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INTERNAL AND EXTERNAL AGROCHEMICAL LOADS, DYNAMICS AND IMPACTS ON THE FRESHWATER ECOSYSTEM OF LAKE ZIWAY, ETHIOPIA

DEPARTMENT OF CHEMISTRY

PhD Thesis

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Declaration by candidate

“I hereby declare that the thesis submitted for the degree of doctor of philosophy (Analytical Chemistry), at Addis Ababa University, Addis Ababa, Ethiopia is my own original work and has not previously been submitted to any other institution of higher education. I declare that all sources cited or quoted are indicated and acknowledged by means of a comprehensive list of references.”

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i. Acknowledgments

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ii. Abstract

Excess agrochemicals input from agricultural activities and industrial effluent around Lake Ziway catchment can pose a serious threat on the lake ecosystem. This study was undertaken to investigate the external and internal agrochemicals load, their dynamics, and impacts on Lake Ziway ecosystem and suggest possible management options for sustainable use of the lake.

Different environmental samples such as water, sediment and fish were collected from nine representative sampling sites of the lake for the measurement of physicochemical parameters, nutrients and pesticides in 2014 and 2015 in both dry and wet seasonal basis. The physicochemical parameters were measured in-situ with portable multimeter and nutrients and chlorophyll a were determined by following the standard procedures outlined in the American Public Health Association (APHA) using UV/Visible spectrophotometer. The trophic status of the lake was determined using the Carlson and Vollenweider models. The external and internal nutrient loads were computed using the methods of Huai-en and Steinman, respectively. Multivariate techniques of cluster analysis (CA), principal component analysis (PCA)/factor analysis (FA) were applied to evaluate water quality of the lake. The lake water quality level was also evaluated using comprehensive evaluation index model.

There were spatio-temporal variations in the physico-chemical parameters and nutrients in the lake ecosystem during the study period. Higher concentrations of nutrients, electrical conductivity (EC) and total dissolved solid (TDS) were recorded in sampling sites of effluents of the floriculture industry (Fb) and around the floriculture industries (Fa) in all seasons. Results of PCA analysis of the four data sets which were explained more than 88 % and 91 % of the total variance in wet and dry seasons, respectively. The pollutant sources were mainly from sampling sites around effluent of floriculture industry (Fb) during dry season and Meki (Mb) and Ketar (Kb) Rivers during wet season, respectively. CA grouped the nine sampling stations into three clusters of similar water quality features and hence the whole lake was categorized into low, moderate and high pollution status. The values of the comprehensive pollution index ranged from 0.69 to 1.80 and 0.38 to 0.68 during dry and wet seasons, respectively. According to the values of com-

prehensive pollution index, the lake is moderately and slightly polluted in dry and wet seasons, respectively.

The vertical nutrient profiles of the lake water showed no significant variability, making it difficult to rely on the observed nutrient concentration profiles to understand the nutrient dynamics in the lake. Ketar and Meki Rivers catchments showed the major sources of external nutrient loads to the lake ecosystem. The study showed a general trend of higher external nutrient load in the wet than in the dry seasons. The nutrient budgets for the lake clearly show the amount of nutrients that enter the lake exceeds the output, indicating that nutrients are being retained in the lake which is important for algal growth. These high nutrient loads indicate the susceptibility of Lake Ziway to eutrophication. Person correlation indicated that precipitation, water level, discharge flow and air temperature had weak to strong positive correlations with SRP, TP, TIN and TN while DO, pH, EC, total alkalinity (TA) and soluble reactive silica (SiO_2-Si) were negatively correlated with water level and discharge flow.

The results of sediment depth profile analyses showed that the mean concentrations of SRP, TP, NO_3-N, NO_2-N and TN were 27.7, 62, 5.28, 8.51 and 1733 mg/kg, respectively in dry season, and 21.2, 73, 7.99, 28.4, 24.2 and 1750 mg/kg, respectively in wet season. The values for SRP, TP, NO_3-N, NO_2-N and TN distributions were higher at sediment top surface and decline with depth of the sediment profiles in most of the sampling sites and seasons. Carlson trophic state and Vollenweider models showed Lake Ziway is eutrophic. In order to stop further deterioration of the lake water quality and to eventually restore the beneficial uses of the lake, management of agrochemicals (fertilizers and pesticides) in the lake catchments should be given urgent priority. It is mandatory to prepare guidelines for the trophic status of the Ethiopian freshwater bodies in the country by making bottom-up-down discussion.

Keywords: *Multivariate analysis, water quality, agrochemical, external and internal nutrient load, trophic state index, eutrophication, Lake Ziway*

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v. Abbreviations

ANOVA	Analysis of Variance
APHA	American Public Health Association
APHRD	Animal and Plant Health Regulatory Directorate
AT	Air temperature
CA	Cluster analysis
Chla	Chlorophyll-*a*
CRV	Central Rift Valley
CTSI	Carlson's Trophic State Index
DF	discharge flow
DLLME	Dispersive liquid-liquid micro extraction
DO	dissolved oxygen
EC	electrical conductivity
EFSA	European Food Safety Authority
EMA	Ethiopia Meteorological Agency
Evp	Evaporation
FA	Factor analysis
FDREMoWIE	Federal Democratic Republic of Ethiopia Ministry of Water, Irrigation and Energy
Ha	Hectare
HGLGIRDC	Halcrow Group Limited and Generation Integrated Rural Development Consultants
IPCC	International Panel on Climate Change
MAE	Microwave assisted extractions
Masl	meter above sea level
MCM	million cubic meters
NH4-N	Ammonia-Nitrogen
NO_2-N	Nitrite-Nitrogen
NO_3-N	Nitrate-Nitrogen
NTU	Nephelometric turbidity units
OECD	Organization for Economic Co-operation and Development
PCA	Principal component analysis

PLE	Pressured liquid extraction
PPT	Precipitation
SD	Secchi depth
SiO_2-Si	Soluble reactive silica
SRP	Soluble reactive phosphorus
T	Tone
TA	Total alkalinity
TDS	total dissolved solids
TIN	Total inorganic nitrogen
TN	Total nitrogen
TP	Total phosphorus
TSI	Trophic state index
USEPA	United States Environmental Protection Agency
WL	Water level
WSSA	Water supply service enterprise
WT	Water temperature

Chapter 1: Introduction

1.1 Background

"L*akes far from being the homogeneous environments we might expect, offer a rich and dynamic heterogeneity at multiple spatial and temporal scales that we are just beginning to understand"* (Kratz *et al*., 2005).

Water pollution is one of the critical issues in environmental conservation. Freshwater resources have been of great importance to both natural ecosystems and human development. They are essential for agriculture, industry and human existence in general. The health of aquatic ecosystems is dependent on the presence of the right proportions of nutrients and requires succession of major nutrients in the water and sediment (Venkatesharaju *et al.,* 2010). Appropriate assemblage of the nutrients ensures the status of water quality in any ecosystem and provides significant information about the available resources for supporting life (Medudhula *et al.*, 2012).

Human impacts on the lakes are linked to many social and economic activities carried out by numerous stakeholders found within the lake basin. These impacts include water pollution, inter-basin water transfer, water abstraction from the lake and from inflowing rivers, siltation of the lake and inflowing rivers, habitat destruction, lake level and surface area recession, decline in fisheries resources, and introduction of alien species of plants and animals. Most of these impacts results in destruction of the littoral zone around the lake shore which is one of the most important portions of the lake ecosystem and which provides a natural filtration system for surface water run-off that enters the lake (Palma *et al.*, 2010; Sridhar *et al*., 2014).

Agrochemicals are employed to increase soil fertility, and to control, or repel pests on agricultural products (Adak *et al*., 2002). Although the main aim is increasing supplies of food, problems do arise when significant amounts of agrochemicals accumulate as residues in soils or transported into surface waters. Under such circumstances, agrochemicals are of great health concern to humans, grazing livestock as well as aquatic biota (Obiri-Danso *et al*., 2011).

Water pollution by agrochemicals has become a growing threat to human society and natural ecosystems in recent decades. The quality of lake water is a reflection of what happens in its catchment as its topography, soil, geology, vegetation and anthropogenic pressures determine the kinds of materials entering into it. Nutrient enrichment of lakes is considered to be one of the major environmental problems in many countries especially in developing ones. Though it stimulates the growth of plants (algae as well as higher plants), nutrient enrichment ultimately leads to deterioration of water quality and degradation of the entire ecosystems (Fianko *et al*., 2011; Erik *et al.*, 2014).

Nitrogen and phosphorus (and silicon too for diatom species) are typical limiting nutrients influencing primary production. Nutrients occur in many different forms and only bio-available forms such as nitrate, nitrite, ammonia, orthophosphate and soluble reactive silica can be utilized directly by phytoplankton. Other forms of nutrients, however, can become bio-available through desorption, dissolution and biomass turnover. Nutrients in the water body may originate from weathering of bedrock, atmospheric precipitation, terrestrial input, storm water runoff, sewage effluent and agricultural discharge (Xagoraraki and Kuo, 2008; Maa *et al.*, 2009).

Surface water can be polluted through direct or indirect discharge of wastes, without adequate treatments, into water bodies including rivers, lakes, wetlands and oceans. Pollutants get into water bodies mainly from anthropogenic activities from point and non point sources (Xagoraraki and Kuo, 2008; Maa *et al.*, 2009). The effect of increasing urbanization and agricultural activities has led to widespread discharges of agrochemicals into water bodies. Excessive inputs can lead to eutrophication with consequent increases in harmful algal blooms and turbidity and expanded regions of hypoxia. Two sources of nutrient load can lead to eutrophication in lakes and reservoirs. These are external and internal nutrient loads (Maa *et al.*, 2009; Abayomi *et al.,* 2011).

In many lakes and reservoirs a substantial portion of nutrients may come from the catchment and tributaries. The external nutrient load mainly occurs when surface runoff from the catchment brings in nutrients from anthropogenic sources, such as sewage plants and agricultural runoff, as well as from natural sources. This kind of loading is frequently considered as the main determining factor in a lake’s trophic status because of its large magnitude. External loading from diffuse sources is often associated with rainfall and the subsequent flow events (Antonio *et al*., 2012). Streams that have large amounts of anthropogenic activities in their basins carry high external agrochemical loads that frequently cause several ecological disturbances in aquatic ecosystems (Mwanuzi *et al*., 2005; Chan, 2011).

External nutrient load is a permanently acting factor, which determines the water quality of a water body (Kondratyev, 2011). Large amounts of nutrients that enter a water body are found in the biota, which includes plankton, macrophytes, fish, and contribute to the pool of recyclable nutrients. However, it is the external nutrient load from human sources (point and nonpoint) that typically results in rapid increases in the rate of biological production and creates a wide range of undesirable water quality problems in ecosystems (Smith et *al.*, 2006; Tammeorg, 2014).

External nutrient loads to lakes are also largely controlled by the land use of surrounding catchments and the intensity, duration and timing of seasonal and annual rainfall pattern (Ramírez *et al*., 2014). Since Lake Ziway experiences a tropical climate, allochthonous nutrient loads typically dominate during the high rainfall season (wet season), whereas autochthonous and internal sources of nutrients often occurs during the dry season. External nutrient loads can be estimated using different models from point sources, rivers and effluents through the measurements of nutrient concentrations and rivers discharge (Usanzineza *et al*., 2015).

External nutrient load describes the amount of nutrients that enter a lake or reservoir from the drainage area (outside the system) but internal load comes from within the system. Internal loading generally refers to the phosphorus and nitrogen species released from anoxic sediment surfaces (Antonio *et al.*, 2012). Under anoxic conditions, these nutrient species (especially nitrate and phosphate) may escape from the sediment into the water column and become a nutrient source for the growth of algae (Brönmark and Hansson, 2005).

Søndergaard *et al*. (2003) reported that sediments play an important role in the overall nutrient dynamics of shallow lakes. Excessive sediment and nutrient load can have adverse ecological impacts on receiving aquatic ecosystems. In shallow aquatic systems, such as lakes and reservoirs, intensive material exchange between the water and the sediment may determine nutrient fluxes and the productivity of the entire ecosystem (Steinman *et al*., 2005; Sobczyński and Joniak, 2009; Ostrovsky and Tęgowski, 2010). Internal nutrient load, particularly that of phosphorus in the water column of a lake system originates from the sediment that is periodically injected from the sediment by action of vertical water cycles or changes in the water chemistry at water-sediment interface (Gertrud, 2009; Antonio *et al.*, 2012). Significant amount of phosphorus in lake sediments may be present bound to redox-sensitive iron compounds or fixed in more or less labile organic forms (Gertrud, 2009). This sediment load plays an important role in lake nutrient dynamics, either as a sink or a source of nutrients (Ogdahl *et al*., 2014). The internal nutrient loads can be estimated in lakes from fluxes across sediment-water interface from nutrient concentration gradients between the pore water and the water (Gertrud, 2009; Antonio *et al.*, 2012).

Different problems of lake include excessive influx of sediments from the lake catchment, through erosion, discharge of untreated or partially treated sewage and industrial waste waters/ solid waste, entry of diffused nutrient from agricultural field and forests through surface runoff, over-exploitation of lake for activities like recreation and fishing (Sharma *et al*., 2010; Ramesh and Krishnaiah, 2014). There is an immediate need to know the pollution status of a lake at any given time so that necessary conservation measures may be undertaken to improve the health of that water body. This can be done by determining the trophic state index (TSI) of the aquatic ecosystem (Sharma et *al*., 2010; Ramesh and Krishnaiah, 2014). Trophic state index involves new methods both of defining trophic status in lakes (Carlson, 1977).

Determining the trophic condition of a lake is an important step in the scientific assessment of the lake ecosystem because of the powerful predictions of statements that can be made to describe abiotic and biotic relationships once the trophic state is known (Ramesh and Krishnaiah, 2014). Various methods have been employed for the classification of lakes and to indicate their trophic status (Carlson, 1977). The most commonly and widely used method is based on productivity, and the frequently used biomass related to trophic state index is that of Carlson (Ramesh and Krishnaiah, 2014). The trophic status refers to the level of productivity in a lake as measured by amount of phosphorus, algae abundance and depth of light penetration (Ramesh and Krishnaiah, 2014). Generally, Lakes are mainly divided into three trophic levels, oligotrophic, mesotrophic, and eutrophic (Carlson, 1977).

Several factors have contributed to eutrophication of lakes in the world including: (1) agricultural- and forestry-related deforestation, (2) nutrient-rich municipal and industrial wastes, (3) residential and recreational developments in riparian areas with ineffectively managed septic systems, and (4) nutrient-rich runoffs from fertilized crop lands and livestock holding areas (French and Petticrew, 2007).

The main symptoms and impacts of eutrophication on surface water are: increase in production and biomass of phytoplankton; production of toxins by certain algae introducing taste and odour problems in the potable water; deoxygenation of water, especially after collapse of algal blooms, usually resulting in economic loss due to change in fish species, fish kills, loss of recreational use of water due to slime, weed infestation, and noxious odour from decaying algae, impediments to navigation due to dense weed growth (Huai-en *et al.*, 2003). Currently, major efforts are made worldwide to improve the ecological quality of eutrophic shallow lakes by reducing external nutrient load (reduced usage of fertilizers and pesticides around the surface water). These have often resulted in lower in-lake total phosphorus and decreased chlorophyll-*a* level in surface water and higher secchi depth (Jeppesen *et al.*, 2007).

Most tropical African lakes are facing problems of pressure from rapid population growth residing in their catchment, which normally discharge pollutants into the lakes. This has led to the deterioration of the water quality in receiving lakes. Some lakes are getting eutrophic due to high nutrient loads whilst others are facing problems of siltation and toxic pollutant discharges, thereby reducing their economic and aesthetic values. Some lakes are experiencing decreases in fish production due to their pollution by different anthropogenic factors (Usanzineza *et al*., 2015).

The rapid urbanization and industrialization together with intensive farming practices are increasingly impacting the rift valley lakes of Ethiopia, particularly Lake Ziway (Figure 1.1). Population increase and rising living standards have also contributed to excessive water withdrawal while escalating the level of external nutrient load and eutrophication that have far exceeded the natural inputs of the lake ecosystem (Herco *et al.*, 2007; Tadele, 2012). This has resulted in major changes in the biological structures and dynamics of the lake, often showing significant shift from clear water to turbid state. Consequently, pollution is becoming a major challenge to the preservation of Lake Ziway (Tilahun, 2006, 2010; Ayenew *et al*., 2007; Tadele, 2012; Tamire, 2012, 2014). Several studies have indicated that the most notable impact on Lake Ziway comes from the massive use of agrochemicals by horticultural and floricultural activities within its catchment (Fianko *et al*., 2011, Tadele, 2012, Beyene *et al*., 2014). Moreover, the water from the lake is also critically needed to supply Ziway Town with potable water. Because of the high fluoride content in the groundwater the Batu (Ziway) Water Supply Service Enterprise (Batu WSSE) had to abandon its groundwater exploration wells approximately 15 years ago, and shifted to using the water from Lake Ziway as drinking water source (APHRD, 2010; Jansen *et al*., 2011).

The water residence time is the time required to refill an empty lake with its natural inflow (Rueda and Cowen, 2005). Water residence time for Lake Ziway has implications for the storage and release of nutrients and contaminants. Water quality problems associated with algal growth, are likely to arise as a consequence of insufficient water inflows to circulate and/or displace the water stored in the lake. Under long residence times, blooms of blue green algae can occur. When the residence time is reduced, the algal biomass becomes regulated by the rate at which it is removed from the shallow lake by flushing. Water residence time analyses are very useful indicators as to whether the water body is at significant risk of algal blooms which indicates lake eutrophication process (Rueda and Cowen, 2005).

The hydrology and nutrients of Lake Ziway can be described in terms of the components of its water and nutrient budgets, respectively. The water budget and the nutrient balance of the lake can be evaluated according to Han (2010) by using the following equations:

$$\Delta S = (\mathrm{PPT} + \mathrm{SW_{in}} + \mathrm{GW_{in}}) - (\mathrm{E_{vap}} + \mathrm{SW_{out}} + \mathrm{GW_{out}}) \qquad 1.1$$

Where ΔS is the change in the volume of water stored in the lake during the period of interest and is equal to the sum of the volume of water entering the lake minus the sum of the volume of water leaving the lake. Water enters to the lake from precipitation (PPT), surface water inflow (SW_{in}), and ground water inflow (GW_{in}). Water leaves the lake through evaporation (E_{vap}), surface water outflow (SW_{out}), and ground water out flow (GW_{out}).

Nutrient balance is described by the following equation:

$$\Delta N = (PPT + N_{in}) - N_{out} \tag{1.2}$$

Where ΔN is the nutrient balance, PPT is nutrients come from the precipitation, and N_{in} is surface nutrient inflow, N_{out} is surface nutrient outflow.

Agrochemical loads to Lake Ziway ecosystems come mainly from two rivers, Meki River that drains part of the western highland which contributes 278 MCM $year^{-1}$ and Ketar River which drains the Arsi Mountains to the east and contributes 302 MCM $year^{-1}$ water to the lake. Moreover, the floriculture effluent, different agricultural activities, animal grazing, irrigation and fishing activities mainly contribute to the external nutrient loading to the lake ecosystem (Figures 1.1 and 1.2).

Lake Ziway is drained by Bulbula River in the south-west which empties into Lake Abijata. The hydrological characteristic of the lake is also affected by water abstractions from the lake for irrigation and industrial uses (Figure 1.1). The nutrient inputs from the Lake Watershed, residence time and water balance as well as nutrient balance have their own contribution for the internal and external nutrient loads and trophic status of the lake ecosystem.

Figure 1.1 Conceptual agrochemical loading model of Lake Ziway

Lake Ziway catchment is currently inhabited by about 2 million people (Ethiopian Central Statistics Authority, 2013, unpublished data) and about 1.9 million livestock (Meshesha *et al.* 2012). Agriculture is the most dominant land use system contributing to the livelihoods of the majority of the catchment population (Figure 1. 2). The agricultural sector is characterized by small-scale subsistence-based farming and rising of livestock. About 74.3 % of the total land-use types within the catchment are agricultural lands (Figure 1. 2). Lake Ziway water demands have massively increased, along with increased population and intensification of agriculture since the end of the last decade (Meshesha *et al.* 2012; Desta *et al*., 2016). The current water abstraction rate is approximately 223 MCM per year (Desta *et al*., 2016). The high agricultural activities around the lake catchment lead to a high external agrochemical load to the lake ecosystem (Meshesha *et al.* 2012).

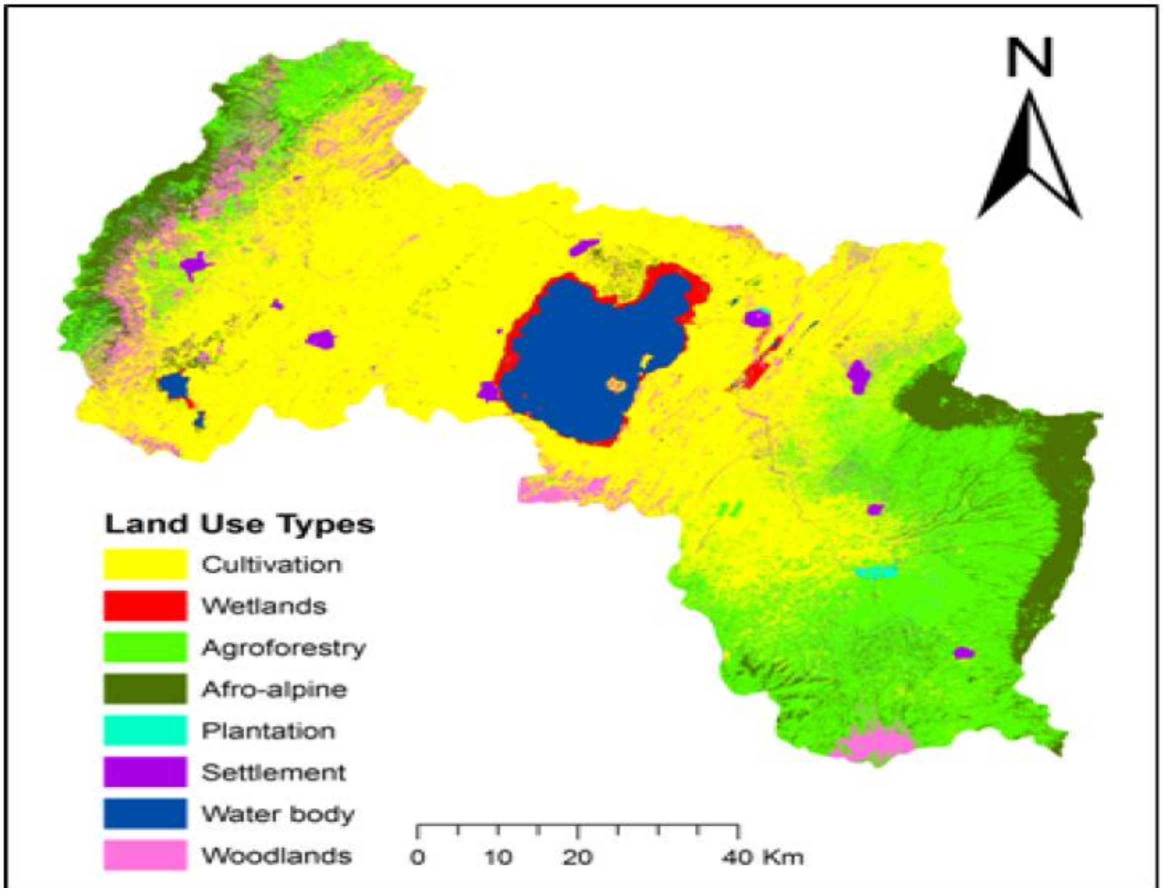

Figure 1.2 Land-use map of the Lake Ziway catchment (source: Desta *et al*., 2016) (Year of satellite image taken, 2013)

More intensive agriculture, coupled with the difficulties of managing the associated discharges of nutrients from these land-use practices, can also adversely affect Lake Ziway water quality (Edgar, 2008). Other human activities like application of fertilizers and pesticides in the lake catchment also affected the lake water quality (Ayenew and Legesse, 2007; Spliethoff *et al.*, 2009). With the increasing impacts of agricultural activities, the presence of water hyacinths near the western shoreline of Lake Ziway is an indicator of eutrophication (Jansen *et al*., 2007).

Moreover, the state of the water quality depends simultaneously on many factors/parameters, monitoring systems are multivariate in nature, and hence, the classification, modeling and interpretation of the monitoring data sets have to be performed by the use of chemometrics and environmetrics (Astel *et al*. 2008). Multivariate methods, such as principal component analysis, cluster analysis and discriminant analysis identify the possible factors/sources that influence water systems (Dolotov *et al.* 2010) and offer valuable tool for developing appropriate strategies for effective management of these water resources (Astel *et al.* 2008; Palma *et al.* 2010).

1.2 Statement of the problem

Accelerated eutrophication caused by the excess inputs of nitrogen (N) and phosphorus (P) from agricultural and industrial activities can pose a serious threat on the lake's ecosystem. The rate of loading of nutrients to lakes varies both in space and time. There have been several studies on various aspects of the ecology of Lake Ziway (Gebre-Mariam, 1998; Kebede and Willen, 1998; Beneberu, 2005; Ayenew *et al*., 2007, 2008; Tilahun, 2006, 2010; Mazengia, 2008; Tadele, 2012; Tamire and Mengistu, 2012, 2014; Beyene, *et al*., 2014). For instance, Tadele (2012) studied the environmental impacts of floriculture industries on lake Ziway: pollution profiles of lake Ziway along floriculture industries; Beyene *et al*., (2014) studied about levels and effects of organochlorine pesticides and heavy metals in aquatic ecosystem on lake Ziway and Hawasa; Tamire and Mengistu, (2014) have investigated macrophytes community diversity, production, decomposition trends and interaction with plankton in lake Ziway; Desta *et al*., (2016) also studied on the degradation of Lake Ziway, Ethiopia: A study of the environmental perceptions of school students, etc.

These and many other works reported that developmental activities such as fisheries, irrigated agriculture (commercial farming), cattle watering, car washing, unhygienic human sanitation, and the rapid expansion of the flower industry may affect the ecological integrity of the lake system. Furthermore, the uncontrolled overuse of pesticides for both the agricultural and industrial activities around Lake Ziway, have been indicated as the other most important potential threats to the lake water quality. Pesticides having high leaching potentials, high surface loss potentials and persistent in the soil and bioaccumulate in the aquatic organisms are of greatest concern (Amare and Abate, 2007; Berhanu, 2008; Fianko *et al*., 2011; Beyene, *et al*., 2014).

All of the aforementioned activities are likely to cause temporal and spatial changes in agrochemical loads, dynamics and impacts in the lake and overall degradation of the water quality.

Most researchers suggested that Lake Ziway is currently has excessive nutrient load, the water is turbid, toxic algae developed, submerged macrophytes disappears, fish stock changed toward less desirable species and top-down control of phytoplankton by zooplankton has disappeared as wells (Tilahun, 2006, 2010; Tadele, 2012; Tamire and Mengistu, 2012, 2014; Teklu *et al.*, 2016). Jansen *et al*., (2007) also recommended that detailed water quality assessment of Lake Ziway should be conducted. Moreover, understanding eutrophication source from the catchments, as well as knowledge about its fate in aquatic system (interaction with bottom sediments) is needed for identifying and reducing the impacts on lake ecosystems. However, studies on internal and external agrochemical loads, dynamics and their impacts on Lake Ziway are very limited. In addition, there are only very little studies on the comprehensive spatio-temporal variations and the systematic identification of the potential pollution sources that affect the water qualities of Lake Ziway. Thus, reliable information on the water quality and pollution sources is important for effective lake water management.

Multivariate statistical techniques have been widely used in the analysis of surface water quality, and in the assessment of temporal and spatial variations caused by natural and anthropogenic factors (Simeonov *et al*., 2010; Camacho *et al*., 2015). The lack of information on the aforementioned pollution related aspects of Lake Ziway has limited the lake and lake basin management decision making on effective ways to reduce the agrochemical loads on the lake ecosystem. Furthermore, the number of studies conducted regarding the release of nutrients from sediment to water and the dynamics of nitrogen and phosphorus species in sediment of Lake Ziway in Ethiopia is extremely low. To the best of our knowledge, there is no previous study reported on nutrient load in sediment depth profiles. Knowledge of nutrient dynamics associated with sediments is therefore of crucial importance in understanding and predicting a lake ecosystem influenced by internal nutrient load. There is also a very limited work done the trophic status associated with nutrient load of Lake Ziway.

Therefore, there is a need to conduct an intensive research to fill these gaps and provide baseline data with regard to spatial and temporal variations in internal and external agrochemical loads, dynamics and impacts of agrochemicals on the lake ecosystem in order to propose suitable measures for sustainable management of the lake.

1.3. Research hypothesis

The main research hypothesis is the contemporary human and animal demographic changes, environmental degradation, agrochemical inputs, and climatic change that are severely affecting Lake Ziway and its watershed. These changes are also likely to have a negative impact on the quality of life that is dependent on the lake. Therefore, in this study, it is hypothesized that the contemporary changes are assessed by using standard chemical methods so as to develop a comprehensive management model towards protection of Lake Ziway for sustainable development. The developed model can be used to identify and manage sources of agrochemical loads and its impact so as to promote protection and restoration of Lake Ziway ecosystem. The generated information can also help to improve the public health in the lake watershed.

1.4. Objective(s)

1.4.1 General objective

The main objective of the study is to investigate the external and internal agrochemical load, their dynamics, and impacts on Lake Ziway ecosystem and suggest possible management options for sustainable use of the lake.

1.4.2 Specific objectives

1. To assess the spatio-temporal variations of nutrients and physicochemical water quality parameters of Lake Ziway
2. To investigate the Nutrient dynamics and external nutrient loading in relation to climatic and hydrological factors in Lake Ziway
3. To evaluate the internal nutrient load dynamics from the sediment in Lake Ziway
4. To determine the trophic status of Lake Ziway based on the trophic state variables.

Chapter 2: Literature review

2.1 Physico-chemical water quality parameters

Environmental water pollution is a serious problem in human life. The health of surface water depends on the quality of its water, which is influenced by the presence of pollutants. The quality of water is generally assessed by a range of water quality parameters, which express physical, chemical and biological composition of water (Medudhula *et al*., 2012). Adak *et al.* (2002) reported that different physico-chemical parameters of water are very important for effective management of water through their appropriate control. In the understanding of the ecology of freshwater systems, analyses of physicochemical parameters are very essential. For instance, DO is a function of temperature, pressure, salinity and biological activity in the water body (Radojevic and Bashkin, 2006). Kaul *et al.* (1980) stated that nutrients have been used as the most reliable parameter of lake eutrophication. According to them a change in the trophic status of a lake is associated with an increase in its nutrient status, thus, an increase in conductivity values indicates a tendency towards higher level of eutrophication. Krishnan (2008) reported that phosphorus appeared to be a limiting factor for growth of the aquatic plants but its excess amount causes water pollution. Water quality parameters such as temperature, pH, DO, EC and alkalinity are major factors that regulate various abiotic as well as biotic activities in the aquatic ecosystem (Ojha and Mandloi, 2004; Radhika *et al.*, 2004; Camacho *et al*., 2015). This survey of the literature on ecological investigations of water bodies showed that long-term monitoring and comprehensive analysis of the physico-chemical parameters is crucial for a holistic approach to solve environmental problems of such systems.

2.2 Agrochemical contaminants on surface water quality

Agrochemicals are an integral parts of current agriculture production systems around the world. Accordingly, the use of agrochemicals (fertilizers and pesticides) remains common practices particularly in many countries in the tropical world (Fianko et *al*., 2011). In recent decades, population growth, agricultural practices and sewage runoff from urban areas have increased nutrient inputs many folds to the level of their natural occurrence, resulting in accelerated eutrophication

(Varol *et al.,* 2009; Razmkhah, *et al*., 2010). Many urban and rural lakes have vanished under this pressure with worldwide environmental concerns (Camacho *et al*., 2015). A good example is Lake Haramaya, Ethiopia (Lemma, 2003). However, in those lakes that continue to “receiving pollution” for drinking water supply is either substantially reduced or it has become non-potable, flood absorption capacity impaired, biodiversity threatened and there is a decrease in fish productivity (Palma *et al.*, 2010; Sridhar *et al*., 2014).

2.2.1 Fertilizers

The use of chemical fertilizers has increased tremendously worldwide since the 1960s and is largely responsible for the green “revolution” that is the massive increase in agricultural production obtained from the same piece of land with the help of mineral fertilizers (nitrogen, phosphorus, potassium) and intensive irrigation (Carvalho, 2006). Use of excessive amounts and improper application of fertilizers may result in harmful chemical contamination of surface and groundwater (David, 2002). Fertilizers are significant pollution threats because of their high solubility and the frequent application of large volumes of irrigation water (Thrupp and Lori Ann, 1998). Nitrogen and phosphorus must be managed carefully to ensure that excess amounts do not degrade water quality. Too much nitrogen and phosphorus along with carbon in surface water cause eutrophication (excessive algae growth) in rivers, lakes, and ponds (David, 2002). The reverse is also true; decreasing the losses of nitrogen and phosphorous from agriculture does not quickly change eutrophic waters to pristine waters (Restrepo, 2002).

Nutrients coming from the application of excessive fertilizers are the primary nutrients that in excessive amounts pollute our lakes, streams, and wetlands. Concentrations of nitrogen and phosphorus species are highly dynamic because they may be utilized, stored, transformed, and excreted rapidly and repeatedly by the various aquatic organisms (Krishnan, 2008). The dynamics of dissolved nutrients depend on their being transported from the catchment to the water column and on all the transfer processes linking the water column to the streambed (Wetzel and Likens, 2000) which eventually become potential sources. Therefore, the main inputs contributing to the nutrient balance and status of these aquatic systems are the external point and diffuse sources plus the internal biogeochemical mineralization processes (Jonathan, 2012**).** Nutrients are essential for survival, reproduction and growth of phytoplankton but the extreme input of nutrients into aquatic ecosystems leads to an excessive algal growth which is referred to as eutrophication (Wetzel and Likens, 2000; Kalff, 2002; Krishnan, 2008).

Nowadays, more than 75 % of the total lands in Lake Ziway catchment are characterized by agricultural land and people use huge amount of fertilizers in these areas. The most important fertilizers distributed around Lake Ziway catchment are urea and DAP (Table 2.1) (Desta, 2016). As shown in Table 2.1, there is an increasing trend of using fertilizers from 2009 to 2013 in Lake Ziway watershed. Moreover, in floriculture farming around Lake Ziway, there is extremely high usage of fertilizer due to high crop demand and maintain a year-round production of cut-flowers. Unfortunately, the data for the use of fertilizers used by floriculture farming around Lake Ziway are not available. The Dutch standards are 1190 kg N /ha and 280 kg P/ha for roses cultivated under artificial light (David, 2002). It is expected that nutrient rates in Ethiopia are in the same range.

Table 2.1 Fertilizers (DAP and urea) used in Lake Ziway Catchment from 2009 to 2014 (in '000 kg) (Desta, 2016)

Year	2009	2010	2011	2012	2013
Total	127	150	149	173	226

2.2.2 Pesticides

The environmental impact of pesticides is usually big. Over 98 percent of sprayed insecticides and 95 percent of herbicides reach destinations other than target species, including non-targeted, air, water, bottom sediments and food. Inappropriate application of pesticides can lead to pest resistance and kill beneficial insects (Tadeo, 2008). The factors that influence the amount of pesticides drifting away from their intended targets are chemical properties of the pesticide, its soil binding ability, its vapour pressure, its water solubility and its resistance to be broken over time (Tadeo, 2008).

The contaminations effects of water by pesticides generally arise from two scenarios: - (i) human health risks when water (e.g., surface water and groundwater) is used for drinking and (ii) Eco-toxicological effects when non-target organisms (e.g., aquatic organisms) are exposed to such water in their habitats (Kishi *et al*., 1995; Tadeo, 2008; Canbay *et al*., 2014). Both the European Union (EU) and the United States have adopted stringent limits for pesticide presence in drinking water. For instance, EU regulations for drinking water quality set a limit of 0.5 mg L^{-1} for the sum of all pesticides and 0.1 mg L^{-1} for each compound. However, when acute or chronic toxicities or other ecological effects (e.g., bioaccumulation) are implied, water quality limits can be much lower than those for drinking water. For instance, in the total maximum daily loads (TMDL) established for diazinon and chlorpyrifos for a catchment in California, the numerical targets for diazinon were set at 80 ng L^{-1} for acute toxicity and 50 ng L^{-1} for chronic toxicity, and those for chlorpyrifos at 20 ng L^{-1} for acute toxicity and 14 ng L^{-1} for chronic toxicity (Canbay *et al*., 2014).

The amount and kind of pesticides in water of a given area depend largely on the intensity of production required and kind of crops. However, the transport of pesticides out of their target area of application results in the presence and accumulation of these compounds in many parts of the hydrosphere (Albanis *et al.*, 1998, Tadeo, 2008). Moreover, distribution and availability into environmental compartments, as well as their toxicological effects is directly related to their mode of action (e.g., herbicides, insecticides, plant growth regulators, fungicides, bactericides, defoliants, desiccants). After applications in the field, pesticides undergo different types of degradation pathways via biotic, abiotic and hydrolysis processes. Following such processes, leaching to groundwater and runoff to surface water occurs after rainfall and/or irrigation practices. Consequently, there is a risk of pesticide contamination of natural waters and that needs to be assessed (Vidal *et al*., 2000; Kuster *et al.*, 2009; Bagheri *et al*., 2009).

2.2.3 Distributions and impacts of pesticide in Ethiopia

Chemical pesticides use in Ethiopia was historically low. However, recent developments in increased food production and expansions in floriculture industry have resulted in higher consumption of chemical pesticides (Wissem *et al*., 2011). Figure 2.1 shows that 2-4 D (2, 4-Dichlorophenoxyacetic acid) is the most imported pesticide between the years 2006 to 2010 followed by glyphosate and endosulfan (APHRD, 2010).

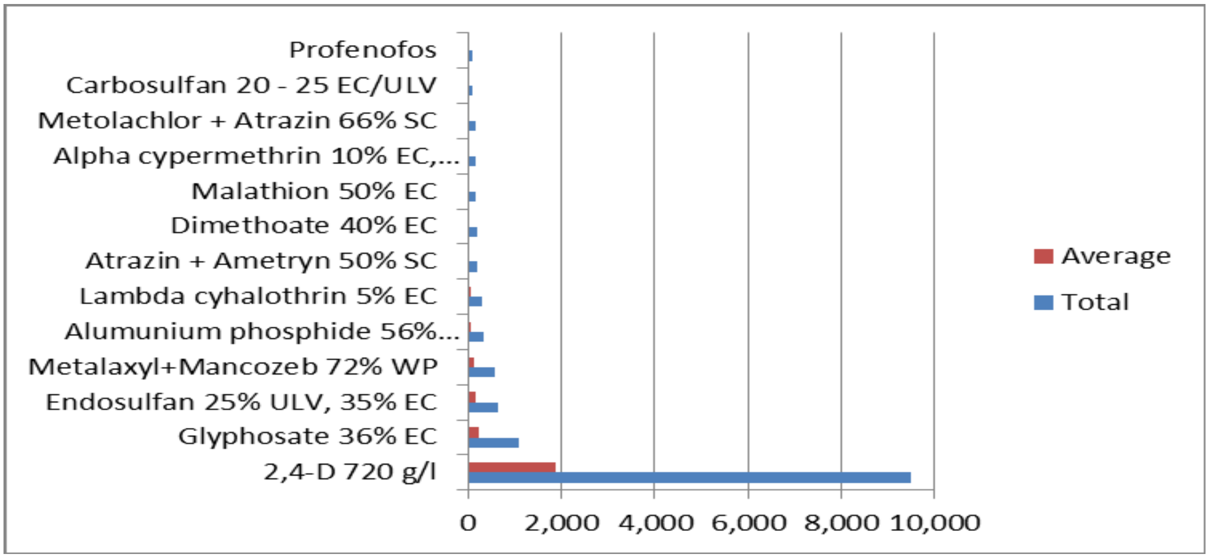

Figure 2.1 Major pesticides imported between the years 2006 - 2010 in Ethiopia (Tones) (APHRD, 2010)

The impacts of pesticides in Ethiopia are likely to be aggravated by the limited knowledge among users on toxicological and chemical properties of these substances. Labels on pesticide containers are in a language which cannot be understood or missing by local population, let alone knowledge of their effects. In other words, little is known about the long term and indirect effects of pesticides on rural and urban communities as well as on local and national food production systems (Taddese and Asferachew, 2008). The awareness of farmers regarding application of pesticides in Ethiopia has been documented as one of the poorest in Africa (Colin and Tingle, 2008; Taddese and Asferachew, 2008.

Exposure to pesticides is also pervasive health threats to Ethiopian children living in rural areas and particularly to those who work in agricultural field. Children of local farmers suffer from frequent exposure to pesticide residues through various exposure routes, including directly in the fields or in the home as their parents track in the toxic residues after returning from work in the fields (Daniel, 2003). For instance, from the case studies done by (Tadesse and Asferachew, 2008; Bezabih *et al*., 2010) in Ethiopia, most farmers are expected to spray their own crop with the technical assistance of development agents, twenty farmers in Garbi Farmers' Association (FA), one farmer each from Hurufalable and Gulba Farmer Associations are currently engaged in pesticide trade in violation to the special decree No. 20/1990.

Moreover, farmers in Abine Germami farmer association are preparing mixtures using different products indicated as follows***:*** *Malathion + Thionex; Thionex + Mancozeb; Selecron + Ridomil; Bayleton + Curzate; Malathion + Karate*. These farmers are attempting to increase the potency of the combined products as a prophylactic blanket application to control pests on vegetables, mostly onions and tomatoes (Tadesse and Asferachew, 2008; Bezabih *et al*., 2010).

After the application of pesticides, their residues enter the aquatic environments through effluent release, discharges of domestic sewage and industrial wastewater, atmospheric deposition, runoff from agricultural fields, leaching, equipment washing, and disposal of empty containers in open field and direct dumping of wastes into the water systems (Yang *et al*., 2005). Pesticides could then get distributed to the ecosystem components, such as water and sediment, and bioaccumulate in organisms of the food chain. The sediment reservoir is important because it serves as a sink from which water and biota are continuously polluted. Aquatic organisms also are directly or in directly linked to the food web of terrestrial organisms, with some aquatic biota, such as fish, being consumed by people and wildlife (William, 2013; Mahboob *et al*., 2013; Beyene *et al.*, 2014). Therefore, pesticide residues in surface water, sediments and biota are extremely important because of their potential impacts on aquatic ecosystems and their implications on drinking water sources (Dem *et al.*, 2007).

2.3 Potential impacts of climatic and hydrological factors on surface water quality

Natural processes influencing water quality include precipitation rate, weathering processes, and sediment transport, whereas anthropogenic activities include urban development and expansion and industrial and agricultural practices. These activities often result in the degradation of water quality, physical habitat, and biological integrity of lotic systems (Varol *et al*., 2009). Seasonal variations in precipitation, surface runoff, interflow, groundwater flow, and pumped in and outflow have a strong effect on river discharge and subsequently on the concentration of pollutants in surface water (Palma *et al*., 2010).

There is increasing evidence that climate change is beginning to have a noticeable effect on lake ecosystems (Solheim *et al*., 2010). The effect of climate change can vary depending on geographical location, regional climate, land use in lake basins and variations in lake characteristics, such as surface area and depth. Besides the expected effects of changes in temperature and precipitation, more projected frequent extreme events (heat waves, storms, extreme rains) may also potentially affect ecosystem stability by enhancing mismatch of species distributions and interactions which lead to greater sensitivity to increasing nutrient load (Figure 2.2) (Mitsch and Gosselink, 2000; Jeppesen *et al*., 2014).

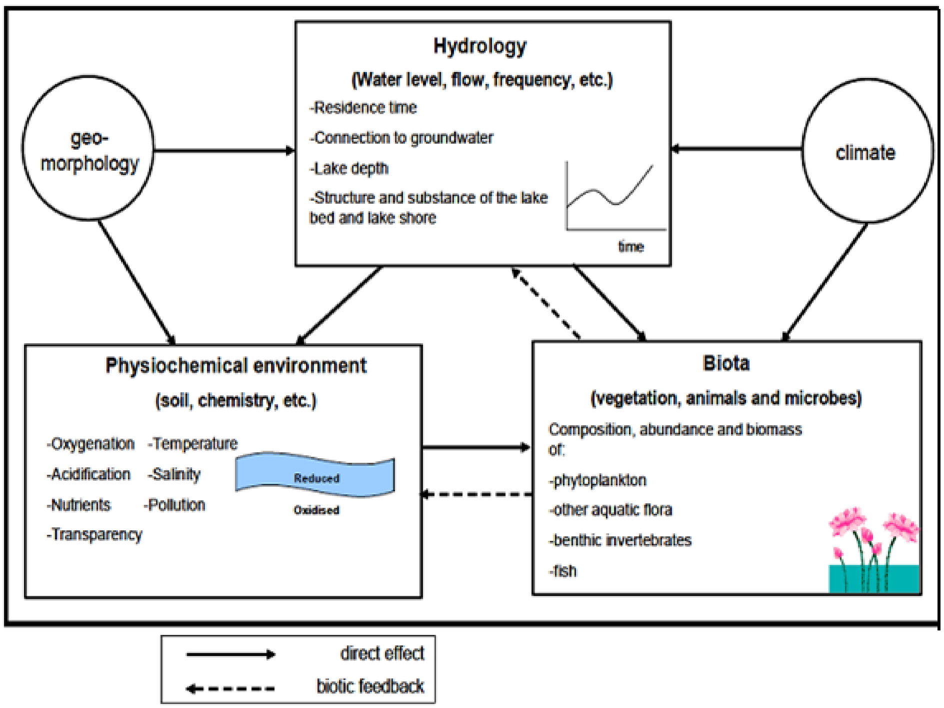

Figure 2.2 Relationships between hydromorphology, biology and physicochemical water quality parameters for Lake Ecosystem (Mitsch and Gosselink, 2000)

According to the IPCC report by 2100 global average air temperature would rise between 1.4 and 5.8 °C and precipitation would vary up to ± 20 % from the 1990 level (Zeray *et al.*, 2007). Being one of the very sensitive sectors, climate change can cause significant impacts on water resources. Developing countries, such as Ethiopia, is currently vulnerable to climate change impacts mainly because of the large dependence of their economy on rain fed agriculture. Hence, assessing vulnerability of water resources to climatic and hydrological factors in relation to external nutrient loading is very crucial. This would require appropriate adaptation measures that must be taken ahead of time (Erik and Brian, 2009). The external nutrient load is generally predicted to increase due to climatic and hydrological factors potentially resulting in eutrophication problems in areas where precipitation and river flow are projected to increase (Moore, 2007).

In tropical Africa, climate is characterized by large fluctuations in rainfall, lake level and river flow regimes **(**Matzinger and Martin, 2007)**.** Changes in annual and seasonal temperature and precipitation serve as primary indicators of climate change. These also drive changes in hydrological and biological indicators as well as increased nutrient loads in the lake ecosystem (Hayhoe *et al*., 2006).

Discharges from point sources like rivers, effluents of the industries, waste disposal and wastewater treatment facilities and non-point sources such as agricultural, urban surface runoff, and other land uses are the major pollution sources of dissolved and particulate nutrients to aquatic ecosystems. At the same time the spatial and temporal distribution of these contaminants are the results of numerous anthropogenic activities developed in the impacted watersheds. Unfortunately, in many parts of the world, such contributions lead to the development of eutrophication of many water bodies (Ismail and Naji, 2011; Jonathan, 2012).

2.4 Sediment nutrient dynamics in lake ecosystems

The most common way in which humans affect aquatic ecosystems is through altering nutrient dynamics. Most tropical African lakes are facing problems of rapid population growth in the riparian communities, which normally discharge pollutants into the lakes. This has led to the rapid deterioration of water quality in receiving lakes, and some lakes are experiencing a decrease in fish production (Wandiga, 2003).

Sediments are known to be the ultimate sinks for contaminants discharged into the environment and become potential sources as they play a role in the remobilization of contaminants in aquatic systems (Doong *et al*., 2002; Malferrari *et al*., 2009). Seasonal riverine intrusions bring a variety of contaminants such as fertilizers, pesticides, manures, terrestrial vegetation and domestic and industrial wastes from upstream catchments to downstream lakes (Chan, 2011).

Internal nutrient loads have significant influence on the water quality of shallow lakes in addition to external nutrient loads. These internal loads occur through diffusive flux from the sediment to the water column above and resuspension of sediments. This source of nutrient is major contributor of phosphorus/ nitrogen concentration in the water column, as well as influencing lake trophic status (Fisher *et al*., 2005). Sediments are important sources of nutrients to freshwater ecosystems (Nowlin *et al*., 2005). According to Niemisto *et al*. (2012) the bottom sediments of lakes contain large pools of nutrients. For numerous reasons, these nutrients stored in the sediment may return to the water column and cause internal nutrient loading, with consequences for the water quality (Steinman *et al*., 2006). For instance, the release of phosphorus and nitrogen species from lake sediments has been examined for decades. Historically, phosphorus input from lake sediments has received much more attention from researchers than nitrogen input because of the complex nature of nitrogen transformations in lake sediments and the fact that phosphorus often limits the biomass and productivity of plankton communities (Nowlin *et al*., 2005).

A conceptual diagram of the processes influencing transformations of nitrogen and phosphorus species in sediment is shown in Figure 2.3. In general, the bottom sediments, which are rich in iron and manganese, will readily desorb phosphorus and release it to the sediment pore water and then into the water column when exposed to anoxic conditions (Hamilton *et al*., 2004; North *et al*, 2015).

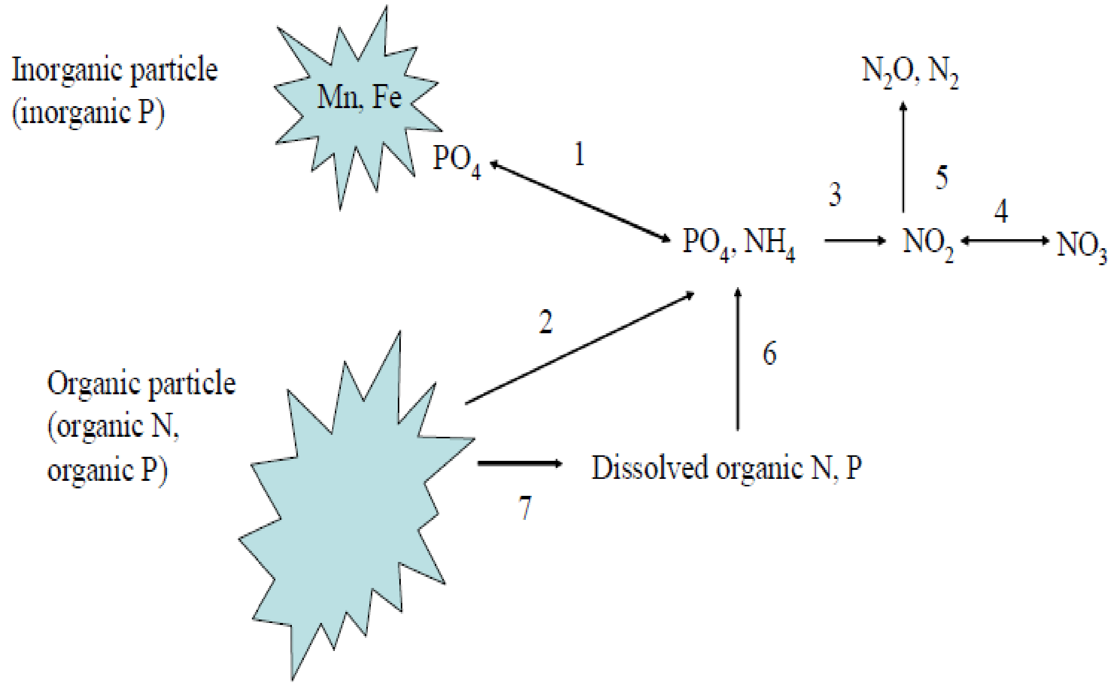

Figure 2.3 Major transformations of phosphorus and nitrogen in bottom sediments 1 (right arrow/ left arrow) = adsorption/desorption of phosphorus from inorganic particles containing oxidized forms of iron and manganese, 2, 6, 7 = production of dissolved forms of phosphorus through breakdown of organic matter, 3, 4 (right arrow) = nitrification, 4 (left arrow), 5 = denitrification (North *et al*, 2015).

Many shallow lakes are unique and vulnerable ecosystems. The structural and functional properties of these lakes like their morphology, biogeochemical cycles and food-web structure, are directly related to lake size, depth and shape (Kangur and Mols, 2008). In shallow lakes like Ziway, wind-induced sediment resuspension is often the main cause of internal load (Steinman *et al.*, 2006). The cumulative impact of multiple anthropogenic factors such as eutrophication and climate factors can result in increased nutrient load from sediments causing declines in water quality manifested as increases in undesirable algal populations, taste, odor, and color problems. These problems are especially important if the lake is used as a drinking water source (North *et al.*, 2015).

2.5 Metrics for eutrophication and its consequences

2.5.1 What is eutrophication?

Assessing the impacts of eutrophication is not a straightforward procedure, since eutrophication occurs as a result of the complex interplay between nutrient availability, light conditions, temperature, residence time and flow conditions (Jeppesen *et al*., 2007). Eutrophication or nutrient enrichment in the broadest sense describes the biological effects of the elevation in the supply of plant nutrients in natural waters either as solutes or bound to organic and inorganic particles, resulting to reduction in water quality (UNEPIETC, 1999). Cooke *et al.* (1993) gave a holistic definition of eutrophication, which includes, organic matter input into lakes and reservoirs leading to loss of volume. This subsequently results to release of nutrients through mineralization or from the sediment when the organic matter stimulates respiration and dissolved oxygen is depleted. However there is a difference between eutrophication and natural aging process of a lakes and reservoirs with the latter reflect the cumulative impacts of all the water and materials flow into the lake.

The lake fills slowly with soils and other materials; either carried by the inflowing waters or organic material from in lake production and eventually becomes a marsh and ultimately, a terrestrial system. This process takes hundreds of thousands of years. Unlike eutrophication, water systems undergoing natural aging process have good water quality and exhibit a diverse biological community throughout most of their existence (Harper 1992). Water bodies can be classified into different trophic categories. The categories generally used today either denote the nutrient "status", or describe the effects of the nutrients on the general water quality and/or trophic conditions of a water body. However, attempts have been made to relate descriptive trophic terms to specific "boundary" values for certain water quality parameters, as illustrated in Table 2.2.

Table 2.2 Indicative limit values for TP, SD and Chla of the quality parameters in surface water (OECD, 1982)

Trophic level		**Ultra-oligotrophic**	**Oligotrophic**	**Mesotrophic**	**Eutrophic**	**Hypereutrophic**
TP(μg/L)	Mean	<4	4 – 10	10 – 35	35 – 100	>100
Chla(μg/L)	Mean	<1	<2.5	2.5 – 8	8- 25	> 25
	Max	< 2.5	< 8	8 -25	25 – 75	>75
SD (m)	Mean	>12	> 6	6 – 3	3 – 1.5	< 1.5
	Min	> 6	> 3	3- 1.5	1.5 – 0.7	< 0.7

KEY

TP = mean annual in-lake total phosphorus concentration (μg L^{-1}; Mean chl-a = mean annual chlorophyll a concentration in surface waters (μg L^{-1}); Maximum chla-a = peak annual chloro-phyll a concentration in surface waters (μg L^{-1}); Mean Secchi = mean annual secchi depth transparency (m); Minimum Secchi = minimum annual secchi depth transparency (m).

With an ever increasing intensity of the exploitation of the lake catchments and their resources, monitoring of water quality variables is imperative to obtain insight into the temporal and spatial variations associated with its prevailing nutrient loads and trophic status. The trophic status of a freshwater ecosystem reflects its environmental quality. That is why several trophic indicators have been developed for such water bodies based on their respective chemical, physical and bio-logical parameters (Kehayias and Doulka, 2014).

The assessment of trophic status of water bodies and determining their limiting factors are key steps in pollution control and eutrophication management (Barki and Singa, 2014). Limnologists have developed many methods to assess the trophic status of surface water. Among these devel-oped methods, Carlson's Trophic State Index (TSI) which is one of the most widely accepted methods in evaluating the trophic status of surface water bodies (Tan *et al.*, 2014). This method is a continuous number in assessing the trophic status, which can provide a more precise assess-ment of the trophic status than other conventional methods which only provide rough typological trophic information (Tan *et al.*, 2014). In addition, Carlson's TSI is easy to implement and ana-lyze the limiting factors of the trophic status of water bodies (Carlson, 1991). Table 2.3 indicates the range of the Carlson's trophic state index (CTSI) values and classification of lakes (Carlson, 1977; Barki and Singa, 2014).

Table 2.3 Classification of lakes based on the Carlson's Trophic State Index values (Barki and Singa, 2014)

TSI values	Trophic status	Attributes
< 30	Oligotrophic	Clear water, oxygen throughout the year in the hypolimnion
30 – 40	Oligotrophic	A lake will still exhibit oligotrophy, but some shallower lakes will become anoxic
40 – 50	Mesotrophic	Water moderately clear, but increasing probability of anoxia
50 – 60	Eutrophic	Lower boundary of classical eutrophy: decrease transparency, warm water fisheries only
60 – 70	Eutrophic	Dominance of blue-green algae, algal scum probable, extensive macrophytes problems
70 – 80	Eutrophic	Heavy algal blooms possible
>80	Hypereutrophic	Algal scum, summer fish kills, few macrophytes

Likewise, OECD, (1982) established trophic classification criteria according to TP, Chl*a*, and SD for the last 34 years (Table 2.2). This trophic classification was accepted by the international community as standards, and many countries use these criteria to determine the quality of surface water bodies.

2.5.2 What causes eutrophication?

Liebig first invented the nutrient-limiting concept, in 1840 (Liebig 1872). He found that, the materials needed by the crop in minute quantities often limited the yield of terrestrial crops. He further found that the ultimate yield of any crop was limited by one essential nutrient, which was most scarce in the environment in relation to the specific needs of the crop (Welch 1980). Despite some minor misuse of this concept (Wetzel, 2000), it has been applied to phytoplankton growth in water systems ever since. Therefore a limiting nutrient in water systems is the nutrient available most closely in amounts below the critical minimum required by the sum of phytoplankton species, thus regulating the algal biomass, hence eutrophication. Tilman *et al.* (1982) suggested that one should not refer to a lake as either "phosphorus" or "nitrogen" limited, but rather recognize individual algal species "not lakes" are the ones limited by a particular nutrient.

The ratio at which these nutrients are taken up and used by the algae, reflect the composition of these elements in their cellular materials. Redfield (1934) determined the cellular content and produced the “Redfield Ratio” of 106 C: 16 N: 1 P. This ratio has become a standard reference in Limnology, although Tilman *et al.* (1982) suggest that, different algal species can assimilate nutrients in different quantities and at different rates, on the basis of “resource competition”. He further provided support of his idea by noting that diatoms grow better under low phosphorus concentration, which indicates that they are superior competitors for phosphorus. Lang and Brown (1981) reported that some cyanobacteria were more efficient in phosphorus uptake, while Smith (1982) showed that the small algal cells are more efficient than the large cells during nutrient-deficit conditions.

Nowadays, with the increase of world population and lack of space, agricultural productivity is increased by intensive practices rather than expanding agricultural fields. This led to further increase in nutrient inputs and intensification of agriculture. In countries like Ethiopia where the plant-soil-water relations are not monitored regularly, excess and untimely application of nutrients into farmlands lead to anthropogenic eutrophication problems in freshwater that are at the receiving ends of the hydrologic system (Erik *et al.*, 2014).

As a consequence of such human actions, eutrophication in freshwater lakes is currently a major environmental concern all over the world due to the high anthropogenic input of phosphorus (P) and nitrogen (N) from agriculture, industry and household waste waters. This high input of nutrients impacted aquatic ecosystems by enhancing lake productivity, leading to undesirable changes in algal community structure, decrease in light availability and consequent eutrophication of these ecosystems (Abayomi *et al*., 2011; Ansari and Gill, 2014; Immers *et al.*, 2015). It is known that if nutrient load is excessive, the growth of phytoplankton is favored and this has significant negative implications for the overall water quality and biodiversity of the lake. As a consequence of these impacts, the water becomes turbid, toxic algae may develop, submerged macrophytes disappear, fish stocks change toward less desirable species and top-down control by zooplankton on phytoplankton disappears (Søndergaard *et al*. 2001).

Chapter 3: Materials and methods

3.1 Description of the study area

Lake Ziway is a shallow freshwater lake found in the northern part of the Ethiopian Rift Valley and is located at $08^{0}01'$N and $38^{0}47'$E (Figure 3.1) and about 163 km south of Addis Ababa, in Oromia Region. The Woredas sharing the lake are Adami Tullu, Jido Kombolcha, Dugda Bora, and Ziway Dugda (Mepham, *et al.*, 1992; Turdu *et al.*, 1999; Legesse *et al*., 2001, Lijalem, *et al.*, 2007). Table 3.1 describes the sampling sites in the study area.

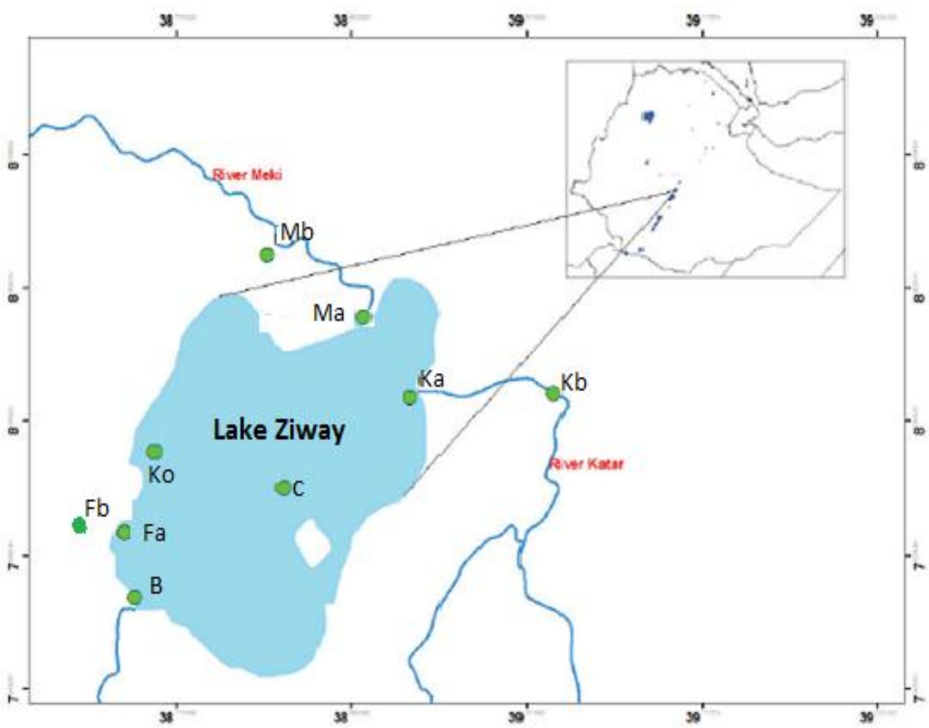

Figure 3.1 Lake Ziway sampling sites in the lake and its feeder rivers in Ethiopia

Table 3.1 Geographic coordinates of the sample sites (Abr. for abbreviation)

Abr.	Sampling site names	Longitude	Latitude
F_b	Floriculture effluent	38.044020	7.54715
B	Bulbula River mouth	38.743261	7.899822
F_a	Around floriculture industries	38.740261	7.917644
C	Central part of the lake	38.841453	7.971989
K_a	Ketar River mouth	38.924100	8.031094
M_a	Meki River mouth	38.848733	8.051128
M_b	Meki River at Meki Gage Station	38.835000	8.103000
K_b	Ketar River at Abura Gage Station	39.019033	8.032822
K_o	Korekonch	38.755692	7.995050

During the last few decades, Lake Ziway has begun to show reduction in its water level because of some climatic factors (e.g. evapotranspiration) and water abstraction for irrigation, municipal and industrial purposes (Ayenew and Legesse, 2007). Moreover, slight increase in its salinity and mineral content were observed during the last four decades which was attributed to evaporation, water abstractions, and changes in the total inflows and outflow (Ayenew and Legesse, 2007).

The lake provides water for domestic use and shares the same water table with key groundwater aquifers that provide borehole water supply for the rapidly-expanding human population in Ziway town and surrounding areas. Currently the population of Lake Ziway catchment is about 2 million (Ethiopian Central Statistics Authority, 2013, unpublished data) and about 1.9 million livestock (Tesfaye *et al.* 2012). The fishery of the lake is also an important source of livelihood to scores of fishermen and their families and provides the sources of food to many families within the lake basin and beyond. Tourism is also a major activity in the area due to the presence of hipotanuse, scenery Islands with monasteries, bird sanctuaries and the presence of rich tropical related biodiversity (IBC. 2005). Other socio-economic activities conducted along the lake's shore include livestock production and small-scale farming (APHRD, 2010; Jansen *et al*., 2011).

The lake's catchment has an area of 7025 square kilometers. Lake Ziway and its catchment are characterized as semi-arid to sub-humid type of climate and have mean annual precipitation varying between 650 mm and 1200 mm and mean annual temperature between 15 and 25 °C

(Mepham, *et al.*, 1992; Turdu *et al.*, 1999; Legesse *et al*., 2001, Lijalem, *et al.*, 2007; Mesfin, *et al.*, 2012). The lake is primarily loaded by two rivers which carry heavy sediment and nutrient loads to the lake ecosystem as mentioned in the introduction part.

Ketar River has a large catchment of 3400 km^2 that includes the Arsi high lands to the Eastern part of the lake. The catchments of Ketar River ascend to over 4100 m above on the summits of mounts Badda and Kaka. Francisco, (2008) reported that the total irrigated area of Ketar River catchment was estimated to be 3,337 ha. Therefore, the prime importance of Ketar River is for irrigation and contribution to feed Lake Ziway. The annual inflow of Lake Ziway from the Ketar River gauged at Abura ($08^0$02.019’ N and $38^0$49.340’ E) was 302 MCM.

3.2 Chemicals, reagents and standards

Analytical reagent grade sodium hydroxide, concentrated hydrochloric acid, concentrated sulfuric acid, concentrated phosphoric acid, anhydrous sodium sulfate, ammonium persulfate, potassium persulfate, Phenol, sodium nitroprusside, sulfanilamide, N-(1-naphthyl)-ethylenediamine dihydrochloride, Potassium chloride, sodium salicylate, potassium sodium tartarate, copper sulfate, silver sulphate, calcium hydroxide, magnesium carbonate, boric acid, potassium antimony tartrate, ammonium molybdate (), ascorbic acid (Sigma-Aldrich, Germany), ethanol (99.99 %, Fisher Scientific, UK), phenolphthalein (Scharlau, European Union), methyl orange (Scharlau, European Union), hypochlorite, acetone. All chemical and reagents are products of Sigma-Aldrich, Germany.

3.3 Apparatus and equipment

Low speed centrifuge (800-1, Germany); high speed centrifuge(Hermle Labortechnik; USA), vacuum pump evaporator (Heidoph, 517/6100/0, Germany); UV-Visible Spectrophotometer (Jenway 6405, UK); Ultrasonicator (Decon, Fs100b, Germany); Shaker Bath (Fifty, GCA, 60647, USA); Gas Chromatography coupled with a Mass Spectrometer (Agilent technologies, 7820A, GC-MS, USA); Kjeldahl apparatus (Gallenhamp, USA); Oven dry (Binder, Germany); Turbidimeter (T-100, Singapore); portable multi meter (HACH MM150, China) were used in the experiments.

3.4 Sampling design and water sample collection for physicochemical, nutrient and chlorophyll-*a* analyses

3.4.1 Sampling design and water sample collection procedures

The proposed project involved the collection of data for analyses of major nutrients, pesticides and physico-chemical water quality parameters in water, soil samples in different depths at the selected sampling sites taken at selected seasons for two years (2014 and 2015). Nine representative sampling sites were selected purposefully based on access, safety, waste disposal activities, lake inflow and outflow and geographical proximity. These sites were evenly distributed along the course of Lake Ziway for estimation of external and internal nutrient loads in water and sediment samples. The specific sampling sites and abbreviations are given in Table 3.1 and Figure 3.1.

Water samples were collected with a Van Dorn water sampler from different depths of the entire water column at 1 m intervals and mixed in equal proportions to produce composite samples. The collected water samples were kept in precleaned polyethylene plastic bottles for nutrient analysis (US EPA, 2014). All water samples were stored in insulated dark ice boxes and taken on the same day to the laboratory and stored at 4 ^{o}C before analysis and the analyses were done before 24 hours.

3.4.2. Sample preparation and analyses for physicochemical and nutrient analyses

3.4.2.1 In-situ measurements of physico-chemical parameters

Physicochemical parameters were measured after all field equipments calibrated according to the manufacturer's specifications:

i. *Temperature, pH, electrical conductivity, total dissolved solid, and dissolved oxygen* were measured with a portable multi meter HACH MM150 model designed for water samples;

ii. *Secchi depth* was measured with a standard Secchi disk of 20 cm diameter with black and white quarters and

iii. *Alkalinity*: Alkalinity of sample was determined by titrating with standard sulphuric acid (0.02 N) by using phenolphthalein and methyl orange indicators. Titration to decolouriation of phenolphthalein indicators were indicated complete neutralization of OH^- and ½ of CO_3^{2-} while sharp change from yellow to orange of methyl orange indicator were indicated total alkalinity (complete neutralization of OH^-, CO_3^{2-}, HCO_3^-) (Standard Method 2320 B; (APHA, 1999)).

Calculations:

$$Alkalinity, \frac{mg\ CaCO_3}{L} = \frac{A * N * 50,000}{mL\ sample} \tag{3.1}$$

where: *A* - volume of standard acid used, mL and *N* - normality of the standard acid.

iv. *Turbidity* was measured with Turbidimeter (T-100, Singapore).

3. 4.2.2 Standard analytical methods for nutrient analysis

In the two year sampling periods (2014 and 2015), the chemical analyses of nutrients (nitrite-nitrogen (NO_2-N), nitrate-nitrogen (NO_3-N), soluble reactive phosphorus (SRP), ammonia-nitrogen (NH4-N), total phosphorus (TP), total nitrogen (TN) and soluble reactive silica (SiO_2-Si) were determined for all monthly samples following the standard procedures outlined in APHA, (1999). The samples used for the analyses of all nutrients except, total nitrogen (TN) and total phosphorus (TP) were filtered through 0.47 µm diameter glass fiber filters (GF/F).

Soluble reactive phosphorus (**SRP**) was measured colorimetrically using ascorbic acid method following the standard procedures outlined in APHA, (1999). The filtered sample was mixed with ammonium molybdate that forms molybdo-phosphoric acid with any phosphate present in the water sample. The acid is then reduced by ascorbic acid to a blue complex known as molybdenum blue. The color intensity, which is proportional to the concentration of phosphate in the water sample, was then measured by a Jenway 6405 UV Visible spectrophotometer at a wave length of 880 nm. Then, concentration of SRP was calculated from standard calibration curve.

Total phosphorus (TP) was analyzed by persulfate digestion followed by the ascorbic acid method. In the persulfate digestion process, the polyphosphates are converted to the orthophosphate form by sulfuric acid digestion and organic phosphorus is converted to orthophosphate. The resulting orthophosphate ion (PO_4^{3-}) without filtering the sample was analyzed by ascorbic acid method (APHA, 1999). Then, concentration of TP was calculated from standard calibration curve.

Ammonia-nitrogen (NH_4-N) was determined by phenate method using spectrophotometry at a wave length of 640 nm where an intensely blue compound, indophenol, is formed by the reaction of ammonia, hypochlorite, and phenol catalyzed by sodium nitroprusside. The intensive color of the blue indophenol is proportional to the ammonia concentration in the sample (APHA, 1999). Then, concentration of NH_4-N was calculated from standard calibration curve.

Nitrite-nitrogen (NO_2–N) was determined by colorimetric method (APHA., 1999) through the formation of a reddish purple azo dye produced at pH 2.0 to 2.5 by coupling diazotized sulfanilamide with *N*-(1-naphthyl)-ethylenediamine dihydrochloride (NED dihydrochloride). The spectrophotometric measurements were done at a wave length of 543 nm. Then, concentration of NO_2-N was calculated from standard calibration curve.

Nitrate-nitrogen (NO_3-N) was determined by salicylate colorimetric method (Yang *et al.*, 1998). The analysis is based on the reaction of the nitrate with sodium salicylate in a sulfuric acid medium, which forms a yellow coloured salt of nitrosalicylic acid. The colour intensity which is proportional to the nitrate concentration and the absorbance was measured using Jenway 6405 UV Visible spectrophotometer at a wave length of 410 nm. Then, concentration of NO_3-N was calculated from standard calibration curve.

Total nitrogen (TN) in water samples was analyzed using Kjeldahl method as stated in APHA, (1999), the methods involves a two-step process. First, the sample was digested with sulfuric acid to convert organic nitrogen compounds to NH_4^+. Then, secondly, the NH_4^+ was converted to NH_3 in an alkali distillation process. The NH_3 liberated in this process was quantified to determine the total N in the original digest. Then, concentration of TN was calculated from standard calibration curve.

Soluble reactive silica (SiO_2-Si) was determined by molybdosilicate method (APHA, 1999) through ammonium molybdate reacts with silica and any phosphate present to produce heteropoly acids. Oxalic acid was added to destroy the molybdophosphoric acid but not the molybdo silicic acid. The intensity of the yellow colour is proportional to the concentration of ‘‘molybdate-reactive’’ silica. Then, concentration of SiO_2-Si was calculated from standard calibration curve.

3.4.2.3 Biomass as chlorophyll-*a* of phytoplankton analysis

Chlorophyll-*a* was determined using acetone extraction method as stated in APHA, (1999), where different volume of water samples were filtered with an electric filtration unit through prewashed Whatman GF/F 0.47 µm diameter filters. Extraction was carried overnight using 5 mL of 90% acetone. Chlorophyll-*a* absorption was then determined using a Jenway 6405 UV/Visible Spectrophotometer by measuring the absorbance at 665 and 750 nm wavelength after zeroing using acetone. The formula by Talling and Driver (1963) was used to calculate the chlorophyll-*a* concentration.

$$\frac{Chl - a\ \mu g}{L} = \frac{13.9 * (E665 - E750) * Ve}{Vf * Z} \qquad 3.2$$

where; E_{665} and E_{750} are absorbance at 665 nm and 750 nm, respectively; V_e is the volume of the extract in mL; V_f is volume of the sample filtered in liter; Z is Path length of the cuvette (1 cm)

3.5. Multivariate statistical data analysis methods

Lake water quality data sets were subjected to three multivariate techniques: cluster analysis (CA), principal component analysis (PCA) and factor analysis (FA) (Zhao, 2012).

3.5. 1 Cluster analysis

Cluster analysis (CA) is a group of multivariate technique, which allows assembling objects based on characteristics. CA classifies objects, so that each object is similar to the others in the cluster with respect to a predetermined selection criterion. Hierarchical agglomerative clustering is the most common approach, which provides intuitive similarity relationships between any one sample and the entire data set and is typically illustrated by a dendrogram (tree diagram). The dendrogram provides a visual summary of the clustering processes, presenting a picture of the groups and their proximity with a dramatic reduction in dimensionality of the original data (Shrestha and Kazama, 2007; Sayadi *et al*., 2014; Camacho *et al*., 2015). In this study, hierarchical agglomerative CA was carried out on the normalized data by means of Ward's method, using squared Euclidean distances as a measure of similarity.

3.5. 2 Principal component analysis/factor analysis

Principal component analysis (PCA) is used to reduce the number of variables and explain the same amount of variance with fewer variables (principal components). Factor analysis (FA) attempts to explain the correlations between the observations in terms of the underlying factors, which are not directly observable (Sayadi *et al*., 2014; Andrea *et al*., 2015). PCA and FA were performed on the water quality data for different seasons to discover the structure in the relationships between water quality parameters, in order to identify the important parameters which affect the chemistry of surface water in each season and to investigate the possible sources of different pollutants (Andrea *et al*., 2015).

In this research, PCA was applied to summarize the statistical correlation among water quality parameters. The magnitudes of physico-chemical parameters and nutrients tend to differ highly; In fact, the statistical results are highly biased by any parameter having a high concentration. Thus, each water quality parameter was standardized before the PCA analysis was performed in order to minimize the influence of different variables and their respective units of measurements. The calculations were performed based on the correlation matrix of chemical components, and the PCA scores were obtained from the standardized analytical data.

3.5.3 Comprehensive evaluation of water quality in the lake

The comprehensive pollution index method has been applied to evaluate water quality qualitatively in many existing studies. The comprehensive pollution index is calculated as follows (Yan *et al*., 2015):

$$P = 1/n \sum_{n=1}^{n} (Ci/Si) \tag{3.3}$$

where P is comprehensive pollution index, C_i is the measured concentration of the pollutant (mg L^{-1}), S_i represents the limits allowed by the State Environmental Protection Administration (SEPA) in the particular country for water quality standard, and *n* is the number of selected pollutants (Bharti and Katyal, 2011; Zhao *et al*., 2012, Rubio-Arias *et al*., 2013, Yan *et al*., 2015). Ultimately, the values determined for P could be used to classify the water quality level of the lake (Table 3.2) (Zhao *et al*., 2012).

Table 3.2 Standard of surface water quality classification

Comprehensive pollution index (P)	Water quality level
$\leq$ 0.20	I cleanness
0.20 to 0.40	II sub-cleanness
0.41 to 1.00	III slight pollution
1.01 to 2.00	IV moderate pollution
$\geq$ 2.01	V severe pollution

3.6 Climatic and hydrological data collection and analysis

Secondary data for air temperatures, wind speed, sunshine, relative humidity, rainfall and evaporation rates collected at a meteorological station at Lake Ziway for the year of 1980 to 2014 were obtained from the Ethiopian Meteorology Agency (Addis Ababa). The hydrological data like water level and rivers discharge flow were taken from the Ministry of Water, Irrigation and Electricity (MoWIE), Ethiopia and nutrient concentrations and other water quality parameters were analyzed according to APHA, (1999) for computing the nutrient load, water balance and water residence time of Lake Ziway as well as analysis of nutrient dynamics.

3.6.1 Rate of eevaporation estimation method

The widely used methods for computing rate of evaporation are using Penman Method (Ayenew and Robert, 2008). According to Penman the potential evaporation E_o (in mm/day) can be calculated as:

$$E_o = \frac{(H\Delta + \gamma E_a)}{\Delta + \gamma} \qquad 3.4$$

where;

E_o = evaporation from open surface water in mm day^{-1};

H = net radiation, expressed in equivalent in mm day^{-1} of evaporation;

$H = R(1 - A)(0.18 + 0.55\frac{n}{N})\text{-}\sigma T_a^4(0.56 - 0.092\sqrt{re_s})(0.10 + 0.90\frac{n}{N})$

R = mean monthly radiation expressed in equivalent mm day^{-1} of evaporation

A = reflection coefficient, i.e., A= 0.05 for water

$\frac{n}{N}$ = percent of possible sunshine; it is the ratio of the actual duration of sunshine to the maximum possible sunshine.

σ = Stefan-Boltzmann constant = 2.01×10^{-9} mm (deg K)$^{-4}$ day^{-1}

T_a = air temperature in deg K

R = relative humidity in percent

e_s = saturated vapor pressure of air in mm Hg

Δ = slope of saturated vapor pressure curve at the air temperature

γ = the psychrometer constant

E_a = a product of wind function and vapor pressure deficit, i.e.

E_a = f (u) (1-r) e_s in mm day^{-1}

where

f (u) = 0.26 (0.5 + 1.2 U_2/100)

U = wind speed in mi day^{-1}

3.6.2 Methods to calculate residence time of the lake water

The water residence time of Lake Ziway was calculated using the volumes of the lake based on measurements of surface area and mean depth and water discharge volume which were measured by Bulbula River outflow from Lake Ziway. The lake water residence time (τ_ω) is calculated by dividing the lake volume (V) by its mean water outflow (Q_o) (Rueda and Cowen, 2005; Rennella and Quiro, 2006).

$$\tau_\omega = {}^{V}/_{Q_o} \quad 3.5$$

Where: τ_ω is lake water residence time; V is Lake Volume and Q_o is mean outflow.

3.6.3 Lake water balance equations

The water balance of a lake is usually evaluated by the basic hydrological equation in which the change in storage of the water volume in the given area per time is equal to the rate of water inflow from all sources minus the rate of water outflow. The annual lake water balance was computed as follows (Ismail *et al*., 2005; Han, 2010):

$$\pm \Delta H = P + Q_{in} - E - Q_{out} \quad 3.6$$

Where ΔH is change in water level; P is rainfall over the lake; Q_{in} is catchment inflow (mainly river Meki and Ketar); E is evaporation from the lake; and Q_{out} is (Bulbula River outflow and abstraction for irrigation).

3.7 External nutrient load models

The major external nutrient sources of Lake Ziway are Ketar and Meki Rivers. The annual nutrient loads to the lake were estimated by multiplying the monthly concentrations of significant forms of nutrients in the rivers by the volume monthly average inflows of the two rivers. Therefore, the external nutrient load of the lake was computed using the method of Huai-en *et al.* (2003) as follows:

$$\mathrm{L} = K\left(\sum_{i=1}^{n} (\mathrm{Ci} * \mathrm{Qi})\right) \quad 3.7$$

Where: L = nutrient load (ton year^{-1}); K = a factor to convert from time period of record to annual value; n = number of samples; Q_i = discharge (m^3 s^{-1}); C_i = concentration (ton m^{-3}). The records of monthly discharges of Meki, Ketar and Bulbula Rivers were obtained from MoWIE.

Vollenweider model: Vollenweider model is one of the most practical models to estimate phosphorus loads in lakes. Vollenweider developed a statistical relationship between phosphorus concentration and hydraulic residence time to predict lake area annual phosphorus loadings (Vollenweider, 1974, 1976; Dennis *et al.*, 1992; Brett and Benjamin, 2008). The Vollenweider (1976) phosphorus loading model is typically express mathematically as:

$$\rho = \frac{Q}{V} \qquad 3.8$$

$$\mathrm{Lp} = TPi \times \rho \times \bar{z} \qquad 3.9$$

$$TP = \frac{Tpi}{(1 + \tau^{-0.5})} \qquad 3.10$$

$$logchla = 1.449 logTP - 1.136 \qquad 3.11$$

$$TSI = 10(6 - log_2^{SD}) \qquad 3.12$$

$$TSI = 10\left(6 - \log_2^{\;7.7/\mathrm{chla}^{0.68}}\right) \qquad 3.13$$

$$TSI = 10\left(6 - \log_2^{\;48/\mathrm{TP}}\right) \qquad 3.14$$

where; LP = annual external P loading (mg m^{-2} yr^{-1}); $\bar{z}$ = lake means depth (m); ρ = flushing rate (out flow rate/lake volume) (1/yr); TP = lake TP concentration (μg L^{-1}); TP_i = mean inflow TP concentration (μg L^{-1}); τ = residence time ; v= lake volume ; TSI = trophic state index; SD= secchi depth (m); Chla = chlorophyll-a (μg L^{-1})???

3.8 Sediment sample collection and extraction procedures for internal nutrient load analyses

Sediment samples were collected using a sediment core sampler from the selected sampling sites. The samples were collected from seven sampling sites in Lake Ziway. In each sampling sites, three sediment samples were collected at three depths (0 - 10 cm, 11– 20 cm and 21 - 30 cm), using a modified sediment core sampler (Figure 3.2).

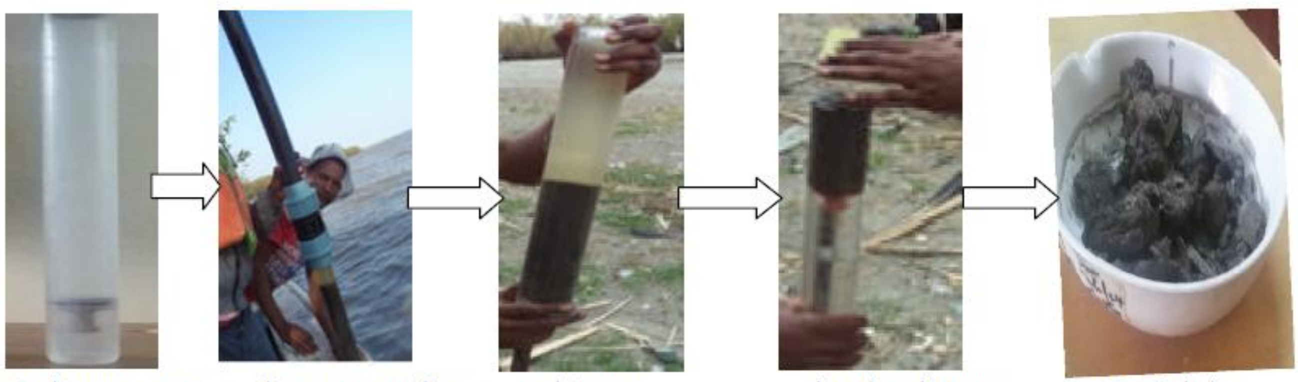

Figure 3.2 sediment sampling producers using modified sediment corer

Nutrients in sediment samples were analyzed by the procedures described in environmental water and soil analysis manual (Trivedi and Raj, 1992; Maria, 1997; EPA, 1993). The sediment samples were air dried with crushing it with a motor and pestle and sieved (< 2 mm) and placed in appropriate petri dishes. After this the appropriate amount of distilled water were added and then homogenized with a mechanical shaker and filtered through a Whatman filter paper grade No. 42 and 50 (Trivedi *et al*., 1992; Maria, 1997; Christensen, *et al*, 2011). Finally, these solutions were analysed according to the standard methods described for water sample analysis for nutrients:

For the determination of SRP, 1 g dry sediment sample was added to 200 mL sulfuric acid (0.002 N) in 500 mL Erlenmeyer flask and was shaken for 30 min. The supernatant was then filtered through Whatman No. 42 filter paper (Trivedi and Raj, 1992; EPA, 1993) and measured for SRP by ascorbic acid method according to APHA (1999).

For the determination of TP, 5 g dry sediment was added to 50 mL deionized water in 500 mL Erlenmeyer flask and was shaken for 30 min. The supernatant was then filtered through Whatman No. 42 filter paper; the soil was wash with additional aliquot of deionized water. The filtrate was collected and diluted to a final volume of 100 mL (Trivedi and Raj, 1992; EPA, 1993). Finally, the concentration was determined by persuphate digestion followed by ascorbic acid according APHA (1999).

For the determination of NO_3-N, 50 g dry sediment sample was added to 500 mL Erlenmeyer flask together with 250 mL extraction reagent solution consisting of 12.5 g copper sulfate and 0.6 g silver sulfate. The solution was shaken for 15 min and mixed with 0.4 g calcium hydroxide and 1 g magnesium carbonate in the same flask. The mixture was then filtered through Whatman No. 50 filter paper (Trivedi and Raj, 1992; EPA, 1993). The NO_3-N from the filtrate was analyzed by sodium salicylate method (Yang *et al.*, 1998).

For the determination of NO_2-N, 10 g fresh sediment sample was added in to an Erlenmeyer flask together with 250 mL 2 M KCl solution. The solution was shaken for 1 hour. Thereafter, the solution was allowed to stand for about 30 min until a clear supernatant was obtained and then the solution was then filtered through Whatman No. 42 filter paper (Trivedi and Raj, 1992; EPA, 1993). The NO_2-N from the filtrate was analyzed by colorimetric method (APHA, 1999).

Determination of TN in sediment was determined using Kjeldahl method according to EPA, 1993 as follows: 1 g of dry sediment samples was transferred into a Kjeldahl digestion flask. After adding of the necessary chemicals, digestion was taken under a hood. The digested solutions were distilled with 2% boric acid solution and finally ammonia was determined by titration with 0.1 N H_2SO_4 solutions.

3.9 Sediment sample collection and preparation for phosphorus release rate determination

Three sediment core samples were collected in a triplicate bases from each sampling site for six consecutive months from January, 2015 to July 2015 during dry and wet seasons in order to study the phosphorus release rate. The sediment corer was constructed from a graduated 0.51 m long polycarbonate tube (5 cm inner diameter). After collection, the core was brought to the surface, and the bottom and upper parts of the polycarbonate tubes were sealed with a rubber stopper in order to protect the outflow of the inside water and sediment. Core tubes were covered with black plastics and placed in a 20 L bucket, and kept in ice during transit. Internal phosphorus release was measured from sediment cores collected in the lake, to identify the relative contribution of internal phosphorus loads. Three sites were sampled over two seasons to estimate seasonal internal phosphorus loading, accounting for spatio-temporal variations in phosphorus flux. Sediment cores were incubated for 5 days under anoxic conditions, and the overlaying water column was sampled for SRP and TP concentrations during the incubation period.

Core processing and phosphorus flux: Internal TP and SRP loads were estimated with methods described in Steinman *et al.* (2004). Briefly, the sediment samples were collected using sediment cores and immediately the cores were covered with black plastic and put in a shaded ice boxed up to the laboratory, then in the Laboratory, these samples were placed in a dark room for five days. Finally, 50 mL water sample was removed by syringe through the sampling port of each core tube after 5 days incubation in each month. Immediately after removal, a 25 mL subsample was refrigerated for analysis of TP, and a 25 mL subsample was filtered through a 0.45 μm membrane filter paper and analyzed for SRP. Both SRP and TP concentrations were determined according to APHA, (1999).

According to the flux (P release rate) calculations were based on the change in water column TP or SRP using the following equation (Steinman *et al.*, 2004):

$$P_{\pi} = \frac{(C_t - C_o) \times V}{(t_t - t_o) \times A} \qquad 3.15$$

where, p_{π} is the net P release rate or retention per unit surface area of sediments, C_t is the TP or SRP concentration in the water column at time t, C_o is the TP or SRP concentration in the water column at time 0, V is the volume of water overlaying the sediment cores, and A is the planar surface area of the sediment cores.

3.10 Determination of the trophic state and trophic state indices

The trophic status of Lake Ziway was determined using the Carlson (1977) and Kretzer and Brezonik (1981) methods. The Carlson's Trophic Status Index (TSIs) is the most important and popular TSI method (Rahimeh *et al*., 2011; Ramesh and Krishnaiah, 2014)**.** TSIs were calculated for the lakes as a whole, using the equations described by Carlson (1977) (Equations 3.16 to 3. 18) and Kretzer and Brezonik (1981) (Equation. 3.19):

$$\text{TSI-TP} = 14.42\ln(TP) + 4.15 \quad 3.16$$

$$TSI - SD = 60 - 14.41\ln(SD) \quad 3.17$$

$$TSI - Chla = 9.81\ln(Chla) + 30.6 \quad 3.18$$

$$TSI - TN = 54.54 + 14.43\ln(TN) \quad 3.19$$

Where, TSI-TP = Trophic state index referred to total phosphorus, (TP) = total phosphorus (μg L^{-1}), TSI-SD = Trophic state index referred to Secchi depth, SD = Secchi depth in meters, TSI-Chla = Trophic state index referred to chlorophyll-*a*, Chla = chlorophyll-*a* (μg L^{-1}), TSI-TN = Trophic state index referred to total nitrogen, (TN) = total nitrogen (mg L^{-1}), while In = natural logarithm.

3.12 Data analysis

Different procedures of statistical analyses were used to analyze the data. Analysis of variance (ANOVA) was conducted to test the differences between, and within, sampling sites at 95 % confidence interval using SPSS (version 20) software (Chicago, USA). The differences between sites were examined to determine the spatial variation while the differences within seasons addressed the temporal variation for both water and sediment samples. Person correlation was chosen to evaluate the correlation and probability values were significant level at 0.05. Depth profiles of water and sediment nutrient distributions were analyzed using sigma plot software (Sigma Stat 10.0) and PAST statistical software (version 1.93) was applied for the principal component analysis and cluster analysis.

Chapter 4: Results and Discussion

4.1 Assessment of spatio-temporal variations of selected water quality parameters of Lake Ziway using multivariate techniques

4.1.1. Spatial and temporal variations of physico-chemical water quality of Lake Ziway

The average spatio-temporal values of physico-chemical water quality parameters in dry and wet seasons are given in Tables 4.1.1 and 4.1.2, respectively.

Temperature: The surface-water-temperature measured during day time between 3 and 9 hours in the study sites ranged from 19.0 to 28.0 ^{o}C and 18.0 to 27.0 ^{o}C in dry and wet seasons, respectively, where the highest values were measured the river inlet (K_a) and outlet (B) while the lowest values were measured in the open water at C both dry and wet seasons (Tables 4.1.1 and 4.1.2). The spatial and temporal variation of mean water temperature in Lake Ziway was not significant ($p > 0.05$) during the study period.

The mean temperature of the lake water was 23.0 ^{o}C in both seasons, which is similar to previously reported mean value of 22.4 ^{o}C (Tilahun and Ahlgren, 2010) but lower than the value (26.1 ^{o}C) reported by Tamire and Mengistou (2012). However, in the wet season, the mean temperature was lower than the previously reported data. Lake Ziway has narrow seasonal fluctuations in water temperature as the lake is a shallow tropical lake. The mean temperature of Lake Ziway is similar to Lakes Hawasa, Chamo, and Naivasha but slightly higher than Lake Hayq (Table 4.1.5).

Table 4.1.1 Means and ranges of the physico-chemical parameters measured at the surface water of Lake Ziway in dry season

Site		Temp	DO	pH	EC	TDS	SD	TA	Turbidity
B	x̄± Std. Err	24.75±1.3	7.3±1.8	8.3±0. 31	385±38	248±24	24.6± 0.5	314±41	159±9
	Range	21-28	4.8-12.4	8-9	289-521	189-335	23-26	216-425	145-175
C	x̄± Std. Err	21.2±1.3	5.2±1.1	8.1±0.17	408±43	268±33.7	27.7±1.3	225±22	180±26
	Range	18-25	4-8.4	8-9	337-558	215-393	23-30	184-300	151-233
F_a	x̄± Std. Err	23.8±0.99	6.8±1.7	8.13±0.23	639.73±114	423.8±83	26± 0.71	320±50	156±44
	Range	21-26	4.2-11.2	8-9	376-1028	249-720	24-28	200-425	88-239
F_b	x̄± Std. Err	23._5±1.4	6.2±1.4	7.56±0.11	1233.6±107	789.6±68.3	25.8± 0.58	463±71.7	17±5
	Range	19-27	2.6-9.3	7-8	1050-1650	672-1056	24-27	200-625	11-27
K_a	x̄± Std. Err	21.3± 0.49	4.4±1.5	8.1± 0.16	382.6±39.4	237.8±18.6	24.4±1.8	24± 29	141±4
	Range	20-23	2.5-9.2	7-8	307-543	196-307	16-30	156-325	135-147
K_b	x̄± Std. Err	20.15±0.23	5.5± 0.64	7.4± 0.08	170.7±14.3	107.7±9	21±.71	187±44	77±6
	Range	20-21	4.0-7.0	7-8	134-204	86-130	19-23	104-275	65-86
K_o	x̄± Std. Err	24.2±1.3	5.4±1.3	7.4± 0.75	399±14.4	254±10.5	25.6±1.1	330±38	172±28
	Range	21-28	2.4-9.0	7-9	362-435	219-278	22-28	200-425	157-210
M_a	x̄± Std. Err	22.2± 0.7	4.4± 0.56	7.98± 0.164	404.13±43	291.9±37.7	27.8±1.8	227.6±26	146±6
	Range	21-25	3.3-6.5	8-9	333-576	213-403	22-31	160-300	139-158
M_b	x̄± Std. Err	22.9± 0.76	7.6±1.6	7.95± 0.22	424±625	267±38	21± 0.71	263±48	59±41
	Range	20-24	3.8-10	7-9	203-584	130-365	19.00	100-375	6-139

- ✓ *Temp for temperature in ^oC; DO for dissolved oxygen in mg L^{-1}; pH for H^+ concentration; EC for electrical conductivity in $\mu S\ cm^{-1}$; TDS for total dissolved solids in mg L^{-1}; SD for secchi depth in cm; TA for total alkalinity in mg L^{-1}; Turbidity in NTU.*

Dissolved oxygen (DO): The level of dissolved oxygen (DO) ranged from 2.42 to 12.4 mg L^{-1} and 1.4 to 7.2 mg L^{-1} in dry and wet seasons, respectively (Tables 4.1.1 and 4.1.2). The lowest values in both seasons were at K_o (2.4 mg L^{-1}) in dry and K_b (1.4 mg L^{-1}) in wet seasons where the highest values were at B (12.4 mg L^{-1}) in dry and F_b (7.2 mg L^{-1}) in wet seasons, respectively. This is probably due to in dry season at K_o, human impacts and low macrophytes and high turbidity as car and human washing and in wet season, K_b is completely muddy due to agricultural runoff. High DO values in sampling site B can be attributed to the presence of macrophytes and phytoplankton with higher biomass and abundance than other sites (Tamire and Mengistu, 2012). However, in the wet season the effluent of floriculture (F_b) was clear water due to high dilution. The overall mean DO concentration of this study was 5.00 mg L^{-1} in lake water samples, which was much lower than the one reported by Roba (2008), which was 8.72 mg L^{-1}. Tadele (2012) reported DO concentration of 1.4 mg L^{-1} around the floriculture effluent which is lower than the present study. When compared the mean concentrations of DO in Lake Ziway is almost similar to most other tropical lakes (Table 4.1.5).

Concentrations below 4.0 mg L^{-1} adversely affect aquatic life (FEPA, 2003). As the dissolved oxygen level decreases in the water, fish and other organisms shift to other areas with more oxygen concentrations (Anonymous, 1999). In Lake Ziway, there was massive fish kill around the outlet of the floriculture industry in January, 2015 (personal observation). This might be due to reduced levels of dissolved oxygen. The value of DO in this study is the minimum permissible values according to EU (1998) and WHO (1996). The standard DO value for fisheries and aquatic life is between 5.0 to 9.0 mg L^{-1}.

pH: The pH values ranged from 7.0 to 9.0 and 6.5 to 9.7 in dry and wet seasons respectively (Tables 4.1.1 and 4.1.2). The maximum pH noticed in the study period was 9.7 at station B during the dry season and the minimum pH recorded was 6.5 at station M_b. The overall mean pH value of the lake water was 8.10 which were in close agreement with previous data reported as 8.39 and 8.44 by Roba (2008) and Tamire and Mengistou (2012) respectively. Similarly, Tilahun and Ahlgren (2010) also reported that the pH values of Lakes Ziway, Hawasa and Chamo were 8.65, 8.66 and 8.84, respectively. The pH of surface water in Lake Ziway showed a slightly alkaline tendency during all the seasons. The pH of most Rift Valley Lakes generally varied between

8 and 9 and remained within narrow range (Table 4.1.5). A pH range of 6.5 to 8.5 is acceptable for aquatic biota according to the APHA (1999).

Electrical conductivity (EC): The EC in the study sites ranged from 134 to 1650 μS cm^{-1} in the dry season and 65 to 496 μS cm^{-1} in the wet season. K_b gave the lowest mean conductivity (134 μS cm^{-1}) in dry and 65 μS cm^{-1} in wet seasons while site F_b recorded the highest mean values of 1650 μS cm^{-1} in dry and K_o mean values 496 μS cm^{-1} in wet seasons, respectively (Tables 4.1.1 and 4.1.2). In general, the overall mean measurement of EC (404 μS cm^{-1}) was comparable with previous reports of Gebre-Mariam *et al.* (2002); Tilahun and Ahlgren (2010) and Tamire and Mengistou (2012) with mean EC values of 410, 478, 419 μS cm^{-1}, respectively. When compared to other African lakes, the EC values of Lake Ziway (404 μS cm^{-1}) was lower than Lakes Chamo (1910 μS cm^{-1}), Hawasa (846 μS cm^{-1}), Hayq (910 μS cm^{-1}), Abaya (623 μS cm^{-1}), Langano (1810 μS cm^{-1}), Bishoftu (1830 μS cm^{-1}), Abijata (15800 μS cm^{-1}), Shalla (19200 μS cm^{-1}), Chitu (28600 μS cm^{-1}) as reported by Tilahun and Ahlgren (2010), Fetahi (2010) and Wood and Talling (1988) (Table 4.1.5), respectively but higher than Lake Tana (115 to 148 μS cm^{-1}) and Lake Naivasha (290) as reported by Wondie (2006) and Momanyi *et al.* (2012), respectively.

The differences in EC over seasons and across different stations were very significant. Higher conductivity values were measured at the floriculture farming sites (F_a and F_b) as compared to other sampling sites probably due to the use of high amount of dissolved agrochemicals from effluents of the floriculture industry (Ayenew, 2005; Tadele, 2012). There were significantly lower values of EC during the main rainy season which may be because of dilution. In the present study, the EC values of different sampling sites were well below the WHO guideline values prescribed for drinking water purpose (1500 μS cm^{-1}) (WHO, 1996). Moreover, Koshy and Nayar (2000) observed that the EC value of 250 μS cm^{-1} in freshwater is conducive for aquatic life. In Lake Ziway, the highest average seasonal EC observed during this study was 1234 μS cm^{-1} at site F_b during the dry season and the lowest EC was 101 μS cm^{-1} at K_b during the wet season. Therefore, the EC values in Lake Ziway may be considered safe for aquatic biota.

Total dissolved solid (TDS): The TDS ranged from 120 to 747 mg L^{-1} with the low values in dry at sampling site K_b and the high values at site F_b while in the wet season it ranged from 130 to

548 mg L^{-1} at sites M_b and F_b, respectively (Tables 4.1.1 and 4.1.2). The overall mean value of TDS in the lake was 263 mg L^{-1}. The TDS at station F_b in general was relatively higher than other stations during the entire period of study. It is due to the increased effect of effluent from the floriculture industry on Lake Ziway, which is a tendency of pollution and must be seriously curbed.

Total alkalinity (TA): TA in the study sites ranged from 100 to 625 mg $CaCO_3$ L^{-1} in the dry season and 60 to 472 mg $CaCO_3$ L^{-1} in the wet season during the study period (Tables 4.1.1 and 4.1.2). M_b showed the lowest mean TA (100 mg $CaCO_3$ L^{-1}) in dry and 60 mg $CaCO_3$ L^{-1} in wet season while site F_b showed the highest mean values of 625 mg $CaCO_3$ L^{-1} in dry and 472 mg $CaCO_3$ L^{-1} in wet season, respectively. The open water TA values of the lake were 225 and 168 mg $CaCO_3$ L^{-1} in dry and wet seasons, respectively which was lower than the values at sampling site Fb. During all the seasons, fluctuations in TA across the sites were significant ($p < 0.05$). TA has generally decreased in all sampling sites in the wet season probably due to the dilution effect of the rains and freshwater incoming runoffs (Singh *et al.*, 2004; Ghafar *et al.*, 2014). Krishnan (2008) reported that alkalinity concentrations more than 60 mg L^{-1} in lake water indicate nutrient rich status of the lakes.

Moreover, Tilahun and Ahlgren (2010) reported that the mean value of TA in Lake Ziway was 248 mg $CaCO_3$ L^{-1} which was similar to the mean value in this study in dry season (239 mg $CaCO_3$ L^{-1}) whereas the mean value in the wet season (155 mg $CaCO_3$ L^{-1}) was much lower. In the lake, TA was solely due to bicarbonates and carbonate alkalinity that could be traced at any station during the entire period of study. According to Camacho *et al.* (2015) nutrient status classifications using TA, Lake Ziway can be considered nutrient rich. In Lake Ziway, the surface water at site F_b when compared to other stations, showed a higher TA in all seasons of the entire period of study. This is due to the effluents of the floriculture industry directly entering into the lake resulting in a high increase in TA in surface waters at this site associated with the use of high amount of dissolved agrochemicals by the floriculture farming. This is supported by Tadele, 2012.

Secchi depth (SD): The different seasonal values of SD at different stations during the two years period of observations are separately given in Tables 4.1.1 and 4.1.2. In general, the shallowest SD was found during the wet season and the deepest during the dry season. Among the different sampling sites deepest SD was recorded at M_a and the shallowest was at site B. The deepest SD recorded during the study period was 0.30 cm at site M_a during the dry season and the shallowest measured was 0.16 m at site K_a during the wet season with overall mean values of 0.20 m. at the center of the lake, SD was 0.22 m which is similar to the overall SD values as mentioned above. For example, the mean SD (0.19) reported by Tilahun (2006) is similar to the result recorded in this study but lower than the ranges of 0.20 to 0.35 m and 0.4 to 1.06 m reported by Dagne *et al*. (2008) and Tilahun (1988) previously, respectively. Moreover, Dagne (2010) also reported that the mean SD value was 0.29 m in Lake Ziway.

As compared to other tropical Lakes, the SD values of Lake Ziway is shallower than in Lakes of Hawasa (0.85 m), Chamo (0.35 m), Hayq (2.7 m), Tana (0.51 – 1.82 m), Navaisha (0.1 – 0.75 m) and Arenguade (0.21 – 0.37 m) as reported by Tilahun and Ahlgren (2010), Fetahi (2010), Wondie (2006), Momanyi *et al.* (2012) and Belachew (2010) (Table 4.1.5), respectively. The declining trend in SD reading is one of the indications which suggest the increasing trend in turbidity of the lake, which can be mainly attributed to catchment degradation and siltation.

Comparison of variations in SD showed that the fluctuations between the seasons were significant whereas those across different sampling sites in all the seasons were not significant (Tables 4.1.1 and 4.1.1.2). In general the SD was found to be at its shallowest during the wet season, and deepest during the dry season at all the sampling sites because of the large amount of silt that enter the lake in the wet season with runoff. Thus, unlike the observations in different tropical freshwater (Ishaq *et al.*, 2013) the transparency of the water in Lake Ziway increased during the dry season. This might be the undisturbed catchment which keeps the soil system intact during dry season.

Turbidity: Turbidity ranged from 88 to 239 and 98 to 399 in dry and wet seasons respectively (Tables 4.1.1 and 4.1.2). Dagne (2010) reported that turbidity of Lake Ziway varied between 49.4 and 299 NTU with mean values of 80.2 NTU. Tamire and Mengistu (2012) also reported that the turbidity of Lake Ziway ranged from 42 to 70 NTU at the study sites (one time measurement) and their range was less than the present work. The turbidity of lake water is high in the rainy season. Higher turbidity during wet season is due to higher impact of silt loaded runoff. This observation is in agreement with other works in which turbidity is 3 to 4 times higher in the rainy season as compared to dry season due to precipitation and erosion (Dagne, 2010).

The overall mean turbidity value of the lake water was 162 NTU. The high turbidity (maximum up to 342 NTU) was the major cause for the decline in most abiotic and biotic components of the lake during the rainy season. The lowest records of SD and DO were recorded during the time of high turbidity due to the surface runoff carry different soils, organic matter, and local wastes from the catchments that leads to decrease both DO and SD values. The increase in turbidity following rainfall is clearly a common limnological feature of the lake especially those whose catchment has intensive agricultural activities. According to the WHO; the turbidity of drinking water should be less than 5 NTU. Therefore, the turbidity of Lake Ziway water is above the acceptable range. According to (US EPA, 2005) turbidity 100-500 NTU or higher is classified as very cloudy to muddy and some fish species may become stressed at prolonged exposures to such water. In the long term it is very likely that Lake Ziway is becoming more turbid as indicated by declining SD as discussed above.

Table 4.1.2 Means and ranges of the physico-chemical parameters measured at the surface water of Lake Ziway in wet season

Site		Temp	DO	pH	EC	TDS	SD	TA	Turbidity
B	x̄± Std. Err	22±0.47	4.72±0.35	8.59±0.09	274.5±9	175.7±58.2	15.3±0.33	207±6.3	191±40
	Range	21.5-23	4.27-5.4	8.4 - 8.7	176 - 456	113-292	15-16	200-220	125-262
C	x̄± Std. Err	21.2±0.25	4.75±28	8.57±0.09	218±44	147.8±37	17.3±0.67	168±6.11	138±24
	Range	20.7-22	4.4-5.3	8.4-8.7	173-306	110-222	16-18	160-180	98-179
F_a	x̄± Std. Err	22±0.56	4.4±0.25	8.78±0.54	353±89	226±56	18.6±0.67	172±14	112±5
	Range	20.8-23	3.95-4.8	7.9-9.7	187-488	120-312	18-20	148- 196	103-124
F_b	x̄± Std. Err	21±1.6	6.2±0.65	8.53±0.14	370±98	216±84	19.6±0.67	250±111	18±7
	Range	18-24	4.9-7.2	8.3-8.7	175-478	49-306	19-21	120-472	10-32
K_a	x̄± Std. Err	22± 0.28	3.1±0.34	8.4±0.08	230±41.4	180±32	16-1.2	117-35	237±77
	Range	20 – 27	2.4 -3.5	8.3-8.5	183-312	117-221	14-18	80-188	129-385
K_b	x̄± Std. Err	20±0.15	2.6±0.64	7.78±0.24	101±17.9	65±11.7	17.3±0.90	72.3±.33	381±230
	Range	20-21	1.4-3.6	7.5-8.3	65-120	42-78.3	16-19	72-73	129-840
K_o	x̄± Std. Err	22.5±0.86	4.8±0.28	8.67±0.10	381±101	234±61	18.3±0.88	175±14.6	115±105
	Range	21-24	4.35-5.3	8.5-8.8	179-496	116-318	17.-20	146-190	105-125
M_a	x̄± Std. Err	23±0.11	3.9±0.12	8.6±0.01	273±49	153±21.3	17±1.15	130±24.9	280±82
	Range	22-23	3.68-4.1	8.6-8.61	176-337	113-185	15-19	100-180	124-399
M_b	x̄± Std. Err	20.4±0.7	4.8±0.75	7.44±0.53	120±3	77±1.9	18±1.73	100±20	266±247
	Range	19.5-22	3.35-5.8	6.5-8.3	115-126	73.7-80.4	15-21.0	60-120.	0-360

- ✓ *Temp for temperature in ^oC; DO for dissolved oxygen in mg L^{-1}; pH for H^+ concentration; EC for electrical conductivity in $\mu S\ cm^{-1}$; TDS for total dissolved solids in mg L^{-1}; SD for secchi depth in cm; TA for total alkalinity, mg L^{-1}; Turbidity in NTU*

4.1.2 Spatial and temporal variations of nutrients in Lake Ziway

The spatial and temporal variations of nutrients are summarized in Tables 4.1.3 and 4.1.4.

Nitrate-nitrogen (NO_3-N): The mean NO_3-N concentration ranged from 0.1 to 5.26 mg L^{-1} and 0.01 to 0.86 mg L^{-1} in dry and wet seasons, respectively (Tables 4.1.3 and 4.1.4). The highest mean NO_3-N was at F_b in dry and at K_b in wet season while M_a has the lowest values in both seasons. The mean NO_3-N value found in this study (0.21 mg L^{-1}) was higher than those values 0.17, 0.003, 0.06 mg L^{-1} reported by Kebede *et al.* (1994), Tilahun and Ahlgren (2010), Tamire and Mengistu (2012), respectively.

As compared to other tropical lakes, Tilahun and Ahlgren (2010) reported that the mean concentration of NO_3-N was about 0.0025 and 0.003 mg L^{-1} in Lakes Hawasa and Chamo which is lower than Lake Ziway (Table 4.1.5), respectively. Similarly, Fetahi (2010) reported that the average concentration of NO_3-N was about 0.042 mg L^{-1} in Lake Hayq which was lower than in this study (Table 4.1.5). The increasing trend in NO_3-N concentration is probably because of nutrient enrichment of the littoral zone of the lake from anthropogenic impacts in the catchment area. Nitrate-nitrogen concentration in the lake water showed that there were significant fluctuations across the different stations during all the seasons but the fluctuations in its value over the different seasons were not significant ($p > 0.05$).

NO_3-N in drinking water has been linked to human health problems such as methaemoglobinemia, stomach cancer and negative reproductive outcomes (Leo *et al.*, 2014). High NO_3-N concentrations have also been linked to lower productivity in livestock (Leo *et al.*, 2014). Because nitrates are endogenously reduced to nitrites at an average percentage of 5 to 10 %, maximum contaminant levels of 10 mg NO_3-N L^{1-} and 1 mg NO_2-N L^{1-} for drinking water have been recommended to prevent methemoglobinemia in humans (USEPA, 2000; WHO, 1996). Several laboratory studies have also shown that a NO_3-N concentration of 10 mg NO_3-N L^{-1} for drinking water can adversely affect, at least during long-term exposures, sensitive aquatic animals (Camargo and Alonso, 2006).

Nitrite-nitrogen (NO_2-N): This ranged from 0.06 to 2.89 mg L^{-1} in dry season and 0.20 to 1.8 mg L^{-1} in wet season during the study period (Tables 4.1.3 and 4.1.4). The lowest concentrations of NO_2-N were at M_a in both dry and wet seasons whereas the highest concentration were at F_b and K_b in dry and wet seasons, respectively (Tables 4.1.3 and 4.1.4). The mean NO_2-N value found in this study (0.5 mg L^{-1}) was higher than those values 0.06, 0.01 mg L^{-1} reported by Beneberu and Mengistu (2005) and Tamire and Mengistu (2012) respectively. Relatively higher NO_2-N concentrations were measured near effluent of the floriculture industry which could be due to the application of high amount of agrochemicals (Tadele, 2012). Comparatively, higher concentrations of NO_2-N values were also measured in Lake Ziway than some other Ethiopian lakes such as, Lake Hayq (0.01 mg L^{-1}) as reported by Fetahi (2010). The mean concentration of NO_2-N in this study is beyond the concentration limit of the EU guidelines for drinking water (0.1 mg NO_2-N L^{-1}) (EU, 1998). Consequently, such results are likely to cause environmental concerns due to NO_2-N toxicity to aquatic biota as well as because of its effects on human health effects. Currently Lake Ziway is serves as a drinking purpose for the people living the city.

The main toxic action of nitrite on aquatic animals, particularly on fish is due to the conversion of oxygen-carrying pigments to forms that are incapable of carrying oxygen, causing hypoxia and ultimately death. In fish, entry of nitrite into the red blood cells is associated with the oxidation of iron atoms ($Fe^{2+} \rightarrow Fe^{3+}$), functional hemoglobin being converted into methemoglobin that is unable to release oxygen to body tissues because of its high dissociation constant (Jensen, 2003). Moreover, the following toxic effects of nitrite on fish have been found: (1) depletion of extracellular and intracellular Cl^{-} levels causing severe electrolyte imbalance; (2) depletion of intracellular K^{+} and elevation of extracellular K^{+} levels affecting membrane potentials, neurotransmission, skeletal muscle contractions, and heart function; (3) formation of N-nitroso compounds that are mutagenic and carcinogenic; (4) damage to mitochondria in liver cells causing tissue O_2 shortage; (5) repression of immune system decreasing the tolerance to bacterial and parasitic diseases (Jensen, 2003; Camargo and Alonso, 2006)

Ammonia nitrogen (NH4-N): Concentration of NH4-N in Lake Ziway ranged from 0.17 to 0.29 mg L^{-1} in dry and 0.08 to 0.15 mg L^{-1} in wet seasons with their lowest concentrations at C and M_a in dry and K_o and M_a in wet seasons while the highest value were at F_b in dry and M_b and K_b in wet seasons, respectively (Tables 4.1.3 and 4.1.4). The mean concentration of NH4-N (0.12 mg L^{-1}) in this study was similar with relatively recent reports by Tilahun and Ahlgren, 2010 (0.11 mg L^{-1}), and Tamire and Mengistu, 2012 (0.14) but higher than that of made reports by Kebede *et al*., 1994 (0.036 mg L^{-1}) indicating increasing trend.

NH_4-N is very toxic to aquatic animals, particularly to fish (Camargo and Alonso, 2006). The toxic action of NH_4-N on fish, may be due to one or more of the following causes: (1) damage to the gill epithelium causing asphyxiation; (2) stimulation of glycolysis and suppression of Krebs cycle causing progressive acidosis and reduction in blood oxygen-carrying capacity; (3) uncoupling oxidative phosphorylation causing inhibition of ATP production and depletion of ATP; (4) disruption of blood vessels and osmoregulatory activity upsetting the liver and kidneys; (5) repression of immune system increasing the susceptibility to bacterial and parasitic diseases (Augspurger *et al.*, 2003). Moreover, it can cause toxicity to Nitrosomonas and Nitrobacter bacteria, inhibiting the nitrification process. This inhibition can also result in increased accumulation of NH_4^+ in the aquatic environment, intensifying the toxicity to bacteria and other aquatic animals (Camargo and Alonso, 2006).

Among the different taxonomic groups of aquatic animals that have been exposed to NH_4-N toxicity, certain freshwater invertebrates and fish seem to be the most sensitive, exhibiting acute toxicities (96-hour LC_{50}) lower than 0.6 mg NH_4-N L^{-1} and chronic toxicities (72-day LC_{50}) of 0.05 mg NH_4-N L^{-1}. On the basis of acute and chronic toxicity data, water quality criteria, ranging 0.05 - 0.35 mg NH_4-N L^{-1} for short-term exposures and 0.01- 0.02 mg NH4-N L^{-1} for long-term exposures, have been estimated and recommended to protect sensitive aquatic animals (USEPA, 2000; Camargo and Alonso, 2006). Moreover, the physiochemical water quality parameters were also changed. For instance, DO concentration decreases.

Total nitrogen (TN): The mean TN concentration ranged from 4.5 to 12.21 mg L^{-1} in dry and 4.98 to 12.0 mg L^{-1} in wet season. The highest concentrations were at K_o and F_b in dry and wet season respectively whereas the lowest concentrations were at B in both seasons (Tables 4.1.3 and 4.1.4). The higher TN concentration in the KO and Fb were due to anthropogenic impacts and application of high amount of agrochemicals by floriculture industry, respectively. There was a seasonal trend of a slightly higher amount of TN during the wet season at most stations. The concentration of organic N in unpolluted surface waters can vary from 0.3 to 2 mg N L^{-1} (APHA, 1999). In eutrophic waters, organic N can reach 7 to 10 mg N L^{-1} and much higher values (> 20 mg N L^{-1}) are found in polluted waters and wastewaters (APHA, 1999).

Soluble Reactive Phosphorus (SRP): The mean values of SRP ranged from 0.05 to 0.08 mg L^{-1} and showed similar concentrations for lower values for most of the sampling sites and high values at F_b in the dry season, while in the wet season it ranged from 0.05 to 0.12 mg L^{-1} (Tables 4.1.3 and 4.1.4). Most sites have also similar concentrations in the wet season and only site F_b has the highest values. The overall mean SRP concentration was 0.06 mg L^{-1} which is higher than the previously reported data of Kebede (1994), Gebre-Mariam (2002), Tilahun and Ahlgren (2010), and Tamire and Mengistou (2012) which was 0.016, 0.035, 0.01 and 0.029 mg L^{-1}, respectively. This is because in recent times Lake Ziway is exposed to strong anthropogenic impacts due to excessive use of agrochemicals like fertilizers and pesticides in which organic and inorganic pollutants are released and discharged from water from domestic sources, agricultural runoff, and horticulture including floriculture activities around the lake. As compared to other tropical lakes, the mean SRP of Lake Ziway (0.06 mg L^{-1}) is lower than in Lakes Chitu (1.7 mg L^{-1}), Shalla (0.76 mg L^{-1}), Chamo (0.118 mg L^{-1}), Tana (0.1 to 1.8 mg L^{-1}), and Arenguade (0.7 to 2.12 mg L^{-1}) as reported by wood and Talling (1988), wood and Talling (1988), Tilahun and Ahlgren (2010), Wondie (2006), and Belachew (2010) but higher than in lakes of Hawasa (0.015 mg L^{-1}), Hayq (0.002 mg L^{-1}) and Navaisha (0.003 mg L^{-1}) as reported by Tilahun and Ahlgren (2010), Fetahi (2010) and Momanyi *et al.* (2012), respectively (Table 4.1.5).

Total phosphorus (TP): The mean TP concentrations ranged from 0.12 to 0.97 mg L^{-1} and 0.23 to 1.02 mg L^{-1} in dry and wet seasons respectively (Tables 4.1.3 and 4.1.4). Mean TP concentration was highest at M_b in both seasons whereas the lowest concentrations were at B and K_o in dry and K_a in wet seasons. The overall mean TP value of the lake water was 0.311 mg L^{-1} which is greater than the previous reported data of Kebede *et al.*, (1994), and Tilahun and Ahlgren (2010), which was 0.219 and 0.069 mg L^{-1} respectively. Tilahun and Ahlgren (2010) also reported that the concentration of TP in Lakes Hawasa and Chamo was 0.034 and 0.182 mg L^{-1}, respectively which is lower than in Lake Ziway (Table 4.1.5).

According to Jeppesen *et al.* (1997), Phosphate concentrations ranging from 0.05 to 0.1 mg L^{-1} are considered to be thresholds for natural waters. SRP is particularly the nutrient considered to be the critical limiting nutrient, causing eutrophication of freshwater systems (Wetzel, 1983, 2001).

Table 4.1.3 Means and ranges of nutrient concentrations measured at the surface water of Lake Ziway in dry season

Site		TP	SRP	NO_2-N	NO_3-N	NH_4-N	TIN	TN	SiO_2-Si
B	x̄± Std. Err	0.12±0.02	0.06±0.01	0.48±0.20	0.17±0.04	0.21±0.05	0.85±0.25	5.7±.25	46.2±6.2
	Range	0.06-0.15	0.04-0.08	0.188-1.3	0.06-0.25	0.1-0.35	0.34-1.8	4.9-6.4	32-68
C	x̄± Std. Err	0.14±0.02	0.05±0.01	0.29±0.05	0.26±0.17	0.17±0.03	0.72±0.22	9.1±0.65	46.8±2.4
	Range	0.1-0.185	0.03-0.07	0.18-0.41	0.01-0.91	0.09-0.26	0.29-1.5	7.34-11.20	39.5-54
F_a	x̄± Std. Err	0.14±0.02	0.05±0.01	0.96±0.22	0.38±0.13	0.24±0.04	1.6±0.36	6.1±.6	46.8±4.9
	Range	0.105-0.23	0.03-0.1	0.6-1.8	0.1-0.75	0.15-0.35	0.9-2.9	4.5-8.3	35-60
F_b	x̄± Std. Err	0.19±0.05	0.08±0.03	1.7±0.44	0.58±0.19	0.29±0.05	2.6±0.6	8.1±.56	91± 10
	Range	0.05-0.32	0.04-0.16	0.72-2.89	0.08-0.97	0.15-0.42	1.0-4.2	6.5-9.8	56.9-114
K_a	x̄± Std. Err	0.13±0.02	0.05±0.01	0.35±0.08	0.12±0.02	0.22±0.05	0.68±0.10	7.1±1.1	50.5±6.7
	Minimum	0.09-0.19	0.04-0.07	0.155-0.64	0.08-0.18	0.10-0.4	0.40-0.95	5.0-11	40.1-77
K_b	x̄± Std. Err	0.17±0.03	0.05±0.01	0.34±0.03	0.22±0.05	0.34±0.03	0.89±0.08	9.2±1.3	68±7.8
	Range	0.08-0.24	0.04-0.09	0.24-0.42	0.07-0.35	0.24-0.42	0.76-1.2	7- 9	43-88.7
K_o	x̄± Std. Err	0.12±0.02	0.05±0.01	0.32±0.09	0.10±0.03	0.2±0.04	0.62±0.14	9.7±.42	40± 3.4
	Range	0.07-0.19	0.04-0.07	0.05±0.188	0.01-0.18	0.09-0.3	0.3-1.2	8.5-11	30-47
M_a	x̄± Std. Err	0.14±0.02	0.05±0.01	0.23±0.08	0.10±0.02	0.17±0.03	0.55±0.08	6.3±.49	49±3.8
	Range	0.09-0.2	0.04-0.06	0.1-0.53	0.04-0.14	0.114-0.3	0.35-0.8	4.8-7.6	38-62
M_b	x̄± Std. Err	0.97±0.75	0.06±0.01	0.41±0.17	0.28±0.19	0.41±0.17	1.3±0.53	9.4±1.2	61.3±3.9
	Range	0.2-3.95	0.04-0.08	0.06-1.1	0.03-1.1	0.1-1.1	0.21-3.2	5.6-12.21	50.8-73

✓ *TP for total phosphorus in mg L^{-1}; SRP for soluble reactive phosphorus in mg L^{-1}; NO_2-N for nitrite-nitrogen in mg L^{-1}; NO_3-N for nitrate-nitrogen in mg L^{-1}; NH4-N for ammonia-nitrogen in mg L^{-1}; TIN for total inorganic nitrogen in mg L^{-1}; TN for total nitrogen in mg L^{-1}; SiO_2-Si for soluble silica in mg L^{-1}*

The seasonal variations of NH_4-N, NO_2-N, NO_3-N, TIN, TN, SRP, TP and SiO_2 were at their highest records at F_b, M_b and K_b sites compared to the other sites. The presence of NH_4-N is very likely to be an indication of domestic waste pollution while the other nutrients are closely associated with agricultural effluents from horticulture and floriculture effluents, domestic wastes and surface runoff into the two rivers (Ayenew and Legesse, 2007; Tadele, 2012). Moreover, redox processes in the system; denitrification as well by the fact that NO_3-N is converted to NH_4-N before being assimilated by plant material. There are also ammonia based fertilizers this suggests that Lake Ziway is experiencing high influxes of phosphorus and nitrogen species from external loads. NO_2-N and SRP concentrations showed little variation between the sampling sites.

The nutrient contamination of the lake water is considered to be mainly a result of domestic wastes and agricultural runoff brought into the lake by Meki and Ketar Rivers watershed, effluent of fishery industry and runoffs from agricultural and irrigation fields (Gebre-Mariam, 2002; Ayenew and Legesse, 2007; Tadele, 2012; Tamire and Mengistu, 2014).

Table 4.1.4 Means and ranges of nutrient concentrations measured at the surface water of Lake Ziway in wet season (TP for total phosphorus in mg L^{-1}; SRP for soluble reactive phosphorus in mg L^{-1}; NO_2-N for nitrite-nitrogen in mg L^{-1}; NO_3-N for nitrate-nitrogen in mg L^{-1}; NH_4-N for ammonia-nitrogen in mg L^{-1}; TIN for total inorganic nitrogen in mg L^{-1}; TN for total nitrogen in mg L^{-1}; SiO_2-Si for soluble silica in mg L^{-1})

Site		TP(mg/L)	SRP(mg/L)	NO_2-N(mg/L)	NO_3-N(mg/L)	NH_4-N(mg/L)	TIN(mg/L)	TN(mg/L)	SiO_2-Si(mg/L)
B	x̄± Std. Err	0.347±0.07	0.046±0.01	0.47±0.06	0.145±0.03	0.108±0.02	0.725±0.08	5.13±1.2	35.5±11.6
	Range	0.21-0.42	0.04-0.06	0.35-0.53	0.08-0.20	0.07-0.13	0.57-0.86	2.8-7.0	12.37- 47.3
C	x̄± Std. Err	0.382±0.023	0.05±0.01	0.33±0.12	0.171±0.12	0.09±0.01	0.59±0.24	6.02±0.26	43.6±.72
	Range	0.34-0.41	0.03-0.08	0.21-0.57	0.05-0.41	0.08-0.10	0.352-1.1	5.60-6.5	42.9-45.1
F_a	x̄± Std. Err	0.29±0.12	0.05±0.01	0.74±0.22	0.26±0.12	0.09±0.03	1.1±0.33	7.0±0.81	36±7.5
	Range	0.176-0.52	0.04-0.07	0.43-1.2	0.03-0.39	0.03-0.14	0.48-1.62	5.6-8.4	22.2-47.7
Fb	x̄± Std. Err	0.416±0.175	0.11±0.04	0.89±0.44	0.44±0.19	0.09±0.04	1.42±0.62	6.66±0.53	39.2±26
	Range	0.17-0.75	0.04-0.16	0.34-1.8	0.17-0.80	0.02-0.15	0.75-2.7	5.6-7.4	6.0 - 90.5
K_a	x̄± Std. Err	0.23±0.02	0.05±0.01	0.84±0.16	0.47±0.04	0.09±0.03	1.39±.18	7.6±0.43	37.9±4.68
	Range	0.20-0.27	0.04-0.07	0.5 - 1.1	0.4-0.54	0.03-0.12	1.1±1.7	7-8.4	30.3 -46.45
K_b	x̄± Std. Err	0.732±0.27	0.06±0.01	1.2±0.20	0.86±0.22	0.15±0.10	2.2±.50	8.1±0.86	38.15±17.10
	Range	0.238-1.2	0.05-0.08	0.89-1.6	0.52-1.3	0.05-0.3	1.5-3.1	7-9.8	11.24-70
K_o	x̄± Std. Err	0.268±0.08	0.05±0.01	0.42±0.12	0.20±0.04	0.08±0.02	0.7±0.12	10±1.9	34.3±11
	Range	0.12-0.376	0.04-0.07	0.2-0.6	0.1-0.3	0.05-0.1	0.5-0.9	8.4-12.0	12.6-48.2
M_a	x̄± Std. Err	0.242±0.04	0.06±0.02	0.76±0.06	0.23±0.11	0.08±0.02	1.06±0.14	6.1±.55	42.62±1.9
	Range	0.19-0.33	0.04-0.082	0.664-0.86	0.01-0.369	0.03-0.11	0.8-1.3	4.97-7	38.96-45.42
M_b	x̄± Std. Err	1.0±0.30	0.09±0.02	1.02±.2	0.50±0.24	0.16±0.06	1.66±.48	8.5±4.5	39.1±14.72
	Range	0.47-1.5	0.06-0.12	0.7-1.42	0.02-0.75	0.05-0.23	0.76-2.4	5.6-12.0	11.2-61.2

Soluble reactive silica (SiO_2-Si): The mean concentration of SiO_2-Si ranged from 39 to 91 and 36 to 43 mg L^{-1} with mean values of 55 and 39 mg L^{-1} in dry and wet seasons, respectively (Tables 4.1.3 and 4.1.4). The lowest amount of silica was recorded in the lake was 30.0 and 6.0 mg L^{-1} and the highest amount was 114 and 91 mg L^{-1} during the dry and wet seasons, respectively. In contrast, Gebre-Mariam (2002) reported that SiO_2-Si concentrations of Lake Ziway ranged from 13 to 31 and 15 to 38 mg L^{-1} with mean values of 19 and 23 mg L^{-1} in dry and wet seasons, respectively. The mean SiO_2-Si concentration in both seasons showed that its fluctuations over the different seasons and across the different sampling sites were significant ($p < 0.05$). The overall mean concentration of SiO_2-Si (41 mg L^{-1}) was higher than the previously reported values of Tilahun and Ahlgren (2010) and Gebre-Mariam (2002) which were 24 and 21 mg L^{-1}, respectively. As compared to other tropical lakes, the mean SiO_2-Si (41 mg L^{-1}) in Lake Ziway was lower than Lakes Chitu (320 mg L^{-1}), Shala (112 mg L^{-1}), Abijata (128 mg L^{-1}) and higher than in lakes like Chamo (1 mg L^{-1}), Hayq (4 mg L^{-1}) and Arenguade (4 to 37 mg L^{-1}) but comparable with Lakes Hawasa (38 mg L^{-1}), Abaya (40 mg L^{-1}), Langano (48 mg L^{-1}) and Bishoftu (38 mg L^{-1}) (Table 4.1.5). Therefore, the amount of dissolved SiO_2-Si in Lake Ziway was very high similar to those reported by Talling, (1992) (> 10 mg SiO_2 L^{-1}) commonly encountered in African lakes.

Table 4.1.5 Comparison of the physico-chemical parameters of Lake Ziway with other tropical lakes (mg L^{-1} for nutrients

Lakes	Temp(^oc)	DO	pH	EC	SRP	TP	NO_3-N	SiO_2-Si	SD	Author
Hawasa	23.5	5 - 7	8.66	846	0.015	0.034	0.025	37.6	0.85	Tilahun and Ahlgren, 2010
Chamo	26.3	5 - 9	8.84	1910	0.118	0.182	0.033	1.0	0.18	Tilahun and Ahlgren, 2010
Hayq	18.2	1- 8.4	9	910	0.022	0.058	0.042	3.7	2.7	Fetahi, 2010
Tana	20 -27	5.9 -7	7.3 - 8.5	115 -148	0.1- 1.8		0.1-1		0.51-1.82	Wondie, 2006
Navaishia	22.4	5.89	8.51	290	0.003	0.027 - 0.41	0.012	-	0.1- 0.75	Momanyi *et al.*, 2012
Arenguade	20.2-24.5	0.4-13.1	9.62 - 9.84	-	0.702 - 2.12	-	0.004 - 0.78	3.5 - 37	0.21- 0.37	Belachew, 2010
Abaya	-	-	8.9	623	0.04	-	-	40	-	Wood and Talling, 1988
Langano	-	-	9.4	1810	0.09	-	-	48	-	Wood and Talling, 1988
Bishoftu	-	-	9.2	1830	0.005 to 0.1	-	-	38	-	Wood and Talling, 1988
Abijata	-	-	10.2	15800	0.05	-	-	128	-	Wood and Talling, 1988
Shala	-	-	9.9	19200	0.76	-	-	112	-	Wood and Talling, 1988
Chitu	-	-	9.8	28600	1.7	-	-	320	-	Wood and Talling, 1988
Ziway	**23**	**5**	**8.1**	**404**	**0.06**	**0.311**	**0.21**	**40.7**	**0.2**	**Present study**

In general high concentration of SiO_2-Si recorded in dry compared to wet season, in the present study is in agreement with to the dry season probably indicating the importance of internal load of silica and dilution in the wet season. Similar results reported by Vessely *et al*. (2005). Wood and Talling (1988) indicated that the SiO_2-Si concentrations in 20 Ethiopian lakes studied were very high by world standards and argued that contributing factors include the great mobility of silicates in most tropical soils, ground-water input for many lakes, and the enhanced dissolution of solid silicates in waters of high alkalinity and pH. Other possible factors responsible for the variations of silicates include silicate removal from solution in the reverse weathering process of sediment formation and the presence or absence of diatoms as major contributors to the flora of a lake.

4.1.3. Multivariate analysis

4. 1.3.1 Principal component analysis (PCA)

Four components of PC analysis showed 88.1 % of the variance in the data set of the wet season, as the Eigenvectors classified the 15 physico-chemical parameters into four groups. PC_1 (38.9 % of the total variance in the data set) has strong positive loads on TP, NH4-N, NO_2-N, NO_3-N, TIN and SD but pH had strong negative loadings with PC_1 (Table 4.1.6). The second component (PC_2) accounted for 24.0 % of the total variance measured, demonstrating strong positive loadings for TN, EC, TDS and TA and the third component (PC_3) demonstrated 16.8 % of the total variance and has strong positive loadings for PO_4-P, DO and temperature but SiO_2-Si, had strong negative loadings with PC_3, while, the fourth component (PC_4) accounts for only 8.4 % of the total variance in the season (Table 4.1.6).

As indicated in the PCA analysis, PC_1 has strong positive loadings for NH4-N, NO_2-N, NO_3-N, SRP, TP, SiO_2-Si, TIN, EC, TDS, TA and SD associated sampling sites M_b and K_b during wet season. The presence of nutrients in PC_1 demonstrated the intensity availability of agricultural products in the catchment of Lake Ziway resulting to pollution with nutrients coming from fertilizers and pesticides in the lake catchment (Meshesha *et al.*, 2012).

One of the main sources of TP in runoff is soils with high phosphorus levels. In other words, the nutrient parameters, pH and SD account for similar patterns seen in lake water samples. This group of nutrient parameters also reflected the degree of eutrophication of the lake, suggesting that the anthropogenic pollution mainly due to the discharge of domestic and agricultural wastes, industrial sewage and agricultural runoff (Meshesha *et al.*, 2012). Moreover, it might be due to ammonium and phosphate based fertilizers and pesticides used by farmers, and the lake receives ammonium via surface runoff and irrigation waters (Desta *et al*., 2016). Nitrate nitrogen source is due to numerous sources, such as, geologic deposits, natural organic matter decomposition and agricultural runoff (Leo *et al.*, 2014). The second component (PC_2) demonstrated strong positive loadings for TN, EC, TDS and TA. The third components (PC_3) demonstrated strong positive loadings for SiO_2-Si, SRP, DO and temperature. This factor indicates that PO_4-P source is from domestic and agricultural wastes, detergents from industries whereas SiO_2-Si is from bed rock materials and compounds containing silica from floriculture industry (Tadele, 2012), while the fourth component (PC_4) had no strong loadings in any measured parameters.

Table 4.1.6 The factor loadings values and explained variance of water quality in two seasons (positive and negative strong correlations are marked bold)

Parameters	**PC1**		**PC 2**		**PC3**		**PC 4**	
	Dry	**Wet**	**Dry**	**wet**	**Dry**	**wet**	**Dry**	**Wet**
TP	0.065	**0.918**	**-0.692**	-0.180	0.483	0.213	0.100	0.225
SRP	**0.93**	0.148	-0.157	-0.179	0.132	**0.850**	-0.034	0.374
NH4-N	**0.907**	**0.853**	-0.039	-0.379	0.265	0.316	-0.105	0.048
NO_2-N	**0.966**	**0.879**	0.099	0.090	-0.073	-0.332	-0.087	-0.145
NO_3-N	**0.963**	**0.897**	-0.040	-0.005	-0.205	0.031	0.104	-0.344
TIN	**0.98**	**0.938**	-0.010	0.027	-0.171	-0.136	0.060	-0.235
TN	-0.097	0.561	-0.315	**0.680**	0.176	-0.277	**0.875**	0.200
SiO_2-Si	**0.791**	0.109	-0.52	-0.096	-0.286	**-0.620**	-0.051	0.485
Temp	0.283	-0.191	**0.793**	0.192	0.431	**0.632**	-0.091	-0.620
DO	0.349	0.078	-0.423	0.551	**0.757**	**0.644**	-0.091	0.396
PH	-0.373	**-0.854**	**0.761**	0.129	0.489	0.004	0.078	-0.165
EC	**0.963**	-0.249	0.159	**0.959**	-0.022	-0.069	0.086	0.030
TDS	**0.955**	-0.255	0.167	**0.954**	-0.049	-0.087	0.077	0.025
SD	0.035	**0.611**	**0.660**	0.580	-0.335	-0.214	0.317	-0.164
TA	**0.801**	0.440	0.538	**0.626**	0.201	0.429	0.112	0.030
Eigenvalues	7.97	5.84	3.051	3.603	1.663	2.515	0.961	1.258
% variance	53.133	38.933	20.34	24.017	11.087	16.764	6.408	8.388
% Cumulativ variance	53.133	38.933	73.473	62.95	84.56	79.714	90.968	88.102

The dry season PCA analysis showed that four principal components (PCs) represented about 91.0 % of the total variation in the entire data set. The first PC accounted for 53.4 % of the total variations between sites and comprised of the following parameters: nutrients (NH4-N, NO_2-N, NO_3-N, TIN, SRP, SiO_2-Si), TDS, EC, TA. The second PC accounted for 20.3 % of the total variance and had strong positive loading with temperature, pH, TP and SD as the associated parameters. The third PC explained 11.1 % of the total variations between sites comprising only DO. Scree plot showed the eigenvalues sorted from large to small as a function of the principal components number after the fourth PC (Figures 4.1.1 and 4.1.2).

In the dry season the PCA performed on the correlation matrix of means of the analyzed water quality parameters by sites showed that four principal components (PCs) represented about 91.0 % of the total variation in the entire dataset. The first PC accounted nutrients (NH4-N, NO_2-N, NO_3-N, TIN, SRP, SiO_2-Si), TDS, EC, TA associated with F_a and F_b sampling sites. The high values in these sampling sites were attributed to the point pollution sources from floriculture industry in dry season.

The second PC had strong positive loadings with temperature, pH, and SD as the associated parameters whereas TP had strong negative loadings. TP demonstrated that intense agricultural activity had occurred at the sampling site M_b causing pollution due to fertilizers and pesticides in the Meki River catchment (Meshesha *et al*., 2012). Singh *et al.* (2004) interpreted as nutrient pollution from external loads, such as eutrophication from domestic wastewater, industrial effluents and agricultural activities. The third PC explained the total variations between sites comprising only DO in sampling site M_b. The inverse relationship between temperature and DO is natural processes because water can hold less DO with increasing temperature (Singh *et al*., 2004). The fourth PC explained site variations with TN only. Liu *et al.* (2003) classified the factor loadings as “strong,” “moderate,” and “weak,” corresponding to absolute loading values of >0.75, 0.75 to 0.50, and 0.50 to 0.30, respectively.

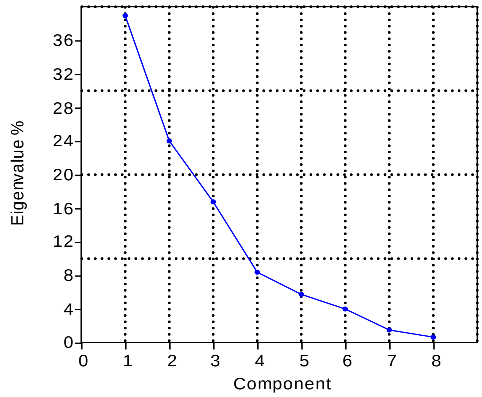

Figure 4.1.1 Wet season scree plot of the eigenvalues.

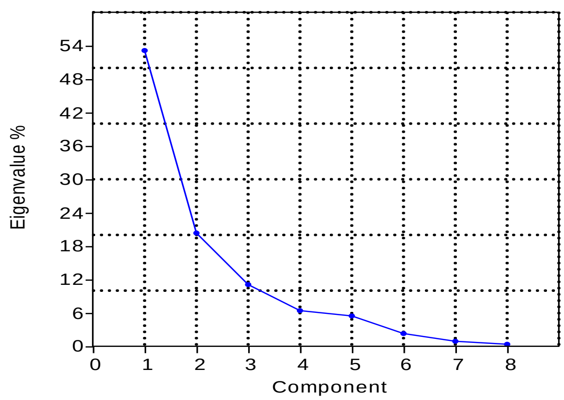

Figure 4.1.2 Dry season scree plot of the eigenvalues

In the present study, a scree plot also showed the eigenvalues sorted from large to small as a function of the principal components number. After the fourth PC (Figures 4.1.1 and 4.1.2), starting in the downward curve, other components can be omitted. The scree plot was used to identify the number of PCs to be retained in order to comprehend the underlying data structure (Palma *et al*., 2010). Thus, a new set of data is obtained. This may explain the variation of data set with fewer variables. Scree plots in PCA/FA to visually assess which components or factors explain most of the variability in the data.

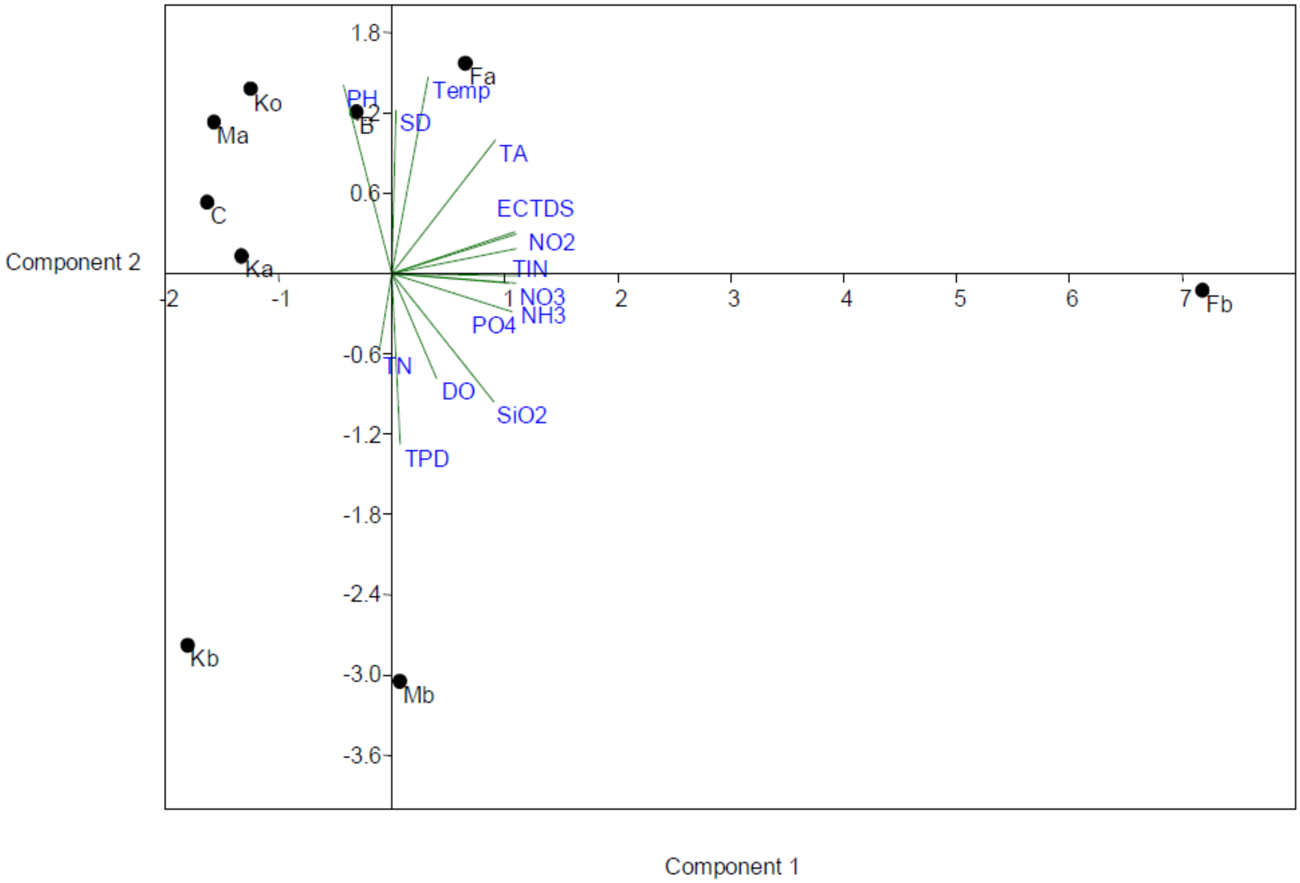

Figure 4.1.3 Results of the bi-plot of the correlation between various water quality parameters with respect to the studied sites using PCA in the dry season in 2014 and 2015

The bi-plot of PCs associated with nutrients (NH4-N, NO_3-N, NO_2-N, SiO_2-Si and SRP), EC and TDS were characterized into the F_b sampling site (Figure 4.1.3), due to the floriculture effluents. Similarly, Tadele (2012) reported that floriculture industries are known for using excessive fertilizers and the effluents from the farms drain directly to the lake. F_a distinctiveness was attributed to temperature, SD and TA. The parameter influencing the distinction in the B site was mainly pH while the M_b site was influenced by DO, TN and TP in the dry season (Figure 4.1.3).

The bi-plot of PCs associated with nutrients (NH4-N, NO_3-N, NO_2-N, SiO_2-Si, TIN, SRP and TP), which were the key parameters characterizing the M_b and K_b sampling sites in the wet season (Figure 4.1.4), suggests the influence of agricultural activities in nutrient input from the catchment of the two rivers feeding the lake (Meki and Ketar Rivers) (Meshesha *et al*., 2012;

Desta *et al.*, 2016). F_a distinctiveness was attributed to temperature, TDS, EC and DO. The parameter influencing the distinction in the K_o site was mainly pH while the F_b site was influenced by DO, TN, TA and SD in the wet season. In the present study, higher EC and TDS values were obtained for sampling points near the floriculture industry (F_b and F_a) in both seasons. In an aquatic environment, EC is an important and a simple indicator to characterize the pollution status of surface waters, as a sudden increase in conductivity can indicate the presence of more dissolved ions, which may have an impact on aquatic life and water quality (Camacho *et al*., 2015).

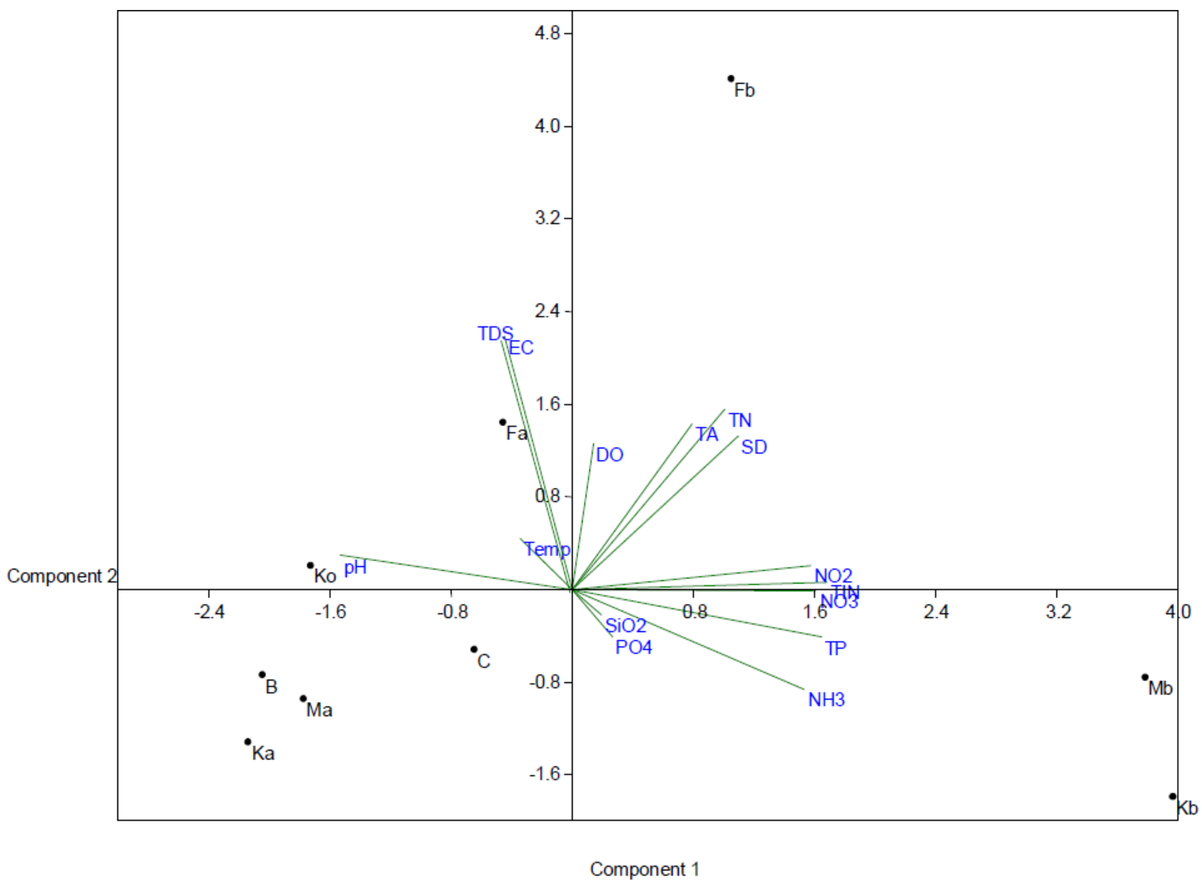

Figure 4.1.4 Results of the bi-plot of the correlation between for various water quality parameters with respect to the studied sites using PCA in the wet season in 2014 and 2015

The results from temporal PCA/FA suggested that agrochemicals were potential pollution sources for both temporal clusters although that the influence of each was different. For the two temporal clusters, 91.0 % and 88.1 % of the variances in dry and wet seasons, respectively, were explained by the four main factors. The results of the present study indicated the existence of contamination of Lake Ziway with both inorganic and organic agrochemicals and other pollutant sources (Meshesha *et al*., 2012; Tadele, 2012). Moreover, there is increasing concentrations of phosphate and nitrate, as well as silicates which all contributed to increases in salinity in Lake Ziway since the 1980s (Ayenew and Legesse, 2007; Tilahun, 2010; Tadele, 2012).

4.1. 3. 2 Cluster analysis (CA)

A dendrogram of sampling sites obtained by the Ward's method is shown in Figure 4.1.5. Nine sampling sites were divided into three groups. Cluster 1 corresponded to site F_b, which is located in the western part of the lake. The sources of pollutants in this site are effluents of floriculture industry. Cluster 2 included site K_b, which is located in the eastern portion of the lake. The pollutants in K_b were determined to be from agricultural and domestic sewage, particularly the dispersed and unsettled wastewaters from the local villages and agrochemicals from agricultural runoff. Cluster 3 contained sites F_a, K_o and B the western part of the lake, C is which in the lake central station; site M_b and M_a in the northern part of the lake and K_a is in the eastern part of the lake. The CA revealed different properties of each site with respect to physical and chemical variables. The three groups vary according to natural background features, land use and land cover, industrial structure and anthropogenic sources of pollution.

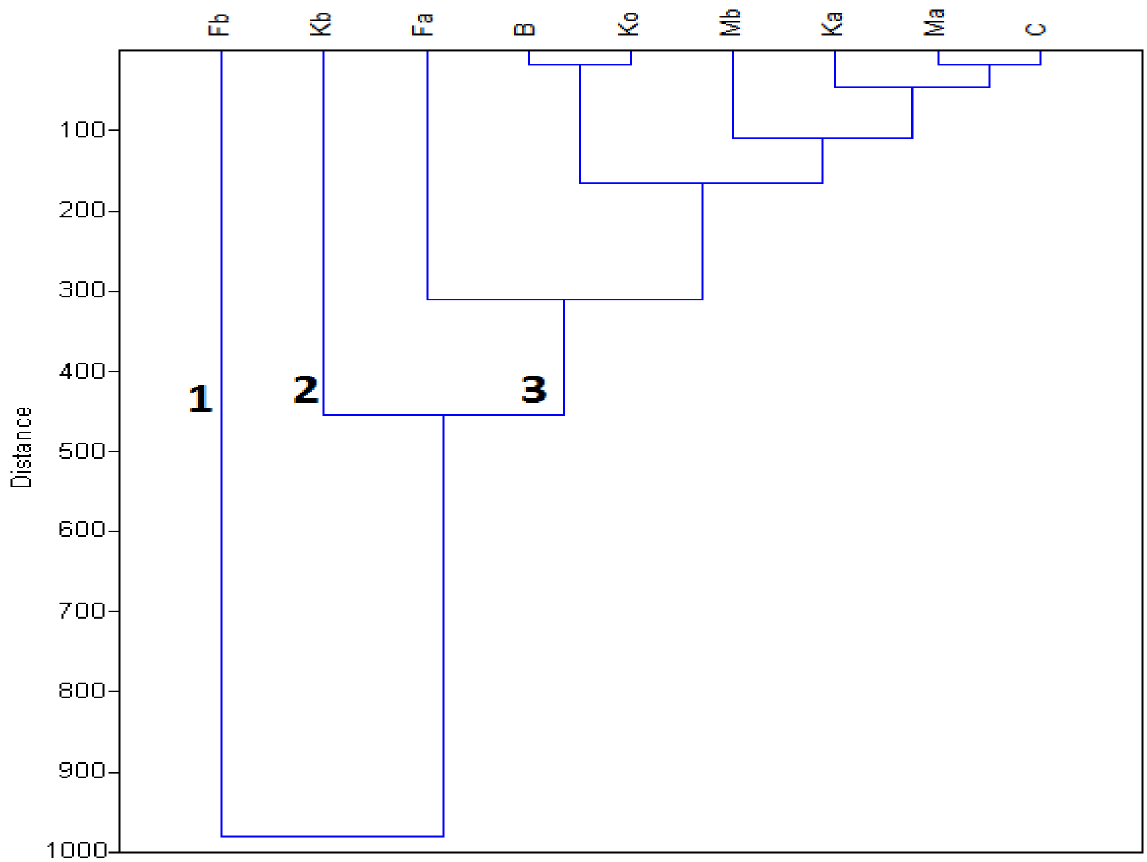

Figure 4.1.5 Dendrogram based agglomerative hierarchical clustering (Wards method) based on the PCA scores in dry season.

In the case of wet season, sampling sites classification was performed by the use of cluster analysis and dendrogram was generated, which grouped all nine sampling sites of the basin into three statistically significant clusters (Figure 4.1.6). Since we used hierarchical agglomerative cluster analysis, the number of clusters was also decided by water quality, which is mainly effected by land use and industrial structure. Grouped stations under each cluster can be seen in Figure 4. 1.6. Based on the results of cluster analysis in the wet season, results can be explained as follows:

Cluster III (Stations C, M_a, K_a, K_o, B and F_a): Sites mainly located different parts of the lake (Stations C, M_a, K_a, K_o, B and F_a) were grouped under Cluster III, which were basically at the center of the lake and shore water. In addition, Site M_a and K_a located upstream of the lake, showed similar water quality characteristics of these stations. Impacts of urbanization and industrialization level are relatively low at these sites. Direct discharged domestic wastewater contaminated the water; cluster III correspond to relatively less polluted (LP), because the inclusion of the sampling location suggests the anthropogenic sources of pollution is less in the study period.

Cluster II (Stations M_b and K_b): The two stations are the rivers of the lake; one is the Meki River that drains part of the western highland and Ketar River which drains the Arsi Mountains to the eastern part of the lake. These two rivers transported many agrochemicals from western and eastern highlands of the watershed. Therefore, these sampling stations received pollutants mostly from agricultural runoffs, domestic wastes and industrial effluents from those parts of the catchment containing Meki and Abura towns. Cluster II corresponds to moderately pollute.

Cluster I (Station F_b): This cluster site is the effluent of the floriculture industries which directly enter into the lake and pollute the lake water. Cluster I corresponds to a relatively highly polluted (HP) site, because the inclusion of floriculture industry, that releases untreated sewage at this site.

Therefore, the results indicate that the CA technique is useful in offering reliable classification of surface water in the selected region and make it possible to design a future spatial sampling strategy in an optimal way to reduce the number of sampling stations and associated costs of sampling. As a result, different measures can be taken to control water pollution in the zones with the additional application of PCA.

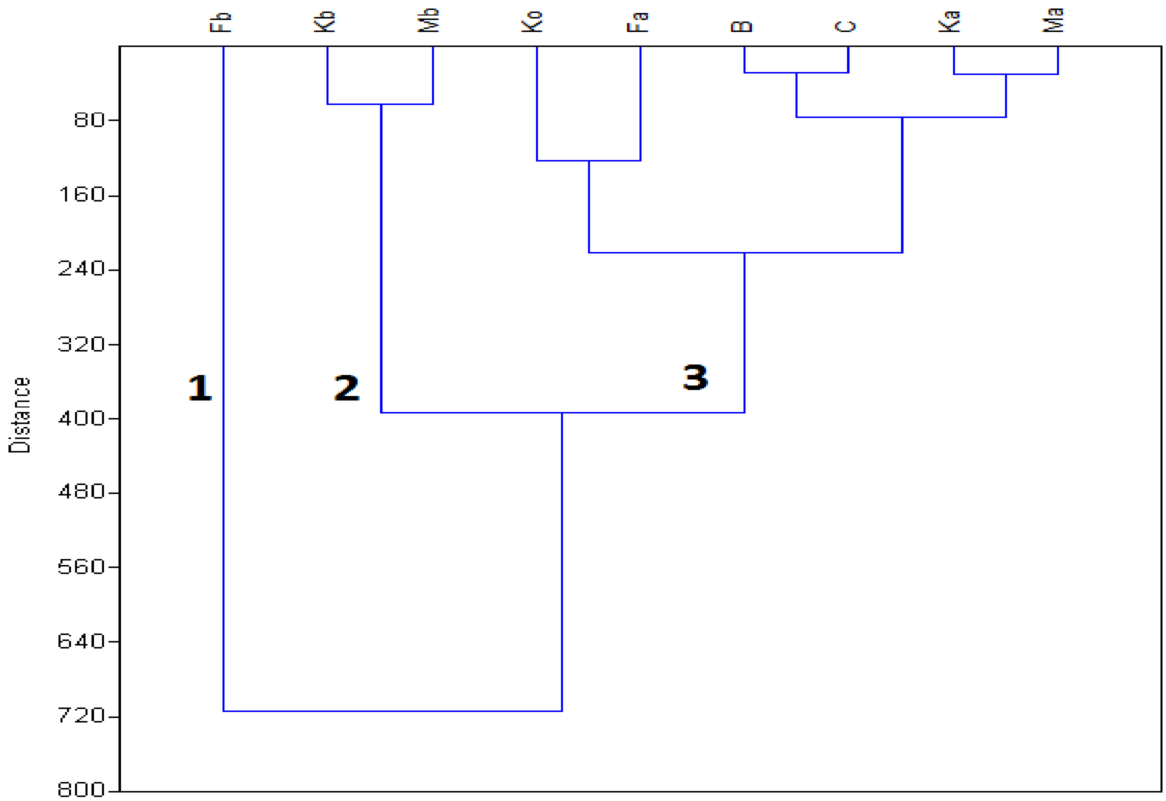

Figure 4.1.6 Dendrogram based agglomerative hierarchical clustering (wards method) based on the PCA scores in the wet season

In summary, Clusters 3 corresponds to sites (B, K_o, F_a, M_b, M_a, K_a and C) and (B, K_o, F_a, M_a, K_a and C) which the lowest pollution levels in dry and wet seasons respectively, Clusters 2 corresponded to site (K_b) in dry and (K_b and M_b) in wet seasons with moderate pollution, whereas Cluster 1 corresponded to site (F_b) demonstrated the highest levels of pollution in both seasons. Accordingly, the spatial variations of water quality in Lake Ziway showed that the water quality was better in the open water than in western and eastern areas during the study seasons. This implies that for a rapid assessment of water quality, only one site in each cluster presents a useful spatial assessment of the water quality for the entire network in different seasons. It is evident that the CA technique is useful in offering reliable classification of surface water throughout a whole region, and will make it possible to accurately perform spatial and temporal assessment in an optimal manner.

4.1.4 Comprehensive evaluation of lake water quality analysis

In Table 4.1.7, shows the values of comprehensive pollution index which were 1.8, 1.0, 1.01 and 1.08 for sites F_b, F_a, B and M_b respectively, which demonstrated moderate pollution in the dry season. The water quality of some selected parameters in these sites was determined to have been influenced by effluents received from the floriculture industry and domestic wastes from Ziway and Meki Towns, while the other sites have pollution index of 0.71, 0.69, 0.81, 0.79 and 0.84 for sites K_a, M_a, C, and K_b respectively, which demonstrated slight pollution in the same season. However, in the wet season, the values of the comprehensive pollution index ranged from 0.38 to 0.68 demonstrating slight pollution of the whole sampling sites. This is due to the dilution process that decreased the amount of nutrients per liter of the lake water in the wet season. The water quality of the lake appeared to be influenced by different major source of pollution such as agricultural activities, domestic wastes, fishing industries, swimming, car washing and floriculture industry (Ayenew and Legesse, 2007; Tadele, 2012; Meshesha *et al.*, 2012; Hayal *et al.*, 2016). Therefore, the comprehensive evaluation of water quality in the lake can tell us additional information regarding the pollution status of the lake in both spatial and temporal variation.

Table 4.1.7 Single pollution and comprehensive pollution indices of nine sampling sites for some selected water quality parameters in the dry and wet seasons in 2014 and 2015

	Dry season							**Wet season**					
Site	P_{SRP}	$P_{NH4\text{-}N}$	$P_{NO2\text{-}N}$	$P_{NO3\text{-}N}$	P_{DO}	**P**		P_{SRP}	$P_{NH4\text{-}N}$	$P_{NO2\text{-}N}$	$P_{NO3\text{-}N}$	P_{DO}	**P**
F_b	0.83	0.20	1.91	0.53	1.20	**1.80**		0.60	0.06	0.99	0.53	1.21	**0.68**
F_a	0.48	0.16	1.06	0.04	1.09	**1.0**		0.50	0.06	0.93	0.04	1.02	**0.51**
B	0.55	0.14	0.53	0.02	1.33	**1.01**		1.10	0.07	0.37	0.02	1.18	**0.55**
K_a	0.50	0.14	0.39	0.01	0.89	**0.71**		0.50	0.06	0.52	0.01	0.78	**0.38**
M_a	0.51	0.11	0.31	0.01	0.88	**0.69**		0.57	0.05	0.84	0.01	0.84	**0.46**
K_o	0.51	0.13	0.36	0.01	1.07	**0.81**		0.50	0.05	0.47	0.01	1.03	**0.41**
C	0.46	0.11	0.32	0.03	1.04	**0.79**		0.51	0.06	0.82	0.03	0.97	**0.48**
K_b	0.52	0.12	0.37	0.02	1.10	**0.84**		0.59	0.10	1.32	0.02	0.70	**0.55**
M_b	0.62	0.15	0.45	0.03	1.43	**1.08**		0.85	0.10	1.13	0.03	1.25	**0.67**

4.1.5 Temporal variation of water quality

Temporal trends were observed in physico-chemical parameters and nutrients of Lake Ziway. Most physico-chemical parameters have significantly higher values in the dry season as compared to the wet season ($p < 0.05$) (Table 4.1.8). Averaged across all sites, the concentrations of physico-chemical parameters and most nutrients showed high values in dry season than the wet seasons, and these variables may be primarily determined by different environmental factors such as dilution, water temperature, wind, natural events (e.g. erosion) and human interference. Sridhar *et al.*, (2015) noted that pollutants that have a high concentration during the dry season and a low concentration during the wet season tend to come from point sources whose supply is constant, whereas the inverse pattern can be attributed to non-point sources that are mobilized by high run-off during wet periods.

Table 4.1.8 Paired samples test for dry and wet seasons

Paired Samples Test					
		Paired Differences			Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	
Pair 1	TP in dry - TP in Wet	-0.200	0.150	0.050	0.004
Pair 2	SRP in dry - SRP in wet	-0.008	0.021	0.007	0.266
Pair 3	NH4-N in Dry - NH4-N wet	0.108	0.049	0.016	0.000
Pair 4	NO_2-N in Dry - NO_2-N in wet	-0.170	0.502	0.167	0.340
Pair 5	NO_3-N in Dry - NO_3-N in wet	0.475	1.68	0.559	0.421
Pair 6	TIN in dry - TIN in wet	0.413	2.14	0.714	0.579
Pair 7	TN in dry - TN in wet	0.565	2.79	0.930	0.560
Pair 8	SiO_2-Si in dry - SiO_2- Si in wet	16.9	15.7	5.226	0.012
Pair 9	Temp in dry - Temp in wet	1.68	1.22	0.406	0.003
Pair 10	DO in dry - DO in wet	0.584	0.599	0.200	0.019
Pair 11	pH in dry - pH in wet	2.971	0.968	0.323	0.000
Pair 12	EC in dry - EC in wet	109	113	37.6	0.020
Pair 13	TDS in dry - TDS in wet	73.1	71.7	23.9	0.016
Pair 14	SD in dry - SD in wet	7.73	2.11	0.704	0.000
Pair 15	TA in dry - TA in wet	93.7	85.24	28.4	0.011

A pattern of low mean concentrations of NH4-N, NO_3-N, TN, TIN, SiO_2-Si, in the dry season have higher mean concentrations than in the wet season. This strongly indicates point source pollution for these parameters, which is associated with industrial effluents, human interference, municipal discharge and animal waste. During the dry season, both decreased precipitation and increased agricultural withdraw for irrigation contribute to lower flow of those nutrients, however, TP, SRP and NO_2-N were observed to have higher concentration during the wet season. Similarly, Singh *et al.*, (2010) reported that high nutrients were observed during the rainy season than in the dry season.

Other water quality studies that applied PCA and CA analysis found the techniques helpful in the interpretation of large datasets. Kazi *et al*., (2009) used PCA and CA in the analysis of water quality in Manchar Lake in Pakistan and found the techniques useful in apportionment of pollution sources based on parameter association. Their findings agree with the present study particularly in the association of nutrients with catchment runoff in the wet season and point sources during the dry season. Magyar *et al.* (2013) used PCA and CA in 33 sampling sites for 13 physico-chemical and biological water quality parameters which helped them in identifying the underlying processes responsible for the heterogeneity in different parts of Lake Neusiedler in Hungary. Their study also showed that the river input region was significantly different. Moreover, Mohammad *et al.*, (2011), 16 water quality parameters; in their finding also agreed with the present study that most parameters increase their concentrations in the dry season due to evaporative effects, whereas lower values are observed in the wet season as the lake water is diluted by rain water. Furthermore, Sridhar *et al.*, (2015) also applied PCA and CA to identify the factors influencing the water quality in different seasons in Hyderabad lakes in India. The study revealed that water pollution was more significant during the dry season as compared to the rainy season because of precipitation and tidal influence which cause dilution. Ndungu *et al.*, 2014, applied PCA and CA in order to provide an insight on water quality in Lake Naivasha, Kenya showed the usefulness of such multivariate analysis in establishing the characteristics of different regions in aquatic ecosystems based on numerous water quality parameters.

Similarly, Zhao *et al.*, (2012) applied comprehensive pollution index model to explain the pollution status of Lake Baiyangdian, china. Their result revealed that Lake Baiyangdian has a pollution status ranging from less polluted to sever polluted.

4.1.6 Conclusion and recommendations

The mean nutrient concentrations showed increasing trends and were higher around the floriculture sampling sites compared to other sites in all seasons. These sites were also characterized by high EC and TDS. CA grouped 9 sampling sites into three clusters of less polluted, moderately polluted and highly polluted sites, based on similarity of water quality characteristics. Accordingly, sampling sites F_b and K_b are highly and moderately polluted in both seasons, respectively. On the other hand, sampling sites at C, M_a, K_a, M_b, K_o and F_a in dry season and K_a, C, M_a, K_o, B and F_a were less polluted during the wet season. PCA analysis also showed the pollutant sources were mainly from F_b during the dry season and M_b and K_b during the wet season. The values of comprehensive pollution index illustrated the lake is moderately and slightly polluted in dry and wet seasons, respectively. Comparatively, the pollution status of the lake is high around the floriculture effluent discharge site and at the two feeding rivers (K_b and M_b) due to increasing trends in agrochemical loads. This may lead to long term ecological changes in the lake unless possible measures are taken. Thus, the study illustrates the useful application of environmetrics techniques for the analysis and interpretation of lake water quality data, their classification on the basis of pollution status and identification of pollution sources as part of the efforts toward management of sustainability of the lake.

Therefore, measures should be taken in order to reduce anthropogenic discharges into the lake; otherwise, high levels of pollution have the potential to endanger to the population and contribute to socio-economic disaster. These results should be considered in setting guidelines for future planning and effective ecosystem management of the lake.

4.2: Nutrient dynamics and external nutrient loading in relation to climatic and hydrological factors in Lake Ziway

4.2.1 Depth profiles of physico-chemical parameters of the lake water column

Spatio-temporal variations in surface water temperature, pH and dissolved oxygen (DO) of Lake Ziway are shown in Figures 4.2.1 and 4.2.2 for monthly sampling intervals from March 2015 to July, 2015.

Temperature profiles of the water column: Temperature variations among sites and between depth profiles were low, ranging from 22.18 to 23.15 and 21.45 to 22.30 ^{o}C in sampling sites 1 and 2, respectively. The difference between the surface and bottom temperatures was in the average 0.85 ^{o}C in sampling Site 1 and 0.98 ^{o}C in sampling Site 2. The two sampling sites were site 1 were at the center (C) and site 2 were another site in the center far from C. The temperature distribution of Lake Ziway was not significantly different within the depth profiles, as the lake is shallow with reasonably strong wind action, thus mixes continuously (Figures 4.2.1 and 4.2.2) which is similar to the report by Tilahun, (2006) for the same lake. Comparison with other East African lakes revealed that the ranges of surface temperature for Lake Ziway (21.45 to 23.15 ^{0}C) are of similar range to those of Lake Nakuru (range 21 to 27 ^{0}C) and Lake Turkana (range 18.1 to 24.8 ^{0}C) Kenya (Ganf and Horne, 1975).

The thermal characteristics of Lake Ziway seems to be consistent with frequent mixing (polymictic condition) which is a typical characteristic nature of shallow East African lakes (Wood *et al*., 1978). They exhibit superficial stratification, generated daily by intense solar heating and destroyed by nocturnal cooling and mixing (Theodor, 1986). Lake Ziway has strong afternoon winds which subside during night-time when cooling results in almost daily short-lived stratification and mixing, with usually well-oxygenated water from top to bottom. In the same way, Gikuma-Njuru *et al*. (2005) reported that the vertical depth profiles of temperature and dissolved oxygen showed even distribution throughout the water column in other tropical African lake, namely, Lake Victoria.

DO profiles of the water column: DO variations among sites and between depth profiles were almost uniform (Figures 4.2.1 and 4.2.2), ranged from 5.65 to 6.40 and 6.45 to 7.24 mg L^{-1} with mean values of 6.76 and 6.04 mg L^{-1} in sampling sites 1 and 2, respectively. More or less even distribution of DO down the water column in the two central stations of Lake Ziway is obviously related to deep-mixing favored by its shallow depth. Similarly, Tilahun and Ahlgren (2010) explained that the depth profiles of oxygen concentration in Lakes Ziway and Hawasa showed uniform distribution nearly up to 15 m depth.

Generally, DO decline with increasing depth, which is related to the progressively lower oxygen contribution of photosynthesis as a consequence of the presumably lower photosynthetic biomass and exponential decline in the level of irradiance and possibly due to the greater demand for oxygen for oxidative decomposition of organic matter by heterotrophy (Wetzel, 2001). Similarly, Ogato *et al*., (2015) also reported that the vertical distribution patterns of DO in another rift valley lake, Lake Chitu and showed low levels of DO down to a depth of 8 m. The profile of oxygen concentration suggests that aeration plays a key role in the distribution of oxygen at depths near the surface of water (Prokopkin *et al*., 2010).

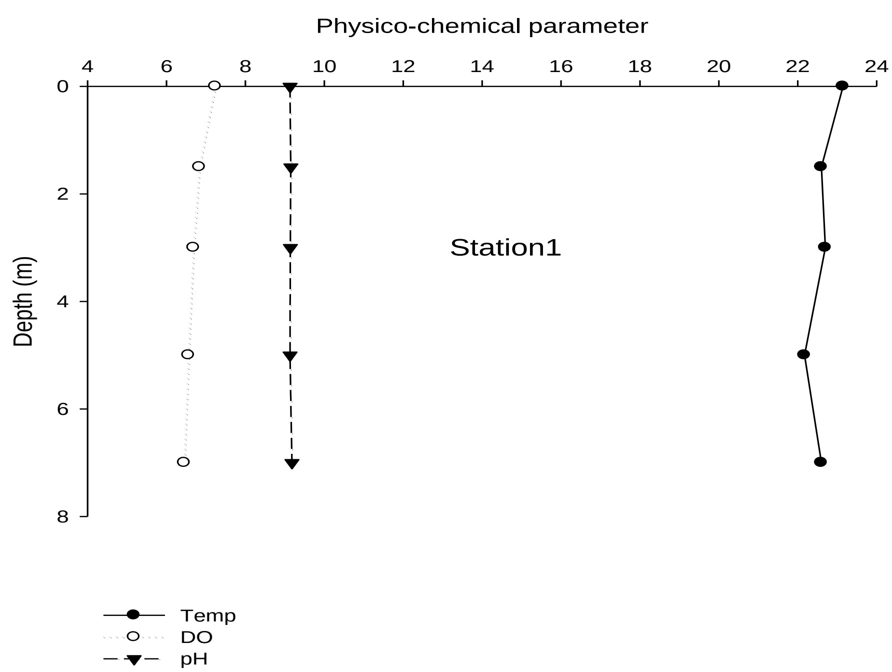

Figure 4.2.1 Profiles of the physico-chemical parameters at the central station 1 (at station C) in Lake Ziway

pH profile in the water column: pH variations among sites and between depths profiles were also almost uniform like DO, ranging from 9.13 to 9.18 and 8.95 to 9.15 with mean values of 9.15 and 9.07 in sampling sites 1 and 2, respectively. The pH of the water in Lake Ziway is slightly alkaline (Figures 4.2.1 and 4.2.2). Lake Ziway is highly exposed to wind action and shallow lake (Tilahun and Ahlgren, 2010). This suggested that the lake is completely mixed during the study period. Similar results were reported by Ogato *et al.*, (2015) on another rift valley Lake in Ethiopia, Lake Chitu. Their results showed that the depth profiles of pH were not significant.

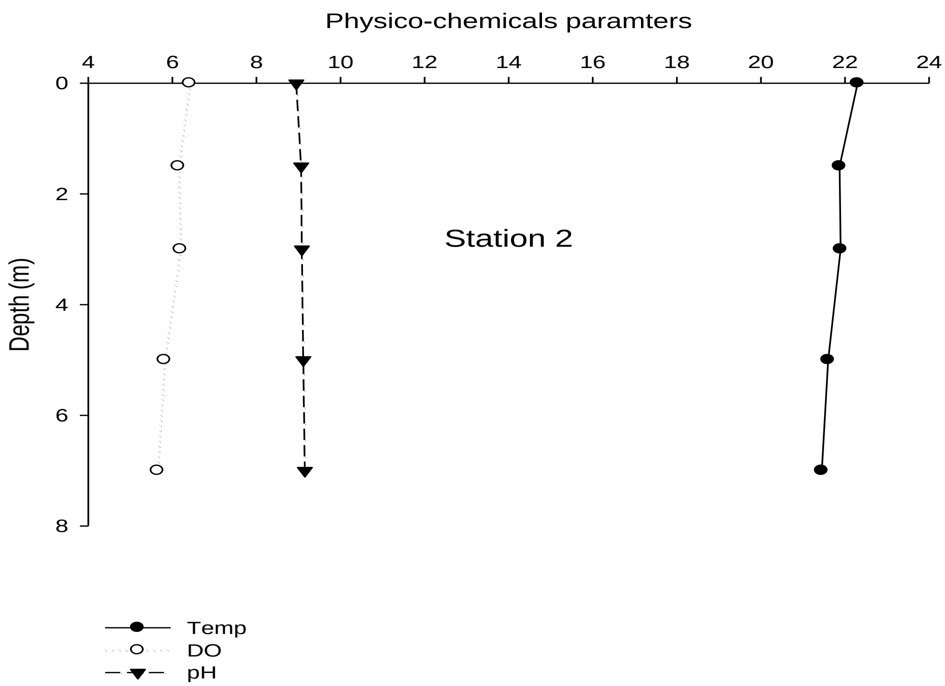

Figure 4.2.2 Depth profiles of physico-chemical parameters at the central station 2, Lake Ziway

4.2.2 Nutrient dynamics and their distribution in Lake Ziway

Mean nitrogen and phosphorus species profiles in the lake water are shown in Figures 4.2.3 and 4.2.4 for monthly sampling intervals from March 2015 to July, 2015. The nutrient levels with depth profiles in Lake Ziway ranged from 0.0047 to 0.005 mg L^{-1} for NO_2-N, 0.14 to 0.31 mg L^{-1} for NO_3-N, 0.005 to 0.235 mg L^{-1} for NH_4-N, 0.049 to 0.475 mg L^{-1} for SRP and 0.160 to 1.650

mg L^{-1} for TP. The mean values were 0.006, 0.21, 0.14, 0.24 and 0.98 mg L^{-1} for NO_2-N, NO_3-N, NH_4-N, SRP and TP, respectively. Depth profiles of NH_3, SRP and NO_3-N showed insignificant variations with increasing depth whereas NO_2-N was very low with almost uniform distribution throughout the water column apart from the increasing depth in both seasons (Figures 4.2.3 and 4.2.4). NH_4-N and NO_3-N have lower values at 1.5 m depth at station 2 and the deeper depths showed very slight changes. The distribution of SRP is approximately uniform but only slightly higher at depth 1.5 m at station 2. The most probable reasons for slight changes in the vertical distribution of most nutrients might be the result of intensive turbulent mixing in the water column and usually have minimum values as the result of the consumption by phytoplankton (Prokopkin *et al*., 2010). Sedimentation/sinking can also remove a huge amount of nutrients from the water column as well especially in turbid systems.

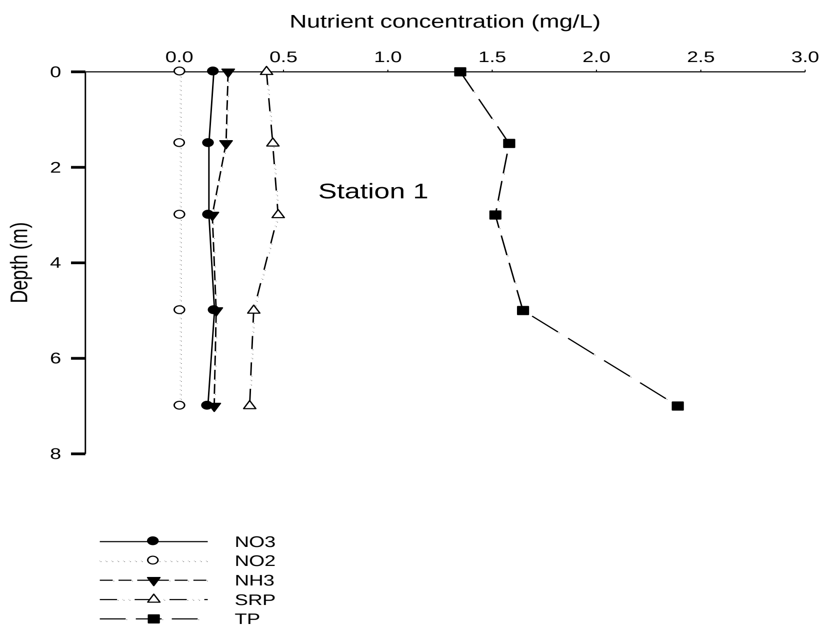

Figure 4.2.3 Depth profiles of nutrients at Lake Ziway central station 1

The mean NO_3-N concentration is uniform from the surface water to the bottom (7 m) at station 1 and it gradually decreased with depth at station 2 (Figures 4.2.3 and 4.2.4). The mean NH_4-N concentration is uniform from the surface water to the bottom (7 m) but only a sharp decrease at depth 1.5 m due to nitrification process (the processes of concerting ammonia to nitrite/nitrate) and increase at 3 m due to ammonification processes (organic nitrogen converts in ammonia) and stays uniform to the last depth (7 m) in station 2 (Figures 4.2.3 and 4.2.4).

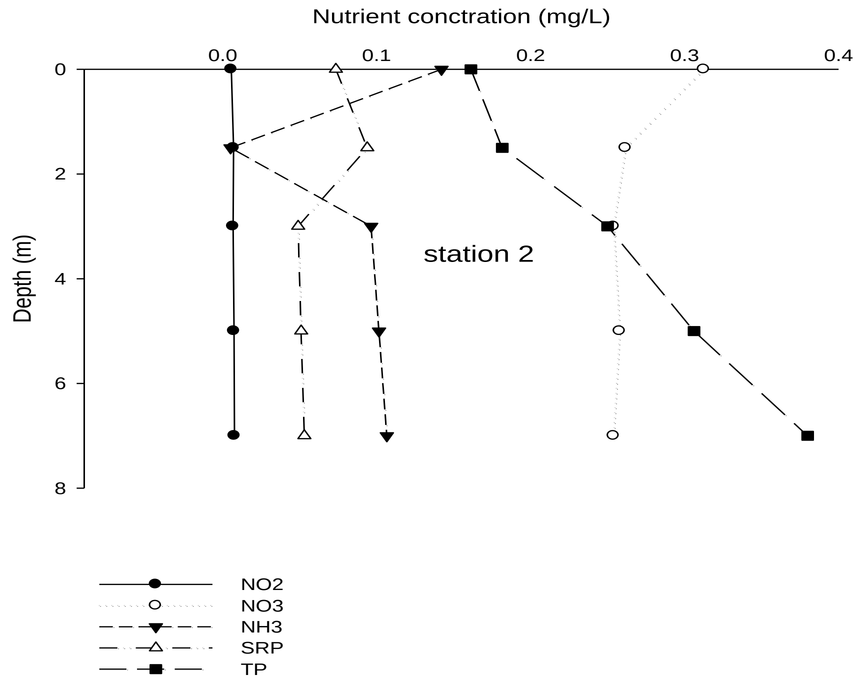

Figure 4.2.4 Depth profiles of nutrients at Lake Ziway central station 2

In contrast to other nutrients, TP concentrations showed an increasing trend with depth and have maximum concentrations near the bottom in both seasons (Figures 4.2.3 and 4.2.4). However, the result of this study is contrary to the results reported for other Rift Valley Lakes. For instance, Ogato *et al*., (2015) reported the depth profiles of NH_4-N and SRP in Lake Chitu increased with increasing depths whereas NO_3-N was undetectable or otherwise very small with almost uniform distribution throughout the water column. It is the result of the accumulation of organic matter in this layer of water over a long period. In turn, such accumulation is the result of the decomposition of the detritus in these layers (Kalacheva *et al*., 2002) and hence deep waters tend to be nutrient rich. Higher nutrient values near the bottom may also probably be caused by the regeneration of particulate matter sedimentation from the epilimnion (Baker and Richards, 2006). Furthermore, an increased nutrient load can occur through settling of nutrients from the top to bottom primarily in particulate form. Increased load can also occur in the bottom when the sediment bed is exposed to anaerobic conditions and releases inorganic phosphorous into the water column (OWRB, 2014).

4.2.3 Climatic and hydrological conditions

Many factors such as temperature, precipitation, evaporation rate, water level, discharge inflow and out flow or geographic location contribute to the dynamic structure of aquatic ecosystems by affecting nutrients, physical forces, or the organisms themselves. Climatic and hydrological factors vary widely throughout Lake Ziway watershed. Though climatic and hydrological conditions throughout the Lake Ziway catchment affect the lake, the rivers in the immediate vicinity provide a good indication of the potential drivers of aquatic chemistry and biology in the lake and the variability over recent years by increasing nutrient load.

4.2.3.1 Climatic factors

4.2.3.1.1 Air temperature

Long-term meteorological measurements were taken at one of the stations of the Ethiopian Meteorology Agency (EMA) found in the vicinity of Lake Ziway located at $07^{0}56'$N and $38^{0}43'$E . The mean air temperature for the period of 1985 to 2014 was 20.87 ^{o}C which is slightly higher than 19.3 °C reported by FDREMoWR, 2008. The temperatures ranged from a minimum of 11.44 ^{o}C in 1986 to a maximum of 27.99 ^{o}C in 2009 during this study.

Table 4.2.1 Mean monthly air temp (^{o}C) in lake Ziway from 1985 to 2014 (The Ethiopian Meteorology Agency)

Temp(^{o}C)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Mean annual
Mean of Max	27.13	28.39	29.25	29.07	29.35	28.00	25.34	25.45	26.76	27.64	27.28	26.68	27.53
Mean of Min	12.44	13.62	14.89	15.58	15.78	15.46	14.99	14.89	14.40	12.93	11.81	11.17	14.00
mean	19.93	21.10	22.15	22.47	22.72	21.86	20.25	20.27	20.67	20.36	19.60	19.01	20.87

Air temperatures in Lake Ziway area vary seasonally, the peak month being May and reaching their lowest in July and August (Table 4.2.1). The higher temperature occurred between March and May, though seasonal variation in monthly temperature is relatively slight small. Spatial variations in temperature are largely the results of differences in altitude though the lapse rates are not uniform and actual temperature variations depend on exposure and seasonal weather characteristics. Figure 4.2.5 shows the increasing annual trends of air Temperature (^oC) in Lake Ziway during 1985 to 2014.

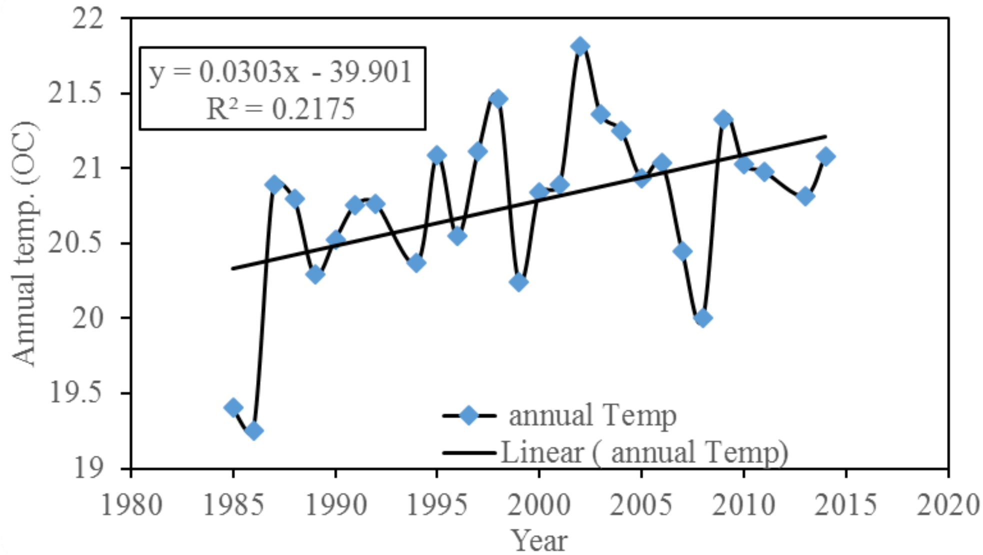

Figure 4.2.5 Mean annual air Temperature (^oC) trends in Lake Ziway from 1985 to 2014 (Source: Ethiopian Meteorology Agency)

HGLGIRDC (2007) reported that climatic factor is a global phenomenon manifested since the last century due to emissions of greenhouse gases. Its effect on climate may appear on an increase of climate variability, changing periods of rain and type of precipitation, as also on a rise of temperatures. Scenarios developed for the years 2001-2099 showed that both temperature and precipitation are likely to increase from the 1981-2000 level. Despite the increasing trend of both climatic variables, the increase in precipitation seems to be obscured by increases in temperature. Hence, the total average annual inflow volume into Lake Ziway might decline significantly and be insufficient to meet future demands of the ever increasing population for water (Zeray *et al*., 2006).

4.2.3.1.2 Precipitation

The annual precipitation distribution of the two major inflowing rivers of the catchments (Meki and Ketar) and the mean monthly rainfall are shown in Table 4.2.2 and Figure 4.2.6. From Figure 4.2.6 one can see that the rainfall in the study area has a decreasing trend currently.

Table 4.2.2 Mean monthly precipitation (mm) of Lake Ziway (Source: Ethiopian Meteorology Agency)

Months	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual rainfall
Mean	13.9	26.0	40.0	74.2	78.0	81.2	143	108	71.9	35.1	10.8	4.41	687

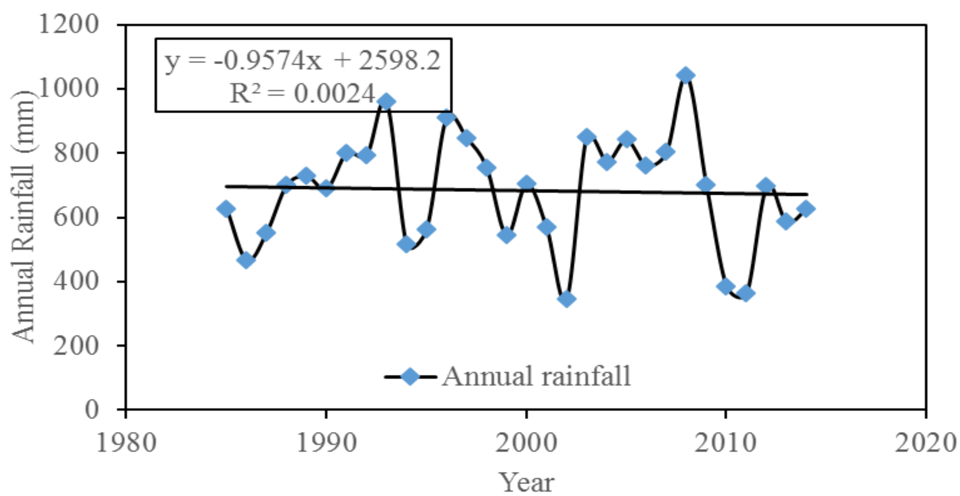

Figure 4.2.6 Mean yearly precipitation (mm) of Lake Ziway from 1985 to 2014 (Source:Ethiopian Metrological Agency)

From the data obtained, the total amounts of water contributed by precipitation were 15 % in dry season and 85 % in wet seasons during the period of 1985 to 2014 (Figure 4.2.7). Although the average amount of rain in most dry seasons was less than 15 %, there were a few dry season months when the rainfall was higher than 15 %. However, generally the dry season had only 12 to 15 % of the total rainfall. Rainfall data obtained during this study period showed that rainfall patterns were not the same from year to year and a month designated as wet in one year was found to be dry month in another year.

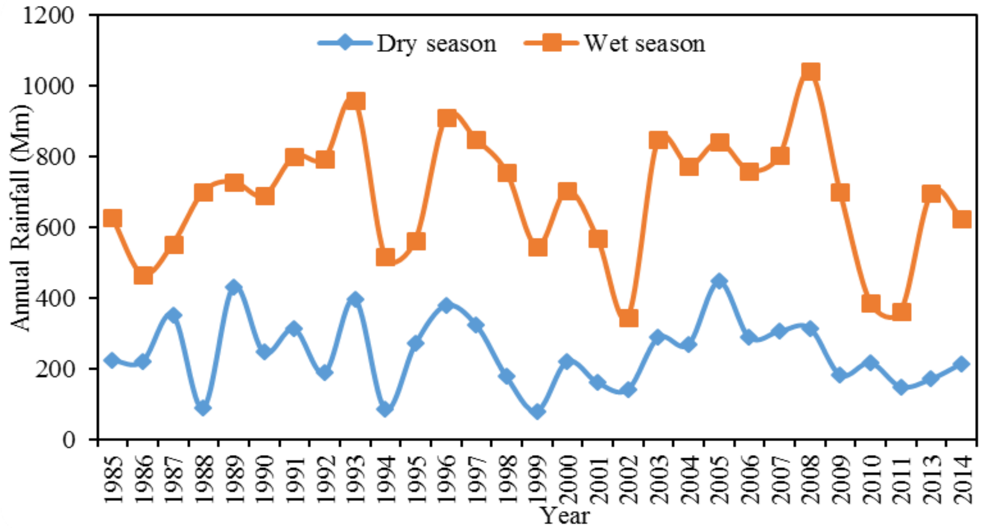

Figure 4.2.7 precipitation pattern in Lake Ziway during wet and dry seasons from 1985 to 2014 (Source: Ethiopian Meteorology Agency)

The different ranges in the amount of precipitation were useful in classifying a month as dry and wet. Such variations in rainfall could have direct effects on the lake as it has been shown to be responsible for within-year variations of the water level and is associated with change in salinity of the lake and alteration in phytoplankton and can affect other communities occur (Talling and Lamoille, 1998). Therefore, an ideal situation was created in this study to look at the effect of rainfall in relation to nutrient load on Lake Ziway ecosystem. On the other hand, classification of the months into dry and wet seasons based on the conventional seasonal classification did not always agree with the rainfall data obtained in the study area. In most of the Ethiopian rift valley, the period between March to October is considered as a wet season and November to February as a dry season (Gamachu, 1977). It is therefore, essential for ecological studies to obtain an actual rainfall data of each sampling month as was done in this study. The total annual precipitation in Lake Ziway from 1985 to 2014 varied between 346 mm to 1042 mm. This range is lower than the range 650 mm to 1200 mm reported by Zeray, *et al.*, (2007).

The higher intensity and frequency of floods and frequent and high precipitation events cause increasing external nutrient loads to Lake Ziway. Heavy rainfall may account for a significant proportion of annual nutrient transport from agricultural soils under arable crops (Torres *et al.*, 2007).

4.2.3.1.3 Evaporation

Increasing temperature generally results in an increase in potential evaporation largely because the water holding capacity of air increases. As it can be seen from the water balance component of this area (next session, Table 4.2.6), the rate of the evaporation is continuously increasing which means the lake level is ultimately decreasing.

Factors affecting evaporation

Wind speed: The wind speed data collected in the study area showed that the high windy periods were June to July for Lake Ziway (Table 4.2.3). The magnitude of the annual wind speed average of the basin is increasing with elevation according to Ziway weather station (Mazengia, 2008).

Table 4.2.3 Mean monthly wind speed of Lake Ziway (Source: Ethiopian Meteorology Agency)

Months	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Mean (m/s)	1.53	1.55	1.37	1.37	1.50	2.08	2.00	1.69	1.23	1.36	1.53	1.63

Relative humidity (RH): According to Ziway station data used for the study, relative humidity is highest (69.7 mm) in April and least (41.2 mm) in November (Table 4.2.4). This station data seem to overestimate the natural relative humidity due to the fact that the meteorology station is located near the lake. The mean annual RH of the basin is decreasing specially within the rift floor.

Table 4.2.4 Mean monthly RH (mm) of Lake Ziway (Source: Ethiopian Meteorology Agency)

Months	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Mean	41.2	57.7	56.4	69.7	46.3	57.9	48.0	46.3	62.2	42.9	41.2	42.0

Temperature: The highest temperatures occur between March and June prior to the start of the rainy season, though a seasonal variation in monthly temperature is relatively insignificant.

Sunshine hours: The annual trends of sunshine (kw/m^2) in Lake Ziway between 2007 and 2014 showed increasing trends (Figure 4.2.8). The lowest values were in 2010 and 2011 but the highest value was during 2009.

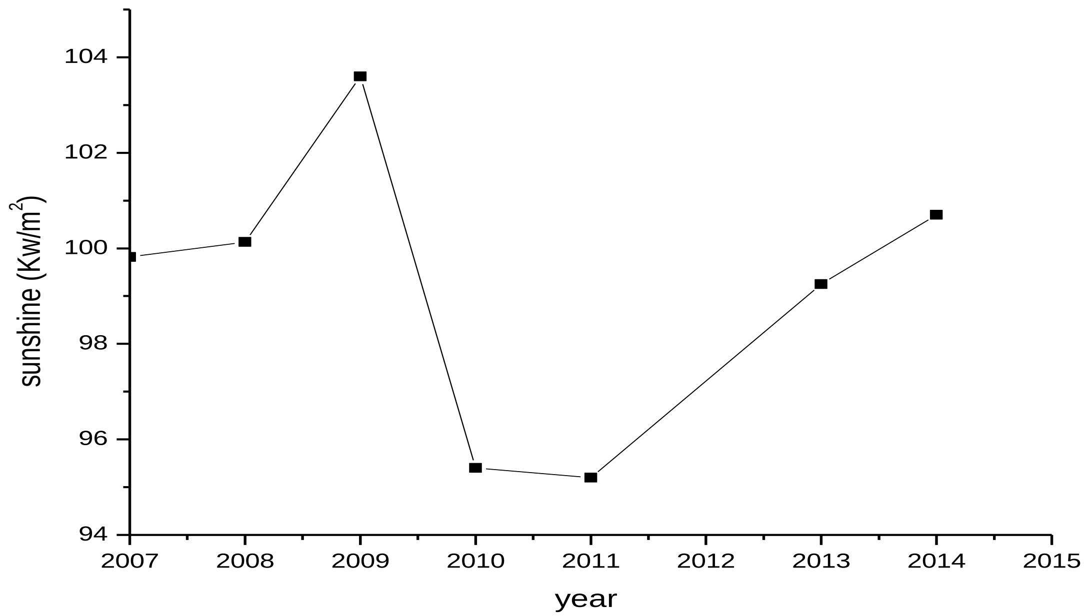

Figure 4.2.8 Sunshine pattern in Lake Ziway during 2007 to 2014 (Source: Ethiopian Meteorology Agency)

The lowest sunshine was recorded in the rainy season while the highest values were generally observed in October to June (Table 4.2.5) and peak for all stations in the month of December. The least value was obtained in the month of July when the precipitation in the basin attains its maximum (Table 4.2.4).

Table 4.2.5 Mean monthly sunshine (kw/m^2) of Lake Ziway (Source: Ethiopian Meteorology Agency)

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
mean	9.65	9.17	8.90	8.55	8.19	8.22	6.00	6.16	6.52	9.50	9.51	9.65

4.2.3.2 Hydrological data analysis

4.2.3 .1.1 River discharges

Discharges through rivers are the most significant sources of water, silt and nutrient imports and exports of Lake Ziway. Originating from within the catchment, these discharges vary in magnitude seasonally, affecting the quantity and quality of waters in Lake Ziway, and ultimately the structure and function of the aquatic ecosystem. The mean monthly discharges to and from Lake Ziway determined for the major inflows, and outflow from, the lake over the period from 1980 to 2014 showed that Ketar River accounted for 63 % and Meki River accounted for 37 % inflow to Lake Ziway. The overall mean monthly inflow and outflow from Lake Ziway through Rivers was 17.7 and 4.92 m^3/s, respectively (Table 4.2.6). The lowest mean monthly discharge into the lake was 2.48 m^3/s by following low precipitation and drought condition in the catchment. The greatest discharge into the lake was 68.8 m^3/s, when precipitation during the heavy rainy season where Lake Ziway catchment recovered from the preceding drought.

Table 4.2.6 River discharge (m^3/s) to and from Lake Ziway from 1980 to 2014 (Source: Ministry of Water, Irrigation and Energy, Ethiopia)

Rivers	**Min**	**Max**	**Mean**
Meki	0.74	23.0	6.62
Ketar	1.74	45.7	11.1
Total inflow	2.48	68.8	17.7
Bulbula (outflow)	1.20	12.7	4.92

4.2.5 .1.1 Meki river

The mean monthly Meki River inflows ranged from 0.74 to 23.0 m^3/s with mean values of 6.62 m^3/s during 1980 to 2014 (Table 4.2.6). Meki River occurred from December to February, associated with a period of drought increase in temperatures which reduced surface runoff in the catchment (FDREMoWIE, 2008). On the average monthly basis the maximum flow occurs in August. As it can be observed from the graph (Figure 4.2.9), the Meki River, discharge at Meki Town near the confluence to Lake Ziway, during February to April the river bed may dry. It can be concluded that the flow of the river can dry out during the severe dry years. The total annual contribution of Meki River to the Lake Ziway is 278 MCM.

Although there is a substantial increase in the exploitation of Meki River tributaries for irrigation, a trend of decrease in the annual flow volume is not discernible in the time series. This could be due to the fact that irrigation practices are of very recent development and the major contribution to the annual flow volume comes from the river in the rainy season with a significant drop of irrigation withdrawal at this time (FDREMoWR, 2008).

4.2.5 .1.2 Ketar river

The discharge measured was very pronounced in August during the high rainfall months (Figure 4.2.9). River discharge recorded from 1980 to 2014 showed the mean monthly Ketar River inflow ranged from 1.74 to 45.72 m^3/s with over all mean values of 11.1 m^3/s. The comparison between the average flow values for Meki and Ketar Rivers clearly illustrate that Ketar River has more volume of inflow as a result of its larger catchment size; consequently Ketar River has a larger irrigational area (3,337 ha) than Meki River which has an irrigational area (1,315 ha) (Francisco, 2008). In contrast to this, Desta (2016) reported that the irrigation scheme at Meki to be 763 ha and 390 ha for Ketar River. According to his report, Ketar River has a relatively small irrigated area than Meki River. Therefore, an intensive research should be done in order to know the exact irrigational coverage of Lake Ziway watershed.

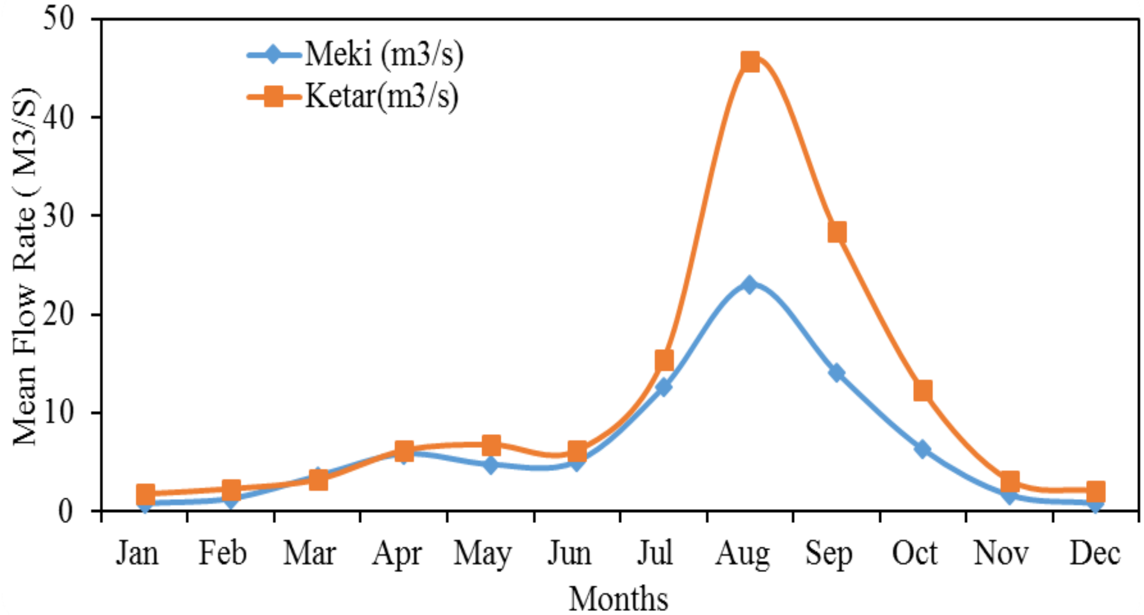

Figure 4.2.9 Mean monthly flow rates of Ketar River at Abura Town station and Meki River at Meki Town station from 1980 to 2014 (Source: Ministry of Water, Irrigation and Energy, Ethiopia)

According to Wetzel (2001), the nutrient load from rivers usually depends on two main factors: flow rate and geology of the drainage basin. However, many other factors such as rainfall, width of river management as well as anthropogenic activities in the catchment such as agriculture, industry and housing play an important role in establishing the nutrient load of a river (Wetzel, 2001; Torres *et al.*, 2007).

4.2.5 .1.3 Bulbula river

The outflow from Lake Ziway is carried by Bulbula River, which flows south for 30 km before entering to Lake Abijata, a terminal lake. Bulbula River descends down to some 58 m over a distance of 30 km between Lakes Ziway and Abijata. Except periodically during the wet season, the water of Bulbula River is largely a spillover from Lake Ziway. However, Bulbula River does have significant catchments of its own with ephemeral tributaries from the east occasionally contributing to the flow (Figure 4.2.10).

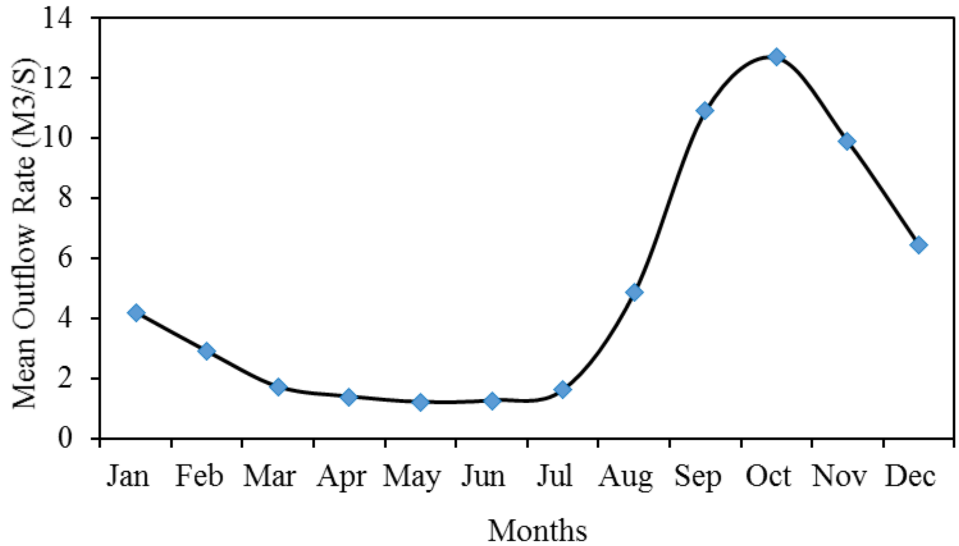

Figure 4.2.10 Mean monthly Bulbula River discharge at Kakarsitu station from 1980 to 2014 (Source: Ministry of Water, Irrigation and Energy, Ethiopia)

The outflow from Ziway Lake recorded from 1980 to 2014 ranged between 1.2 to 12.7 m^3/s with mean value of 4.92 m^3/s (Table 4.2.6) and is controlled by the height of the rock sill in the Bulbula channel near Adamitulu. Outflow ceases when the lake falls to this level which is 1636 masl or 0.46 m on the staff gauge, at Ziway town (Mazengia, 2008). The total mean annual outflow from Lake Ziway measured at Kakarsitu was 156 MCM. Therefore, the outflow from this river has its own impacts on the Lake water level and water balance. Bulbula River out flow is the only outlet for Lake Ziway.

4.2.5. 2 Lake Ziway water level

In this study, the water volume of Lake Ziway was observed to fluctuate following seasonal changes with slight rise in wet seasons and decline in the dry seasons within each year (Figure 4.2.12). During dry seasons and frequent low rainfall years, the discharge of the feeder rivers are low, 2.23 m^3/s from Meki River and 3.19 m^3/s from Ketar River and as a result the surface area of the lake is reduced (Figure 4.2.11). Variations in lake water level may result from the large difference in rainfall between wet and dry seasons coupled with increase in temperature especially during the dry season. Consequently, high evaporation rate and abstraction particularly due to global warming as part of climate change, wind, rainfall, inflows, outflows and abstractions play a major role due to high demand for irrigation (FDREMoWR, 2008).

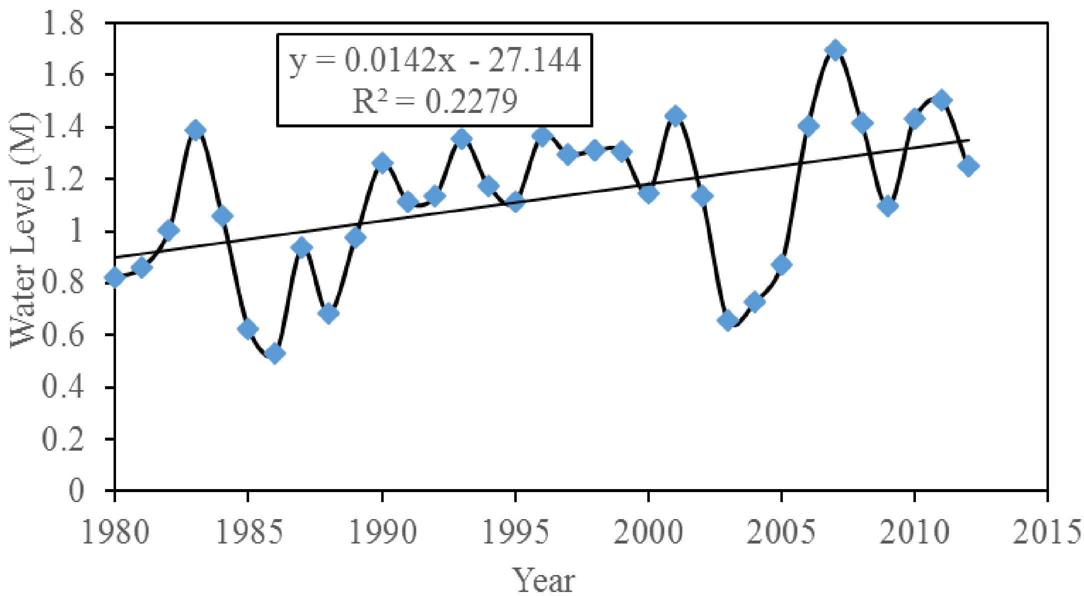

Figure 4.2.11 Mean annual water level measurement of Lake Ziway from 1980 to 2014 (Source: Ministry of Water, Irrigation and Energy, Ethiopia)

The monthly distribution of the water level of the lake is also described in Figure 4.2.12. The trend shows that high water level occurred since July (wet season) and reached its peak in September for the whole period of the years and in contrast decreased in the dry seasons.

Currently, plenty of variable capacity pumps are abstracting freshwater from the lake by the state, investors and private commercial farms throughout the year (about 223 MCM) (Desta *et al*., 2016). In personal observation, even during the rainy season water for horticultural crops is pumped from the lake. Hence, the current irrigation practices in the upstream areas might have considerably reduced the volume of the inflowing water from Meki and Ketar Rivers and the lake itself, critically affecting the water level of Lake Ziway. As a result, the lake ecosystem is influenced by catchment degradation, siltation, imbalance between water inflow and outflow.

Scholten, (2007) reported that the average level of Lake Ziway decreased by approximately 0.5 m between 2000 and 2006.

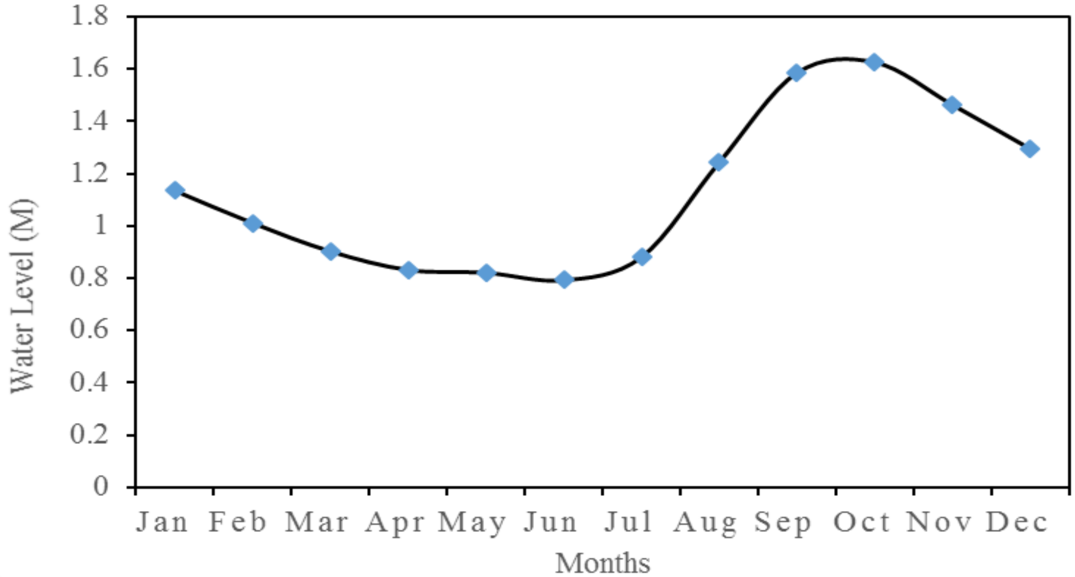

Figure 4.2.12 Mean monthly water level measurement of Lake Ziway from 1980 to 2014

According to Scholten *et al*. (2007), the decrease in discharge of the Bulbula River and the lowering of the water level of Lake Ziway are results of the development of 7500 to 10 000 ha of newly irrigated lands. Their study showed that, most of these irrigated areas are concentrated around Lake Ziway and about 1000 ha are situated along the Bulbula River. Their reports have also showed that the intensively cultivated areas have also increased since 1973, especially in the catchment of Ziway. Abraham (2006) reported that the demands of irrigation, coupled with increasing mean temperature and decreasing annual rainfall, will also eventually reduce Lake Ziway's water level so much that the largest body of freshwater in the CRV in particular Lake Ziway will become saline; if this occurs, it will negatively affect the livelihoods of all water users, fisheries, domestic water users, livestock, irrigated farms and ecosystems (Meshesha *et al*., 2012).

Nowadays, water abstractions are completely uncontrolled and unmetered throughout the Lake Ziway catchment. The reduction of the lake water level might be further aggravated by water abstractions from the Ketar and Meki Rivers. The high seasonal variation in water level in the lake might also be attributed to seasonal rainfall. It was also reported that high lake evaporation, which was estimated at 890 MCM annually, contributed to the imbalance between water inflow and outflow, and the lake showed a net loss of 74 MCM volume of water annually (Ayenew and Legesse, 2007; Ayenew and Robert, 2008). To conclude, the vulnerability of Lake Ziway to changes in climatic and hydrological parameters and anthropogenic factors, the lake has exhibited decrease in water level which might consequently influence physico-chemical characteristics of the lake particularly resulting to increase in nutrient concentrations and decrease water clarity.

4.2.5. 3 Lake water residence time

Based on these data and the model (in 3.6.2), the hydraulic residence time for Lake Ziway was about 6.67 years and this long residence time accelerated the deterioration of the aquatic environment and enhanced the process of eutrophication. This study is similar to the World Lake Data Base (1999), which was 6.3 years but much higher than the reported (1.5 to 2 years) by Spliethoff *et al.* (2009) for the same lake.

4.2.5. 4 Evaluation of water balances

There are several contributors to the water balance of the lake. The inputs to the lake consist of rainfall, surface runoff from ungauged catchment and inflowing Rivers. The outputs include evaporation from the lake, water abstraction and out flowing River from the lake. The approximate annual water budget of Lake Ziway was computed according to Han (2010) (Table 4.2.7).

Table 4.2.7 The water balance for Lake Ziway in MCM

Process	1980 to 2014	References
Inflow		
Precipitation on the lake (P)	687	
Inflow rivers (R_i)	580	
Surface runoff from ungauged catchments (S_r)	125	Ayenew and Legesse, 2007
Outflow		
Evaporation from lake (E)	890	Ayenew and Robert, 2008
Bulbula river out flow (R_o)	156	
Abstraction by man (A)	223	Desta *et al*., 2016
Change in storage ($\pm\Delta$H)(MCM)	123	

Table 4.2.7 indicated that the water balance of the lake is small, which is only on average 123.18 MCM from its storage. Ayenew and Legesse, (2007) reported that the lake showed a net loss of 74 MCM volume of water annually which is much lower than the current study. From the above one can conclude that Lake Ziway has been exposed to human interventions, where in the first scenario man has removed water beyond the water budget of the lake could allow. As a consequence the lake continued to decrease in volume if all the conditions continue as by the current scenario, Lake Ziway will be dry like Lake Haramaya. Therefore, the lake needs attention.

4.2.6 External nutrient load

Water quality and quantity data are used to describe the recent loads of TP, SRP, NO_3-N, NO_2-N, NH4-N, TIN, TN and SiO_2-Si to Lake Ziway over the study period. The results of the study are shown on spatial and seasonal bases in Tables 4.2.7 and 4.2.8.

4.2.6 1 External soluble reactive phosphorus load

Soluble reactive phosphorus (SRP) load to Lake Ziway ranged from a value of 0.0 to 33 kg day^{-1} and 25 to 245 kg day^{-1} during the dry and wet seasons, respectively (Tables 4.2.8 and 4.2.9). Mean SRP loads were 14.1 and 102 kg day^{-1} during the dry and wet seasons, respectively. SRP loads were significantly different between rivers ($p < 0.05$) in dry season.

Table 4.2.8 Mean, mean standard error, minimum and maximum values of the external nutrients loading (kg day^{-1}) in Ketar River (Kb) and Meki River (Mb) in dry season

site		TP	SRP	NO_3-N	NO_2-N	NH4-N	TIN	TN	SiO_2-Si
Kb	x̄± Std. Err	86.4 ±21.1	16.4±4.3	60.1±17.2	174.7±74.1	53.6±8.2	288.3±88.3	1558.4±383.8	19526±4515
	Min	37	8	36	45	42	148	733	12149
	Max	154	33	144	536	94	722	3347	41565
Mb	x̄± Std. Err	22.3±8.8	11.9±5.0	65.9±47.4	161.9±98.4	44.83±27.2	87.17±34.4	500.1±114.1	5828±1801
	Min	0	0	0	0	0	0	0	0
	Max	62	30	295	590	177	203	798	12399
Total	x̄± Std. Err	54.4±14.6	14.1±3.2	63.0±24.0	168.3±58.8	49.2±13.6	187.7±54.4	1029.3±248.8	12677±3104
	Min	0	0	0	0	0	0	0	0
	Max	154	33	295	590	177	722	3347	41565

Table 4.2.9 Mean, mean standard error, minimum and maximum values of the external nutrient loads (kg day^{-1}) in Kb and Mb in wet season

site		TP	SRP	NO_3-N	NO_2-N	NH_4-N	TIN	TN	SiO_2-Si
Kb	x̄± Std. Err	1528±1121	110.8±47.9	1510.5±1220.7	2182.7±1413.5	323.7±258.1	4017±2889	13974±8832	44833±2266
	Min	97	28	45	487	43	584	2117	38453
	Max	4821	245	5159	6378	1098	12634	40041	49170
Mb	x̄± Std. Err	1138±626	92.83±46.8	346.3±111.6	1005.3±315	127.2±80.8	1793.2±622.3	8194±3976	29124±5931.9
	Min	146	25	45	434	5	764	1961	21365
	Max	2913	230	515	1782	355	3512	19164	46726
Total	x̄± Std. Err	1333±599	102±31	928±608	1594±706	225±131	2905±1431	11084±4615	36979±4178
	Min	97	25	45	434	5	584	1961	21365
	Max	4821	245	5159	6378	1098	12634	40041	49170

*. Correlation is significant at the 0.05 level
**. Correlation is significant at the 0.01 level.

An increasing SRP load has been observed in Lake Ziway, where the inflow of K_b contributes greater than M_b (Tables 4.2.8 and 4.2.9). The seasonal variability in SRP loads to Lake Ziway is mostly determined by variability in seasonal inflows of Ketar and Meki Rivers, as demonstrated by the relationship between seasonal inflows of the two rivers and seasonal SRP concentration in the two rivers. This indicated that nutrient loads are higher during rainfall period due to agricultural runoff. Similarly, Moore, (2007) reported that increasing SRP loading during rainy season is attributed to the increased river flow with precipitation. Jeppesen *et al*., (2009; 2014) also reported heavy rainfall has significant impact on annual phosphorus transfer from agricultural soils under arable crops to the lake ecosystem. An excessive loading of nutrients from a number of anthropogenically influenced sources in the lake catchment is indicated as the main reason by other recent studies (Granlund *et al*., 2005).

4.2.6.2 External total phosphorus load

The external TP load to Lake Ziway ranged between 0 to 155 kg day^{-1} and 96.77 to 4821 kg day^{-1} with mean TPs values of 54.4 and 1333 kg day^{-1} in the dry and wet seasons respectively (Tables 4.2.8 and 4.2.9). ANOVA (Kruskal-Wallis) result showed that TP values between sampling sites were significantly different ($p < 0.05$) during the dry but not significantly different ($p > 0.05$) during the wet season.

The temporal variability in external TP loads to Lake Ziway is mostly determined by variability in temporal river inflows, as demonstrated by the relationship between temporal river inflow and temporal variability in TP concentrations in a similar trend for SRP present above. The external TP load was maximum in the wet season and minimum in the dry season which might be due to the seasonality of precipitation, land use, and periods when fertilizer is applied on farmlands (Alan *et al*., 2007; May *et al*., 2012; Mihkel *et al*., 2013).

In both seasons Ketar River TP load was higher than that of Meki River (Figures 4.2.13 and 4.2.14). The result is supported by the data from the reports of FDREMOWIE (2008). Ketar River inflow accounts for 63 % of the variability in TP load. In contrast, only about 37 % of the variability in TP load can be attributed to Meki River inflow. The major reason for the lower TP input from River Meki could be either the volume of Meki River decreases extremely in the dry season or it completely dries out at the warmest peak during the dry season, due to excessive water abstraction for irrigation conducted upstream. Thus the difference between this two could be the intensity of the irrigation practices, slope and even geology.

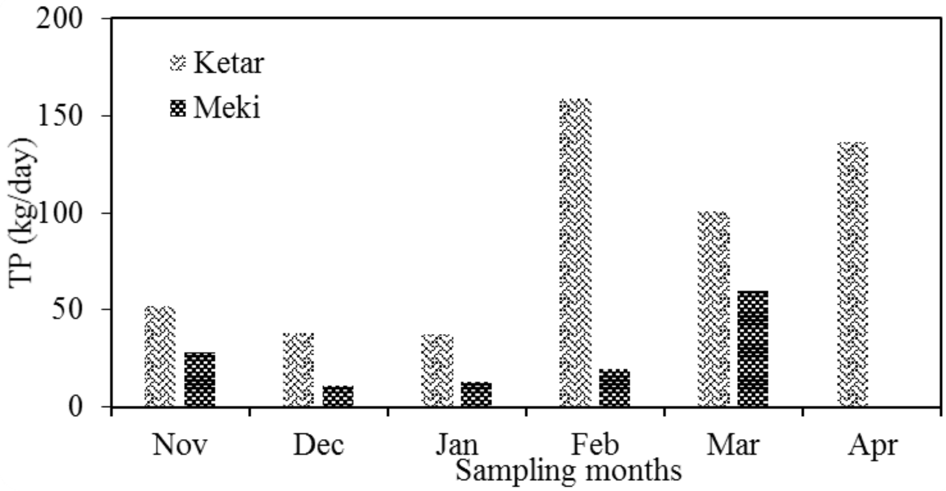

Figure 4.2.13 External TP load dynamics from the Meki (Mb) and Ketar (Kb) rivers during dry season in 2014 and 2015

A significant source of TP in water bodies can be attributed to runoff containing fertilizers, pesticides, detergents, or cleaning chemicals. These products can contain phosphorous and commonly end up in the local waterways. According to the U.S. Geological Survey (USGS), the Environmental Protection Agency (EPA) has recommended that TP concentrations should not exceed 0.1 mg L^{-1} in rivers (Martin *et al.*, 1999; Rebecca, 2007; Hou *et al*., 2013). Therefore, TP concentrations in the two rivers of Ziway are beyond this value.

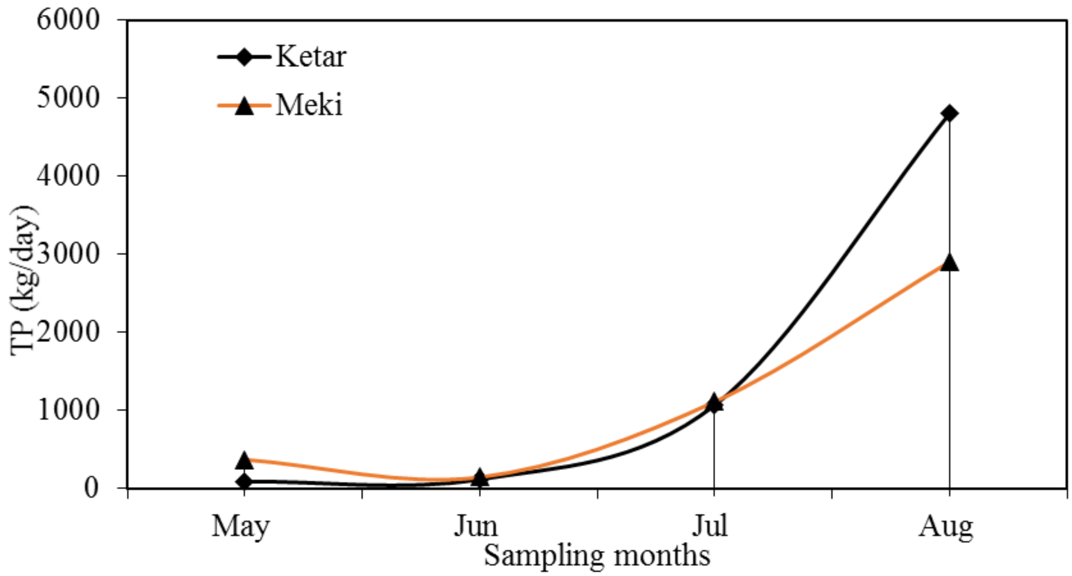

Figure 4.2.14 Seasonal variation in external TP load to Lake Ziway from the Meki and Ketar rivers in wet season in 2014 and 2015

The increased anthropogenic developmental activities within the catchment might be the main cause of the higher external TP loading in the lake ecosystem as observed in the Land-use map of the lake Ziway catchment (Figure 1.2).

This spatial variation in external TP sources suggests that different management strategies may be needed within the catchment based on unique major River basin characteristics. For example, limiting sediment erosion may be an effective management practice to reduce TP in the two rivers basin.

Phosphorus (P) loading, has been considered as important limiting nutrient for phytoplankton production in lakes (Moss *et al.*, 2012). Eutrophication of lakes causing high phytoplankton production with severe implications for both the ecological state and drinking water quality which is the current world-wide problem (Schindler, 2006; Søndergaard *et al*., 2012) and for Lake Ziway, which is no exception to this problem.

4.2.6.3 External nitrate-nitrogen load

The external nitrate-nitrogen (NO_3-N) load to Lake Ziway ranged between 0 to 295 kg day^{-1} and 45 to 5189 kg day^{-1} with mean values of 63 and 1928 kg day^{-1} in the dry and wet seasons respectively. NO_3-N loads were significantly different between sampling sites ($p < 0.05$), with K_b having significantly greater than M_b during the wet season (Tables 4.2.8 and 4.2.9). The mean NO_3-N loads were higher in the wet season than the dry season. The higher NO_3-N load in the wet season might be attributed to the application of nitrogen fertilizers and pesticides in the Meki and Ketar rivers' catchment during this season. The intensive agricultural practice in the lake catchment area resulting in the excess enrichment of nutrients through agricultural runoff has been reported by other studies (Meshesha *et al.*, 2012; Desta *et al.*, 2016) in the same lake. Solheim *et al.*, (2010) also reported that extreme precipitation increases the NO_3-N load to the lake ecosystem.

4.2.6.4 External nitrite-nitrogen load

Nitrite-nitrogen (NO_2-N) load ranged from a maximum of 598 kg day^{-1} in March to a minimum of 0.0 kg day^{-1} in April at Meki River during the dry season and a maximum of 6378 kg day^{-1} in August at Ketar and minimum of 434 kg day^{-1} in May during the wet season in Meki River (Tables 4.2.8 and 4.2.9). The total mean NO_2-N loads were 168 kg day^{-1} and 1594 kg day^{-1} during the dry and wet seasons respectively and the mean NO_2-N loads were not significantly different between sampling sites ($p > 0.05$) in both seasons. The higher NO_2-N load during wet seasons was due to agricultural runoff from the catchment precipitation.

4.2.6.5 External ammonium-nitrogen load

The ammonium-nitrogen (NH_4-N) load to Lake Ziway ranged between 5 to 1098 kg day^{-1} and 0 to 177 kg day^{-1} with mean values of 225 and 49.2 kg day^{-1} in the wet and dry seasons respectively (Tables 4.2.8 and 4.2.9). Through the mean NH_4-N loads were not significantly different between sampling sites ($p > 0.05$) in both seasons; similar results reported by the seasonal variability of the load with maximum values in the wet season and minimum in the dry season can likely be attributed to the seasonality of climatic and anthropogenic activities like precipitation, land use change and periods of fertilizer and pesticides application on farmland (May *et al*., 2012; Meshesha *et al.*, 2012; Jeppesen *et al*., 2014; Desta *et al.*, 2016).

The greatest external NH_4-N loads to Ziway Lake occurred in August at Ketar River (1098 kg day^{-1}) and the lowest loads occurred in June (5 kg day^{-1}) at Meki River during wet season while in dry season highest and lowest NH_4-N load were in March (178 kg day^{-1}) and April (0 kg day^{-1}) at Meki River, respectively. In general, Ketar River was the dominant source of external NH_4-N load, but there were only for a few months, when Meki River contributed more NH_4-N load than Ketar River.

4.2.6.6 External total inorganic nitrogen load

Total inorganic nitrogen (TIN) load in the study sites ranged from 0 to 722 kg day^{-1} and 584 to 12634 kg day^{-1} in dry and wet season respectively during the study period (Tables 4.2.8 and 4.2.9). The highest load of TIN in wet season could be due to climate changes in particular to rainfall. The greatest external TIN loads to Lake Ziway occurred in August (12634 kg day^{-1}) and the lowest loads occurred in May (584 kg day^{-1}) at Ketar River during the wet season while in the dry season the lowest and highest values were in April (0 kg day^{-1}) in Meki and March (261.8 kg day^{-1}) at Ketar Rivers, respectively. However, ANOVA (Kruskal-Wallis) result showed that TIN values between sampling sites were significantly different ($p < 0.05$) during the dry season but not ($p> 0.05$) during the wet season. In general, the results showed Ketar River is the dominant source not only for SRP and TP described above but also for TIN too to Lake Ziway throughout the study period (Figures 4.2.15 and 4.2.16).

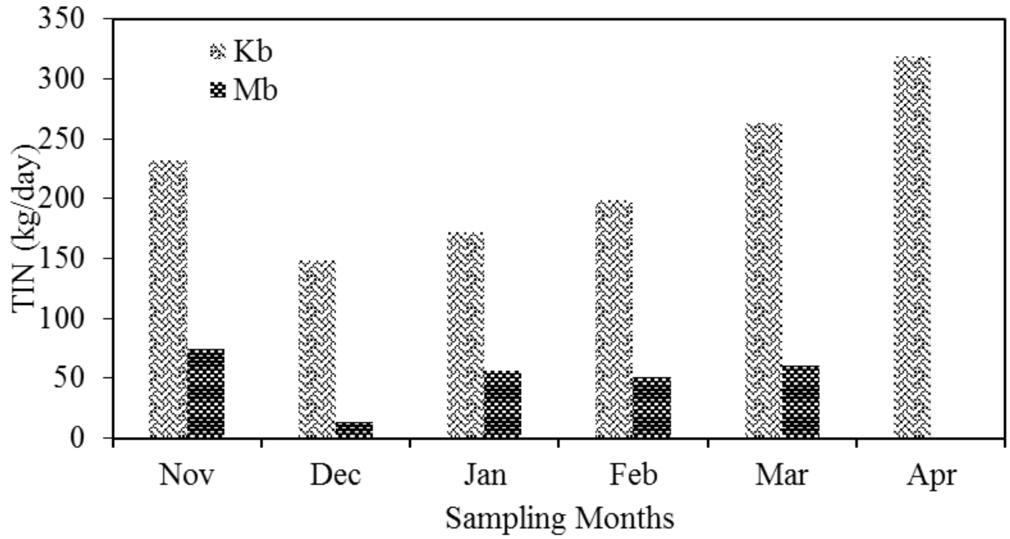

Figure 4.2.15 External TIN load dynamics from the Meki (M_b) and Ketar (K_b) rivers during dry season in 2014 and 2015

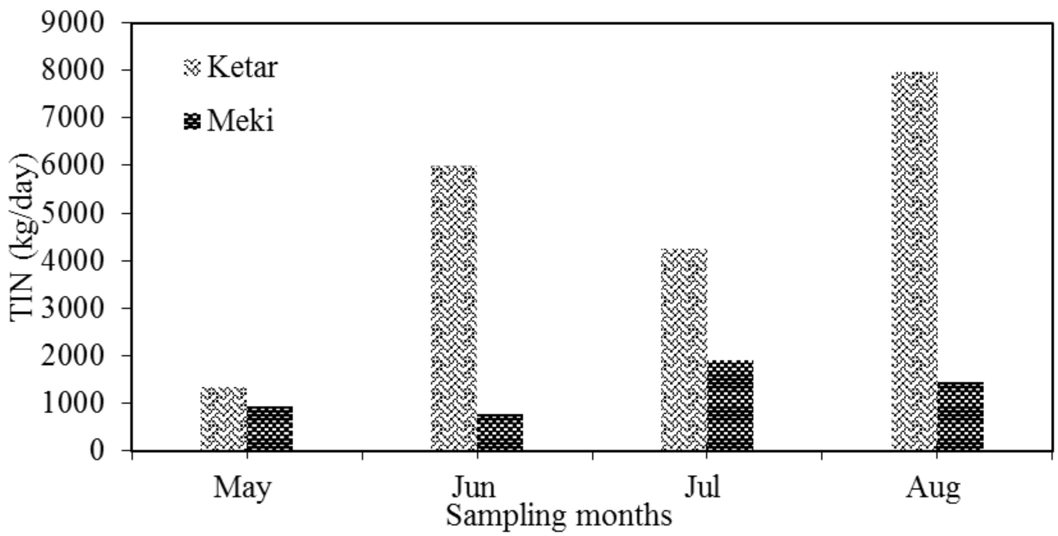

Figure 4.2.16 External TIN load dynamics from the Meki (M_b) and Ketar (K_b) rivers during wet season in 2014 and 2015

Increased TIN load in this study might be associated with anthropogenic factors around the Lake Catchment and climate changes. The rainfall increase may cause flushing of upland soils. In the dry season increased temperature, reduced inflow and increased residence time result in enhanced denitrification and lower TIN concentrations. However, further downstream, where the input from agriculture and point sources is larger, the effect of reduced dilution in dry season becomes more important than that of increased denitrification, giving increased concentrations also in the dry season (O'sullivan *et al.*, 2004).

4.2.6.7 External total nitrogen load

The total nitrogen (TN) load ranged from 0 to 3347 kg day^{-1} and 1961 to 40041 kg day^{-1} during the dry and the wet seasons, respectively (Tables 4.2.8 and 4.2.9). The TN load to Lake Ziway was an average of 1029 kg day^{-1} and 11084 kg day^{-1} in dry and wet seasons, respectively. ANOVA (Kruskal-Wallis) result showed that TN values between sampling sites were significantly different ($p < 0.05$) in dry season but not in wet season ($p > 0.05$).

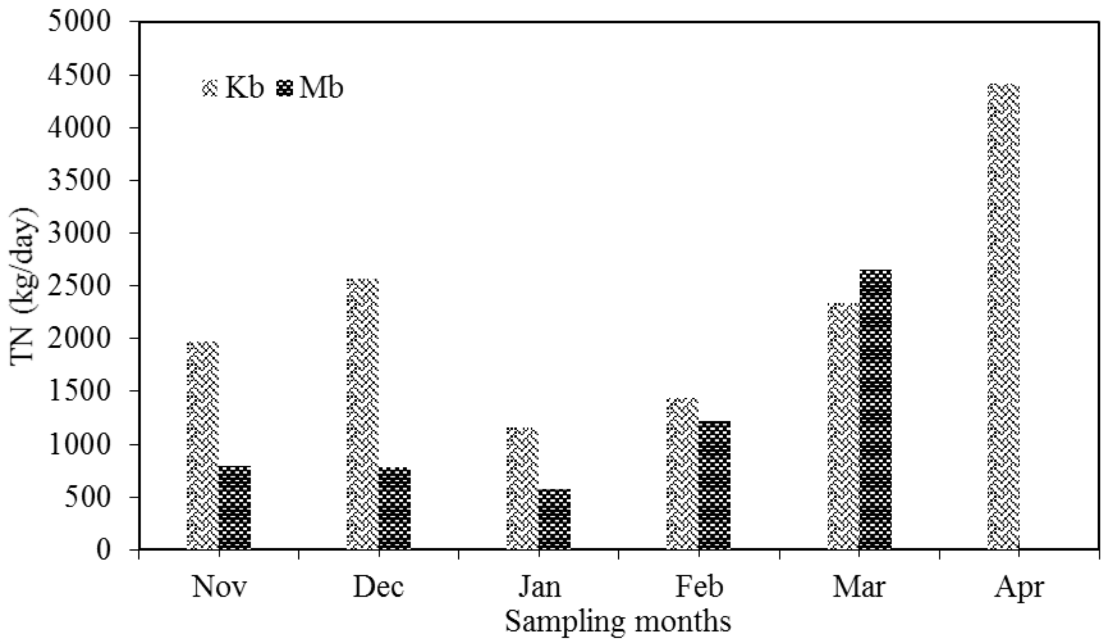

Figure 4.2.17 External TN load dynamics from the M_b and K_b rivers during dry season in 2014 and 2015

Low TN load in Meki River during April (Figure 4.2.17) is associated with the lowest monthly inflows from the river in dry season as the river dried out during (Personal observation) while high TN load occurred during the wet season in August at Ketar River (Figure 4.2.18). Based on the discharge flow data in this study, Ketar River contributed 56 % and 63 % of the TN load over the study period in dry and wet seasons, respectively.

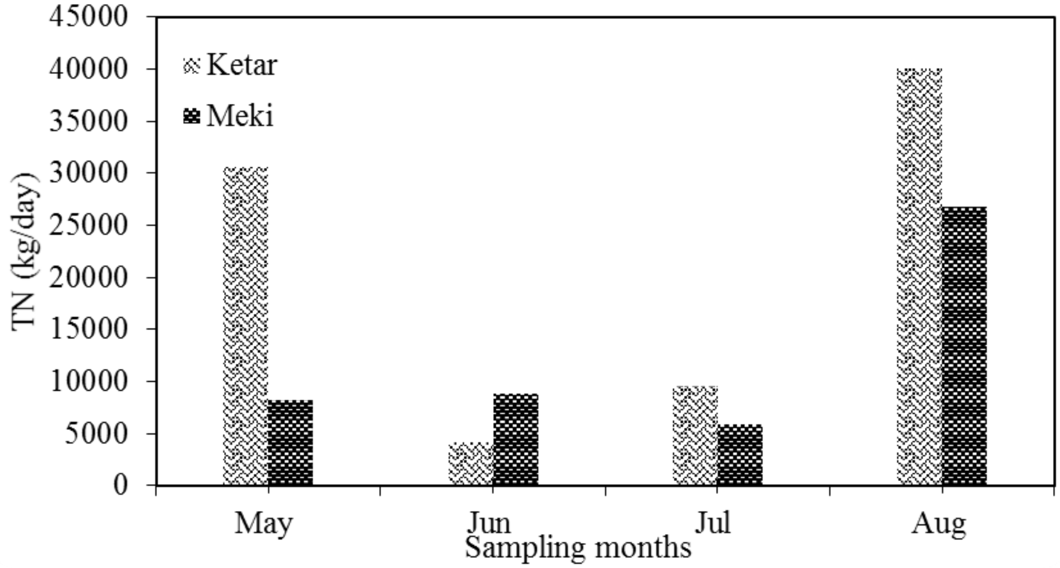

Figure 4.2.18 External TN load dynamics from the Meki and Ketar rivers during wet season in 2014 and 2015

4.2.6. 8 Soluble reactive silica load

Soluble reactive silica (SiO_2-Si) load to Lake Ziway ranged from 0 to 41565 kg day^{-1} and 21365 to 49170 kg day^{-1} during dry and wet seasons respectively (Tables 4.2.7 and 4.2.8). The mean SiO_2-Si loads were 12677 and 36979 kg day^{-1} in dry and wet seasons, respectively. SiO_2-Si loads were significantly different between sampling sites ($p < 0.05$) in both seasons.

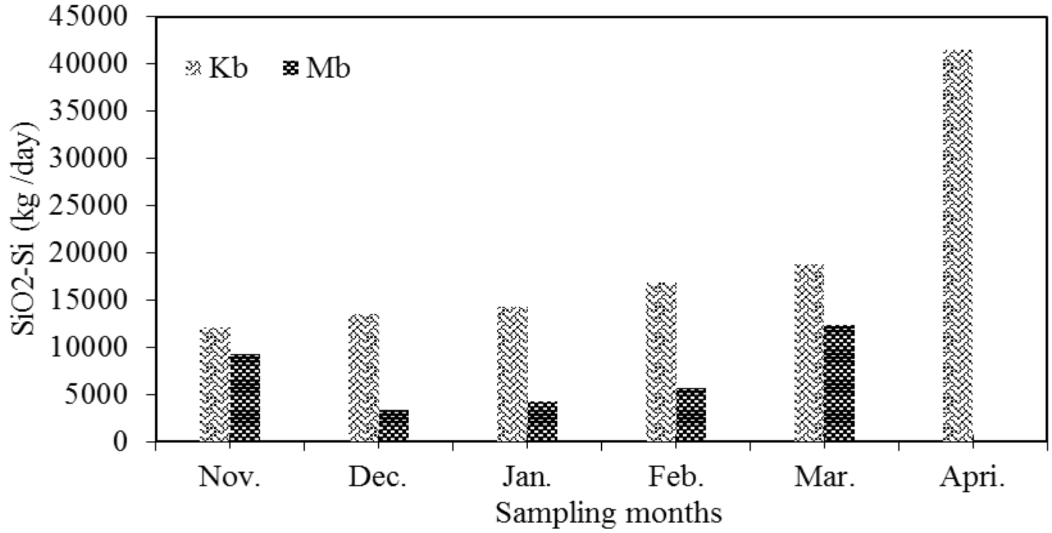

Figure 4.2.19 External SiO_2-Si load dynamics from the Meki River (M_b) and Ketar River (K_b) during dry season in 2014 and 2015

The SiO_2-Si load is highest in April at Ketar River and the lowest in the same month at Meki River (Figure 4.2.19) during the dry season. The nutrient load patterns in the two rivers have low values during the dry season and an extended rainy season which was high load. When compared the SiO_2-Si load for the two rivers, is very low in Meki River in all sampling months except July in which both have similar external SiO_2-Si load (Figure 4.2. 20).

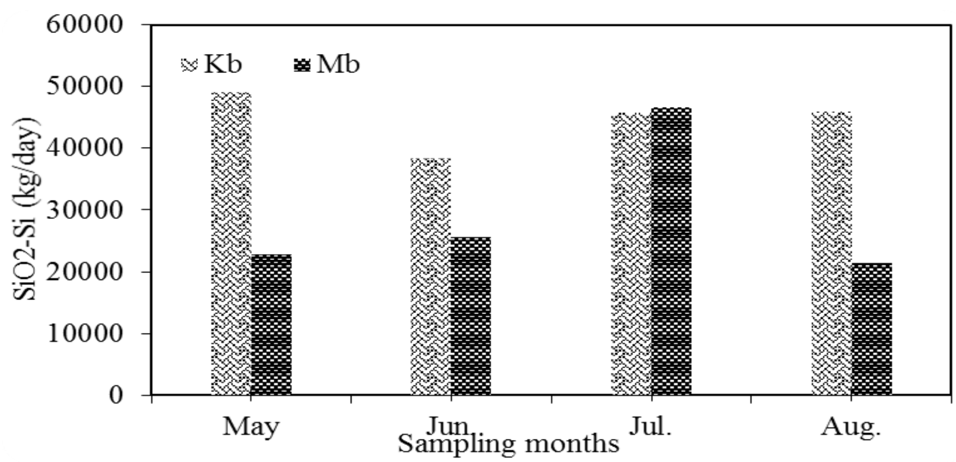

Figure 4.2.20 External SiO_2-Si load dynamics from the Meki River (M_b) and Ketar River (K_b) during wet season in 2014 and 2015

The two major rivers showed systematic variations in SiO_2-Si loads as a function of inflow with higher loads under high flow conditions and the lowest loads at low inflows. Therefore flow rate seems to be a parameter that increases external SiO_2-Si load. The annual external SiO_2-Si load in Lake Ziway is estimated 8938 t yr^{-1} which is closely similar to the external SiO_2-Si load of Lake Kivu, Congo (7200 t yr^{-1}) as reported by Amisi, 2010.

In conclusion, this study showed the direct impact of the two rivers, Meki and Ketar, effluents from floriculture and high human interference around korekonch sites of Lake Ziway imposed a significant effect on the high nutrient loads to the lake. Other reports on the same lake have also shown that these factors have a decisive effect on the high nutrient loads to the lake (Ayenew and Legesse, 20007; Tadele, 2012; Meshesha *et al*., 2012, Desta *et al*., 2106). Several recent studies have also shown that hydrological processes (e.g., hydraulic residence time, water-level change, and floods) can greatly influence lakes' nutrient load and dynamics in many regions of the globe (Chen *et al*., 2010; Meshesha *et al.*, 2012). Owing to its shallowness and relatively long water residence time (about 6.67 years), the ecological state of the lake might also be strongly influenced by natural processes, like periodic fluctuations of water level and temperature. The results of this study agrees with the reports by Jeppesen *et al.*, (2009; 2014) which state that higher intensity and frequency of floods and more frequent extreme precipitation events cause increased surface runoff and erosion, consequently increase in nutrient load to the surface water systems.

Comparisons with other lakes (Table 4.2.10), showed that, the external TP and TN load in Lake Ziway is higher compared to some Tropical Lakes like Lake Lewisville (Gain and Baldys, 1995) and Ibirité reservoir (Antonio *et al.*, 2012), however, lower than that of Chaohu (Yang *et al*., 2013) and Victoria (Mnyanga *et al.*, 2005). TP loads for Lake Ziway is similar with the TP loads of Lake Kasumigaura (Havens *et al*. (2001)) and Okeechobee (Havens *et al*. (2001) however its TN load is lower than that of the mentioned lakes. TN load of Lake Ziway is comparable with the TN load of Lake Donghu and Ibirité reservoir (Havens *et al*. (2001). All lakes listed in Table 4.2.10 are under eutrophic conditions.

Table 4.2.10 Comparisons of the external nutrient loads (t yr^{-1}) of different lakes

Lakes	TP	TN	References
Victoria (Rivers total loading)	9270	38828	Mnyanga *et al.* (2005)
Chaohu	2700	4350	Yang *et al*. (2013)
Kasumigaura	220	3890	Havens *et al*. (2001)
Donghu	95	1480	Havens *et al*. (2001)
Okeechobee	426	5550	Havens *et al*. (2001)
Lewisville	9.26	57.3	Gain and Baldys (1995)
Ibirité reservoir	97	1526	Antonio *et al.* (2012)
Ziway	**208**	**1817**	**Present study**

4.2.7 Evaluation of the nutrient load balance of Lake Ziway

Nutrient load calculation and budget of Lake Ziway is shown in Table 4.2.11. The total load of the input TP was 2399 t $year^{-1}$ and the output was 186 t $year^{-1}$, resulting in a net retention of 2213 t $year^{-1}$, with a 92.3 % increase. The total load of input SRP was 215 t $year^{-1}$ and the output was 41.27 t $year^{-1}$, resulting in a net retention of 174 t $year^{-1}$ and 80.8 % increase. The overall percentage of the retention value found in the present study is about 80.8 %. Similar findings were observed in the study of phosphorus mass balance in the eutrophic lake Paranoá (Brazil), which has a phosphorus input of approximately 115 t $year^{-1}$ with a retention of 80 % in the reservoir (Guariento *et al.*, 2007).

Furthermore, the total input load of TIN was 3828 t $year^{-1}$ and the output was 616 t $year^{-1}$, resulting in a net retention of 3211 t $year^{-1}$, meaning 83.9 % was produced within the lake. In addition, the total input load of TN was 20329 t $year^{-1}$ and the output was 3595 t $year^{-1}$, with a net retention of 16734 t $year^{-1}$, with an increase of 82.3 % (Table 4.2.11). Therefore, the nutrients budget for Lake Ziway clearly shows that the amount of nutrients that enters the lake exceeds the output, indicating that nutrients are being retained in the lake which might lead to eutrophication of the lake. In a similar way, Hamilton *et al.* (2006) estimated that around 86 % and 72 % of phosphorus and nitrogen entering Lake Tarawera are retained within the lake.

Table 4.2.11 Nutrient load and balance of Lake Ziway with in the study period (**ton year** $^{-1}$)

Nutrient Load Balance	**TP**	**SRP**	**TIN**	**TN**
Ketar River	993	78.5	2239	9597
Meki River	1405	137	1589	10732
Total input	2399	215	3828	20329
Total output	186	41.3	616	3595
Input – output	2213	174	3211	16734
Percentage (%)	92.3	80.8	83.9	82.3

The fluctuations in the quantities of the retained nutrients depend on the river discharge and nutrient concentrations (Havens *et al.*, 2001). According to Ismail *et al*., (2011) hydraulic retention time is the major factor influencing nutrient retention in a lake ecosystem. The hydraulic retention time of Lake Ziway is 6.67 years which is suitable for phytoplankton growth. Because of the characteristically high water discharge rates of Ketar and Meki Rivers, the nutrient loads from this system were higher than those of the lake.

A clear seasonal effect was observed in this study on the external input of nutrients, with higher inputs during the rainy season. In addition, this study demonstrated that Lake Ziway has high nutrient load which might lead for eutrophication of the lake unless possible measures are taken in the lake water management.

4.2.8 Analysis of the relationship of climatic, hydrological factors and surface water quality parameters

The results in Tables 4.2.12 and 4.2.13 revealed that there are significant correlations of climatic, hydrological and water quality parameters. Precipitation had strong positive correlations with mean water level, discharge and fair positive correlation with mean air temperature; however had weak negative correlations with evaporation in both dry and wet seasons. Increase in temperature generally results in an increase in potential evaporation largely because the water holding capacity of air is increased (Carthy *et al*., 2001). As a consequence, the precipitation will increase, resulting in increase in both river discharge flow and water level. Mean water level and discharge flow showed the strongest positive correlations compared to the other parameters (Tables 4.2.12

and 4.2.13). According to the hydrological cycle, when precipitation increases, it results to more surface runoff reaching hence high water levels in rivers (Prathumratana *et al.,* 2008). High water level is followed by increasing flow velocity and discharge (Prathumratana *et al.,* 2008). , consequently more water delivered to the recipient water body of which in this case is Lake Ziway.

Although there are positive correlations between precipitation and discharge (Tables 4.2.12 and 4.2.13), some other factors within a basin that influence the precipitation–stream flow relationship include the area of the basin, the slope of the ground, the permeability of the soil, and the area of impervious surface within the basin (Prathumratana *et al*., 2008). A wide river will intercept more direct precipitation/rainfall than a narrow stream. Steeper slopes and larger amounts of impervious surface will increase the amount of runoff in a basin and decrease infiltration thus reducing the amount of precipitation that becomes groundwater (Prathumratana *et al*., 2008).

DO had from weak to strong negative correlations with mean precipitation, water level and discharge during the dry season and the wet seasons, respectively (Tables 4.2.12 and 4.2.13). This might be possibly explained by the transportation of different organic and inorganic matter by high discharge of rivers which increases oxygen demand hence decreasing the DO (Prathumratana *et al.,* 2008).

Table 4.2.12 Pearson correlations matrix showing climatic, hydrological factors and some water quality parameters of Lake Ziway in dry season

	PPT	WL	AT	Evp	DF	TP	SRP	TIN	TN	SiO2	WT	DO	pH	EC	TDS	TA
PPT	1	.933**	.430	-.138	.942**	.930**	.965**	.922**	.499	-.562	-.691	-.218	.857*	-.729	-.795	-.829*
WL	.933**	1	.364	-.365	.900*	.879*	.817*	.917*	.647	-.565	-.755	-.288	.640	-.585	-.617	-.669
AT	.430	.364	1	.022	.118	.502	.543	.493	-.377	.322	.290	.128	.510	-.218	-.487	-.794
Evp	-.138	-.365	.022	1	-.140	.027	.045	-.069	-.173	-.093	.198	.178	.205	-.484	-.380	-.135
DF	.942**	.900*	.118	-.140	1	.872*	.861*	.868*	.719	-.781	-.847*	-.195	.725	-.756	-.732	-.635

*. Correlation is significant at the 0.05 level
**. Correlation is significant at the 0.01 level.

Table 4.2.13 Pearson correlations matrix showing climatic, hydrological factors and some water quality parameters of Lake Ziway in wet season

	PPT	WL	AT	Evp	DF	TP	SRP	TIN	TN	SiO2	WT	DO	pH	EC	TDS	TA
PPT	1	.540	-.278	-.434	.457	.652	.670	.762	.442	-.240	-.766	-.611	-.729	-.423	-.423	.195
WL	.540	1	-.452	-.930	.763	.620	.864	.766	.777	-.083	-.751	-.464	-.926	-.876	-.873	-.022
AT	-.278	-.452	1	.736	-.921	-.909	-.793	-.801	-.912	.911	.805	-.464	.663	-.034	-.040	.864
Evp	-.434	-.930	.736	1	-.936	-.792	-.942	-.855	-.946	.406	.844	.119	.933	.648	.643	.387
DF	.457	.763	-.921	-.936	1	.936	.956*	.924	.999**	-.700	-.920	.123	-.890	-.356	-.350	-.628

*. Correlation is significant at the 0.05 level
**. Correlation is significant at the 0.01 level.

Abbreviations:-PPT-precipitation; WL-water level; AT-air temperature; DF-discharge flow; Evp-evaporation, TP-total phosphorus, SRP-soluble reactive phosphorus, TIN-total inorganic nitrogen, TN-total nitrogen, WT-water temperature, DO-dissolved oxygen, EC-electrical conductivity, TDS-totals dissolved solid, TA-total alkalinity

The nutrient parameters (SRP, TP, TIN and TN) in this study showed strong positive correlations with climatic (PPT and AT) and hydrological (WL and DF) parameters except evaporation for which the correlation was weak negative in the dry and strong negative in the wet season (Tables 4.2.12 and 4.2.13). For instance, these nutrient parameters showed strong positive correlation with discharge in both seasons. Alexander *et al.* (1996) suggested that nutrient loadings to receiving from the catchment would vary primarily with stream flow volume. The above mentioned nutrient parameters showed strong positive correlations with precipitation. Studies also proved that an increased frequency of heavy rainfall would adversely affect water quality by increasing pollutant loads flushed into the river (Prathumratana *et al*., 2008). In a Similar way, Ventela *et al.*, (2010) reported that high nutrient loads occur during the wet season as a result of their displacement by caused by high precipitation.

From the study, TA fairly (dry season) to strong (wet season) showed a negative correlations with the mean water level, discharge and precipitation in the dry season and weakly negative correlation with discharge and water levels. Similar findings have been reported by the study of Welsch *et al.* (2006). Their study focused on simulation of future stream, TA under changing deposition and climate scenarios and they found that stream water TA continued to decrease for all scenarios of climate change except where climate was gradually warming and becoming moister. TA could be considered as an important indicator for the impact of climate change.

Electrical conductivity (EC) has strong negative correlations with the mean water level and discharge flow and precipitation. The EC of the water generally increases as the levels of dissolved pollutants (such as nitrate, ammonium, phosphate, sulfate and potassium) increases (Kenneth *et al*., 2005). The negative correlation of EC with water level, discharge flow and precipitation is mainly due to dilution effect. Similarly, Gebre-Mariam (2002) reported that the EC of the Ethiopian Rift Valley lakes generally have lower values during the rainy season than the dry season; which is due to dilution by rain coupled with lower/minimal evaporation rates during the rainy season.

4.2.9 Conclusions and recommendation

According to the results of this study, the vertical nutrient profiles of Lake Ziway showed no significant variability, making it difficult to rely on the observed nutrient concentration profiles to understand the temporal nutrient dynamics in the lake. As expected there is a general trend of higher nutrient load in the wet than in the dry seasons in Lake Ziway for the study periods. The long term effects of high nutrient load and decreased water level in the lake could bring severe negative consequence which might be difficult to reverse unless immediate possible measures are taken on the lake water management, such as a resumption of the natural flow practice around the Lake catchment and mobilization of overall stakeholders to conserve the lake.

There were significant correlations between climatic, hydrological and water quality parameters of Lake Ziway which outlines their importance in the lake characteristics and functions. However, precipitation, the mean lake level, discharge and the mean air temperature had weak to strong positive correlations with nutrients. Negative correlations of DO, pH, EC, TA and SiO_2 were found with all of the hydrological parameters. Since the lake is an intensive agricultural site, it is high time to develop the lake catchment protection management practice in order to mitigate the destruction of the lake.

4.3: Analysis of internal nutrient load dynamics from the sediment in Lake Ziway

4.3.1. Spatial and seasonal trends in nutrients analysis in the sediment depth profiles

The results of the study for the spatial and temporal values of NO_3-N, NO_2-N, SRP, TP and TN concentrations and loads in the lake sediment samples in both composite and depth profiles are presented below:

4.3.1.1 Vertical soluble reactive phosphorus distributions in sediment depth profiles

Soluble reactive phosphorus (SRP) distributions were analyzed in all sediment samples collected in Lake Ziway in both the dry and wet seasons with depth profiles and the spatio-temporal depth profiles results are shown in Figure 4.3.1 a and b.

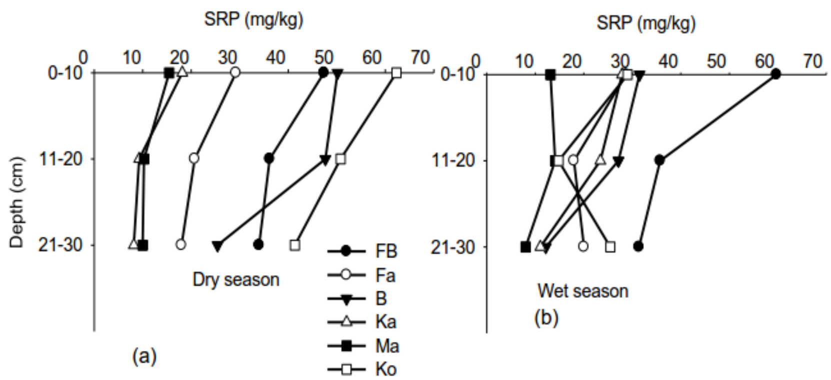

Figure 4.3.1 a and b Vertical profiles of sediment SRP from the six different sampling sites in dry and wet seasons in 2014 and 2015

SRP concentrations ranged from 8.15 to 62.0 mg/kg and 8.01 to 60.0 mg/kg in the dry and wet seasons respectively. Higher SRP concentrations occurred in the upper layer and declined with depth in most sampling sites in both seasons (Figure 4.3.1 a and b). Similar results were reported by Yang *et al*., (2008), Sobczyński and Joniak, (2009) and Kangur *et al*., (2013). The main reason for the declining of SRP along depths of the sediment might be the 'bound up' of SRP with other metal complexes and not being actively released to the overlying water column. Similarly, Søndergaard *et al*., (2003) agreed that phosphorus in the upper approximately 10 cm is considered to take part in the whole lake metabolism, but mobility of phosphorus from depths down to the bottom is decreasing. Similar results also were obtained by Pettersson, (1998) working in oxic condition that explained the vertical profiles of sediment phosphorus concentration expressed on dry weight basis showed an increasing trend towards the sediment surface.

According to Teichreb *et al*., (2013), the disturbance of the overlying sediment would result in chemical reactivation and release of SRP from lower depths. Other studies also showed, as far as internal inputs are concerned, phosphorus is typically released from the sediment to the overlying water column through organic matter decomposition and geochemical processes (Vadrucci *et al*., 2004). The high SRP concentrations at the top sediment layer might also be due to the active layer of anaerobic decomposition of organic matter which is indicated by low DO concentration at the lake bottom.

The mean concentrations of SRP were 27.7 mg/kg and 21.2 mg/kg in the dry and wet seasons respectively. The value of sediment SRP in Lake Ziway is in the same range of its value in other Ethiopian lakes like Lake Tana (ranged between 9.6 to 52.2 mg/kg with the overall mean value of 21.8 mg/kg) reported by Kebede and Muhabaw, (2015). Similarly, Wang *et al*., (2014) and North *et al*, (2015) reported that released SRP in the sediment is available for algal growth and can further sustain the eutrophication processes. Therefore, this result indicated that the sediment might be an important internal source of SRP for Lake Ziway ecosystem in increasing eutrophication process.

In the case of temporal variations, the dry season SRP concentrations were slightly higher than the wet season, due to its internal load enhanced by warm temperature and biological activities in the lake ($p < 0.05$) (Pettersson, 1998; Javaid *et al.*, 2014). Similarly, Feuchtmayr *et al*., (2009) reported that higher temperature increases the release of phosphorus from bottom sediments. Others also explained that because mixing prevents a buildup of high phosphorus gradients at the sediment-water interface which hamper further phosphorus release, and because higher hypolimnetic temperature enhances mineralization of organic matter and phosphorus release from the sediment (Wilhelm and Adrian, 2008). On the other hand, higher wind speed could enhance the mixing of nutrients (George *et al*., 2007). So, the higher sediment wind induced and wave disturbance in the lake during the dry season, with a decline in lake level might be one reason for the higher sediment SRP concentration during the dry season.

Besides, in shallow lakes, internal release of nutrients and pollutants was drastically influenced by wind induced and wave disturbance particularly in shallow lakes (Zhu, *et al*., 2004). Robarts et *al*., (1998) also reported that the concentration of SRP in lake water increased. In Lake Taihu, it was also found that SRP concentration in lake water increased over 2 times during the strong wind course, with a wind speed of over 12 m s^{-1} (Guangwei *et al.,* 2006). Therefore, like Ziway sediments wind induced and wave disturbance could be the main means of internal releasing of phosphorus in Lake Ecosystem. Spatial variation of SRP concentration in the sediments was also highly significant ($p < 0.05$) in both seasons. This spatial variation might be due to the difference in natural (climatic and hydrological factors) and anthropogenic (agricultural, fishing, swimming, washing of cloths and cars, etc) around the lake as discussed above.

4.3.1.2 Vertical distributions of total phosphorus in sediment depth profiles

Total phosphorus (TP) concentrations varied within the range of 16.2 to 207 mg/kg and 24 to 192 mg/kg with mean value of 62 and 73 mg/kg in the dry and wet seasons respectively. The vertical distribution of sediment TP concentration was higher at the top sediment depth (0 - 10 cm) and lower in the middle (11-20 cm) in most sampling sites in the wet season but showing a decreasing trend down the depth profiles in the dry season (Figure 4. 3.2).

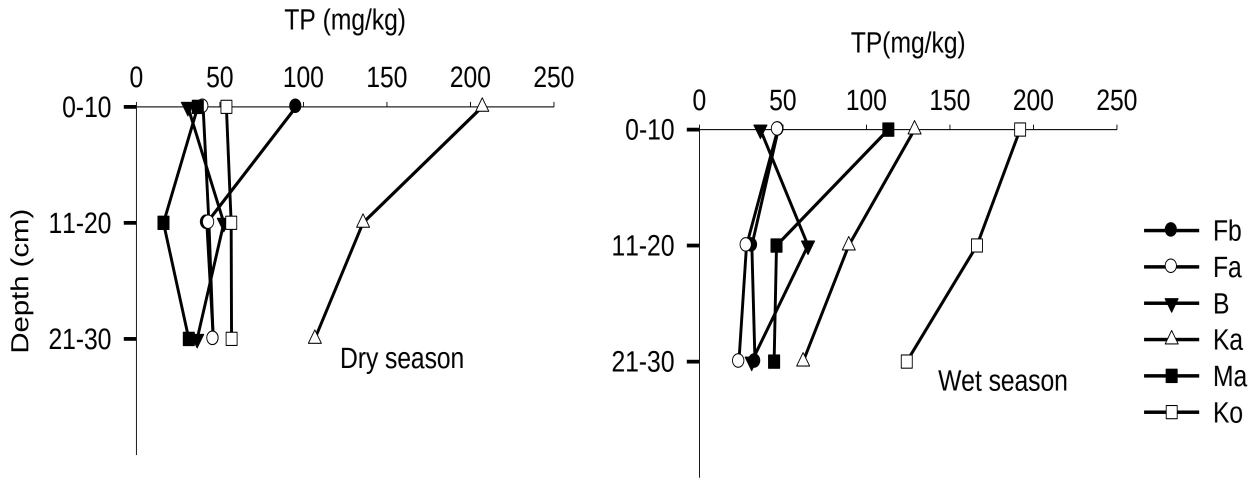

Figure 4.3.2 Vertical distributions of TP in sediment from the six different sampling sites in dry and wet seasons in 2014 and 2015

Similarly, Jellison *et al.* (2003), Sobczyński and Joniak (2009), Ye *et al.* (2009) and Chang *et al.* (2010) reported the concentration of TP in sediment depth profiles of lakes decreasing with depth. A greater localized external agrochemical load might be given as a cause increasing nutrient load for this variation. Similarly, Kelderman *et al.* (2005) and Trolle (2009) suggested that the elevated TP concentrations in the uppermost sediment layers of the lake are due to high localized external agrochemical load. Kim *et al*. (2004) also reported decreasing TP concentrations with increasing sediment depth might, which they explained that could be due to biodegradation, or release due to the changing conditions caused by biodegradation. Gertrud (2009) found that internal TP loading from bottom sediments was higher in the dry season in several lakes, and that had measurable effects on the water quality. Therefore, TP this study identifies that nutrient concentration in sediment have an effect on Lake Ziway water quality.

In general, higher concentrations of TP profiles in the uppermost sediment layers, is similar to that of SRP. Similarly, Chao *et al.*, (2007) studied the vertical variation of the phosphorus species in sediments of three typical shallow urban lakes in China, and reported that in all the three studied lakes, TP concentrations increased in the upper 10-cm of sediment cores and decrease with the depth, suggesting that the pollution status of these lakes became more serious with the development of industry and economy of these cities. In this study, TP had significant seasonal variation ($p < 0.05$).

The TP concentrations in sediment depth profiles exhibited different patterns at different parts of Lake Ziway. For example, there was low TP concentration gradient at M_a and B during the dry and wet seasons, respectively. This probably indicates delayed mineralization of settled material either due to increase in sedimentation rate or reduction in biological activity (Kitaka, 2000). K_a and K_o sampling sites showed high TP concentration in the dry and wet seasons, respectively. The higher values of TP concentrations in these sampling sites might be due to the higher external nutrient loads at K_a and the anthropogenic impacts on K_o sampling sites that can in turn have lead to high accumulation of nutrients in the top layer of sediments.

4.3.1.3 Vertical distributions of nitrate-nitrogen in sediment depth profiles

Sediment NO_3-N concentrations in depth profile ranged from 2.52 to 7.99 mg/kg and 2.95 to 61.8 mg/kg with mean values of 5.28 and 28.4 mg/kg in the dry and wet seasons respectively. ANOVA (Kruskal-Wallis test) analyses showed that NO_3-N concentrations among sampling sites were significantly different during the wet season ($p < 0.05$) but not during the dry season ($p > 0.05$). High NO_3-N concentrations were obtained during the wet season than the dry season which might be associated with high inflows from the catchment. The sampling sites K_o and F_b have high NO_3-N concentration in both seasons as compared to other sampling sites (Figure 4.3.3). This could be due to high animal and human interference (mainly from fish marketing activities and animal grazing) in K_o and effluents of the floriculture industry in F_b.

The vertical distribution of NO_3-N concentrations in the lake decreased with sediment depth in most sampling sites in both seasons (Figure 4. 3.3). Similarly, Dasm *et al*. (2013) reported that the NO_3-N concentration in the lake sediment were typically lower in the deeper depth (>10 cm) than the shallower depth (0-10 cm) in both seasons. The decreasing trends of NO_3-N with depth might be the conversion of nitrate to nitrite and then to nitrogen gas through microbially mediated denitrification (Lehmann *et al*., 2007).

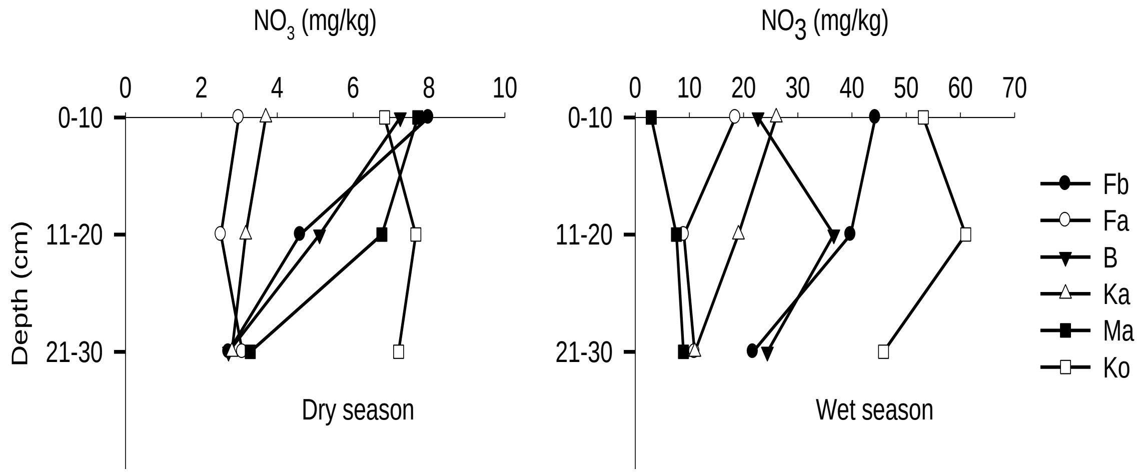

Figure 4.3.3 Vertical distributions of NO_3-N concentrations in sediment depth profiles in dry and wet season in 2014 and 2015

Other studies also suggested that the population of nitrifying bacteria, free living nitrogen fixing bacteria and total bacterial population showed a slight decreasing trend with gradual increase in sediment depth (Lehmann *et al*., 2007). Moreover, Zhang *et al*. (2014) explained that NO_3-N diffusion from the water column to the sediment decreased severely with sediment depth due to the denitrification processes as oxygen level decreases.

4.3.1.4 Vertical nitrite-nitrogen distributions in sediment depth profiles

Nitrite-nitrogen (NO_2-N) concentrations ranged from 0.84 to 20.0 mg/kg and 11.3 to 45.3 mg/kg and the mean concentrations of NO_2-N were 8.51 mg/kg and 24.2 mg/kg in the dry and wet seasons, respectively. In the study, there were strong seasonal variations ($p < 0.05$).

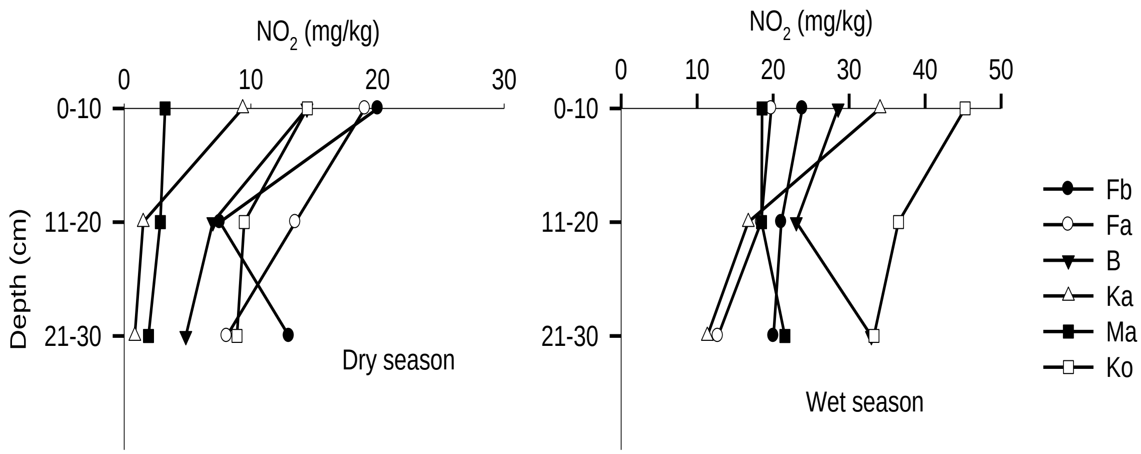

Figure 4.3.4 Vertical profiles of sediment NO_2-N from the six representative sampling sites in dry and wet seasons in 2014 and 2015

Most sampling sites had high NO_2-N concentrations at the top sediment samples and decreased with depth in both seasons (Figure 4.3.4). Similar results were reported by Trolle (2009), Dasm *et al*. (2013) and Zhang *et al*. (2014) in their studies in other different lakes in the world.

In the study, spatial trends were also observed in NO_2-N concentrations in most sampling sites. Most sediment cores the bottom sediment was relatively low NO_2-N concentrations in sediment depth in both seasons (Figure 4. 3. 4). However, profiles from sampling sites of F_b and K_o generally had high NO_2-N concentrations in the uppermost sediment layers during the dry and wet seasons, respectively. Wet season NO_2-N concentrations were higher than the dry season. This most probably might be related to excessive sedimentation due to anthropogenic input from agricultural runoff, industrial effluents and domestic sewage from the surrounding lake catchment, similar to report from other studies on the same lake (Meshesha *et al.*, 2012, Desta *et al*., 2016).

4.3.1.5 Vertical total nitrogen distributions in sediment depth profiles

The mean TN concentrations in the sediment depth profile ranged from 508 to 3200 mg/kg and 443 to 3753 mg/kg, with over all means of 1511 and 1631 mg/kg in the dry and wet seasons, respectively. Though TN concentration variations between seasons were not significant ($p < 0.05$), the wet season values were slightly higher than the dry season in most sampling sites. The probable reasons for increasing TN in wet season is similar to that for NO_2-N as mentioned above. The depth profiles of TN concentrations decreased with sediment depth in both seasons (Figure 4.3.5). Similar results has been reported in different lakes by Meng and Zhao (2013); Ye *et al.*, 2009; Trolle (2009); Kim *et al.* (2004); Kelderman *et al.* (2005). The higher TN concentrations in the uppermost sediment layer of the lake might be due to aerobic condition at the sediment-water interface for decomposition and break down of binding molecules and the higher localized external loading (Kelderman *et al*., 2005). Similarly, Jinglu *et al*. (2007) and Trolle (2009) explained that the increased top surface nutrient concentrations in the sediment could be due to the urbanization, industrialization and agricultural intensification in the lake catchment. There were also spatial differences, in depth profile concentrations of TN during the dry and wet seasons in most sampling sites. It could also indicate high N fixing by sediment benthic algae especially relevant in shallow systems.

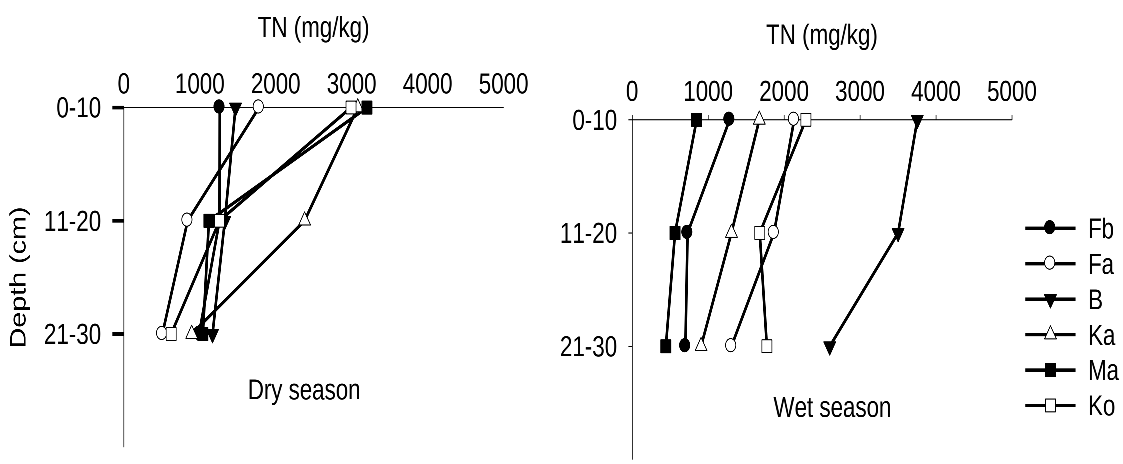

Figure 4.3.5 Vertical profiles of sediment TN from the six representative sampling sites in dry and wet seasons in 2014 and 2015

As can be seen from Figure 4.3.5, M_a (3200 mg/kg) and B (3753 mg/kg) have the highest concentrations of TN in the dry and wet seasons, respectively at the top sediment layers. The highest values of TN in these sites are probably due to the differences in the origins of the sediments and related anthropogenic factors. According to EPA, (1994), the evaluation criteria of TN pollution in the sediment sampling sites of M_a in the dry season and B in wet season in Lake Ziway have reached severe pollution, and the rest sampling sites have reached mild pollution. Throughout the whole lake sediment TN concentration shows Lake Ziway sediment pollution is very high. Therefore, the endogenous load cannot be ignored.

As a summary, the nutrient distribution in depth profiles of SRP, TP, NO_3-N, NO_2-N and TN were higher at sediment top surface (0 - 10 cm depth) and declined with depth of the sediment profiles in most of the sampling sites in both seasons which might be probably due to aerobic condition at the interface than at the bottom for decomposition and break down of binding molecules and longer time period strata formation at the bottom. Internal nutrient load can be especially high in shallow lakes like Ziway where mixing at the sediment-water interface effectively maintains nutrients in the water which depends on climate and external nutrient load conditions (Sorann *et al*., 1997; Jinglu et *al*., 2007, Ye *et al.*, 2009, Zhang *et al*., 2014). According to Christensen *et al.*, (2011), large nutrient concentrations in bottom sediment and sediment-water interface samples could indicate a release of nutrients from sediment to the water column. Therefore, the internal load in Lake Ziway could be one of the major determining factors for its water quality and should not be ignored in any lake water management plan.

4.3.2 Seasonal variations of composite sediment nutrient analyses at the central sampling site of Lake Ziway

The mean concentrations for SRP, TP, NO_3-N and NO_2-N were 10.4, 58.7, 10.6, 38.4 mg/kg and 6.32, 46.2, 3.19, 63.6 mg/kg for the wet and dry seasons respectively (Figure 4.3.6). Wet season values were higher than the dry season in all nutrients except NO_2-N. There are seasonal variations of nutrient concentrations for the sediment samples; this might be the seasonal cycles of nutrients due to imbalances in the processes of mineralization and consumption (Adeyemo *et al.*, 2008)**.** Zhang *et al*., (2014) reported that lake sediment has a significant effect on nutrient transfer in lakes, especially shallow ones.

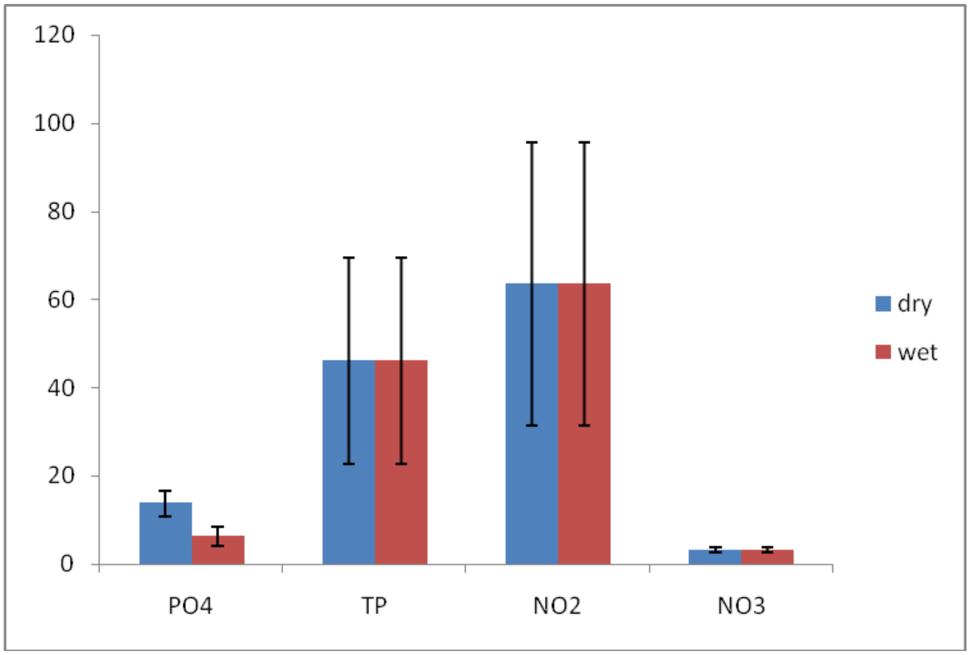

Figure 4.3.6 Mean concentrations of nutrients in composite sediment samples at the centre sampling site for the wet and dry seasons in 2014 and 2015.

There are significant variations in SRP concentrations in sediment samples between the dry and wet seasons ($p < 0.05$). For instance, lake's sediments SRP showed higher concentration in the wet season and lower concentration in the dry season (Figure 4.3.6). Similarly, Kebede and Muhabaw, (2015) reported that SRP concentration in sediment samples in another Ethiopian lake, Lake Tana has higher values in wet season than the dry season. This could be attributed to the fact that this season follows immediately during the heavy rain season and most of the sediments from the rivers and discharge points have been washed into the lake (Vincen *et al.*, 2007).

According to the index system of the UK Agricultural Development and Advisory Service, higher SRP concentrations in sediment (> 46 mg/kg) indicate a high nutrient status (Dasm *et al.*, 2013). Therefore, according to this index system Lake Ziway has high nutrient status. Kangur *et al.*, (2013) explained that increasing nutrient concentrations appeared to be a general phenomenon in shallow eutrophic lakes and in most cases this increase can only be the result of increased sediment load, implying that seasonal nutrient concentrations are largely controlled by internal processes.

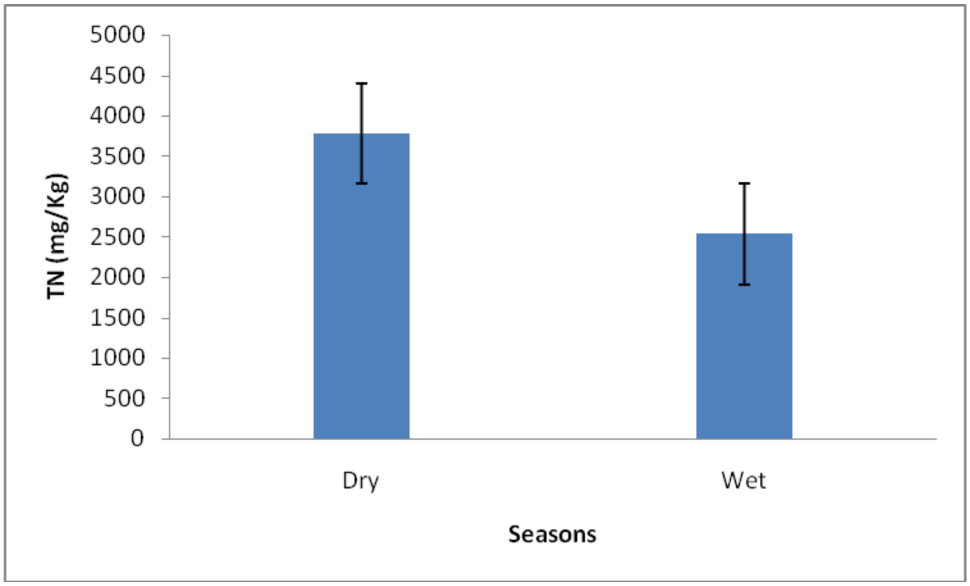

Figure 4.3.7 Mean concentrations of TN in composite sediment samples at the centre sampling site for the wet and dry seasons in 2014 and 2015.

The results in Figure 4.3.7 show that the mean concentrations of TN in sediments were 3780 and 2537 mg/kg in the dry and wet seasons, respectively. Relatively lower mean concentrations were obtained in wet season as compared to the dry season. Similarly, Kebede and Muhabaw, (2015) and Adeyemo *et al.*, (2008) have reported similar situation with maximum sediment TN value recorded during the dry season for Lake Tana, Ethiopia and Ibadan River, Nigeria, respectively. However, the overall mean values of sediment TN of Lake Ziway (3158 mg/kg) is found to be much higher than that of Lake Tana, Ethiopia (180 mg/kg) reported by Kebede and Muhabaw, (2015). According to EPA (1993), guidelines for contaminated freshwater sediments, TN concentrations in sediment of 550 and 4800 mg/ kg cause lowest and sever effects on aquatic biota, respectively.

High sediment concentrations of TN in the present study might be attributed to the increased agricultural activities and rural and urban wastewater effluents in the area as well as increased decomposition of organic matter with warm temperature (Meshesha *et al.*, 2012; Desta *et al.*, 2016) as shown above in 4.1.3. Similarly, Landkildehus *et al.*, (2014) reported that the TN concentration increased with increasing temperature, possibly resulting to reduced nitrogen retention in the sediment under warmer conditions.

4.3.3 Seasonal evaluation of phosphorus flux from lake sediments as a measure of internal phosphorus load

Incubated phosphorus fluxes were displayed in Table 4.3.1. The results showed that the flux ranged from -1.64 to 32.6 and -1.31 to 6.92 mg m^{-2} day^{-1} for SRP and -3.08 to 116 and - 4.33 to 28.2 mg m^{-2} day^{-1} for TP in dry and wet seasons, respectively. There were significant differences in the mean release rates between sampling months ($p < 0.05$) but not across sampling sites ($p > 0.05$). The mean TP and SRP release rates were 5 times and 3 times higher in the dry season as compared to the wet season, respectively. The mean release rates were significantly higher in January, 2015 than all other months followed by March 2015 at sampling site $F_{a,}$ which in turn were significantly higher than the rest of the months. Phosphorus concentrations were highest in the dry season; perhaps the high water temperature increased the activities of microorganisms, and thus stimulated the degradation of organic matter (OM) by microbiological agents, which enhanced the further release of phosphorus. Similar results have reported that in many shallow nutrient-rich lakes, P concentrations in the dry season are considerably higher than in the rainy season (Clavero *et al.*, 2000; Søndergaard, 2007; 2013). Moreover, Kangur *et al.* (2013) and Zhang *et al*. (2013) also reported that increased temperatures increase microbial processes and diffusion from the sediments resulting in elevated phosphorus concentration in the overlying water column. Furthermore, Søndergaard (2007) explained that the increased temperature augments the rate of chemical diffusion and chemical processes, but the most significant impact on nutrient release is often via biological processes. As result enhanced temperature stimulate the mineralization of organic matter in the sediment and the release of inorganic phosphate increased in the sediment. Also chemical binding and release can play a very big role especially if anoxixcity is reported at the water-sediment interface, since Lake Ziway is alkaline in nature so change in pH causing more release rates of phosphorus.

Spatial variability was also evident when comparing SRP and TP release rates within Lake Ziway sediment. The highest mean SRP and TP release rates were measured from cores sampled at site F_a as compared with other sites; this might be attributed to its location close to the floriculture industry. There was a higher turbidity in this site indicating high sediment loading with high nutrient concentration as mentioned above. A similar approach has been suggested for Lake

Okeechobee, Florida, where differing phosphorus release rates are related to sediment characteristics throughout the large, subtropical lake (Steinman *et al.*, 2007) in another lakes in the world.

The negative values showed that phosphorus species generally diffused from the water column to the sediment where as positive results showed that phosphorus species diffused from the sediment to the water column and thus played a key role as a source of phosphorus species. Phosphorus in pore water might come from the degradation of OM in sediment, and the diffusion of phosphorus can be controlled by the concentration gradient in pore water and the overlying water. Phosphorus fluxes are attributed to the integrative result of dissolution, diffusion and adsorption/desorption, moreover, might be related to the form of SRP and the redox situation in the sediment (Zhang *et al*., 2014). At the same time, iron hydroxide adsorption/desorption to phosphorus would alter the concentration of phosphorus (Zhang *et al*., 2014). High concentrations of phosphor species were observed the sites F_a (near floriculture industry) in both seasons, which could suggest the overuse of agrochemicals by the floriculture industry. The fluxes indicated that SRP mainly diffused from sediment to the water column and the sediment was the sources of SRP. Similar results were reported by Steinman and Ogdahl (2006) and Zhang *et al*. (2014).

As has been documented in aquatic systems in different parts of the world, sediments almost invariably act as sinks and sources of SRP and TP (Steinman *et al.*, 2007). The same author explained that what varies among ecosystems and sediment types is the order of magnitude of these internal fluxes and the proportion released into the external loads. Moreover, Shah *et al.,* (2014), reported that the concentration of phosphorus in shallow lakes is slightly controlled by external phosphorus loading; however, internal lake processes have a major impact on the functioning of shallow lakes and proposed few criteria for the lakes having high internal phosphorus loading which include:(i) lake morphometry (shallow depth, large surface area and long fetch), (ii) intensely agricultural surrounding and (iii) increase of temperature with elevated pH and decreased light penetration. All these criteria fit to Lake Ziway, therefore, justify its high internal phosphorus loading.

Table 4.3.1 Lake Ziway sediment TP and SRP release rates incubated in 5 days under anaerobic condition (mg m^{-2} day^{-1})

		Dry season						Wet season		
Site	Nutrients	Jan, 2015	Feb, 2015	Mar, 2015	April, 2015	$\bar{x}\pm$ Std. Err		May, 2015	Jul, 2015	$\bar{x}\pm$ Std. Err
Fa	SRP	32.6	9.09	12.3	0.33	13.57± 6.82		6.92	0.33	3.63±3.29
Fa	TP	116	62.5	59.6	-0.56	59.44±23.86		28.2	-1.54	13.31±10.25
B	SRP	0.21	1.64	-4.58	9.09	1.59±2.83		0.70	0.98	0.84 ± 0.14
B	TP	11.3	10.4	20.8	16.4	11.56±4.78		1.31	2.87	2.09 ± 0.78
Ka	SRP	-1.64	1.82	7.20	6.78	3.54±2.12		1.96	-1.31	0.33±0.16
Ka	TP	-3.08	8.51	7.20	13.1	6.43±3.41		-4.33	-3.01	-3.67±0.66
	Mean SRP					***6.23±2.81***		*Mean SRP*		***1.60±1.15***
	Mean TP					***25.8±10.3***		*Mean TP*		***3.91±1.50***

✓ *Positive numbers indicated fluxes out of the sediment and negative numbers indicated fluxes into the sediment.*

The TP release rates ranged from -3.08 to 116 mg m^{-2} day^{-1} in Lake Ziway under anaerobic conditions, this indicated that internal load might be a significant source of phosphorus in the lake ecosystem. Similar results have been reported by Steinman *et al.*, 2007. Nowlin *et al.,(* 2005) that nutrients release from the lake sediment are ecologically more important than inputs from external nutrient sources because SRP released from sediments often contains a larger portion of immediate SRP. Steinman *et al.* (2004); Søndergaard *et al*. (2012) also reported that internal phosphorus load can be a significant source of nutrients in shallow eutrophic lakes, and can result in serious impairment to water quality. Increased release of phosphorus into the water column further stimulates the growth of algae and cyanobacteria causing nuisance algal blooms (Christensen *et al*., 2013).

Wetzel (2000) reported that even though the overall flux of TP in the lake sediment, the biogeochemical processes that are unique to the sediment environment if capable of transforming relatively refractory phosphorus compounds that are deposited on the sediment surface to more bioavailable forms. Bioavailable phosphorus is then released to the water column and this internal phosphorus source can become a major factor in regulating lake productivity.

Fisher *et al.* (2005) also explained that, even though internal load does not (usually) represent a net source of nutrients to the lake, it can be a significant source of phosphorus and is therefore an important regulator of lake trophic conditions. Based on the above facts, this study suggested that internal nutrient load contributes much of phosphorus loads to Lake Ziway causing its current trophic status.

As compared to other lakes, the release rate of SRP (3.9 mg P m^{-2} d^{-1}) in Lake Ziway was similar to the release rates of SRP of Lakes Alderfen Broad (3.5 mg P m^{-2} d^{-1}), Neagh (4.4 mg P m^{-2} d^{-1}), Scharmutzelsee (2.6 mg P m^{-2} d^{-1}) and Long (2.6 mg P m^{-2} d^{-1}) (Table 4.3.2). The SRP release rate of Lake Ziway was higher than Lakes Okeechobee (0.83 mg P m^{-2} d^{-1}) and Beaver Reservoir (0.31 mg P m^{-2} d^{-1}) but slightly lower than Lakes Agmon (6.0 mg P m^{-2} d^{-1}) and Klamath (6.0 mg P m^{-2} d^{-1}), respectively (Table 4.3.2). The release rate of TP (16.1 mg P m^{-2} d^{-1}) in Lake Ziway was higher than Lakes White (3.75 mg P m^{-2} d^{-1}) and Mona (4.44 mg P m^{-2} d^{-1}) but similar to Lake Spring (15.6 mg P m^{-2} d^{-1}) (Table 4.3.2). All the above lakes suffer from eutrophication.

Table 4.3.2 Comparisons of P release from bottom sediments of different lakes

Lake	P release rate (mg P m^{-2} d^{-1})	Reference
Long (WA, USA)	2.6	Steinman and Rediske (2004)
Klamath (OR, USA)	6.0	Steinman and Rediske (2004)
Alderfen Broad (UK)	3.5	Steinman and Rediske (2004)
Neagh (UK)	4.4	Steinman and Rediske (2004)
Okeechobee	0.83	Fisher *et al.* (2005)
Beaver Reservoir (USA)	0.31	Sen *et al.* (2007)
Scharmutzelsee (Germany)	2.6	Kleeberg and Kozerski (1997)
Agmon (Israel)	6.0	Kowalczewska-Madura and Gołdyn (2009)
Ziway	3.9	This study
	TP release rate (mg P m^{-2} d^{-1})	
White	3.75	Steinman (2006)
Mona	4.44	Steinman (2006)
Spring	15.6	Steinman and Mary (2005)
Ziway	16.1	This study

4.3.4 Conclusion and recommendations

In this study the spatial and temporal variability of nutrients in depth profiles of sediment samples were observed. The values of nutrient distributions in depth profiles were higher at the sediment top surface and decline with depth of the sediment profiles in most of the sampling sites and seasons. From the results internal nutrient load might be sources of eutrophication of the lake ecosystem. Pore water phosphorus changed distinctly in different seasons with higher values at the sites near the floriculture.

Therefore, in shallow eutrophic lakes like Ziway, quantification of internal nutrient load as well as vertical distribution of nutrients in sediment profile is a critical issue in identifying management strategy to improve the water quality conditions. The findings from the current study indicate that internal sources of nutrients to Lake Ziway vary across time and space. Understanding this variation may help in developing mitigation and restoration strategies for the lake and other aquatic ecosystems in Ethiopia.

4.4: Determination of the trophic status of Lake Ziway

4.4.1. Analysis of trophic state variables (physico-chemical and biological parameters)

The water quality data measured (total phosphorus (TP), total nitrogen (TN), chlorophyll-*a* (Chl-*a*) and secchi depth (SD)) for the analysis of the trophic status of Lake Ziway are shown in Figures 4.4.1 to 4.4.4.

Total phosphorus (TP): TP ranged between 108 μg L^{-1} to 340 μg L^{-1} with an average concentration of 212 μg L^{-1}. No statistically significant differences among the six sampling sites were found (Kruskal-Wallis test, $p > 0.05$). The lowest phosphorous concentrations measured were in April (108 μg L^{-1}) during the dry season (Figure 4.4.1). Concentration of TP fluctuated significantly during the study periods while the higher values were in July (337 μg L^{-1}) and August (340 μg L^{-1}) in the wet season (Figure 4.4.1). The relatively high concentration of phosphorous in Lake Ziway during the rainy season could be attributed to fertilizer runoff from the surrounding agricultural fields and may be from internal phosphorous loading as discussed in the previous sections (section 4.3 and 4.2.6). Furthermore; the external nutrient load interms of the mean TP concentration due to the two feeding rivers (Meki and Ketar) was 0.25 mg L^{-1} and 0.76 mg L^{-1} in the dry and wet seasons, respectively. From this study the mean annual TP concentration due to the two rivers is 0.51 mg L^{-1}. According to Lau et *al*., 2002, the mean annual TP of eutrophic lake is between $0.047 < x \leq 0.13$ mg L^{-1} and annual TP > 0.13 mg L^{-1} in hypertrophic lake. Therefore, the lake is currently eutrophic based on TP concentrations.

According to Wetzel (2000), TP concentration less than 10.0 μg L^{-1} in a lake are generally considered to be oligotrophic while 100 μg L^{-1} often is used as the threshold for hyper-eutrophication. Apart from this, according to the Organization for Economic Development and Co-operation (OECD, 1982) (Table 2.3) for trophic state classification, the limit of TP for define eutrophic is 35.0 μg L^{-1}. Similarly, Ndungu *et al.* (2013) reported that the TP concentration of Lake Naivasha, Kenya ranged from 27 to 410 μg L^{-1}. Thus, the value for Lake Ziway is 5.73 times greater than the prescribed limit for eutrophication. Moreover, both the internal and external TP loads showed the lake is in eutrophic state.

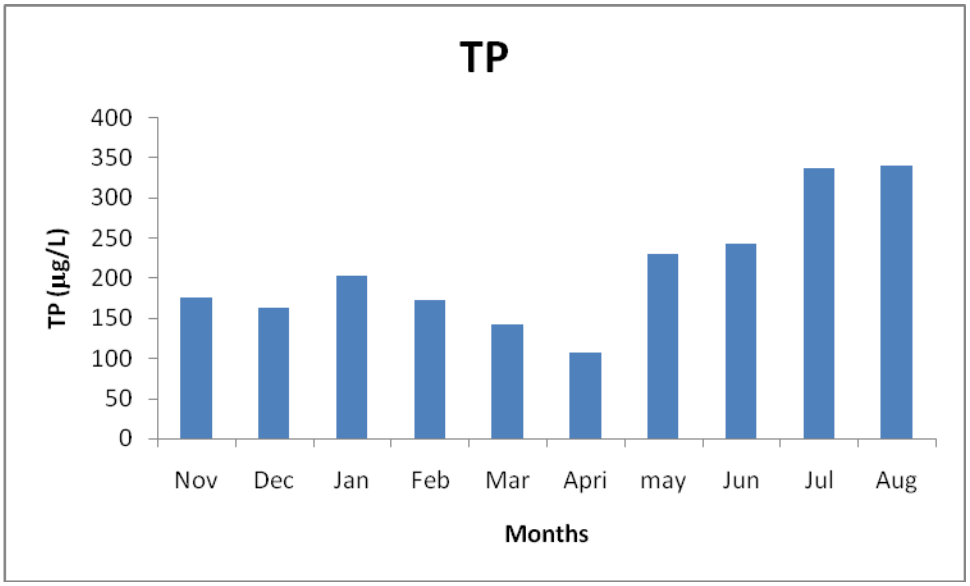

Figure 4.4.1 Monthly mean values in TP concentration in Lake Ziway

Total nitrogen (TN): TN ranged from 5.54 mg L^{-1} to 7.49 mg L^{-1} with mean concentration of 6.70 mg L^{-1}. ANOVA (Kruskal-Wallis test) result showed that TN concentrations among sampling sites were significantly different ($p < 0.05$). The lowest TN concentrations measured were in May (5.54 mg L^{-1}) and the highest TN concentration was recorded in July (7.50 mg L^{-1}) (Figure 4.4.2). The relatively high concentration of TN in July (Figure 4.4.2) could be from the application of fertilizers on crop land and decomposition of organic matters washed off into the lake as important source of nutrient loading available to phytoplankton.

Limnologists and lake managers have developed a general consensus about freshwater lake responses to nutrient additions, that essentially an ambient TP concentration of greater than about 0.01 mg L^{-1} and/or TN of about 0.15 mg L^{-1} are likely to predict blue-green algal bloom problems during the growing season (O'Sullivan and Reynolds, 2004). Similarly, chronic over enrichment leads to lake quality degradation manifested in low dissolved oxygen, fish kills, algal blooms, expanded macrophytes, likely increased sediment accumulation rates, and species shifts of both flora and fauna (US EPA, 2000). From the study, it was found that Lake Ziway, concentrations of TP and TN obtained are greater than the limit of 0.01 mg L^{-1} and 0.15 mg L^{-1}, respectively.

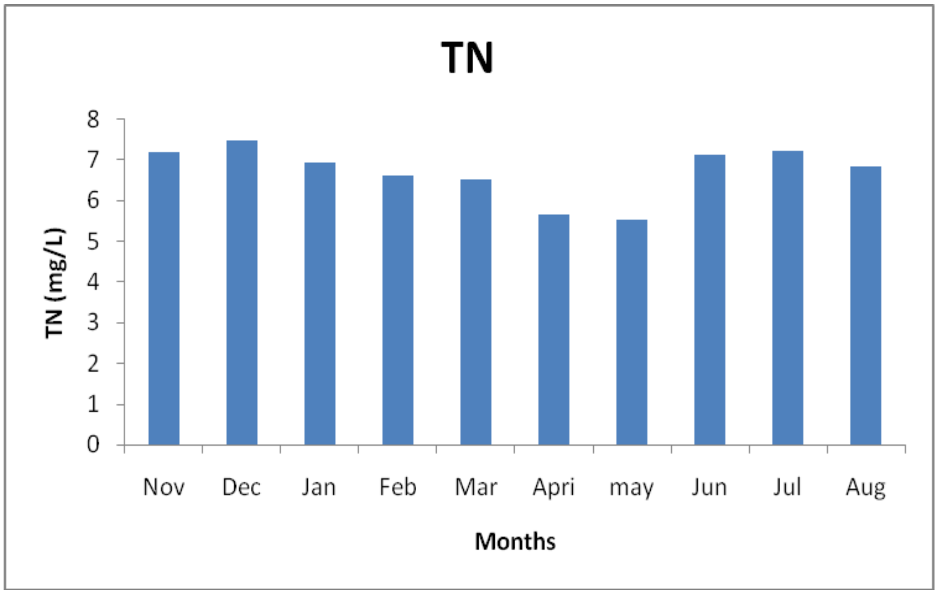

Figure 4.4.2 Monthly trends of TN concentrations in Lake Ziway

In addition, both the internal and external TP and TN loads showed the lake is in eutrophic state. For instance, the external TP and TN load in Lake Ziway is higher compared to some tropical eutrophic Lakes like Lake Lewisville (Gain and Baldys, 1995) and Ibirité reservoir (Antonio *et al.*, 2012), and TP loads for Lake Ziway is in the same range with that of eutrophic lakes, Lake Kasumigaura (Havens *et al*. (2001)) and Okeechobee (Havens *et al*. (2001). Moreover, the TN load in Lake Ziway is also in the same range with that of another eutrophic lake, Lake Donghu (Havens *et al*. (2001). Explanations of internal and external nutrient loads are presented in section 4.3 and 4.2.6 so as the results of these sources of nutrient loads have high contributions for eutrophication. Therefore, it can be stated that reduction in nutrient concentration will be an essential mechanism to control the process of eutrophication in the lake.

Chlorophyll-*a* (Chl*a*): The mean concentration of Chl-*a* in Lake Ziway ranged from 28 to 76 μg L^{-1} with mean values of 42 μg L^{-1}. The lowest measurements were in July (28 μg L^{-1}) and the highest chlorophyll-*a* concentration was in June (76 μg L^{-1}) (Figure 4.4.3) which is mainly due to high nutrient and turbidity rainfall in relation with plankton abundance. No significance differences among the six sampling sites were found (Kruskal-Wallis test, $p > 0.05$). Therefore, relatively higher concentrations of chlorophyll-*a* observed in the rainy season due to increase in nutrient input from the catchment. Similar results were reported by Tilahun, (2006) in the same lake and Lake Hawasa. According to OECD, 1982 classification of trophic state, 8.00 μg L^{-1} of chlorophyll-*a* concentration is the threshold for eutrophication and in the present study; all in the sampling sites were found to have chlorophyll-*a* concentrations beyond the prescribed limit.

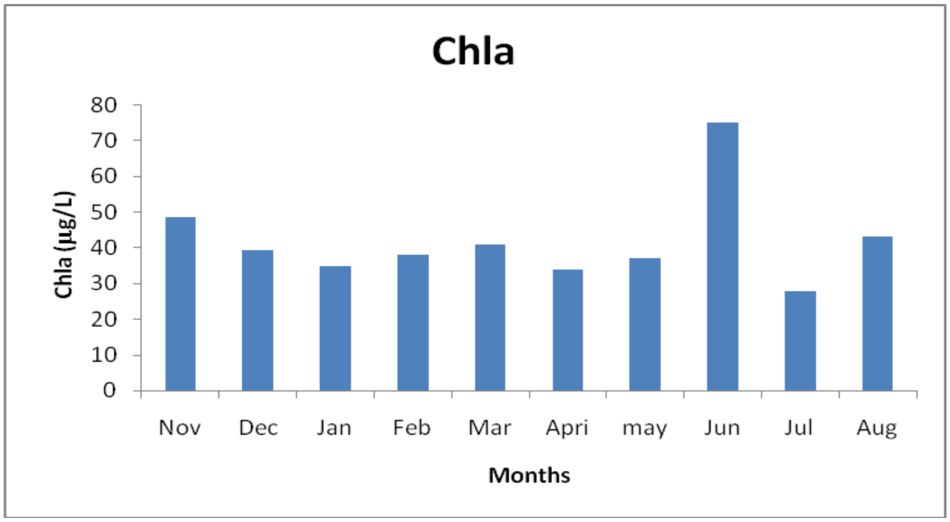

Figure 4.4.3 Monthly trends of chlorophyll a concentrations in Lake Ziway

According to Carlson (1977) model, Table 4.4.4, the trophic state condition's using the concentrations of chlorophyll-*a* in lake Ziway have shown three scenarios: before 1966, the lake was oligotrophic but between the years 1980 to 2002, the lake was approaching to hypereutrophic state. For instance, high phytoplankton biomass of 91 μg Chl-*a* L^{-1}, 48 to 334 μg Chl-*a* L^{-1} and 150 to 212 μg Chl-*a* L^{-1} was reported by Belay and Wood (1984), Kebede *et al*. (1994) and Tilahun (1988), respectively. Gebre-Mariam *et al*. (2002) was also reported a mean value of 82.4 μg L^{-1} with a range of 23.0 to 224 μg L^{-1} of chlorophyll-*a* for Lake Ziway, again much higher than the values obtained during this study. After 2006 up to the present the lake is in eutrophic state. For instance, moderate phytoplankton biomass of 39.2, 38, 56.3 and 42 μg Chl*a* L^{-1} was reported by Tilahun (2006), Beneberu and Mengistu, (2009), Tamire and Mengistu (2012) and the present study respectively (Table 4.4.4). Previous studies based on time series of chlorophyll-*a* analysis speculated that Lake Ziway showed a progressive increase towards eutrophy (Gebre-Mariam *et al*., 2002), the result of the present study also agreed with the trend of eutrophication condition of Lake Ziway. The eutrophication of Lake Ziway might have been intensified after the rapid expansion of the flower industry, widespread fisheries, and fast population growth, industrialization and intensive use of agrochemicals in the lake watershed.

Table 4.4.4 Tends of Chl-*a* μg L^{-1} concentrations during the years from 1937 to 2015 in Lake Ziway

Year	**Chla(μg L^{-1})**	**References**
1937 to 1938	Clear water	Cannicci and Almagia (1947)
1966	7	Wood *et al.* (1978)
1980	91	Belay and Wood (1984)
1986	48 -334	Kebede *et al.* (1994)
1987 to 1988	150-212	Tilahun (1988)
1991	154	Kebede and Willen (1998)
2002	82.4	Gebre-Mariam *et al.* (2002)
2006	39.2	Tilahun (2006)
2009	26.3-57.9	Beneberu and Mengistu (2009)
2011 to 2012	56.34	Tamire and Mengistu(2012)
2013 to 2015	28 -76	Present work

The decrease in biomass in the present study as compared to previous results can be attributed either to zooplankton grazing, other biota and/or increased non-algal turbidity. The declining trend in SD reading is one of the indications which suggest the increasing trend in turbidity of the lake, which can be mainly attributed to catchment degradation and siltation. The increase in turbidity was reflected by the low SD measured during the study period as compared to previously reported values (Table 4.4.4). The mean turbidity measurement in this study is 162 NTU (as discussed in section 4.1.1). The low biomass but high nutrients in the lake might be due to increasing turbidity and the effect of macrophytes, as macrophytes compete for the same nutrients with algae (Tamire and Mengistu, 2012). Besides this, macrophytes might also suppress the growth of algae through the production of suppressive chemicals and/or shading (Tamire and Mengistu, 2012).

As compared to other lakes, the mean concentration of chlorophyll-*a* in Lake Ziway (42 μg L^{-1}) is higher than most Ethiopian lakes Chamo, Hawasa, Koka, Babogaya, Abaya, Kuriftu and Hayq but much lower than some East African Lakes like Chitu, Arenguade and Lakes Victoria and Naivasha among others (Table 4.4.5).

Table 4.4.5 Comparisons of phytoplankton biomass of Lake Ziway with other lakes

Lakes	**Chla(μg L^{-1})**	**References**
Chamo	31.2	Tilahun and Ahlgren (2010)
Hawasa	10.4 to 25.2	Fetahi (2010)
	13 to 26	Tilahun and Ahlgren (2010)
Koka	16	Elizabeth and Willen (1998)
Chitu	2600	Wood and Talling (1988)
	72 to 233 (150)	Ogato *et al.* (2015)
Babogaya	4 to 20	Major (2006)
Hora	29	Gebre-Mariam and Taylor (1997)
Abaya	0 to 33	Gebre-Mariam (2002)
Kuriftu	17.24 to 55.6	Dessalegn (2007)
Bishoftu	60	Gebre-Mariam and Taylor (1997)
Arenguade	41.7 to 271	Belachew (2010)
	917 to 2170	Talling *et al*. (1973)
Hayq	12.9	Fetahi (2010)
Naivasha	40 to 210	Ndungu *et al.* (2013)
Ziway	28 to 76	Present work

Secchi depth (SD): The lowest depth measurements were in May (0.16 m) and Jun (0.16 m) while the deepest measurements were in November (0.26 m) and December (0.27 m) (Figure 4.4.4). The mean SD in Lake Ziway ranged between 0.16 to 0.27 m with a mean value of 0.20 m. The SD was lower in May to August of 2014 and 2015 which could be due to high turbidity where as in November and December when the turbidity was low, the SD was at 0.27 m, indicating the lake was clearer than it was before the rainfall (Table 4.2.2). ANOVA (Kruskal-Wallis Test) showed that SD values between sampling sites were not significantly different ($p > 0.05$).

According to OECD, (1982) the hypereutrophic lakes generally showed the maximum transparency values at ≤ 1.5 m and minimum transparency ≤ 0.7 m (Table 2.2). Therefore, the present data of 0.20 m indicate Lake Ziway is a highly productive ecosystem having low euphotic zones with an indication of eutrophication. Moreover, the detailed explanation regarding SD is present in section 4.1.1.

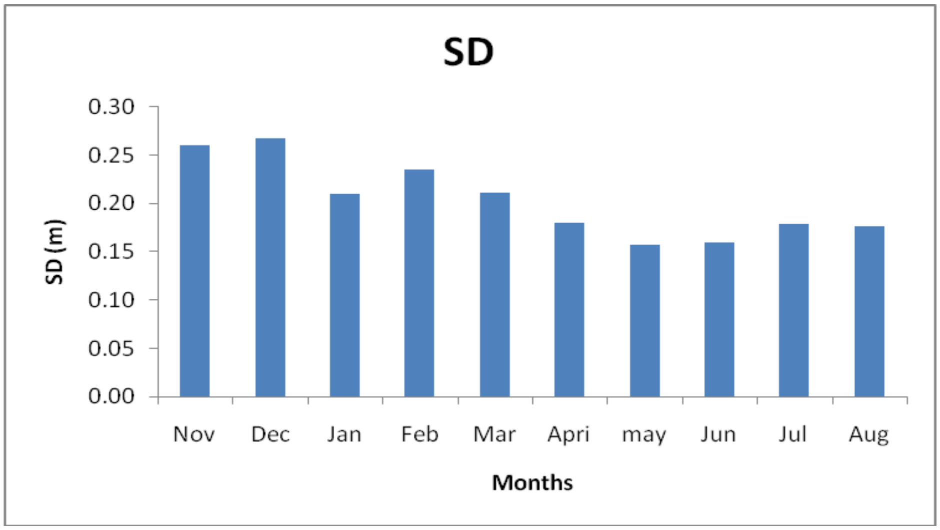

Figure 4.4.4 Monthly trends of SD transparency in Lake Ziway

4.4.2. Evaluation of the trophic status of Lake Ziway using different models

4.4.2.1 Carlson Trophic State Index (TSI) model

The trophic status of Lake Ziway is computed using Carlson trophic state index and Kretzer and Brezonik models which assume there is a close relationship between total phosphorous (TP), chlorophyll-*a* (chla), secchi depth (SD), and total nitrogen (TN). The analytical results of the six sampling sites and Trophic State Index (TSI) are summarized in Table 4.4.6.

Table 4.4.6 Analytical results of the six sampling sites and trophic state index in 2014 and 2015

Sites	TSI-TP	TSI-Chla	TSI-SD	TSI-TN
Fa	79.9	66.8	82.7	79.8
B	76.7	64.6	84.0	77.5
Ka	80.4	65.5	83.7	81.9
Ma	80.0	66.3	82.7	79.3
Ko	79.3	67.0	82.4	87.3
C	78.6	64.7	82.9	82.4
Mean	79.0	66.0	83.0	81.0

ANOVA (Kruskal-Wallis test) showed that, the TSI -TN value was significantly different ($p < 0.05$) among sampling sites whereas TSI-TP, TSI-Chla and TSI-SD values were not significantly different ($p > 0.05$)

The mean values of TSI-TP, TSI-Chl-*a*, TSI-TN and TSI-SD were 79, 66, 81 and 83, respectively (Table 4. 4. 6) and are graphically presented in Figure 4.4.5. All the TSI values of TP, Chla, SD and TN were above the eutrophic threshold values (Figure 4.4.5). The overall average value of Trophic State Index (TSI) of Lake Ziway is found to be 77. Generally the TSIs value below 40 corresponds to oligotrophic, between 40 and 60 - mesotrophic, from 60 to 80 - eutrophic, and above 80 - hypertrophic of the lake (Jarosiewicz *et al*., 2011).

Table 4.4.7 Carlson TSI classification

Trophic state	TSI
Ultra-Oligotrophic	< 20
Oligotrophic	20 – 40
Mesotrophic	45 – 40
Eutrophic	50 - 60
Hyper-eutrophic	>70

Moreover, these TSI values based on Carlson's trophic state classification criteria (Table 4.4.7) (Carlson, 1977) clearly indicate that Lake Ziway is found in hyper-eutrophic stage during the entire study period. Likewise, when the TSI values computed in this study are compared with the OECD's standard (OECD, 1982), it can be seen that Lake Ziway is in eutrophic state based on the Chl-*a* and TP and in hypereutrophic state based on the SD and TN.

The trophic state index of TP and TN exhibited higher trophic state probably due to the run off that comes from the Ketar and Meki Rivers catchment (Figure 4.2.9) and section 4.3 also clearly showed how internal loading is significant in the trophic status of Lake Ziway. Other studies have indicated that urban development contributes to increased TP and TN load to nearby streams (Bech *et al*., 2005). The nutrient may enter into lakes as agricultural runoff, sewage, or wastewater and also by cattle ranching; causing over enrichment of nutrients in water bodies leading to algal bloom (Ramesh and Krishnaiah, 2013). The decaying process of dead algal bio-mass may also result in the depletion of dissolved oxygen in the lakes causing anoxic environ-ment (Prasad and Siddaraju, 2012), which enhances nutrients release from the sediment.

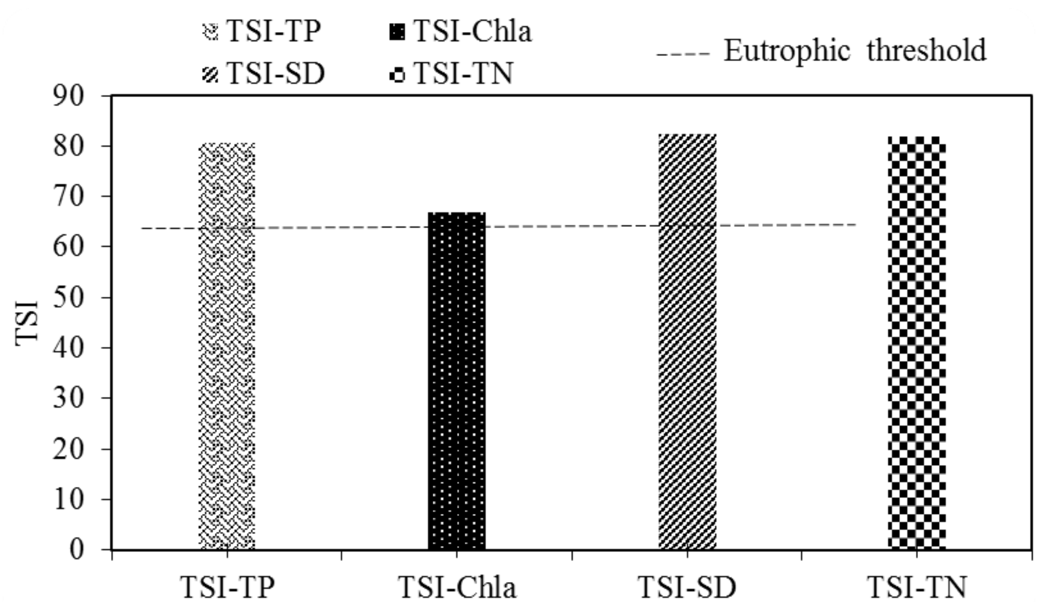

Figure 4.4.5 Trophic State Index of Ziway Lake in 2014 and 2015

This result is supported by Zeray *et al*. (2007) which states that human-induced changes in land- and water-use have resulted in environmental perturbations in Lake Ziway ecosystem, transforming its waters from a clear oligotrophic state, to turbid eutrophic state. Moreover, Gebre-Mariam *et al*. (2002) also supported the present explanation for eutrophic status of Lake Ziway. The TSI value of Lake Ziway interms of TP, Chl-*a* and SD (TP-TSI = 79; Chl*a*-TSI = 66; SD-TSI = 83) is higher than that of other Ethiopian eutrophic lakes like Lake Hayq (TP-TSI = 63; Chl*a*-TSI = 55.7) and (SD-TSI = 62; Chl*a* –TSI = 59.5) for Lake Hawasa studied by Fetahi (2010). In a similar way, Kitaka *et al.* (2002); Matthews *et al.* (2002); Ndungu *et al.* (2013); Alemayehu *et al*. (2016) also reported the trophic status of Lakes Naivasha, Whatcom, Naivasha and Kaw using Carlson trophic state index model, respectively.

4.4.2.2 TSI value based on external TP load computed from Vollenweider model

The trophic level of the lake is estimated using the Vollenweider model based on the following information in Table 4.4.8.

Table 4.4.8 Data for determination of the trophic status for the lake water in 2014 and 2015

Sources	**Values**	**Remark**
Mean total inflows (m^3 yr^{-1})	5.6 *10^8	Calculated from flow rate of two rivers (this study)
Volume of lake (m^3)	1.6 * 10^9	Ayenew and Legesse, 2007
Mean out flow (m^3 yr^{-1})	1.6 *10^8	Calculated from flow rate of Bulbula river (this study)
External TP loading (mg m^{-2} yr^{-1})	191	Calculated using Vollenweider model (this study)
Lake TP load (mg m^{-2} year $^{-1}$)	54.0	Calculated from Vollenweider model
Residence time (year)	6.67	Calculated from Bulbula River outflow and lake volume
Surface area (km^2)	485	Ayenew and Legesse, 2007
Mean depth (m)	2.5	Ayenew and Legesse, 2007
Mean inflow TP (μg L^{-1})	510	Experimental results from this study
TSI	**62**	**Calculated using Vollenweider model**

According to Vollenweider model the TSI values of Lake Ziway is 62 which is smaller than the values as computed using the Carlson's TSI model presented above. This is due to the internal TP load (Gertrud, 2009; Dennis *et al*., 1992). Even if the Vollenweider model underestimates the values of TSI of the lake, the lake is still under eutrophic based on the trophic state boundary conditions indicating external load has a higher contribution for Lake Ziway's present eutrophic condition. Lake Ziway is eutrophic according to both standards of OECD fixed boundary system or diagnostic model (OECD, 1982) (Table 2.3) and Carlson's trophic state classification criteria

(Table 2.2) (Carlson, 1977 and Jarosiewicz *et al*., (2011). It is known that eutrophication of water bodies is a worldwide predicament resulting in high phytoplankton production with severe repercussion for both the ecological state and drinking water quality in the water bodies (Shah *et al.*, 2014). Therefore, the current eutrophication of Lake Ziway might cause ecological impacts on the lake ecosystem. Furthermore, Brett and Benjamin (2008) demonstrated that increasing input nutrient concentrations has a direct effect on a lake trophic state, but increasing nutrient loading has only an indirect effect whose magnitude depends on lake hydraulic retention time and whether the increase in loading was due to changes in inflow rate or input nutrient concentrations.

4.4.3 Total Nitrogen to Total Phosphorus (TN: TP) ratio

The ratio of total nitrogen (TN) to total phosphorous (TP) of Lake Ziway was evaluated to determine the limiting nutrient of the phytoplankton in the lake (Smith, 1982). The mean TN: TP ratio of Lake Ziway is 48.1. Kalff (1983) in his study on some tropical African lakes has shown nitrogen or phosphorus or both as growth limiting nutrients. It is well known that the TN: TP ratio in an aquatic environment is an important variable since it can indicate which of these nutrients appears to be in excess or limiting growth. The Swedish (Fish, 2005) work concluded that TN: TP ratios over the range 10 to 17 by weight show P or N (or both) limited growth, while higher ratio (>20) denoted P limitation and lower ratio (<10) shows N limitation. According to these authors Lake Ziway with mean TN: TP ratio of 48.1 is phosphorus limited. This result is supported by Wetzel, (2000) in which phosphorus is the most probable limiting nutrient for phytoplankton growth in freshwater. Moreover, Smith, (1984) reported that the TN: TP ratios have been used as a basis for estimating which nutrient limits algal growth. Galvez-Cloutier et *al*., (2010) also suggested that, in freshwater where the TN: TP ratio is greater than 7, phosphorus will be the limiting nutrient, whereas for TN: TP ratios below 7, nitrogen will be the limiting nutrient for algal growth. Similarly, Tilahun, (2006) reported that the TN: TP ratios were 20.8, 47.5 and 9.6 for Lakes Ziway, Hawasa and Chamo, respectively. However, Deriemaecker (2013) reported that the other two Rift Valley lakes of Ethiopia, Chamo and Abaya are nitrogen limited, as the TN: TP ratios are 1.21 and 1.31 respectively. In a similar way, Kalff (1983), in his study of the neighbouring Kenyan lakes has reported moderate P deficiency in the freshwater lakes of

Naivasha (mean TN: TP ratio 30) and high P deficiency in Oloiden (mean TN: TP ratio 48), However currently Lake Naivasha has been classified as eutrophic condition (Kitaka *et al*., 2002; Ndungu et al., 2013).

4.4.4 Deviations between trophic state indices

In the present study, the trophic state index determined with chlorophyll-a showed lower values than those determined with all trophic state index values of TN, TP, and SD, indicating that factors other than phosphorus and nitrogen limited algal growth, and the deviation of this study indicated that wind mixing and non-algal turbidity affected light attenuation in lake Ziway. Figures 4.4.6 and 4.4.7 clearly show that non-algal turbidity was the major factor for deviations between trophic state indices in Lake Ziway.

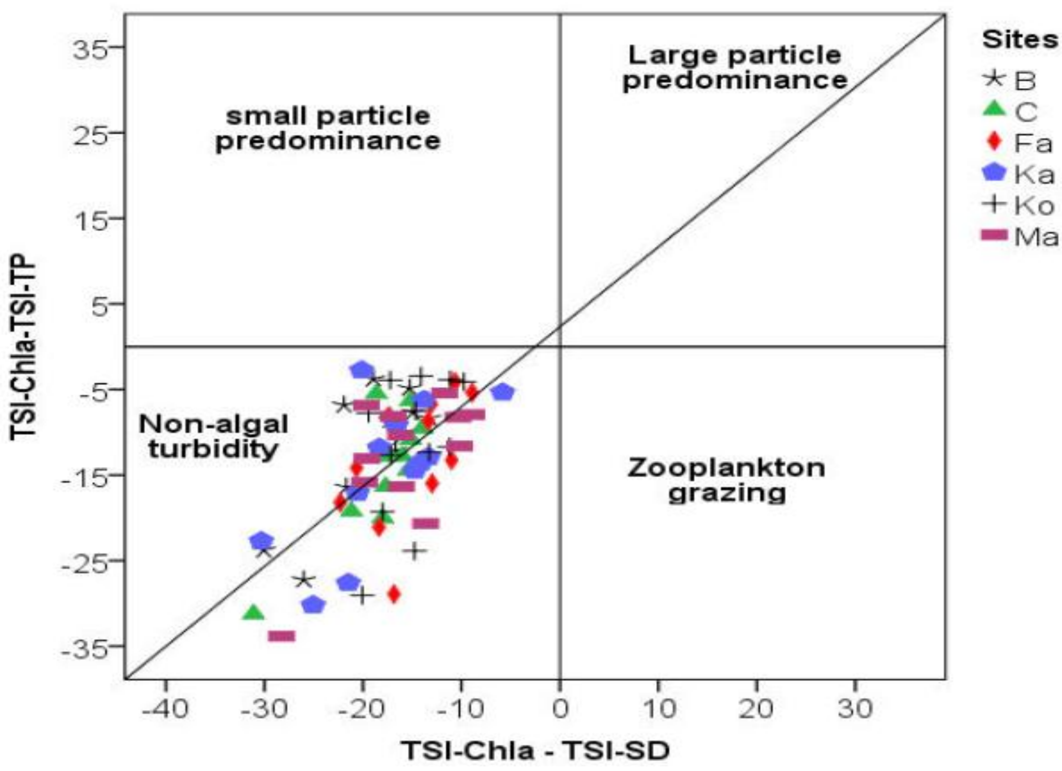

Figure 4.4.6 A plot of the deviation of TSI (Chla) from TSI (SD) versus the deviation of TSI (Chla) from TSI (TP) in 2014 and 2015

Deviations of all values were negative which lie in the non-algal turbidity (Figures 4.4.6 and 4.4.7). According to Kalff (1983), deviations of the TSI-Chla from the TSI-TP emphasized phosphorus limitation on phytoplankton biomass, as expected for tropical freshwater ecosystems. However, negative values occurred coincident the TP and TN concentration were high because of catchment and urban runoff or internal mixing.

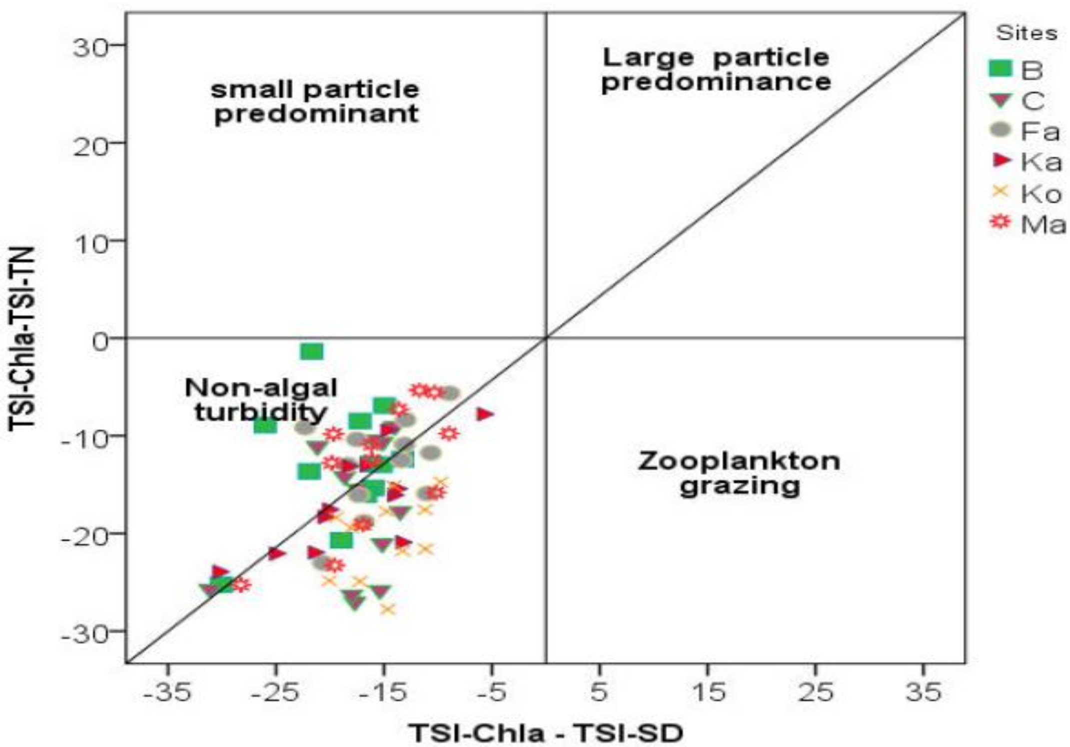

Figure 4.4.7 A plot of the deviation of TSI (Chla) from TSI (SD) versus the deviation of TSI (Chla) from TSI (TN) in 2014 and 2015

Moreover, Carlson's initial intention with the TSIs was to create equations that would produce the same TSI for a particular lake regardless of whether chlorophyll-*a*, TP, TN or SD were used to generate the index. In theory, subtracting TSI-Chla from any other TSI will be equal to zero, or nearly so, with only random variation causing deviations from zero. In reality, there are usually predictable deviations between TSI-Chla and nutrient or TSI-SD that can be used to assess the degree and type of nutrient limitation in lakes (Carlson, 1991; Carlson and Havens, 2005).

According to Carlson and Havens (2005), When TSI-Chla is equal to or greater than TSI-SD, one may infer that algae dominate light attenuation. When TSI-Chla is substantially lower than TSI-SD, this provides evidence that something other than algae, perhaps non-algal turbidity, is contributing to light attenuation. When TSI-Chl-*a* is equal to or greater than TSI-TP, phosphorus generally is limiting to algal growth. When TSI-Chl-*a* is substantially lower than TSI-TP, this indicates that there is less algal material present than expected based on TP, and that some other factors may be limiting. In the same manner, nitrogen limitation is indicated when TSI (Chl-*a*) - TSI (TN) > 0 and TSI (TN) < TSI (TP). According to this the results of this study showed TSI-Chla is lower than TSI-SD, providing evidences that non-algal turbidity is contributing to light attenuation. These relationships have been extensively used by most related studies (e.g., Matthews *et al.*, 2002; An and Park, 2003). For instance, Matthews *et al.* (2002) employed the concept of TSI differences to assess the trophic state and nutrient limitation of Lake Whatcom (USA). An and Park (2003) used deviations of the trophic state index to illustrate that factors other than phosphorus limited algal growth, and that non-algal particles affected light attenuation in an Asian reservoir. Furthermore, Ndungu *et al.* (2013) also used deviations of the trophic state index to illustrate that factors other than phosphorus limited algal growth, and that small and large particles predominates affected light attenuation in an Lake Naivasha, Kenya.

4.4.5 Conclusions and recommendations

In conclusion, there is a high external nutrient load from the two feeding rivers of Lake Ziway with Ketar River accounting more than Meki River for the entire nutrient loads. The general trend which is also expected is that the nutrient load in the wet season was much higher than the dry season. As a consequence of high external nutrient load, eutrophication of the lake ecosystem is increasing rapidly. Therefore, the overall evaluation of the trophic status of the lake indicated that clear signals of eutrophication were observed in Lake Ziway during the study period. The results of the TN: TP ratio also indicated that phosphorus was the limiting nutrient in the lake water. Moreover, the trophic state index determined with chlorophyll-*a* showed lower value than those determined with all trophic state index values of TN, TP, and SD which indicated that wind mixing and non-algal turbidity affected light attenuation for algal growth.

In order to stop further deterioration of the lake water quality and to eventually restore the beneficial uses of the lake, management of phosphorus and nitrogen load into the lake should be given urgent priority. Measures should be taken to reduce the external nutrient loads by a multiple approaches such as catchment management to minimize soil erosion and nutrient runoff;

sewage diversion; increased use of phosphorus free detergents; establishing animal fertilizer storage capacity; wetland restoration. Furthermore, the Ethiopian Environmental Protection Authority should prepare guidelines for the trophic status of the freshwater bodies in the country by making bottom-up top-down discussions.

Chapter 5: General conclusion and recommendations

5.1 Conclusion

Lake Ziway has shown some undesirable changes in terms of hydrology and lake water quality due to loads, dynamics and impacts of agrochemicals in the lake ecosystem. Mean nutrient concentrations showed increasing trend and were higher in F_b and Fa sampling sites in all seasons. These sites were also characterized by high EC and TDS and are flowing from catchment dominated by flower farming.

There were spatio-temporal variations in the physicochemical parameters and nutrients in the lake ecosystem. In the multivariate statistical data analysis techniques, CA grouped nine sampling sites into three clusters according to similar water quality features and by which all the sampling sites were categorized into three levels. Sampling sites F_b and K_b are highly polluted and moderately polluted in both seasons, respectively while sampling sites at C, M_a, K_a, K_o and F_a in dry season and K_a, C, M_a, M_b, K_o, B, F_a were less polluted during the wet season. PCA analysis identifies the major sources of pollution responsible for water quality variations besides seasonal variations and these pollutant sources were mainly from sampling sites F_b during the dry season and M_b and K_b during the wet season (effluent from the flower farms and rivers Meki and Ketar, respectively). The PCA analysis of the four data sets explained more than 88.1 % and 91.0 % of the total variance in the wet and dry seasons, respectively. The values of comprehensive pollution index also illustrated the lake is moderately and slightly polluted in dry and wet seasons, respectively. Comparatively, the pollution status of the lake is high around the floriculture effluent discharge site and at the two feeding rivers.

From the results of this study, the vertical nutrient profiles of the lake water samples show no significant variability, making it difficult to rely on the observed nutrient concentration profiles to understand the nutrient dynamics in Lake Ziway. Ketar and Meki Rivers catchment showed the major sources of external nutrient loadings to the lake ecosystem. The study showed a general trend of higher external nutrient load in the wet than in the dry seasons. There were also significant correlations between climatic, hydrological and water quality parameters of Lake Ziway. Precipitation, lake water level, discharge flow and air temperature had weak to strong positive correlations with nutrients. Negative correlations of DO, pH, EC, TA and SiO_2 were found with all of the climatic and hydrological factors.

In the study the spatial and temporal variability of nutrients in the depth profiles of sediment samples were observed. The values of nutrient distributions in depth profiles were higher at sediment top surface and decline with depth in most of the sampling sites and seasons indicating high localized external input of nutrients. The results of the seasonal evaluation of phosphorus flux from lake sediments showed that sediments were acting both as sources of phosphorus rather than a sink. Moreover, the overall dynamics of nutrient loads in the lake shows increasing trends. Moreover, the nutrient budget for Lake Ziway clearly shows the amount of nutrients that enters the lake exceeds the output, indicating that nutrients are being retained in the lake. This can explain the high nutrient concentration obtained in the sediment and also infers that it is important for algal growth. Consequently, the overall evaluation of the trophic status of the lake is indicated by clear signals of eutrophication during the study period.

5.2 Recommendations

Based on the results of this study, the lake shows some changes in terms of some physico-chemical parameters and internal and external nutrient loads. For instance the lake has higher nutrient concentrations compared to previous studies; therefore, further research should be done on the dynamics of the watershed's response to runoffs due to non-point agrochemical pollution sources and land management practices under varying climatic conditions to better understand the complex physical and chemical processes causing the degradation observed in the present study. It is better to study the sedimentation load of Ketar and Meki Rivers. Moreover, the seasonal impact of nutrients on Lake Ziway can be controlled by improving the current practices in the catchments. These include regulated use of farm inputs improving waste disposal practices and factory effluents to the lake ecosystem. The following measures should be taken to reduce the external nutrient loads by a multiple approaches such as catchment management to minimize soil erosion and nutrient runoff; sewage diversion; increased use of phosphorus free detergents and wetland restoration. The Ethiopian Environmental Protection Authority (EEPA) should prepare guidelines for the trophic status of the freshwater bodies in the country by making bottom-up top-down discussions. Moreover, it is recommended to discourage farming activities along the lakeshore and to set a standardized buffer zone around the lake shore beyond which no farming should be allowed.

In order to stop further deterioration of the lake water quality and to eventually restore the beneficial uses of the lake, management of phosphorus and nitrogen load (such as regular monitoring of the soil-plant-water relations and the appropriate fertilizer use should be a priority in the lake watershed. Most of all free access policy (no ownership scenario) to water bodies may have to change for Lake Ziway by giving concession rights to users with the appropriate environmental regulatory protocols. Understanding this variation may help in developing mitigation and restoration strategies for the lake and aquatic ecosystems in Ethiopia.

The study focused only on the qualitative assessments of pesticides in the study area; therefore, further and intensive researches in both qualitative and quantitative analyses of pesticides as well as toxicity of pesticides in fish and other biota should be done. Moreover, regular monitoring program should be designed in order to provide a hazard free environment to the aquatic biota and to ensure safe and healthy supply of drinking water and fish for human consumption.

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