28 to 8.70 measured in the water samples are still within the limits of different guidelines for drinking water (6.5-9.2), livestock watering and irrigation (6.5-9.0) (DWAF, 1996; UNEPA, 2011; WHO, 2011; Fernández-Luqueño *et al*., 2013). Our result is coherent with the finding of Kassa (2016), Mengesha *et al*. (2013) and Wondimu (2016), who reported a pH of 8.92, 8.2 and 8.4 in littoral area of Lake Tana, Angereb reservoir and Megech River mouth, respectively. Similarly, DO range in the present study (7.45 - 9.88 mg L^{-1}) was within the standards for aquatic life (WHO, 2011). The highest DO value measured at site M1 indicated relatively low anthropogenic influence and the slight decrease in the downstream might be due to the possible entry of oxygen demanding wastes from surface runoff and agricultural fields which promote decomposition (Wendie, 2006; Kassa, 2016).

Maximum EC measured at site M2 is an indicator for high concentrations of metallic ions or dissolved solids derived from domestic and industrial effluent of Gondar and Azezo towns (Akele *et al*., 2016). It can also probably be due to the excavation and sand mining activities, which allow soil particle to dissolve. Conversely, the minimum EC measured at M6 could be attributed to filtration and absorption of metal ions by water hyacinth and other macrophytes (Ratan and Verma, 2014; Admas *et al*., 2017). EC observed at site M2 was within the WHO (2011) limit of 2500 µS cm^{-1} for natural water. The maximum turbidity observed at M5 could

be due to surface runoff during sampling and poor farming practice which provoke the top soil erosion (Kassa, 2016). Wondimu (2016), observed significant difference in turbidity of Lake Tana tributaries measured before and after rain. The findings of our present study are in consensus with the reports of Wondimu (2016).

5.2. Nutrient concentrations in the water samples

In the present study, highest concentrations of nutrients such as SRP, TN, NO_3-N and NO_2-N measured at site M2 can probably be associated with intensive anthropogenic activities including sewage and industrial effluents from nearby highly populated (323,900 inhabitants) Gondar and Azezo towns with poor wastewater drainage system (Admassu *et al*., 2003; Alemu *et al*., 2017; CSA, 2017). According to Mekonen (2012), in Ethiopia more than 80 % of wastewater generated is directly discharged in to rivers and streams without treatment. Similarly, Megech River is also used as waste dumping site. Carpenter (2005), Marti *et al*. (2006) and Kassa *et al*. (2016) explained the strong associations of domestic wastewater and industrial effluents with high nutrient contents. Moreover, excavations for construction works might led minerals to dissolve and to leach in to the water (Wudneh *et al*., 2014).

The lowest concentrations of SRP, NO_3-N and NH_4-N measured at site M6 in the littoral region of Lake Tana might be due to uptake by algal communities, bacteria and by the highly infested water hyacinth or adsorbed by sediment (Baldwin and Mitchell, 2000; Gerhardt *et al*., 2010). The current mean range values of SRP are lower than the findings by Kassa (2016) who reported 110-470 μg L^{-1} from the littoral area of Lake Tana. This could be due to the difference in sampling season, where surface runoff and municipal waste discharge increase during rainy season (Alemayehu, 2001). Alemu *et al*., (2017) stated the distinct pattern in concentration of SRP during rainy and dry season with higher values recorded in August. Conversely, concentration of NO_3-N measured in our study (1.25 – 1.94 mg L^{-1}) was relatively higher than results reported from other Ethiopian water bodies. Mengesha *et al*. (2013) reported a NO_3-N

value of 0.5 mg L^{-1} from Angereb reservoir, Wondie *et al*. (2007) and Kassa (2016) reported a value of 1.83 mg L^{-1} NO_3-N from littoral area of Lake Tana. Tibebe *et al*. (2018), has also reported NO_3-N value of 1.86 mg L^{-1} from Ketera and Meki rivers during the dry season. The increasing trend in concentration can probably ascribed to nutrient enrichment derived from sever anthropogenic activities and fertilizers. Akale *et al*. (2018) also reported greater NO_3-N concentrations, in water bodies close to agricultural land use due to the modest application of nitrogen fertilizers (100 kg N ha^{-1}) which easily leached in the form of NO_3-N to nearby water bodies.

On the other hand, higher concentrations of nutrients measured at M5 and M6 could be associated with point and non-point sources of pollutants such as animal defecations, phosphate containing detergents used for washing and bathing, runoff from croplands and pasture which might cause nutrient enrichment (Li *et al*., 2014; Alemu *et al*., 2017). Gerhardt *et al*. (2010), Lampert and Sommer (2007) and Strokal *et al*. (2016) observed inevitable contributions of bacterial decomposition of detritus, dissolved organics and animal excretion for high TP/SRP content in water. Similarly, Akale *et al*. (2018) and Alemu *et al*. (2017) indicated increased use of fertilizers and pesticides in the catchment of Lake Tana. TN measured in our study is lower than previous values reported from different Ethiopian inland water bodies. Tibebe *et al*. (2018), reported mean TN values of 6.96 and 9.6 mg L^{-1} from Ketera and Meki rivers, respectively.

In general, freshwater systems respond to excess nutrient enrichment in various ways. According to O'sullivan and Reynold (2004), Tibebe *et al*. (2018), TN concentration greater than 0.3 mg L^{-1} and TP above 0.01 mg L^{-1} are enough to cause eutrophication. Hence, TP and TN measured in our study were higher than the above values. Therefore, Megech River has an inevitable contribution in the recent infestation of water hyacinth and eutrophication of Lake Tana.

5.3. Nutrient concentrations in the sediment samples

In the present study, TP concentration from sediment samples of Megech River were generally high ranging from 375.67 to 581.67 µg g^{-1} measured at site M4 and M5, respectively. The highest TP value noted at site M5 might be attributed with the poor farming and soil conservation practice in the near catchment which allow more surface soil erosion (Hou *et al*., 2013; Kassa *et al*., 2016; Akale *et al*., 2018). Akoma and Imoobe (2009) and Wondimu (2016), mentioned the close interaction of nutrient enrichment in the sediment with agricultural runoffs in the Bahir Dar gulf of Lake Tana.

Soluble reactive phosphorus extracted from sediment samples decreased in downstream sites. However, the concentrations measured (208.17 – 333.50 µg g^{-1}) were relatively higher than the maximum values (108.79 mg kg^{-1}) reported by Wondimu (2016), from Lake Tana. Apart from sampling season, presence of detritus and animal excreta in the sediment surface, the difference can possibly be ascribed to aerobic condition and presence of clay particle from the excavation site that facilitate P adsorption thus increasing its concentration in the sediment (Baldwin and Mitchell, 2000; Lampert and Sommer, 2007). Gerhardt *et al*. (2010) also reported the high TP/SRP content of sediments due to adsorption of phosphate by some metals such as Ca^{2+}, Fe^{3+} and Al^{3+} in the bottom.

5.4. Alkali and earth alkaline metals in the water and sediment samples

In the present study, maximum concentrations of Ca and Mg from water and sediment samples were measured at site M2 and M3. This could be attributed to the dissolution of calcite, dolomite and related minerals in the soil and catchment (Sun *et al*., 2014). Walle *et al*. (2000) also described massive depositions of limestone, marble and granite in the Northern (Gondar and Tigray) and west-central parts of Ethiopia. In addition, excavation of rocks, construction materials like gypsum, cement and sand mining activities used for dam construction on the

river might have increased considerable amount of those alkali and alkaline earth metals in to the water and sediment of the river (Potasznik and Szymczyk, 2015). On the other hand, lower concentration of alkali and alkaline earth metals observed at site M6 possibly be due to absorption by some aquatic animals, algal communities and water hyacinth (Sun *et al*., 2014; Potasznik and Szymczyk, 2015).

5.5. Heavy metals concentration in the water and sediment samples

The concentrations of Cu, Zn, and Cr in the water samples of Megech River were found below the international guidelines for drinking purpose. However, Cd and Pb remained above the permissible limits of standards (DWAF, 1996; USEPA, 2011; WHO, 2011). The observed high concentrations of Cd and Pb could be associated with leachates discarded batteries from the garages, car washings and sewages (Gebreyohannes and Gebrekida, 2018). Concentrations of heavy metals analysed in the present study were lower than values reported from different Ethiopian water bodies (Asefa and Berhanu, 2015; Akele *et al*., 2016; Dribaba *et al*., 2018). This might be due to dilution or formation of less soluble metal complexes (Dribaba *et al*., 2018; Kassegn *et al*., 2018)

In the present study, higher concentrations of heavy metals in the sediment were measured at site M2. This might be due geological presence and intensive anthropogenic activity including excavation, metal work effluents, garages and open burning of municipal solid waste (Hou *et al*., 2013; Dribaba *et al*., 2018; Kassegn, *et al*., 2018). The order of abundance for heavy metals from sediment samples was Cu > Zn > Cr > Pb > Cd. Moreover, an attempt was made to compare the concentrations of heavy metals from Megech River with sediment quality guideline (SQG) standard for freshwater systems (Table 9) to describe the current pollution status of the systems to cause an adverse effect on organisms. The SQG includes the threshold effect concentration (TEC) where the concentrations are lower than the expected to cause

adverse effect; and the probable effect concentration (PEC) which is high concentration where adverse effects are expected to occur (Decena *et al*., 2018).

Table 9. Mean concentrations of heavy metals from sediment samples of Megech River with SQG and other literature values from Ethiopian water bodies (mg/kg).

Reference		**Cu**	**Zn**	**Cr**	**Cd**	**Pb**
SQG	TEC	32	120	43	0.99	36
	PEC	150	460	110	5	130
Present study	Min	8.02	3.74	1.34	0.68	1.02
	Max	12.68	6.06	2.56	1.24	1.82
	Mean	10.60	4.92	1.96	0.96	1.43
Other studies (2015 - 2018)	L.Akaki	59.06	228.53	70.96	ND	238.17
	G. Akaki	4.2	21.8	24.5	2.6	137.7
	Aba Yohannes	45	10	25	2.6	136.8
	Elalla	40.03	387.5	47.2	16.25	1.58
	Awash	79.43	382.73	120.58	2.60	13.53
	Tendaho	10.35	21.89	2.52	1.03	5.78
	L. Awassa	8.69	93.80	8.27	0.21	15.7

NA = Not available; *ND = Not detected*

Value below TEC value *Value above TEC and below PEC* *Value above PEC*

(Assefa and Berhanu, 2015 = Tendaho reservoir; Akele *et al*., 2016 = Little Akaki River; Dribaba *et al*., 2018 = Awash River; Gebreyohanes and Gebrekidan, 2018 = Elalla River; Kassegne *et al*., 2018 = Great Akaki River and Aba Yohannes River).

5.6. Heavy metal contents and distribution in *E. crassipes*

As an important component of aquatic systems, macrophytes play a significant role in biological filtration of water (Admas *et al*., 2017). Furthermore, positive advantages of aquatic macrophytes include their potential to accumulate excess chemicals and heavy metals in their plant body (Kabeer *et al*., 2013). In contrast to previous reports that described root as primary site of accumulation for heavy metals in *E. crassipes*, the finding of the present study revealed

stem has high concentrations than roots and leaves. This may be due to over accumulation of metals caused by prolonged low-level exposure of roots and metals may move to stem together with other minerals via transport tissue (Ndimele *et al*., 2012). Furthermore, less differentiation between root and stem could facilitate fast translocation rate of heavy metals in to aerial part (Williams *et al*., 2000). In addition, Kabeer *et al*. (2013), explained the different factors that affect metal accumulation in aquatic macrophytes, such as variation in plant species, growth stage, physiological adaptations and demand for absorption are among the major once (Jones *et al.*, 2018). The current result corroborates with Kabeer *et al*. (2013) who disclosed high accumulation of metals in the floating (aerial) parts of the macrophyte such as stem and leaf. The abundance pattern of heavy metals in *E. crassipes* samples were in the order Cu > Zn > Cr >Pb > Cd in the stem, root and leaves. In comparison with water samples, higher concentrations of metals were recorded in the *E. crassipes* sample. This could be attributed to bioconcentration of metals in the macrophyte body. Ndimele *et al*. (2012) and Jones *et al*. (2018) elaborated the best quality of aquatic macrophytes to absorb metals from water and make their internal concentration several fold greater than the surrounding environment.

CHAPTER 6: CONCLUSIONS

External point and nonpoint sources of pollutants together with anthropogenic activities in the watershed including excavation sand mining and water abstraction severely impact the natural conditions of the river. Therefore, industrial and municipal effluents from Gondar and Azezo towns are assumed to be major causes of pollution.

Although, there were variation in spatial concentrations of nutrients assessed from Megech River, the mean concentrations exceed USEPA standards to cause eutrophication. Therefore, the river might have an inevitable contribution in the recent infestation of water hyacinth and eutrophication of Lake Tana.

The concentrations of more than half of the heavy metals assessed from surface water samples are below the maximum permissible limits for natural waters. However, concentrations of Cd and Pb in the water are above the standard for drinking water. Hence, future ecological and health problems are expected.

Concentrations of all heavy metals assessed in the sediment samples are below the sediment quality guideline to cause adverse effects on organisms (TEC). Generally, nutrient and heavy metal concentrations values recorded in the present study are relatively lower than values reported from different Ethiopian water bodies.

CHAPTER 7: RCOMMENDATIONS

Since this research was done within a short period during dry season focusing on the current status of nutrients and heavy metals pollution, further studies including temporal variation (wet season) and more sampling sites (tributaries of the river) are essential to have a complete assessment of Megech River.

Despite the laboratory facility limitations and working conditions, further studies including other aquatic macrophytes, benthic organisms, sediment characterization, and estimation of loading in to the lake are of great importance.

Community based awareness creation on the values of water bodies, integrated watershed management and continuous monitoring are essential to reduce the risk of pollution and its impact on organisms in the future. Furthermore, legislating abiding law to municipalities and industries not to discharge untreated effluents in to the rivers.

References

Abebe, E. and Kebede, A. (2017). Assessment of Climate Change Impacts on the Water Resources of Megech River Catchment, Abbay Basin, Ethiopia. *Open J. of Modern Hydrology, 7,* 141-152.

Ackova, D. G. (2018). Heavy metals and their general toxicity on plants. *Plant Sci. Today, 5*(1), 14-18.

Admas, A., Sahle, S., Belete, E., Agidie, A. and Alebachew, M. (2017). Controlling Water Hyacinth in Lake Tana Using Biological Method at Green House and Pond Level. *Eur Exp. Biol., 7*(5:30), 1-5.

Admassu, M., Wubshet, M. and Tilaye T. (2003). Sanitary Survey in Gondar Town. *Ethiop. J. Health Dev., 3,* 215-219.

Agbaji, E. B., Anhwange B. A. and Gimba E. C. (2012). Impact Assessment of Human Activities and Seasonal Variation on River Benue, within Makurdi Metropolis. *Inter. J. of Sci. and Tech., 2*(5), 2224-3577.

Aghoghovwia, O.A., Miri, F.A. and Izah, S.C. (2018). Impacts of anthropogenic activities on heavy metal levels in surface water of Nun River around Gbarantoru and Tombia Towns, Bayelsa State, Nigeria. *Annals of Ecol. and Environ. Sci., 2*(2), 1-8.

Aghoghovwia, O.A., Miri, F.A. and Izah, S.C. (2018). Impacts of anthropogenic activities on heavy metal levels in surface water of Nun River around Gbarantoru and Tombia Towns, Bayelsa State, Nigeria. *Annals of Ecol. and Environ. Sci., 2*(2), 1-8.

Ahemad, M., Zaidi, A., Khan, M. and Oves, M. (2009). Biological importance of phosphorus and phosphate solubilizing microbes - an overview. *Nova Sci. Publishers,* 1-14. ISBN 978-1-60876-112-8.

Akale, A. T., Moges, M. A., Dagnew, D. C., Tilahun, S.A. and Steenhuis, T. S. (2018). Assessment of Nitrate in Wells and Springs in the North Central Ethiopian Highlands. *Water, 10*: 476. DOI: 10.3390/w10040476.

Akele, M. L., Kelderman, P., Koning, C.W. and Irvine, K. (2016). Trace metal distributions in the sediments of the Little Akaki. River, Addis Ababa, Ethiopia. *Environ. Monit. Assess., 188*:389: 1-13. DOI: 10.1007/s10661-016-5387-z.

Akoma, O. and Imoobe, T. (2009). Limnological and Phytoplankton Survey of Bahir Dar Gulf of Lake Tana, Ethiopia. *AJST., 10,* 91-98.

Alemayehu, T. (2001). The impact of uncontrolled waste disposal on surface water quality in Addis Ababa, Ethiopia. *SINET Ethiop. J. Sci., 24*(1), 93-104.

Alemu, M. L., Geset, M., Mosa, H. M., Zemale, F.A., Moges, M.A., Giri, S.K., Tillahun, S. A., Melesse, A. M., Ayana, E. K. and Steenhuis, T.S. (2017). Spatial and temporal trends of recent dissolved phosphorus concentrations in Lake Tana and its four main tributaries. *Land Degrad. Develop., 28,* 1742–1751.

American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation (1999). Standard methods for the examination of water and wastewater (20th edd.): Washington, D.C.

Anteneh, W., Mengist, M., Wondie, A., Tewabe, D., WeldeKidan, W., Assefa, A. and Engida, W. (2014). Water hyacinth coverage survey report on Lake Tana, *Technical Report Series 1*, 1 – 29.

Appenroth, K.J. (2010). What are ‘‘heavy metals’’ in Plant Sciences? *Acta Physiol. Plant, 32*, 615-619.

Asefa, W. and Beranu, T. (2015). Levels of Some Trace Metals in Fishes Tissues, Water and Sediment at Tendaho Water Reservoir, Afar Region, Ethiopia. *J. Environ. Anal. Toxicol., 5*(5), 1- 6. DOI: 10.4172/2161-0525.1000313.

Arhonditsis, G. B., Stow, C. A., Paerl, H. W., Valdes-Weaver, L. M., Steinberg, L. J. and Reckhow, K. H. (2007). Delineation of the role of nutrient dynamics and hydrologic forcing on phytoplankton patterns along a freshwater–marine continuum. *Ecological modelling, 208*, 230-246.

Arimoro, F. O., Olisa, H. E., Keke, U. N., Ayanwale, A. V. and Chukwuemeka, V. I. (2018). Exploring Spatio-temporal patterns of plankton diversity and community structure as correlates of water quality in a tropical stream. *Acta Ecologica Sinica, 38,* 216-223.

Arnot, J. A. and Gobas, F. A. P. C. (2006). A review of bioconcentration factor (BFA) assessment for organic chemicals in aquatic organisms. *Environ. Rev., 14*: 257-297.

Ateka, A., Zimale, F. A., Sishu, F. K., Maglwa, T., Kokou, K., Schmitter, P., Steenhuis, T. S. and Tilahun S. A. (2018). Spatial and temporal variation of nutrient availability in the Lake Tana, upper Blue Nile Basin. Bahir Dar University. pp. 8.

Awulachew, S. B., Erkossa, T., Smakhtin, V. and Fernando, A. (2009). Simulation of water resource development and environmental flows in the Lake Tana Sub basin: *Inter. Water Manag. Institute, 18,* DOI: 10.3910/2009.201.

Awulachew, S. B., Yilma, A. D., Loulseged, M., Loiskandl, W., Ayana, M. and Alamirew, T. (2007). Water Resources and Irrigation Development in Ethiopia. *Intern. Water Manag. Institute*. Sri Lanka pp 78.

Baldwin, D. S. and Mitchell, A. M. (2000). The effects of drying and re-flooding on the sediment and soil nutrient dynamics of lowland river–floodplain systems: a synthesis. *Regul. Rivers. Res. Mgmt., 16,* 457-467.

Bennett, M.G., Schofield, K. A., Lee, Y. S. and Norton, S. B. (2017). Response of chlorophyll *a* to total nitrogen and total phosphorus concentrations in lotic ecosystems: a systematic review protocol. *Environ Evid., 6*(18), 1-13.

Beyene, H. and Redaie, G. (2011). Assessment of Waste Stabilization Ponds for the Treatment of Hospital Wastewater: The Case of Hawassa University Referral Hospital. *World Applied Sci. J., 15* (1), 142-150.

Bhuyana, M. S., Abu-Bakarb, M., Akhtara, A., Hossainc, M. B., Alid, M. M. and Islam, M. S. (2017). Heavy metal contamination in surface water and sediment of the Meghna River, Bangladesh. *Environ. Nano technol. Monitoring and Manag., 8,* 273-279.

Bouwman, A. F., Bierkens, M. F. P., Griffioen, J., Hefting, M. M., Middelburg, J. J., Middelkoop, H. and Slomp, C. P. (2013). Nutrient dynamics, transfer and retention along the aquatic continuum from land to ocean: towards integration of ecological and biogeochemical models. *Biogeosciences, 10,* 1–23.

Butusov, M. and Jernelöv, A. (2013). Phosphorus: An Element that could have been called Lucifer. *Briefs in Environ. Sci. 9,* 13-17.

Canli, M. Ay, O. and Kalay, M. (1998). Levels of heavy metals (Cd, Pb, Cu, Cr and Ni) in tissue of *Cyprinus carpio, Barbus capito* and *Chondrostoma regium* from the Seyhan river, Turkey. *Tr. J. of Zoo., 22,* 149-157.

Carpenter, S. R. (2005). Eutrophication of aquatic ecosystems: Biostability and soil phosphorus. *National academy of Sci., 102*(29), 10002-10005.

Çelik, K. (2013). The Relationships between Chlorophyll-a Dynamics, Certain Physical and Chemical Variables in the Temperate Eutrophic Çaygören Reservoir, Turkey. *Iranian J. of Fisheries Sci., 12*(4), 770-782.

Central Statistical Agency of Ethiopia (2017). Ethiopian population and housing census. Data capturing and processing implementation strategy. http://www.csa.gov.et/component/phocadownload/category/301-census-tables

Costa, J. A., Souza, J. P., Teixeira, A. P., Nabout, J. C. and Carneiro, F. M. (2018). Eutrophication in aquatic ecosystems: a scientometric study. *Acta Limnologica Brasiliensia, 30*(2), 1-11.

Datri, C. W., Pray, C. L., Zhang, Y. and Nowlin, W. H. (2015). Nutrient enrichment scarcely affects ecosystem impacts of a non-native herbivore in a spring-fed river. *Freshwater Biol., 60,* 551-562.

Decena, S. C. P., Arguelles, M. S. and Robel, L. L. (2018). Assessing Heavy Metal Contamination in Surface Sediments in an Urban River in the Philippines. *Pol. J. Environ. Stud., 27*(5), 1983-1995.

Dejen, E., Vijverberg, J., Nagelkerke, L. and Sibbing, F. (2004). Temporal and spatial distribution of micro crustacean zooplankton in relation to turbidity and other environmental factors in large tropical lake (Lake Tana, Ethiopia). *Hydrobiologia*. 513:39-49.

Demeke, A., 1998. Age and growth determination of tilapia, *Oreochromis niloticus* L. (Pisces: Cichilidae) in some lakes of Ethiopia. Unpubl. Ph.D. Thesis, School of Graduate Studies, Addis Ababa University, Addis Ababa, pp: 115.

Desta, Z., Borgstrom, R. and Gebremariam, Z. (2003) Habitat use and trophic position determine mercury concentration in the straight fin barb *Barbus paludinosus,* a small fish species in Lake Awassa, Ethiopia. *J. Fish Biol., 73*(3), 477-497.

Dham, C. N., Grimm, N. B., Marmonier, P., Valet, H. M. and Vervier, P. (1998). Nutrient dynamics at the interface between surface water and groundwater. *Freshwater Biol*., *40*, 427-451.

Dimari, A. G., Abdulrahman, F. I., Akan, J. C. and Garba, S.T. (2008). Metals Concentrations in Tissues of *Tilapia gallier*, *Crarias lazera* and *Osteoglossidae* Caught from Alau Dam, Maiduguri, Borno State, Nigeria. *American J. of Environ. Sci., 4*(4), 373-379.

Dirbaba, N. B., Yan, X., Wu, H., Colebrooke, L. L., and Wang, J. (2018). Occurrences and Ecotoxicological Risk Assessment of Heavy Metals in Surface Sediments from Awash River Basin, Ethiopia. *Water 10*(535), 1-14.

Dirilgen, N. (2001). Accumulation of heavy metal in fresh water organism: Assessment of toxic interaction. *Turk. J. Chem*. *25*(3): 173-179.

Dsikowitzky, L., Mengesha, M., Dadebo, E., Carvalho, C. E. V. and Sindern, S. (2012). Assessment of heavy metals in water samples and tissues of edible fish species from Awassa and Koka Rift Valley Lakes, Ethiopia. *Environ. Monitoring Assess., 185*(4), 3117-3131. DOI: 10.1007/s10661-012-2777-8.

Durand, P., Breuer, L., Johnes, P.J., Billen, G., Butturini, A., Pinay, G. (2011) European Nitrogen Assessment. *Cambridge University Press*, Cambridge, pp.126-146. ISBN 781107006126.

DWAF (1996) South African Water Quality Guidelines. 1: Domestic Uses (2nd edn.). Department of Water Affairs & Forestry, Pretoria.

Ebro, A., Berhe, K., Getahun, Y., Adane, Z., Alemayehu, N., Fayisa, Y. and Tegegne, A. (2017). Water hyacinth (*Eichhornia crassipes* (Mart.): Land use/land cover changes and community-based management in East-Shoa zone, Ethiopia. *Inter. J. Environ. Agri. Res*., *3*(5), 1-11.

Elisabeta, C. A., Michael, G. H. and Paul, S. A. (2010). Advection-dispersion model for nutrient dynamics in river Swale. *Int. Conference on Water Resources*, pp.10.

El-Sayed, A. E, El-Ayyat, M. S., Nasr, E. and Khater, Z. (2011). Assessment of heavy metals in water, sediment and fish tissues, from Sharkia province, Egypt. *Egypt J. Aquatic Biol. and Fish*. *15*(2), 125- 144.

Emama, E. L., K.ahloun, M. and Meire, P. (2010). Ecohydrological status of Lake Tana- A shallow highland lake in the Blue Nile (Abbay) basin in Ethiopia: Review. *Ecohydrology and hydrobiology, 10*(2-4), 109-122. DOI: 10.2478/v10104-011-0021-8.

FAO (2017). Food and Agriculture Organization of the United Nations Rome and the International Water Management Institute on behalf of the Water Land and Ecosystems research program. Colombo. http://www.fao.org/3/a-i7754e.pdf

Fernández-Luqueño, F., Valdez, F. L., Melo, P. G., Suárez, S. L., Gonzále, E. N. A., Martínez, A. I., Guillermo, M. S. G., Martínez, G. H., Mendoza, R. H., Garza, M. A. A. and Velázquez, I. R. P. (2013). Heavy metal pollution in drinking water - a global risk for

human health: A review. *African J. Environ. Sci. Tech., 7*(7), 567-584. DOI: 10.5897/AJST12.197.

Fetahi, T. (2010). Plankton Communities and Ecology of Tropical Lakes Hayq and Awasa, Ethiopia. *PhD Dissertation submitted to Vienna University*, pp. 98.

Förstner, U., Wittmann, G. T. W. (1983). Metal pollution in the aquatic environment. *Folia Geobotanica*, 18: 194-194.

Gebremariam, Z., Kebede, E. and Desta, Z. (2002). Long-term changes in chemical features of waters of seven Ethiopian rift-valley lakes. *Hydrobiologia, 477*(1), 81-91.

Gebremedhin, S., Getahun, A., Anteneh, A., Bruneel, S. and Goethals, P. (2018). A Drivers-Pressure-State-Impact-Responses Framework to Support the Sustainability of Fish and Fisheries in Lake Tana, Ethiopia. *Sustainability, 10*, 2957. DOI: 10.3390/su10082957.

Gebreyohannes, F. and Gebrekidan, A. (2018). Health risk assessment of heavy metals via consumption of spinach vegetable grown in Elalla river. *Bull. Chem. Soc. Ethiop., 32*(1), 65-75.

Gerhardt, S., Boos, K. and Schink, B. (2010). Uptake and release of phosphate by littoral sediment of a freshwater lake under the influence of light or mechanical perturbation. *J. Limnol., 69*(1), 54-63.

Gichuki, J., Omondi, R., Boera, P., Okorut, T., Matano, A. S., Jembe, T. and Ofulla, A. (2012). Water Hyacinth *Eichhornia crassipes* (Mart.) Solms-Laubach. Dynamics and succession in the Nyanza gulf of Lake Victoria (East Africa): Implications for water quality and biodiversity conservation. *East Africa Community Lake Victoria Basin Commission.*

Goshu, G. and Aynalem, S. (2017). Problem Overview of the Lake Tana Basin. *Social and Ecological System Dynamics, 9*(23), DOI: 10.1007/978-3-319-45755-0_2.

Gurebiyaw, K. and Yigzaw, M. (2018). Landowners' Outlook Towards Soil Erosion Problem and Conservation Strategies in Maksegnit Province, Ethiopia. *Int. J. Photochem. and Photobiol., 2*(1), 22-27. DOI: 10.11648/j.ijpp.20180201.15.

Hakanson, L. and Eklund, J. M. (2010). Relationships between Chlorophyll, Salinity, Phosph orus, and Nitrogen in Lakes and Marine Areas. *J. of Coastal Res., 26*(3), 412-423.

Halliday, S. J., Skeffington, R. A., Bowes, M. J., Gozzard, E., Newman, J. R., Loewenthal, M., Felgate, P. E. J. Jarvie, H. P. and Wade, A. J. (2014). The Water Quality of the River Enborne, UK: Observations from High-Frequency Monitoring in a Rural, Lowland river system. *Water, 6*, 150-180.

Hauer, F. R. and Lamberti, G. A. (2007). Methods in stream ecology. Second edition, *Elsevier, 895*. DOI: 10.1016/B978-0-12-332908-0.X5001-3.

Hillbricht-Ilkowska, A. (2005). Protection of lakes and lake district landscape-problems, processes and perspectives. Features regional and research problems lake district landscape. KOSMOS. *Problems of Biological Sci., 54*(2-3), 285-302.

Hou, D., He, J., Lü, C., Sun, Y., Zhang, F. and Otgonbayar, K. (2013). Effects of environmental factors on nutrients release at sediment-water interface and assessment of trophic status for a typical shallow Lake, Northwest China. *The Sci. World J.,* 1-16.

Ibrahim, S. and Sa'id, H. A. (2010). Heavy metals load in tilapia species: a case study of Jakara river and Kusalla dam, Kano state,Nigeria. *Bayero J. Pure App. Sci., 3*(1), 87 – 90.

Inamdar, S., Dhillon, G., Singh, S., Parr, T. and Qin, Z. (2015). Particulate nitrogen exports in stream runoff exceed dissolved nitrogen forms during large tropical storms in a temperate, headwater, forested watershed. *J. Geophys. Res. Biogeosci., 120*, 1548–1566.

Jafari, N. (2010). Ecological and Socio-economic utilization of water hyacinth (*Eichhornia crassipes* Mart Solms). *J. Application of Sci. and Environ. Manag., 14*, 43-49.

Jan, A. T., Azam, M., Siddiqui, K., Ali, A., Choi, I. and Haq, Q. M. R. (2015). Heavy metals and human health: mechanistic insight into toxicity and counter defence system of antioxidants. *Int. J. Mol. Sci*., *16,* 29592–29630.

Jones, J.L., Jenkins, R. O. and Haris P. I. (2018). Extending the geographic reach of the water hyacinth plant in removal of heavy metals from a temperate Northern Hemisphere river. *Scientific Reports. 8, 11071.* DOI:10.1038/s41598-018-29387-6 1.

Kabeer, R., Varghese, R., Jaysooryan, K. K., George, J., Ambily, V. and Sylas, V. P. (2013). Removal of zinc lead and cadmium by water hyacinth (*E. crassipes*). *Int. J of Curr. Res*., *5*(9), 2506-2509.

Karl, D. M. and Bjorkman, K. M. (2002). Biogeochemistry of marine dissolved organic matter. 2nd edition, *Elsevier* academic press, 250-366.

Kassa, Y. (2016). Macrophyte ecology, nutrient dynamics and water quality of the littoral zone and Yitamot Wetland, Lake Tana, Ethiopia. *PhD thesis submitted to Addis Ababa University*. pp. 157.

Kassegne, A. B., Esho, T. B., Okonkwo, J. O. and Asfaw, S. L. (2018). Distribution and ecological risk assessment of trace metals in surface sediments from Akaki River catchment and Aba Samuel reservoir, Central Ethiopia. *Environ. Syst. Res*., *7,* 24 l. DOI: 10.1186/s40068-018-0127-8.

Kavanova, M., Lattanzi, F. A., Grimoldi, A. A., and Schnyder, H. (2006). Phosphorus deficiency decreases cell division and elongation in grass Leaves. *Plant Physiology, 141,* 766–775.

Kebede, A. and Wondimu, T. (2004). Distribution of race elements in muscle and organs of Tilapia, Oreochromis niloticus, from Lake Awassa and Ziway, Ethiopia. *Bull. Chem. Soc. Ethiop., 18*(2), 119-130.

Kelderman, P., and Osman, A. A. (2007). Effect of redox potential on heavy metal binding forms in polluted canal sediments in Delft (The Netherlands). *Water Res., 41,* 4251-4261.

Kerketta, P., Baxla, S. L., Gora, R. H., Kumari, S. and Roushan R. K. (2013). Analysis of physico-chemical properties and heavy metals in drinking water from different sources in and around Ranchi, Jharkhand, India. *Vet World, 6*(7), 370-375. DOI: 10.5455/vetworld.2013.370-375.

Khan, F. A. and Ansari, A. A. (2005). Eutrophication: An Ecological vision. *The Botanical Review, 71*(4), 449-482.

Kyambadde, J., Kansiime, F. and Dalhammar, G. (2005). Nitrogen and phosphorus removal in substrate-free pilot constructed wetlands with horizontal surface flow in Uganda. *Water, Air, and Soil Pollution*., *165*, 37–59.

Lampert, W. and Sommer, U. (2007). Limnoecology. 2nd edition, *Oxford University*, pp.234-284.

Lanckriet, S., Nyssen, J. and Adgo, E. (2017). Environmental change in lake catchments of Ethiopia. *Land Degrad. Develop*., *28*, 1793–1794.

Lawson, E.O. (2011). Physico-chemical parameters and heavy metal contents of water from the mangrove's swamps of logos lagoon, logos, Nigeria. *Advances in biological Res.*, *5*(1), 8-21.

LFDP, (1997). Lake fisheries development program, Hand book for fishery Officers. Commission of the European Communities (EDF VI). Animal and Fisheries Development Technology Team (MoA), *GOPA Consultants*, pp: 1-125.

Li, G., Li, H., Leffelaar, P. A., Shen, J. and Zhang, F. (2014). Characterization of Phosphorus in Animal Manures Collected from Three (Dairy, Swine, and Broiler) Farms in China. *PLoS ONE, 9*(7), e102698. DOI: 10.1371/journal.pone.0102698.

Li, H., Shi, A., Li, M. and Zhang, X. (2013). Effect of pH, Temperature, Dissolved Oxygen, and Flow Rate of Overlying Water on Heavy Metals Release from Storm Sewer Sediments. *J. of Chem.*, DOI: 10.1155/2013/434012.

Lokhande, V. H., Srivastava S., Patade V. Y., Dwivedi, D., Tripathi, R. D., Nikam T. D. and Suprasanna P. (2011). Investigation of arsenic accumulation and tolerance potential of Sesuvium portulacastrum (L.) L. *Chemospher, 82*, 529-534. DOI: 10.1016/j.chemosphere.2010.10.059.

Lopes, P., Caliman, A., Carneiro, L., Bini, L., Esteves, F., Farjalla, V. and Bozelli, R. (2011). Concordance among assemblages of upland Amazonian lakes and the structuring role of spatial and environmental factors. *Ecological Indicators, 11*, 1171–1176.

Malone, T. C., Crocker, L. H., Pike, S. E. and Wendler, B. W. (2018). Influences of river flow on the dynamics of phytoplankton production in a partially stratified estuary. *Mar. Ecol. Prog. Ser., 48*, 235-249.

Martí, E., Sabater, F., Riera, J. L., Merseburger, G. C., von Schiller, D., Argerich, A., Caille, F. and Fonollà, P. (2006). Fluvial nutrient dynamics in a humanized landscape. Insights from a hierarchical perspective. *Limnetica, 25*(1-2), 513-526.

Mehari, M., Dessie, M. and Abate, M. (2014). Bed Shear Stress under Complex Flow Conditions - The Case of Megech River, Ethiopia. *Geophysical Res., 16*, 1-1.

Mekonnen, F. H. (2012). Liquid waste management: The case of Bahir Dar, Ethiopia. *Ethiop. J. Health Dev., 26*(1), 49-53.

Melaku, S., Wondimu, T., Dams, R and Moens, L. (2007). Pollution status of Tinishu Akaki River and its tributaries (Ethiopia) evaluated using physico-chemical parameters, major ions, and nutrients. *Bull. Chem. Soc. Ethiop., 21*, 13–22.

Mengesha, A., Mekuria, A. and Husen, A. (2013). Algal biomass and nutrient enrichment in the Angereb reservoir, Gondar, Ethiopia. *Environ. and Experimental Biol., 11,* 91–98.

Moss, B. (2010). Ecology of freshwaters. *John Wiley & Sons Ltd*. 4th edition 25-36.

Muhammd, B. L., (2018). Determination of Cadmium, Chromium and Lead from Industrial Wastewater in Kombolcha Town, Ethiopia Using FAAS. *J. Environ. Anal. Chem., 5*(3), 1-5.

Mulholland, P. J. and Webster, J. R. (2010). Nutrient dynamics in streams and the role of J-NABS. *J. N. Am. Benthol. Soc., 29*(1), 100–117.

Mulugeta, M. and Gashaw, T. (2017). Determination of selected essential and non-essential elements in different Beer brands of Ethiopia. *Food Sci. and Quality Manag., 69,* 6-11.

Ndimele, P. E. (2012). The effects of water hyacinth (*Eichhornia crassipes*); Infestation on the physico-chemistry, nutrient and heavy metal content of Badagry Creek and Ologe Lagoon, Lagos, Nigeria. *J. Environ. Sci. and Tech., 5*, 128 – 136.

Nigatu, M., Alemayheu, M. and Haile-Sillassie, A. (2018). Optimum rate of NPS fertilizer for economical production of irrigated onion (Allium cepa L) in Dembyia District of Amhara Region, Ethiopia. *Ethiop. J. Sci. & Technol., 11*(2), 105 – 119.

Niirnberg, G. K. (1994). Phosphorus release from anoxic sediments: what we know and how we can deal with it. *Lirnnetica, 10*(1), 1-4.

O'sullivan, P. and Reynolds, C. 2004. The Lakes Handbook Volume 2 Limnology and Limnetic Ecology, *Blackwell Publisher*, USA. Pp. 708. ISBN: 0-632-04797-6.

Ogundiran, M. A. and Fawole, O. O. (2018). Toxic Effects of Water Pollution on Two Bio-indicators of Aquatic Resources of Asa River, Nigeria. *J Fisheries Sci., 12*(2), 20-27.

Okalebo, J. R., Gathua, K. W. and Woomer P. L. (2002). Laboratory methods of soil and plant analysis. Working manual, 2nd edition. TSBF-CIAT and *SACRED Africa*, Kenya.

Okunowo, W. O. and Ogunkanmi, L. A. (2010). Phytoremediation potential of some heavy metals by water hyacinth. *Int. J. Biol. Chem. Sci., 4*(2), 347-353.

Olowu, R. A., Osundiya, M. O., Onwordi, C. T., Denloye, A. A., Okoro, C. G., Ovide, O. O., Majolagbe, A. O., Omoyeni, O. A. and Moronkola B. A. (2012). Pollution status of brewery sewage sludge in Lagos, Nigeria. *IJRRAS., 10* (1), 159-165.

Orosun, M. M., Tchokossa, P., Orosun, R. O., Akinyose, F.C. and Ige, S.O. (2016). Determination of selected heavy metals and human health risk assessment in Fishes

from Kiri dam and river Gongola, North-eastern Nigeria. *J. Phys. Chem. Biophys.*, *6*(5), 229. DOI: 10.4172/2161-0398.1000229.

Paerl, H. W. (2006). Assessing and managing nutrient-enhanced eutrophication in estuarine and coastal waters: Interactive effects of human and climatic perturbations. *Ecological Engineering, 26,* 40–54.

Paerl, H. W., Gardner, W. S., Havens, K. E., Joyner, A. R., McCarthy, M. J., Newell, S. E., Qin, B. and Scott, J. T. (2016). Mitigating cyanobacterial harmful algal blooms in aquatic ecosystems impacted by climate change and anthropogenic nutrients. *Harmful Algae, 54,* 213–222.

Pigłowski, M. (2018). Heavy Metals in Notifications of Rapid Alert System for Food and Feed. *Int. J. Environ. Res. Public Health, 15,* 1-13.

Pizarroa, J., Vergara, P. M., Rodríguez, J. A., Sanhueza, P. A. and Castro S. A. (2010). Nutrients dynamics in the main river basins of the centre-southern region of Chile. *J. Hazardous Materials, 175,* 608–613.

Potasznik, A. and Szymczyk, S. (2015). Magnesium and calcium concentrations in the surface water and bottom deposits of a river-lake system. *J. Elem*., *20*(3), 677-692.

Pretty, J. L., Hildrew, A. G. and Trimmer M. (2006). Nutrient dynamics in relation to surface–subsurface hydrological exchange in a groundwater fed chalk stream. *J. of Hydrology, 330,* 84-100.

Rabalais, N. N. (2002). Nitrogen in aquatic ecosystem. *J. of the Human Environ*., *31*(2), 102-112.

Rachel, E. S. and Deborah, A. B. (2015). Biogeochemistry of marine dissolved organic matter. 2nd edition, *Elsevier academic press,* 127-232.

Rajeshkumar, S. and Li, X. (2018). Bioaccumulation of heavy metals in fish species from the Meiliang Bay, Taihu Lake, China. *Toxicology Reports, 5,* 288–295.

Ratan, A. and Verma, V. N. (2014). Photochemical studies of *Eichhornia crassipes* (Water Hyacinth). *Int. Letters of Chem. Phy. and Astro*., 11(3), 214-222.

Robson, B.J. (2014). State of the art in modelling of phosphorus in aquatic systems: Review, criticisms and commentary. *Environ. Modelling and Software, 61,* 339-359.

Saha, P. and Paul, B. (2016). Assessment of Heavy Metal Pollution in water resources and their Impacts: A Review. *J. of Basic and App. Eng. Res*., *3*(8), 671-675.

Sarneel, J. M., Geurts, J. J. M., Beltman, B., Lamers, L. P. M., Nijzink, M. M., Soons, M. B. and Verhoeven, J. T. A. (2010). The effect of nutrient enrichment of either the bank or the surface water on shoreline vegetation and decomposition. *Ecosystems, 13,* 1275–1286.

Setegn, S.G., Srinivasan, R. and Dargahi, B. (2008). Hydrological Modelling in the Lake Tana Basin, Ethiopia Using SWAT Model. *The Open Hydrology J., 2,* 49-62.

Shao, W. L. and Chang, W. L. (2004). Heavy metal phytoremediation by water hyacinth at constructed wetlands in Taiwan. *J. of Aqua. Plant Manag., 42*, 60-68.

Showqi, I., Lone, F. A. and Naikoo, M. (2018). Preliminary assessment of heavy metals in water, sediment and macrophyte (*Lemna minor*) collected from Anchar Lake, Kashmir, India. *Applied Water Sci., 8*(80), 1-11.

So, L. M., Chu, L. M. and Wong, P. K. (2003). Microbial enhancement of Cu^{2+}removal capacity of *Eichhornia crassipes* (Mart.). *Chemosphere, 52*: 1499-1503.

Strokal, M., Kroeze, C., Wang, M., Bai, Z. and Ma, L. (2016). The MARINA model (Model to Assess River Inputs of Nutrients to seas. Model description and results for China. *Science of the Total Environ., 562*, 869–888.

Sun, H., Alexander, J., Gove, B., Pezzi, E., Chakowski, N. and Husch, J. (2014). Mineralogical and anthropogenic controls of stream water chemistry in salted watersheds. *Applied Geochemistry, 48*, 141-154.

Sunday, M. and Agbaji, E. B. (2012). The influence of hospital waste dumps and incinerator ash on the receiving Environment. *Advances in App. Sci. Res., 3*(5), 2884-2889.

Tadesse, M, Tsegaye, D. and Girma, G. (2018). Assessment of the level of some physico-chemical parameters and heavy metals of Rebu river in Oromia region, Ethiopia. *MOJ Biol. Med., 3*(4), 99-118.

TaSBO (Tans Sub-basin Organization), 2011. Annual Report on Lake Tana Water Quality Baseline monitoring, Northern Ethiopia, Bahir Dar, Ethiopia, *Unpublished Working paper*: WQM-03.

Tibebe, D., Zewge, F., Lemma, B., Kassa, Y. and Bhaskarwar, A. N. (2018). External Nutrient Load and Determination of the Trophic Status of Lake Ziway. *CSVTU Int. J. Biotech. Bioinfor. and Biomed., 3*(2), 01–16.

Tudorancea, C. and Taylor, W. D. (2002). Ethiopian Rift Valley Lakes. – *Backhuys Publishers, Leiden.* pp 284.

Velez, D. and Montoro, R. (1998). Arsenic speciation in manufactured seafood products: a review. *J. Food. Protect., 61* (9), 1240-1245.

Voegborlo, R.B., El-Methnani, A.M., Abedin, M.Z. (1999). Mercury, cadmium and lead content of canned tuna fish. *Food Chem., 67*, 341-345.

Walle, H., Zewde, S. and Heldal, T. (2000). Building stone of central and southern Ethiopia: deposits and resource potential. *NGU-BULL, 436*, 175-182.

Williams, L. E., Pittman, J. K. and Hall, J. L. (2000). Emerging mechanisms for heavy metal transport in plants. *Biochimica et Biophysica Acta, 1465*, 104 – 126.

Wondie, A., Mengistou, S., Vijverberg, J. and Dejen E. (2007). Seasonal variation in primary production of a high-altitude tropical lake (Lake Tana, Ethiopia): effects of nutrient availability and water transparency. *Aquat. Ecol., 41*, 195–207.

Wondim, Y. K. (2016). Water Quality Status of Lake Tana, Ethiopia. *Civil and Environ. Res., 8*(9), 39-51.

Wudneh, A., Erkossa, T. and Deci, P. (2014). Sediment nutrient lost by runoff from two watersheds of Blue Nile basin, Ethiopia. *Afr. J. of Environ. Sci. and Tech., 8*(9), 498-510.

Wudneh, T. (1998). Biology and Management of Fish Stocks in Bahir Dar Gulf, Lake Tana, Ethiopia. Ph.D. thesis, *Wageningen Agricultural University*.

Yan, X., Liu, M., Zhong, J., Guo, J. and Wu, W. (2018). How human activities affect heavy metal contamination of soil and sediment in a long-term reclaimed area of the Liaohe River Delta, North China. *Sustainability, 10*(338), 1-19.

Yun, Y. J. and An, K. G. (2016). Roles of N:P ratios on trophic structures and ecological stream health in lotic ecosystems. *Water, 8*(22), 1-19.

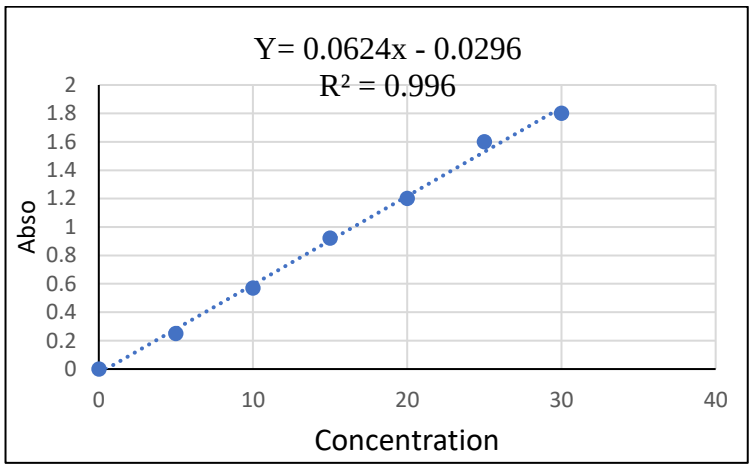
Zhang, J., Zhu, L., Li, F., Liu, C., Qiu, Z., Xiao, M. and Cai, Y. (2018). Comparison of toxic metal distribution characteristics and health risk between cultured and wild fish captured from Honghu city, China. *Int. J. Environ. Res. Public health, 15(*334), 1-6.

Appendices

Appendix 1. Standard series for Heavy metal

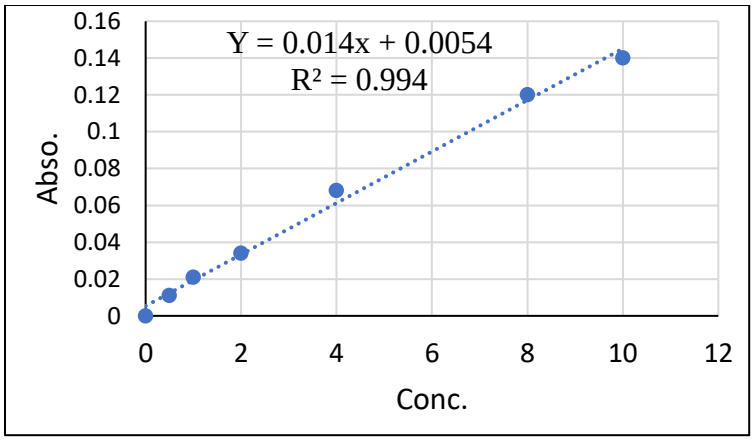
Ca and Mg

Std. Series	(mg/l)	Absor.
Cal Zero	0	0
Cal Std 1	5	0.25
Cal Std 2	10	0.57
Cal Std 3	15	0.92
Cal Std 4	20	1.2
Cal Std 5	25	1.6
Cal std 6	30	1.8



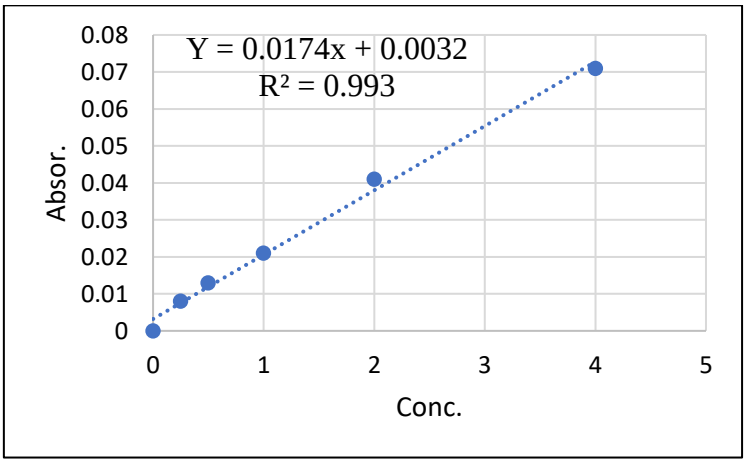
Fe and Mn

Std. Series	(mg/l)	Absor.
Cal Zero	0	0
Cal Std 1	0.5	0.011
Cal Std 2	1	0.021
Cal Std 3	2	0.034
Cal Std 4	4	0.068
Cal Std 5	8	0.13
Cal std 6	10	0.14



Cu, Zn, Cr, Pb, Cd

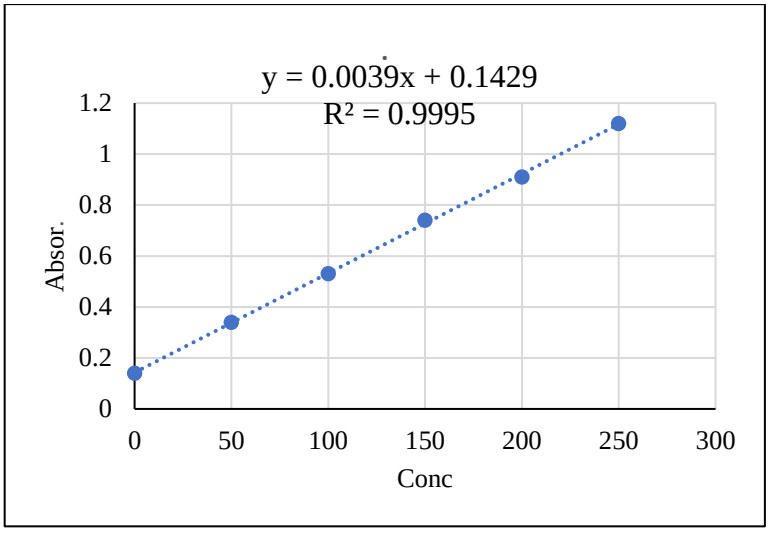
Std. Series	(mg/l)	Absor.
Cal Zero	0	0
Cal Std 1	0.25	0.008
Cal Std 2	0.5	0.013
Cal Std 3	1	0.021
Cal Std 4	2	0.041
Cal Std 5	4	0.071



Appendix 2. Some standard series for nutrients

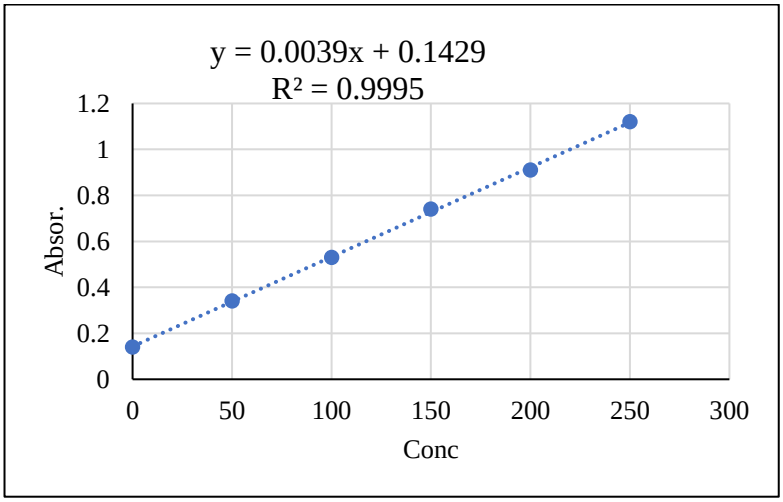
TP and SRP

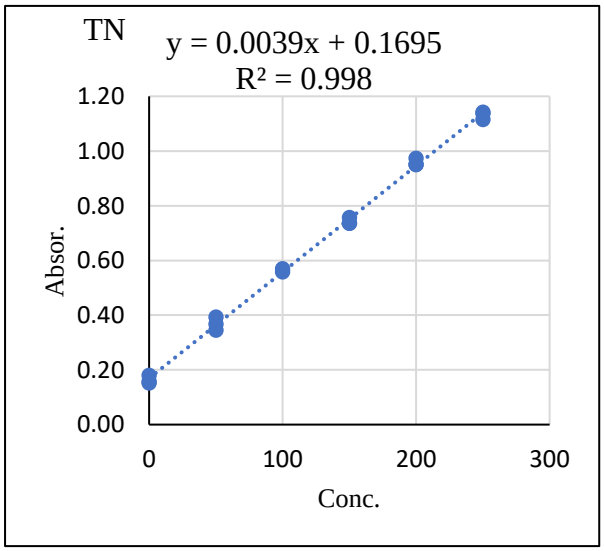
Std Series	(µg/l)	Abso.
Cal zero	0	0.044
Cal std 1	10	0.011
Cal std 2	20	0.049
Cal std 3	50	0.044
Cal std 4	100	0.112
Cal std 5	200	0.19
Cal std 6	400	0.351
Cal std 7	500	0.411

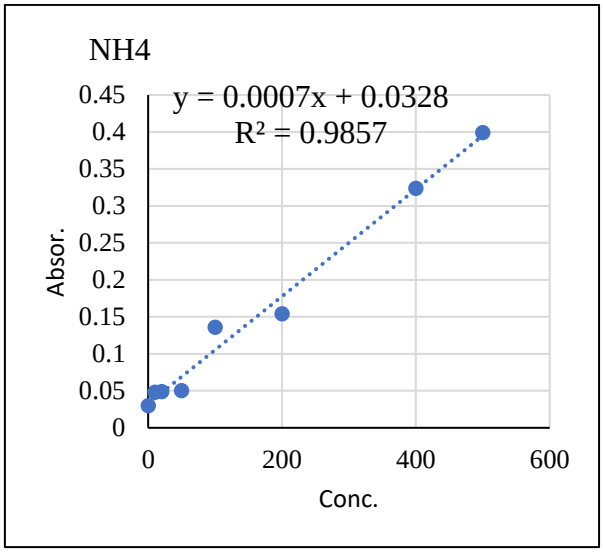


NO_3-N

Std Series	(µg/l)	Abso.
Cal zero	0	0.017
Cal std 1	10	0.041
Cal std 2	20	0.038
Cal std 3	50	0.05
Cal std 4	100	0.087
Cal std 5	200	0.155
Cal std 6	400	0.314
Cal std 7	500	0.395







Appendix 2. Optimization procedure for digestion of water, sediment and macrophyte samples

Sample	Trial	HNO3 (ml)	HCl (ml)	$HClO_4$ (ml)	H_2O_2 (ml)	Colour of Solution	Remark
Water	A	5	8			Not clear	rejected
	B	6	10			clear	Selected for water
	C	4	6			Not clear	rejected
Sediment	A	6		2	3	clear	Selected for sediment
	B	5		3	4	Not clear	rejected
	C	4		4	3	Not clear	rejected
Macrophyte	A	5	5			Not clear	rejected
	B	6	4			Clear	Selected for macrophyte
	C	4	5			Not clear	rejected

Appendix 3. Wave length, slit width, percent of recovery and MDL of cations and heavy metals using argon flame system.

Element	Wave length	Slit width	% Recovery			MDL
			Water	Sediment	Macrophyte	
Cu	324.8	0.7	95.85	89.50	98.20	0.024
Zn	213.8	0.7	105.17	93.76	106.15	0.024
Cr	357.9	0.7	89.29	111.07	92.68	0.018
Cd	228.8	0.7	97.19	96.26	90.19	0.018
Pb	283.3	0.7	91.46	86.58	97.56	0.017
K	766.5	0.7	96.44	86.63	108.33	0.022
Ca	422.7	0.7	88.38	91.43	96.78	0.014
Mg	279.5	0.7	101.61	104.04	96.42	0.018

Appendix 4. **Some pictures of sampling sites**