ANALYSIS OF INTERNAL NUTRIENT LOAD DYNAMICS FROM THE SEDIMENT IN LAKE ZIWAY

Dessie Tibebe1, Feleke Zewge2, Brook Lemma2, Yezbie Kassa4

1 Department of Chemistry, College of Natural and Computational Sciences, University of Gondar, Gondar, Ethiopia.
Email: dessie9277@gmail.com
2 Department of Chemistry, College of Natural and Computational Sciences, Addis Ababa University, Addis Ababa, Ethiopia.
Email: flshabk@yahoo.com
3 Department of Zoological Sciences, College of Natural and Computational Sciences, Addis Ababa University, Addis Ababa, Ethiopia.
Email: brknnn909@gmail.com
4 Department of Biology, College of Natural and Computational Sciences, University of Gondar, Gondar, Ethiopia.
Email: yezbie.kassa.brknnn@gmail.com

ABSTRACT

Lake Ziway is shallow freshwater located in Northern part of Ethiopian Rift Valley. Expansions of the flower industry, widespread fisheries, intensive agricultural activities, fast population growth lead to deterioration of both water and sediment qualities and depletion of aquatic biota. The main objective of this study is to evaluate the internal nutrient load dynamics from the sediment. Nutrients in sediment samples were analyzed according to the standard procedures outlined in EPA, 1994 and phosphorus release rate were estimated with the methods described in Steinman, et al. [3]. The results of sediment depth profile analyses showed that the mean concentrations of SRP, TP, NO3-N, NO2-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 all the studied nutrients distribution were higher at sediment top surface and decline with depth of the sediment profiles in most of the sampling sites and seasons. The results of the seasonal evaluation of phosphorus flux from lake sediments showed that sediments were sources of phosphorus. The findings from the current study indicate that internal sources of nutrients to Lake Ziway vary across time and space. Understanding this variation and internal nutrient load is important in developing mitigation and restoration strategies for the lake ecosystems.

Contribution/Originality: The main objective of this study is to evaluate the internal nutrient load dynamics from the sediment. Nutrients in sediment samples were analyzed according to the standard procedures outlined in EPA, 1994 and phosphorus release rate were estimated with the methods described in Steinman, et al. [3].

1. INTRODUCTION

Lake sediment is an important component in the lake ecosystem acting as a sink and/or sources of nutrients. Seasonal Riverine intrusions brings a variety of contaminants such as sediments, fertilizers, pesticides, manures, terrestrial vegetation and domestic and industrial wastes from upstream catchments to downstream lakes. Sediments can act as a buffering system for the overlying water, retaining allochthonous and autochthonous nutrients [1]. Excessive sediment and nutrient load can have major adverse ecological impacts on receiving aquatic
ecosystems. In shallow aquatic systems such as lakes, and reservoirs, intensive material exchange between the bottom and the water may determine nutrient fluxes and the productivity of the entire ecosystem [2-4]. Factors causing internal nutrient load include low redox potential, elevated pH, and sediment resuspension caused by water currents and animal activities. In shallow lakes like Ziway, wind-induced sediment resuspension is often the main cause of internal load [5]. 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 resource [6].

Sediment analysis is increasingly important in evaluating qualities of the ecosystem of a body of water, in addition to the water sample analysis practiced for years [7, 8]. Although a substantial amount of data are available on primary productivity, dynamics of the major phytoplankton and zooplankton communities, macrophytes and fishery in Lake Ziway water samples but studies on the contribution of internal nutrient load in the sediment to the functions of the system give less attention. To the best of our knowledge, there is no previous study reported on nutrient load in sediment depth profiles in Lake Ziway. The main objective of this study is to evaluate the internal nutrient load dynamics from the sediment depth profile in Lake Ziway and to analyze the temporal and spatial patterns of phosphorus release rate from sediment to the water column.

2. MATERIALS AND METHODS

2.1. Description of the Study Area

Lake Ziway is a shallow freshwater lake found in the most northern section of the Ethiopian Rift Valley and is located at 08°01’N and 38°47’E Figure 1.

Lake Ziway is well known for its aquatic bird life and other aquatic animals such as the different fish species, various species of phytoplankton, zooplankton and other micro flora, there are also terrestrial plants and animals found around the lake constituting its fauna and flora [9]. The lake's catchment has an area of 7025 square kilometers. Lake Ziway catchment is currently inhabited by about 2 million people (Ethiopian Central Statistics
Authority, 2013, unpublished data) and about 1.9 million livestock \[10^7\]. The Lake Ziway region is characterized a semi-arid to sub-humid type of climate and has mean annual precipitation varying between 346 mm and 1042 mm and mean annual temperature between 11.44 to 28 °C. Table 1 showed the selected sampling sites of the lake for sediment sample analyses in Lake Ziway.

| Sampling site description       | Abr. | North   | East     | Elevation |
|--------------------------------|------|---------|----------|-----------|
| Floriculture effluent          | Fb   | 07°54.715' | 038°44.020' | 1642      |
| Floriculture after mixing      | Fa   | 07°54.79'   | 038°44.111' | 1639      |
| Bulbula River mouth            | B    | 07°53.943' | 038°44.134' | 1641      |
| Ketar River mouth              | Ka   | 07°53.398' | 038°52.086' | 1640      |
| Meki River mouth               | Ma   | 08° 08.379' | 038°56.459' | 1633      |
| Korekonch                      | Ko   | 07°55.494' | 038°43.697' | 1637      |
| Central station                | C    | 07°55.49'  | 038°52.934' | 1635      |

2.2. Chemicals and Reagents

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)-ethylendiamine dihydrochloride, Potassium chloride, sodium salicylate, potassium sodium tartarate, copper sulfate, silver sulphate, calcium hydroxide, magnesium carbonate, potassium antimony tartrate, ammonium molybdate, ascorbic acid, ethanol, phenolphthalein, methyl orange, hypochlorite, acetone. All chemical and reagents are products of Sigma-Aldrich, Germany.

2.3. 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); Kjeldahl apparatus (Gallenhamp, USA); Oven dry (Binder, Germany); Turbidimeter (T-100, Singapore); portable multi meter (HACH MM150, China) were used in the experiments.

2.4. 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 2.

![Figure 2. Sediment sampling producers using modified sediment corer.](image-url)
Nutrients in sediment samples were analyzed by the procedures described in environmental water and soil analysis manual [11-13]. 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 [11, 12, 14]. 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 [11, 13] and measured for SRP by ascorbic acid method according to American Publica Health Association (APHA) [15].

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 washed with additional aliquot of deionized water. The filtrate was collected and diluted to a final volume of 100 mL [11, 12, 14]. Finally, the concentration was determined by persuphate digestion followed by ascorbic acid according [15].

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 [11, 13]. The NO$_3$-N from the filtrate was analyzed by sodium salicylate method [16].

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 [11, 13]. The NO$_2$-N from the filtrate was analyzed by colorimetric method [15].

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$_2$SO$_4$ solutions.

2.5. 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 overlying 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. [4]. 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 American Public Health Association (APHA) [15].

According to the flux (P release rate) calculations were based on the change in water column TP or SRP using the following equation [3]:

$$p_n = \frac{(C_t - C_o) \times V}{(t - t_0) \times A}$$  

where, $p_n$ 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.

2.6. Data Analysis

Different procedures of statistical analyses were used to analyze data. SPSS software version 20 (SPSS Inc, Chicago, USA) was employed to test spatial heterogeneity of sediment concentrations. Person correlation was chosen to evaluate the correlation and probability values were significant level at 0.05. Differences in mean concentrations of nutrients were analyzed using ANOVA test. Depth profiles of sediment nutrient distributions were analyzed using Sigma Plot Software (SigmaStat 10.0).

3. RESULTS AND DISCUSSION

3.1. Analysis of Internal Nutrient Load Dynamics from the Sediment in Lake Ziway

3.1.1. 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:

3.1.2. Vertical Soluble Reactive Phosphorus Distributions in Sediment Depth Profiles

Soluble reactive phosphorus (SRP) concentration 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 3. Similar results were reported by Yang, et al. [17]; Sobczyński and Joniak [4] and Kangur, et al. [18]. 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. [19] 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.

![Figure 3](image.jpg)  

**Figure 3.** Vertical profiles of sediment SRP from the six different sampling sites in dry and wet seasons in 2014 and 2015.
Similar results also were obtained by Pettersson [20] 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. [21] 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 [22].

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 Mosa [8]. Similarly, Wang and Morrison [23] and North, et al. [6] 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) [20, 24]. Similarly, Feuchtmayr, et al. [25] reported that higher temperature increases the release of phosphorus from bottom sediments.

### 3.1.3. 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 and lower in the middle in most sampling sites in the wet season but showing a decreasing trend down the depth profiles in the dry season Figure 4.

**Figure 4.** 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. [26]; Sobczyński and Joniak [4]; Ye, et al. [27] and Chang, et al. [28] 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. [29] and Trolle [30] 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. [31] 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.
In general, higher concentrations of TP profiles in the uppermost sediment layers, is similar to that of SRP. Similarly, Chao, et al. [32] 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).

3.1.4. 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 5. 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 5. Similarly, Dasm, et al. [33] 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 [34].

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 [34]. Moreover, Zhang, et al. [35] 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.

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 depth profiles of TN concentrations decreased with sediment depth in both seasons Figure 6. Similar results has been reported in different lakes by Ye, et al. [27]; Trolle [30]; Kim, et
al. [31]; Kelderman, et al. [29]. 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 [29]. Similarly, Jinglu, et al. [36] and Trolle [30] 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 6](image_url)

**Figure 6.** 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 6, Mₐ (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 [18] the evaluation criteria of TN pollution in the sediment sampling sites of Mₐ 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.

3.1.6. Seasonal Variations of Composite Sediment Nutrient Analyses at the Central Sampling Site of Lake Ziway

The mean concentrations for SRP, TP, NO₃-N and NO₂-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 7. Wet season values were higher than the dry season in all nutrients except NO₂-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. [37]. Zhang, et al. [35] reported that lake sediment has a significant effect on nutrient transfer in lakes, especially shallow ones.

![Figure 7](image_url)

**Figure 7.** 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 7. Similarly, Kebede and Mosa [8] 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.

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 [33]. Therefore, according to this index system Lake Ziway has high nutrient status. Kangur, et al. [18] 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.

The results in Figure 8 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 Mosa [8] and Adeyemo, et al. [37] 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 Mosa [8]. According to EPA [19] 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 [10, 38]. Similarly, Landkildehus, et al. [39] reported that the TN concentration increased with increasing temperature, possibly resulting to reduced nitrogen retention in the sediment under warmer conditions.

3.1.7. Seasonal Evaluation of Phosphorus Flux from Lake Sediments as a Measure of Internal Phosphorus Load

Incubated phosphorus fluxes were displayed in Table 2. 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 [40-42]. Moreover, Kangur, et al. [18] and Zhang, et al. [43] 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 [42] 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 anoxiocity 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. 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 [3] 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 species 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 [35]. At the same time, iron hydroxide adsorption/desorption to phosphorus would alter the concentration of phosphorus [35]. 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, et al. [5] and Zhang, et al. [35].

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 [5]. 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. [24] 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.
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. [3] 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. [3]; Sondergaard, et al. [41] 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 [14]. 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 3.

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 3. 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 3.

Table 3. Comparisons of Phosphorus release from bottom sediments of different lakes.

| Lake               | P release rate ( mg P m⁻² d⁻¹) | Reference                      |
|--------------------|-------------------------------|--------------------------------|
| Long (WA, USA)     | 2.6                           | Steinman, et al. [3]            |
| Klamath (OR, USA)  | 6.0                           | Steinman, et al. [3]            |
| Alderfen Broad (UK)| 3.5                           | Steinman, et al. [3]            |
| Neagh (UK)         | 4.4                           | Steinman, et al. [3]            |
| Okeechobee         | 0.83                          | Fisher, et al. [44]             |
| Beaver Reservoir (USA) | 0.31                  | Sen, et al. [45]                |
| Scharmutzelsee (Germany) | 2.6                       | Kleeberg and Kozerski [46]     |
| Agmon (Israel)     | 6.0                           | Kowalczewska-Madura and Goldyn [47] |
| Ziway              | 3.9                           | This study                      |

| Lake | TP release rate ( mg P m⁻² d⁻¹) | Reference                      |
|------|--------------------------------|--------------------------------|
| White| 3.75                          | Steinman, et al. [3]            |
| Mona | 4.44                          | Steinman, et al. [3]            |
| Spring| 15.6                      | Steinman and Ogilah [48]       |
| Ziway| 16.1                          | This study                      |

4. CONCLUSION

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 industry. The results of the seasonal evaluation of phosphorus flux from lake sediments showed that sediments were as sources of phosphorus. 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.

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REFERENCES

[1] W. Chan, "Spatial and temporal features of hydrodynamics and biogeochemistry in Myponga reservoir," PhD Thesis, The University of Adelaide, South Australia, 2011.

[2] I. Ostrovsky and J. Tęgowski, "Hydroacoustic analysis of spatial and temporal variability of bottom sediment characteristics in Lake Kinneret in relation to water level fluctuation," *Geo-Marine Letters*, vol. 30, pp. 261-269, 2010. Available at: https://doi.org/10.1007/s00367-009-0180-4.

[3] A. Steinman, R. Rediske, and K. R. Reddy, "The reduction of internal phosphorus loading using alum in Spring Lake, Michigan," *Journal of Environmental Quality*, vol. 33, pp. 2040-2048, 2004. Available at: https://doi.org/10.2134/jeq2004.2040.

[4] T. Sobczyński and T. Joniak, "Vertical changeability of physical-chemical features of bottom sediments in three lakes in aspect type of water mixis and intensity of human impact," *Polish Journal of Environmental Studies*, vol. 18, pp. 1093-1099, 2009.

[5] A. D. Steinman, L. Nemeth, E. Nemeth, and R. Rediske, "Factors influencing internal P loading in a western Michigan, drowned river-mouth lake," *Journal of the North American Benthological Society*, vol. 25, pp. 304-312, 2006. Available at: https://doi.org/10.1899/0887-3593(2006)25[304:fipli]2.0.co;2.

[6] R. L. North, J. Johansson, D. M. Vandergrucht, L. E. Doig, K. Liber, K.-E. Lindenschmidt, H. Baulch, and J. J. Hudson, "Evidence for internal phosphorus loading in a large prairie reservoir (Lake Diefenbaker, Saskatchewan)," *Journal of Great Lakes Research*, vol. 41, pp. 91-99, 2015. Available at: https://doi.org/10.1016/j.jglr.2015.07.003.

[7] S. U. Pravin, M. P. Trivedi, R. M. Mishra, and D. Dagli, "Assessing the physico-chemical parameters of sediment ecosystem of Vasai Creek at Mumbai, India," *Marine Science*, vol. 1, pp. 22-29, 2011. Available at: https://doi.org/10.5923/j.ms.20110101.03.

[8] Y. W. Kebede and H. M. Mosa, "Spatial variation of sediment physicochemical characteristics of lake Tana, Ethiopia," *Journal of Environment and Earth Science*, vol. 5, pp. 95-109, 2015.

[9] IBC, *Site action plan for the conservation and sustainable use of Lake Ziway Biodiversity (Rift Valley Lakes Project)*. Addis Ababa, Ethiopia: Institute of Biodiversity, 2005.

[10] D. T. Meshesha, A. Tsumekawa, and M. Tsubo, "Continuing land degradation: cause–effect in Ethiopia's Central Rift Valley," *Land Degradation & Development*, vol. 23, pp. 130-145, 2012. Available at: https://doi.org/10.1002/ldr.1061.

[11] P. Trivedi and G. Raj, *Environmental water and soil analysis*. New York: Lewis Publisher, 1992.

[12] C. Maria, *Environmental sampling and analysis laboratory manual*. New York: Lewis Publisher, 1997.

[13] EPA, "Methods for chemical analysis of water and wastes," *Method 365 No. 351.3 [EPA/400/4-79/029], 1993.

[14] G. Christensen, P. Maki, and R. Kiesling, "Relation of nutrient concentrations, nutrient loading, and algal production to changes in water levels in Kabetogama Lake, Voyageurs National Park, northern Minnesota, 2008–09: U.S.," *Geological Survey Scientific Investigations Report*, 5096, 2011.

[15] American Publica Health Association (APHA), *Standard methods for the examination of water and wastewater*, 20th ed. Washington D.C: American Publica Health Association, 1999.
J. Yang, E. Skogley, B. Schaff, and J. Kim, "A simple spectrophotometric determination of nitrate in water," *Soil Science Society of America Journal*, vol. 62, pp. 1108 – 1115, 1998.

F. Yang, B. Xiong, and M. Yang, "Seasonal dynamics of phosphorus forms in water body and sediments of Nanhu Lake," *Wuhan, China Article*, vol. 1, pp. 2029 – 2034, 2008.

M. Kangur, L. Puusepp, O. Buhvestova, M. Haldna, and K. Kangur, "Spatio-temporal variability of surface sediment phosphorus fractions and water phosphorus concentration in Lake Peipsi (Estonia/Russia)," *Estonian Journal of Earth Sciences*, vol. 62, pp. 171-180, 2013. Available at: https://doi.org/10.3176/earth.2013.14.

M. Sondergaard, J. P. Jensen, and E. Jeppesen, "Role of sediment and internal loading of phosphorus in shallow lakes," *Hydrobiologia*, vol. 506, pp. 135-145, 2003. Available at: https://doi.org/10.1023/b:hydrr.0000008611.12704.dd.

K. Pettersson, "Mechanisms for internal loading of phosphorus in lakes," *Hydrobiologia*, vol. 373, pp. 21-25, 1998. Available at: https://doi.org/10.1007/978-94-011-5266-2_2.

C. Teichreb, B. Peter, and M. Dyer, "Overview of pigeon lake water quality, sediment quality, and Non-Fish Biota," *Alberta Environment and Sustainable Resources Development*, p. 84, 2013.

M. Vadrucci, A. Semeraro, N. Zaccarelli, and A. Basset, "Nutrient loading and spatial–temporal dynamics of phytoplankton guilds in a Southern Italian coastal lagoon (Lake Alimini Grande, Otranto, Italy)," *Chemistry and Ecology*, vol. 20, pp. 285-301, 2004. Available at: https://doi.org/10.1007/s10494-004-0054-z.

C. Wang and R. J. Morrison, "Phosphorus speciation and changes with depth in the sediment of Lake Illawarra, New South Wales, Australia," *Environmental Earth Sciences*, vol. 71, pp. 3529-3541, 2014. Available at: https://doi.org/10.1007/s12665-013-2742-2.

J. A. Shah, A. K. Pandit, and G. M. Shah, "Spatial and temporal variations of nitrogen and phosphorus in wular lake leading to eutrophication," *Ecologia*, vol. 4, pp. 44-55, 2014. Available at: https://doi.org/10.3923/ecologia.2014.44.55.

H. Feuchtmayr, R. Moran, K. Hatton, L. Connor, T. Heyes, B. Moss, I. Harvey, and D. Atkinson, "Global warming and eutrophication: Effects on water chemistry and autotrophic communities in experimental hypertrophic shallow lake mesocosms," *Journal of Applied Ecology*, vol. 46, pp. 713-725, 2009. Available at: https://doi.org/10.1111/j.1365-2664.2009.01644.x.

R. Jellison, K. Rose, and J. Melack, *Assessment of internal nutrient loading to Crowley Lake*. Mono County, California: Final Report, 2003.

W. Ye, X. Liu, S. Lin, J. Tan, J. Pan, D. Li, and H. Yang, "The vertical distribution of bacterial and archaeal water and sediment of Lake Taihu," *FEMS Microbiology Ecology*, vol. 70, pp. 263-276, 2009. Available at: https://doi.org/10.1111/j.1574-6941.2009.00761.x.

F. Chang, X. Pan, Y. Li, D. Li, G. Li, Y. Liu, and Y. Liu, "Contamination assessment and potential mobility of sediment phosphorus from Dianchi Lake, China," *Fresenius Environmental Bulletin*, vol. 19, pp. 42-46, 2010.

P. Kelderman, Z. Wei, and M. Maessen, "Water and mass budgets for estimating phosphorus sediment–water exchange in Lake Taihu (China PR)," *Hydrobiologia*, vol. 544, pp. 167-175, 2005. Available at: https://doi.org/10.1007/s10750-005-0542-5.

D. Trolle, "The influence of sediment nutrient dynamics on the response of Lake Ecosystems To Restoration And Climate Change," The University Of Waikato, PhD Thesis, 2009.

L.-H. Kim, E. Choi, K.-I. Gil, and M. K. Stenstrom, "Phosphorus release rates from sediments and pollutant characteristics in Han River, Seoul, Korea," *Science of the Total Environment*, vol. 321, pp. 115-125, 2004. Available at: https://doi.org/10.1016/j.scitotenv.2003.08.018.

W. Chao, Q. Jin, G. Zhi-Yong, Z. L. Z., and L. X. Li, "Vertical distributions of phosphorus fractions in sediments of three typical shallow urban lakes in P.R. China," *Polish Journal of Environmental Studies*, vol. 17, pp. 155-162, 2007.

S. Dasm, D. Ganguly, T. Maiti, A. Mukherjee, K. Jana, and K. De, "A depth wise diversity of free living N2 fixing and nitrifying bacteria and Its seasonal variation with nitrogen containing nutrients in the mangrove sediments of sundarban," *Journal of Marine Science and Engineering*, vol. 3, pp. 112-119, 2013.
M. F. Lehmann, D. M. Sigman, D. C. McCorkle, J. Granger, S. Hoffmann, G. Cane, and B. G. Brunelle, "The distribution of nitrate $^{15}$N/$^{14}$N in marine sediments and the impact of benthic nitrogen loss on the isotopic composition of oceanic nitrate," Geochimica et Cosmochimica Acta, vol. 71, pp. 5384-5404, 2007. Available at: https://doi.org/10.1016/j.gca.2007.07.025.

L. Zhang, L. Wang, K. Yin, Y. Liu, Y. Yang, and X. Huang, "Spatial and seasonal variations of nutrients in sediment profiles and their sediment-water fluxes in the Pearl River Estuary, Southern China," Journal of Earth Science, vol. 25, pp. 197-206, 2014. Available at: https://doi.org/10.1007/s12583-014-0413-y.

W. Jinglu, H. Chengmin, Z. Haiao, G. Schleser, and R. Battarbee, "The vertical distribution of bacterial and archaeal communities in the water and sediment of Lake Taihu," Journal of Paleolimn., vol. 38, pp. 13 - 25, 2007.

O. Adeyemo, O. Adedokun, R. Yusuf, and E. Abeleye, "Seasonal changes in physico-chemical parameters and nutrient load of river sediments in Ibadan city, Nigeria," Global Nest. The International Journal, vol. 10, pp. 326-336, 2008. Available at: https://doi.org/10.3176/gnj.000458.

H. Desta, B. Lemma, G. Albert, and T. Stellmacher, "Degradation of Lake Ziway, Ethiopia: A study of the environmental perceptions of school students," Lakes & Reservoirs: Research & Management, vol. 20, pp. 249-255, 2015. Available at: https://doi.org/10.3176/eco.2014.2.02.

F. Landkildehus, M. Søndergaard, M. Beklioglu, R. Adrian, D. G. Angeler, J. Hejzlar, E. Papastergiadou, P. Zingel, A. I. Cakiroglu, and U. Scharfenberger, "Climate change effects on shallow lakes: Design and preliminary results of a cross-European climate gradient mesocosm experiment," Estonian Journal of Ecology, vol. 63, pp. 71-89, 2014. Available at: https://doi.org/10.3176/eco.2014.2.02.

V. Clavero, J. Izquierdo, J. Fernandez, and F. Niell, "Seasonal fluxes of phosphate and ammonium across the sediment-water interface in a small estuary (Palmones River, southern Spain)," Marine Ecology Progress Series, vol. 198, pp. 51-60, 2000. Available at: https://doi.org/10.3354/meps198051.

M. Søndergaard, R. Bjerring, and E. Jeppesen, "Shallow lake restoration by nutrient loading reduction some recent findings and challenges ahead," Hydrobiologia, vol. 10, pp. 1081 – 1091, 2012.

M. Søndergaard, "Nutrient dynamics in lakes-with emphasis on phosphorus, sediment and lake restoration," PhD Thesis, Aarhus Universitet, Danmarks Miljøundersøgelser, 2007.

L. Zhang, L. Wang, K. Yin, Y. Lü, D. Zhang, Y. Yang, and X. Huang, "Pore water nutrient characteristics and the fluxes across the sediment in the Pearl River estuary and adjacent waters, China," Estuarine, Coastal and Shelf Science, vol. 133, pp. 182-192, 2013. Available at: https://doi.org/10.1016/j.ecss.2013.08.028.

M. Fisher, K. Reddy, and R. T. James, "Internal nutrient loads from sediments in a shallow, subtropical lake.," Lake and Reservoir Management, vol. 21, pp. 338-349, 2005. Available at: https://doi.org/10.1080/07438140509354439.

S. Sen, B. Haggard, I. Chaubey, R. Bryce, T. Costello, and M. Matlock, "Water air soil pollut," vol. 179, pp. 67-76, 2007.

A. Kleeberg and H. Kozerski, "Phosphorus release in Lake Grober Muggelsee and its implications for lake restoration," Hydrobiologia, vol. 342, pp. 9 -18, 1997.

K. Kowalczewska-Madura and R. Goldyn, "Internal loading of phosphorus from sediments of Swarzędzkie Lake (Western Poland)," Polish Journal of Environmental Studies, vol. 18, pp. 635-643, 2009.

A. Steinman and M. Ogden, "Internal phosphorus loading in spring Lake Eight months following an alum treatment," Scientific Technical Reports Paper 10, 2005.

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