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Research Article

Analyses of Potential Heavy Metals and Physico-chemical Water Quality Parameters on Lake Tana, Ethiopia

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Abstract

The study was made to investigate the potential heavy metals and physico-chemical water quality of Lake Tana. Water samples were collected from 15 sampling sites of the lake for the measurement of heavy metals, nutrients and physico-chemical water quality indicators in both dry and wet seasons. Nutrients were determined by following the standard procedures outlined in the American Public Health Association (APHA) using UV/Visible spectrophotometer and heavy metals were measured using atomic spectrophotometry (AAS). There were spatio-temporal variations in the physico-chemical water indicators and heavy metals 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 some resort and the major feeding rivers in all seasons. The mean concentrations of heavy metals were Zn (1.66 mg/L, 1.04 mg/L), Cu (1.4 mg/L, 0.23 mg/L), Pb (0.75 mg/L, 0.25 mg/L), Mn (1.26 mg/L, 0.99 mg/L), Cr (0.07 mg/L, 0.2 mg/L), Cd (0.029 mg/L, 0.009 mg/L) in dry and rainy seasons respectively. Where as in Gumara river; Zn (0.69 mg/L ,0.62 mg/L), Cu (0.88 mg/L, 0.2 mg/L), Pb (0 mg/L, 0.25 mg/L), Mn (0.11 mg/L, 0.45 mg/L), Cr (0.07 mg/L, 0.2 mg/L), Cd (0.069 mg/L, 0.008 mg/L) in dry and rainy seasons respectively. In order to stop further deterioration of lake water quality and to eventually restore the beneficial uses of the lake, management of agrochemicals in the lake watershed should be given urgent priority.

Keywords: Heavy metals, physico-chemical water quality, spatio-temporal variations, electrical conductivity.

Introduction

The physical and chemical characteristics of any lake under natural conditions are influenced by a number of factors including topography, geology and inputs through rainwater, water/rock interactions and climate variability (Han *et al.*, 2004). Lake systems are also influenced by anthropogenic factors of the people residing in the watershed; disturbance due to pollution and other human interferences giving rise to specific problems (Davide *et al.*, 2003) that correlate with the changes of the respective factors mentioned above. Moreover, agricultural runoff is an important source of pollutants in the catchments of freshwater bodies (Markich and Brown, 1998). Historically, human populations have lived close to freshwater resources in Ethiopia and elsewhere in the world. Currently, lakes of Ethiopia in particular to Lake Tana, population increase, rising living standards, intensive farming practices, industrial developments and expansion of water hyacinth have all contributed to excessive water withdrawal while increasing the level of external nutrient loading in the remaining natural freshwater systems. This resulted in major changes in biological structures and dynamics of the lakes and other fresh waters, often showing significant shift from clear water to turbid state.

As a consequence, water pollution and coverage of water hyacinth is currently a major environmental challenge to Lake Tana (Wondie *et al.*, 2007, 2014; Vijverberg *et al.*, 2009; Wassie *et al.*, 2014; Yezbie, 2016). Nowadays, Lake Tana has shown signs of eutrophication. Algae and 40,000 ha water hyacinths currently are being found in the Lake Tana near the Fogera and Dembia plains which have the greatest acreage with intensive agriculture and the release of untreated wastewater from industries around the lake adds to the deterioration of the lake ecosystem (Wassie *et al.*, 2014). Moreover, the lake's resources have been misused causing resource degradation and ecosystem disturbances. Delays in reversing the deterioration process may result, not in a distant future, in the depletion/extinction of the lake's biodiversity. Developing good understanding of such spatial and temporal variability as well as the fate and dynamics of these chemicals in the lake is critical for developing integrated approaches to managing lake water quality. All these activities as mentioned above are therefore likely to cause temporal and spatial changes in agrochemical loads, dynamics and impacts in the lake with the resulting proliferation of eutrophication and overall degradation of the water quality.

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But studies on potential heavy metals and nutrient concentrations on the Northern and southern shore of Lake Tana are very limited. Therefore, there is a need to conduct an intensive research to give possible solutions for these crucial problems and consequently, improve understanding of spatial and temporal variations of potential heavy metals and nutrient concentrations on the northern and southern shore of the lake ecosystem to propose suitable measures for sustainable management of the lake. The main objective of this project is to investigate the potential heavy metal analyses and nutrient concentrations in Lake Tana Ecosystem

Materials and methods

Description of the study area: Reducing the discharge of nutrients from point and non-point sources is the primary measure to control eutrophication. Recent researches on nutrient removal by different macrophytes have proven that they are effective for water quality improvement (Wu *et al.,* 2011; Borin and Salvato, 2012; Xu, *et al.,* 2014). Changes in ecosystem properties like water transparency and nutrient concentrations can be caused by changes in the composition of aquatic plants (Lopes *et al.,* 2011).

Due to climatic and land use changes, shallow lakes may be threatened: For instance, increased water demand or climate change leading to a shift in the water balance and lake levels, increased land degradation and soil erosion in the riparian zones leading to sediment pollution and deposition in the lakes, thereby reducing their storage capacity, change in ecosystem services and hence the livelihood for the people that depend on these lakes (Yezbie, 2016). The area around the lake has been cultivated for centuries. Recent studies have shown that the increasing trend in cultivated land use on the lake watershed which has great effects on current point and non-point sources of sediment and nutrient input (Andualem and Gebremariam, 2015) with the recent infestations of water. This lake and adjacent wetlands provide directly and indirectly a livelihood for more than500, 000 people. The lake is important for fisheries, local transport, hydroelectric power generation, ecological restoration, and dry season irrigation supply and tourism attractions. Also the basin's biodiversity is striking with the presence of many endemic plant species, endemic birds, endemic fishes and large areas of wetlands (Colot, 2012; Poppe *et al*., 2013; Setegnet *al*., 2009, 2010).

Sample collection and sampling site for nutrients and heavy metal analyses: Water and sediment samples were collected for the analyses of heavy metals and physicochemical water quality indicators of from the selected sampling sites in dry and wet seasonal basis.

Fifteen sampling sites were selected based on their distance from human settlements and anthropogenic effect and accessibility for quantitative study. These Sampling sites were grouped into the following areas: Six Rivers mouth (Abay Inlet (AIn), Rib (RB), Gumara (GU), Megech (MG), Derma (DM), and Abay outlet (AIn), Abo (ABO), Tana Hotel (TR) Ab restaurant (AB), Mango (MA), at the center of the lake in the Southern part (C_1) and at the center of the lake in northern part (C_2) sites and Kuriftu (KU).

Sample preparation and analyses for physicochemical and nutrient analyses:

In-situ measurements of physico-chemical parameters: Physicochemical parameters including Dissolved Oxygen (DO), pH, electrical conductivity (EC), Total Dissolved Solid (TDS), temperature, Secchi depth, Depth of the water level and nutrients as nitrate, Soluble Reactive Phosphate (SRP) and Total Phosphorus (TP) were measured seasonally according to standard protocols describe in APHA, 1999 (dry, pre-rainy, main-rainy, post-rainy) in the study period. DO, pH, EC, TDS and temperature were measured in situ using an YSI 556 multi-probe system. Transparency of the water was measured by lowering a 20 cm diameter circular disc (Secchi disc) into the water column and Nitrate) was determined by salicylate colorimetric method (Yang *et al.,* 1998).

Digestion procedure of water sample for heavy metals analysis: About 50 mL of water measured and put in a clean conical flask and 5 mL of nitric acid added. The mixture was heated at 95°C with the addition 2 mL of hydrogen peroxide until clear solution and the volume reduced to about 15 mL. The mixture was then filtered using Whatman no.1 filter paper in a 50 mL volumetric flask and filled to the labeled mark. The samples of water were digested in triplicates and then transferred into separate plastic bottles, labeled and stored until for analysis. For background correction, three blanks were digested as pre-test samples and each analyzed for Pb, Ni, Zn, Cd, Cu and Cr by atomic absorption spectrophotometer.

Method validation for heavy metal analysis: The reproducibility and reliability of the analytical procedures adopted in this study was tested in terms of sensitivity, limit of detection, limit of quantification and recovery.

Recovery tests: The method recoveries for all elements were tested by performing repeated spiked water samples at different concentration levels. The average recovery was determined Table 4.1.The recovery of Cu, Cr, Pb, Zn, Mn, and Cd is 87.5, 94.6, 90, 91, 85, and 100 for water samples, respectively. The acceptable values are ranging from 80 to 120. So these values were acceptable (Table 1).

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Table 1. Recovery and Limit of Detection (LOD).

Metal	Recovery of Water	LOD in water sample
Cu	87.5	0.0128
Cr	94.6	0.17
Pb	90	0.0017
Zn	91	0.0104
Mn	85	0.0017
Cd	100	0.029

Table 2. Means and ranges of the physico-chemical parameters measured at the surface water of Lake Tana in dry season (Temp for temperature in °C; DO for dissolved oxygen in mg L-1; pH for H+ concentration; EC for electrical conductivity in µS cm-1; TDS for total dissolved solids in mg L-1; Secchi depth in cm; Depth for depth in cm, Salinity in mg/L); Aberration of sampling sites: (Abay Inlet (AIn), Rib (RB), Gumara (GU), Megech (MG), Derma (DM), and Abay outlet (AIn), Abo (ABO), Tana Hotel (TR) Ab restaurant (AB), Mango (MA), at the center of the lake in the Southern part (C1) and at the center of the lake in northern part (C2) sites and Kuriftu (KU).

Site	DO	pH	EC	TDS	Temp.	Secchi	Depth	NO3-N	SRP	TP(mg/L)	Salinity
GU	3.83	7.29	373	211	30.37	-	-	0.42	0.14	0.81	0.16
AB	4.06	9.23	153	98	26	90	150	0.79	0.47	1.20	0.07
DB	4.88	7.45	144	97	23.28	-	-	0.28	0.17	0.70	0.08
ABO	4.98	6.8	151	103	22.6	163	2400	0.91	0.31	1.06	0.7
C1	5.35	7.35	142	96	23.75	76	510	0.46	0.11	0.51	0.07
MG	5.27	7.46	140	92	21.83	-	-	0.96	0.32	0.81	0.07
DM	5.48	7.3	144	97	22.85	-	-	0.79	0.16	0.44	0.07
RB	4.43	7.8	141	94	24.39	-	-	1.43	0.20	0.55	0.07
ABL	5.17	7.15	146	98	23.46	61	210	0.58	0.19	0.80	0.07
KU	4.71	8.75	158	101	25.9	83	231	1.56	0.38	1.07	0.07
AIn	5.6	7.5	135.02	78.01	25.4	-	-	0.58	0.15	0.51	0.07
MA	4.35	8.5	160	101	26.62	71	160	1.32	0.35	0.62	0.07
C2	5.84	7.98	141	95	25.4	-	-	0.56	0.32	0.61	0.07
TR	4.39	8.19	155	100	24.98	78	168	0.45	0.34	0.85	0.07

Limit of Detection (LOD): One of the initial concerns was the quality of the LOD data submitted. In order to evaluate its quality, the supporting data was request as well. In addition, typical blank results were request to assess blank response and concentration at the theoretical LOD level. All the LOD values of water samples were less than one and were acceptable (Table 1).

Limit of Quantification (LOQ): The lowest practical limit of quantization of each element was estimated by repeat the analysis of spiked water samples on about the expected lowest (Table 1).

Results and discussion

Assessment of spatio-temporal variations of selected water quality parameters of Lake Tana: The mean values ranged between, 21.83 to 30.37°C and 17.5 to 27.5°C in dry and wet seasons for temperature. The mean temperature of Lake Tana water was 23.90°C in both seasons, which is similar to mean value of 22.4°C in one of the rift valley of Lake Ziway which is reported by Tilahun and Ahlgren (2010). However, in the wet season, the mean temperature was lower than the previously reported data.

Lake Tana has narrow seasonal fluctuations in water temperature as the lake is a shallow tropical lake. The mean temperature of Lake Tana was similar to Lakes Hawassa and Navaishia but slightly higher than Lake Hayk. The values of electrical conductivity (EC) ranged from 140 to 375 and 37 to 172 µS cm^{-1} in the dry and wet seasons, respectively. Sampling sites MG gave the lowest mean conductivity (140 µS cm^{-1}) in dry and GU (37 µS cm^{-1}) in wet seasons while site GU has highest mean values of 375 µS cm^{-1} in dry and MA mean values 172 µS cm^{-1} in wet seasons, respectively (Tables 2 and 3). Overall mean values of EC was 148.5 µS cm^{-1}. When this value compared to other Ethiopian lakes, the EC values of Lake Tana (148.5 µS cm^{-1}) was much 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 3), respectively but similar to the max values 148 µS cm^{-1} as previous reported data by Wondie (2006) in the same Lake. The TDS ranged from 92 to 211 mg L^{-1} with the low values in dry at sampling site MG and the high values at site GU while in the wet season it ranged from 28 to 115 mg L^{-1} at sites GU and MA (Tables 2 and 3).

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Table 3. Means and ranges of the physico-chemical parameters measured at the surface water of Lake Tana in wet season (Temp for temperature in °C; DO for dissolved oxygen in mg L^{-1}; pH for H^+ concentration; EC for electrical conductivity in µS cm^{-1}; TDS for total dissolved solids in mg L^{-1}; SD for Secchi depth in cm; Depth in cm & salinity in mg/L; Aberration of sampling sites: (Abay Inlet (AIn), Rib (RB), Gumara (GU), Megech (MG), Derma (DM), and Abay outlet (AIn), Abo (ABO), Tana Hotel (TR) Ab restaurant (AB), Mango (MA), at the center of the lake in the Southern part (C_1) and at the center of the lake in northern part (C_2) sites and Kuriftu (KU).

Site	DO	pH	EC	TDS	Temp.	Secchi	Depth	NO3-N	SRP	TP(mg/L)	Salinity
GU	8.86	6.52	37	28	17.5	-	-	0.88	0.73	1.73	0.07
AB	6.18	7.45	256	176	22.39	96	175	0.79	0.34	1.20	0.13
DB	5.89	7.89	146	96	24.34	-	-	0.8	0.48	0.70	0.07
ABO	5.89	7.29	159	90	22.1	100	225	0.91	0.31	1.06	0.08
C1	6.01	7.85	135	93	22.3	62	510	0.46	0.23	0.51	0.07
MG	4.31	7.86	160	99	27.5	-	-	0.98	0.88	1.36	0.07
DM	5.62	7.87	153	98	25.39	-	-	0.79	0.26	0.44	0.07
RB	8.27	7.64	72	52	19.2	-	-	1.03	0.75	1.77	0.04
ABL	5.96	7.75	129	89	22.32	28	89	0.58	0.29	1.04	0.06
KU	5.52	7.78	154	103	23.69	85	250	0.6	0.38	0.95	0.07
AIn	5.00	6.97	140	84	24.6	-	-	0.58	0.24	0.81	0.07
MA	5.06	7.8	172	115	23.73	145	178	0.97	0.35	0.62	0.08
C2	5.17	8.05	151	97	25.4	-	-	0.84	0.41	0.85	0.07
TR	6.05	7.68	143	96	23.15	73	210	0.87	0.35	0.78	0.07

Table 4. Comparison of the physico-chemical parameters of Lake Tana with other tropical lakes (mg L^{-1} for nutrients and DO; µS cm^{-1} for EC and m for SD).

Lakes	Temp (°c)	DO	pH	EC	SRP	TP	NO_3-N	Author
Hawasa	23.5	5 - 7	8.66	846	0.015	0.034	0.025	Tilahun and Ahlgren, 2010
Chamo	26.3	5 - 9	8.84	1910	0.118	0.182	0.033	Tilahun and Ahlgren, 2010
Hayq	18.2	1- 8.4	9	910	0.022	0.058	0.042	Fetahi, 2010
Navaishia	22.4	5.89	8.51	290	0.003	0.027 - 0.41	0.012	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	Belachew, 2010
Abaya	-	-	8.9	623	0.04	-	-	Wood and Talling, 1988
Langano	-	-	9.4	1810	0.09	-	-	Wood and Talling, 1988
Bishoftu	-	-	9.2	1830	0.005-0.1	-	-	Wood and Talling, 1988
Abijata	-	-	10.2	15800	0.05	-	-	Wood and Talling, 1988
Shala	-	-	9.9	19200	0.76	-	-	Wood and Talling, 1988
Chitu	-	-	9.8	28600	1.7	-	-	Wood and Talling, 1988
Tana	22°C	4.06-6.2	6.8-9.4	96-256	0.1-1.8	0.83	0.1-1	Present study

The overall mean value of TDS in the lake was 77.5 mg L^{-1}. The TDS at station GU 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 surrounding highly agricultural areas on Lake Tana, which is a tendency of pollution and must be seriously curbed. The level of dissolved oxygen (DO) ranged from 3.83to 5.84 mg L^{-1} and 4.31 to 8.86 mg L^{-1} in dry and wet seasons, respectively (Tables 2 and 3). The lowest value at GU (3.83 mg L^{-1}) in dry and MG (4.31 mg L^{-1}) in wet seasons where the highest values were at C_2 (5.84 mg L^{-1}) in dry and GU (8.86 mg L^{-1}) in wet seasons, respectively. This is probably due to in dry season at GU, human impacts and some unseasonal rain that cases high turbidity of the river and in wet season, MG is completely muddy due to agricultural runoff. The overall mean DO concentration of this study was 5.80 mg L^{-1} in lake water samples, which was in the range of WHO guidelines.

When compared the mean concentrations of DO in Lake Tana is almost similar to most other tropical lakes (Table 4). According to EU (1998) and WHO (1996), the standard for DO value for fisheries and aquatic life is between 5.0 to 9.0 mg L^{-1}. 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 another area (Anonymous, 1999). The value of DO in this study is the minimum permissible values of EU (1998) and WHO (1996). The pH values ranged from 6.8 to 9.35 and 6.52 to 8.1 in dry and wet seasons respectively. The maximum pH noticed in the study period was 9.35 at station AB during the dry season and the minimum pH recorded was 6.52 at station GU. The overall mean pH value of the lake water was 7.9 which were in close agreement with previous data reported as 7.7 (Wondie 2006).

Similarly, Tilahun and Ahlgren (2010) also reported that the pH values of another Ethiopian Lakes of Ziway, Hawassa and Chamo were 8.65, 8.66 and 8.84, respectively. The pH of surface water in Lake Tana showed a very slightly alkaline tendency during all the seasons.The pH of most Ethiopian Lakes generally varied between 7.5 and 9 and remained within narrow range (Table 2). A pH range of 6.5 to 8.5 is acceptable for aquatic biota according to the APHA (1999). The different seasonal values of Secchi depth (SD) at different stations during the one year period of observations are separately given in Tables 2 and 3. 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 C_1 and the shallowest was at site ABL. The deepest SD recorded during the study period was 1.63 m at site ABO during the dry season and the shallowest measured was 0.28 m at site ABL during the wet season with overall mean values of 0.865 m. As compared to other tropical Lakes, the SD values of Lake Tana is shallower than in Lakes of Hawassa (0.85 m), Chamo (0.35 m), Hayk (2.7 m), Tana (0.51–1.82 m), Navaishia (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 4.3), respectively. Thus, unlike the observations in different tropical freshwater (Ishaq *et al.*, 2013) the transparency of the water in Lake Tana increased during the dry season. This might be the undisturbed watershed which keeps the soil system intact during dry season.

Spatio-temporal variations of nutrients in Lake Tana: The spatial and temporal variations of nutrients are summarized in Tables 2 and 3. The mean NO_3-N concentration ranged from 0.28 to 1.56 mg L^{-1} and 0.58 to 1.03 mg L^{-1} in dry and wet seasons, respectively (Tables 2 and 3). The highest mean NO_3-N was at KU in dry and at MG in wet season while DB has the lowest values in dry season and ABL in wet season. The mean NO_3-N value found in this study (0.763 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 Hawassa and Chamo which is lower than Lake Tana (Table 4), respectively. Similarly, Fetahi (2010) reported that the average concentration of NO_3-N was about 0.042 mg L^{-1} in Lake Hayk which was lower than in this study (Table 4). 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 ($p>0.05$). 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 methaemoglobinemia in humans (WHO, 1996; USEPA, 2000). 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.

The mean values of SRP ranged from 0.11 to 0.47 mg L^{-1} and showed similar concentrations for lower values for most of the sampling sites and high values at AB in the dry season, while in the wet season it ranged from 0.23 to 0.88 mg L^{-1} (Tables 2 and 3). The overall mean SRP concentration was 0.326 mg L^{-1} which is higher than the other Ethiopia Lakes reported data of Kebede (1994), Gebre-Mariam (2002), Tilahun and Ahlgren (2010), and Tamire and Mengistu (2012) which was 0.016, 0.035, 0.01 and 0.029 mg L^{-1}, respectively. This is because in recent times Lake Tana 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 Tana (0.326 mg L^{-1}) showed 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). The mean TP concentrations ranged from 0.44 to 1.20 mg L^{-1} and 0.44 to 1.73 mg L^{-1} in dry and wet seasons respectively (Tables 2 and 3). Mean TP concentration was highest at AB in dry season and GU in wet season whereas the lowest concentrations were at C_{1in} dry and DM in wet seasons. The overall mean TP value of the lake water was 0.862 mg L^{-1} which is greater than the most Ethiopian Lakes reported by 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 Hawassa and Chamo was 0.034 and 0.182 mg L^{-1}, respectively which is lower than in Lake Tana (Table 4). 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).

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Table 5. Heavy metal concentrations in Lake Tana water samples.

Sampling sites	Dry season (conc. mg/L)						Wet season (conc. mg/L)					
	Zn	Cu	Pb	Mn	Cr	Cd	Zn	Cu	Pb	Mn	Cr	Cd
KU	0.38	1.05	0.75	0.11	-	0.05	0.04	0.33	0.25	0.21	0.6	0.001
MA	1.2	1.25	1.25	0.11	-	0.05	0.53	0.18	0.25	0.10	0.4	0.03
AB	1.34	0.49	-	0.18	-	0.05	0.20	0.14	-	0	0.4	0.03
TR	0.72	1.25	1	0.11	-	0.08	0.40	0.14	-	0.22	0.4	0.05
Abo	0.51	1.1	1	0.78	-	0.06	0.38	0.18	0.5	-	0.8	0.01
C_1	0.66	3.08	1.5	0.1	-	0.09	0.44	0.16	-	-	0.4	0.02
C_2	0.66	3.48	1.25	0.1	0.07	0.07	0.51	0.2	0.5	-	0.4	0.02
DM	0.38	0.88	0.5	0.61	-	0.05	0.39	0.16	0.25	0.22	0.2	0.02
MG	0.66	0.68	1.5	0.22	0.2	0.1	0.11	0.2	0.25	-	0.4	0.01
DB	0.46	1.12	0.5	0.11	-	0.06	0.18	0.24	0.25	0.10	0.4	0.01
AIn	0.71	1.12	0.5	0.11	-	0.04	0.29	0.18	0.25	0.10	0.6	0.01
Rb	1.66	1.4	0.75	1.26	0.07	0.029	1.04	0.23	0.25	0.99	0.2	0.009
GU	0.69	0.88	-	0.11	0.07	0.069	0.62	0.21	0.25	0.45	0.2	0.008
Mean	1.05	1.23	0.82	0.54	0.06	0.05	0.63	0.21	0.25	0.51	0.28	0.01

Table 6. Comparison of heavy metals in water samples of Lake Tana (mg/L) with reported literatures.

Heavy Metals	Concentration (mg/L)	Location	References
Cd	0.222-0.304	Ethiopia	Carignan-Dugas *et al.*, 2017
	0.066	Ethiopia	Denussa, 2017
	0.031-0.103	Ethiopia	Abduro, 2017
	0.003	-	Organization, 2011
	0.05-0.1	Ethiopia	Present study
Cr	0.014-0.046	Ethiopia	Carignan-Dugas *et al.*, 2017
	0.072-0.097	Ethiopia	Melku *et al.*, 2014
	0.05	-	Organization, 2011
	ND - 0.22	Ethiopia	Present study
Cu	0.051-0.092	Ethiopia	Bedada *et al.*, 2014a
	0.03-0.21	Ethiopia	Bedada *et al.*, 2014b
	2.0	-	Campo *et al.*, 2011
	0.49 - 3.48	Ethiopia	Present study
Pb	0.294-2.663	Ethiopia	Carignan-Dugas *et al.*, 2017
	0.36	Ethiopia	Denussa, 2017
	0.01	-	Organization, 2011
	ND- 1.5	Ethiopia	Present study
Mn	0.061-0.092	Ethiopia	Abduro, 2017
	0.4	-	Organization, 2011
	0.11-1.26	Ethiopia	Present study
Zn	0.011-0.022	Ethiopia	Carignan-Dugas *et al.*, 2017
	0.069-0.18	Egypt	Authman and Abbas, 2007
	0.01-5.62	Tanzania	Kisamo, 2003
	3.0	-	Campo *et al.*, 2011
	0.38-1.34	Ethiopia	Present study

The mean concentrations of metals in the surface water of Lake Tana are shown in Fig. 1, 2 and Table 5 in dry and wet seasons. Based on the mean values of the heavy metals concentrations, the target elements in the surface water of the lake exhibited the following descending order: Cu> Zn> Pb>Mn > Cr >Cd and Zn >Mn > Cr > Pb > Cu >Cd in dry and wet seasons respectively.

In dry season, Mango, Tana Hotel and AB resort has recorded the highest mean concentration of Zn; center 1 and 2, Mango and Tana Hotel, has recorded the highest mean concentrations of Cu; Tana Hotel, Megech and center1 has recorded the highest Pb concentration; Abo and Derma highest Mn detected; Megech maximum Cr and Cd detected.

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Fig. 1. Means of metal concentration in Lake Tana Surface water from the different sampling sites in the dry season.

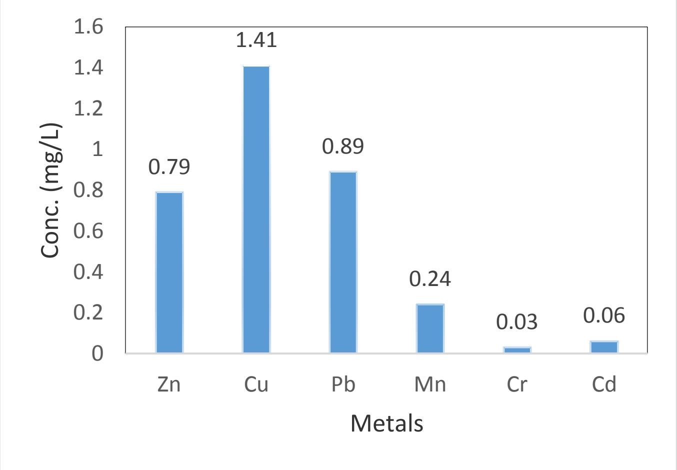
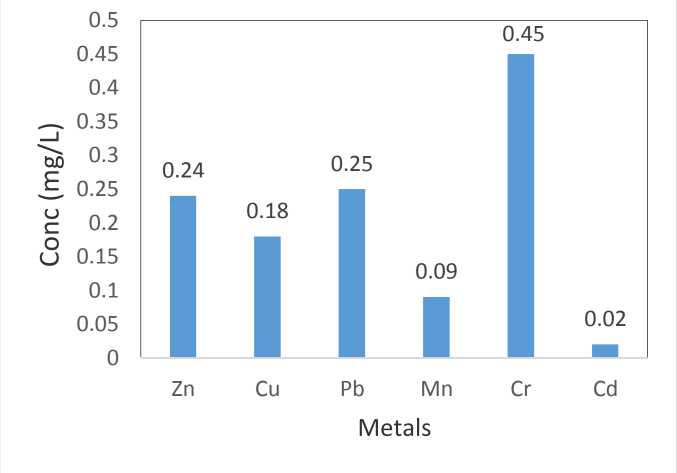


Fig. 2. Means of metal concentration in Lake Tana Surface water from the different sampling sites in the wet season.



During the rainy season Mango has recorded the maximum Zn concentration; Kuriftu detected the maximum Cu concentration; Abo and center 2 detected the maximum Pb concentration; Derma, Kuriftu and Tana Hotel detected the maximum Mn; Abo detected the maximum Cr and Tana Hotel detected the maximum Cd so that the distribution of heavy metals in the rainy and dry season was too different also it needs more research about the case and distribution of toxic heavy metals in Lake. The mean concentrations of metals were variable and some of them did not show significant variation among sampling sites (ANOVA, $P > 0.05$). From the above the Table 5, Cr was not detected in most sampling sites in the dry season, this study indicating that wastewater receives little effluents contaminated with Cr metal. The mean concentrations of Mn and Cr in the different sampling sites of the lake were under the Ethiopian effluent allowable discharge limits into water courses in both seasons (5 mg/L, 1 mg/L) (EEPA/UNIDO, 2003).

On the other hand, the mean concentrations of Cu, and Zn in all sampling sites were higher than the limits (0.1 mg/L and 1 mg/L, respectively) (EEPA/UNIDO, 2003). And the mean concentrations of Cr, Cu and Mn were also higher than the maximum allowable concentration ranges for fisheries and aquatic life set by Environment Canada (1987) (0.02 to 0.002 mg/L, 0.002 to 0.004 mg/L, 0.3 mg/L, respectively) which shows that Lake Tana can be regarded as relatively influenced by anthropogenic pollution. Heavy metals such as cadmium, chromium, copper, lead and zinc exhibit aquatic toxicity when present above recommended standard. In view of the fact that the major use of water in the study area is for cattle drinking, domestic and irrigation, the concentration levels of heavy metals Cu, Zn and As recorded exceeded the limit for aquatic ecosystem, therefore it is of great concern since these metals are extremely toxic and the consumption of water high in these metals could cause adverse health effect to end users. The high concentration of Cu, Zn, and Pb in the study area could be attributed to the discharge of domestic wastewater containing compounds of these metals. The domestic wastewater discharged into the lake could be composed of grey water that may consist of: the bath, dishwasher products, personal care products and laundry detergents; which are good sources of these metal elements (Tjandraatmadja *et al.*, 2008; Diaper *et al.*, 2008). Also dumping of wood treated with chemicals made from salts of these metals (Cr and Cu and Zn) to prevent fungi and pest attack might provide a potential source of chemical spills and drainage from the treated wood around the Lake, this is in support of other findings (Ndiokwere, 2004). The higher mean concentrations of metals among sampling sites were also recorded for example, the increased mean concentrations of Zn, Cu, Pb and Mn in the sampling sites of AB resort, Mango, Central sites 1 and 2, Tana hotel and Rib river mouth, respectively in the dry season were due to different anthropogenic sources of pollution in the lake ecosystem. Moreover, high levels of copper above the limits could be due to the effluent containing copper metal chips from metal engineering operations involving Cu scrap. Although copper toxicity in humans is rare, aquatic organisms are potentially at risk from Cu exposures (Paul, 2011). The comparisons of heavy metal analysis in this study with different literatures are summarized in Table 6.

Conclusion

There were spatio-temporal variations in the selected physicochemical water quality indicators in the lake ecosystem. From the result, five major Rivers' catchments showed the major sources of high nutrient concentrations to the lake ecosystem. Based on the results of this study, the lake shows some changes in terms of some physico-chemical water quality indicators and heavy metals.

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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. These include regulated use of farm inputs improving waste disposal practices and factory effluents to the lake ecosystem. Tana center is known by the concentration of an element copper. The concentration of chromium is high around AB resort. The location of the lake at Abay outlet is known by the high concentration Cadmium. The concentration and absorbance of heavy metals such as Copper, Cadmium, Chromium, Zinc, Lead and Manganese were linearly related to each other. Furthermore, 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.

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