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Investigating the Current Level of Heavy Metals and Physico-Chemical Parameters in Water of Lake Ziway, Oromia Region - Ethiopia

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Abstract: Background: Pollution from a single, easily identifiable source, such as an industrial facility or sewage treatment plant, is referred to as point-source pollution. Nonpoint-Source pollution is contamination that originates from multiple sources rather than just one. Lake Ziway is one of the Ethiopian Rift Valley lakes that have been impacted by both anthropogenic and natural activities. Large-scale projects, domestic waste influents, pesticide use that wasn't foreseen, industrial and domestic wastes, etc. are a few of the factors contributing to the pollution. Objective: The goal of this study was to determine the current concentrations of a few specific heavy metals and physicochemical components in the water of Lake Ziway (Ethiopia) as a result of point and nonpoint influent discharges. Method: The physico-chemical parameters including electrical conductivity, total dissolved solids, pH, turbidity, ammonia, nitrites, nitrates, phosphates, sulfates, and total hardness were investigated using the Palin test photometer, while the Cr, Pb, and Ni concentrations in collected water samples were determined using the Flame Atomic Absorption Spectroscopy (FAAS). Result: Phosphorus, turbidity, chemical oxygen demand, biochemical oxygen demand, magnesium, calcium, chromium, lead, and nickel are just a few of the parameters that were over the standard limit values at location "A", and they are also revealed to be above the standard limit values at site "B" and site "C" chromium, nickel, and zinc requirements are higher than recommended by WHO standards. Conclusion: In this article we investigated the levels of some heavy metals, i.e. chromium, lead, nickel, Zinc and physicochemical paramters including BOD, COD, PH, total dissolved solids, turbidity, nitrates, phosphates, and total hardness. The expansion of large-scale investment projects, such as irrigation-based agricultural development activities, floriculture industries, unplanned use of agrochemicals, domestic waste influents from Ziway/Batu town, and rivers like the Meki Rivers in Meki town (about 30 km far from Ziway) that flow into Lake Ziway carry contaminated discharge from industrial and domestic sources, are currently putting pressure on Lake Ziway.

Keywords: Biochemical Demand, Meki River, Heavy Metals, Lake Ziway, Palint Test, East Shoa

1. Introduction

Ethiopia is one of the nations in Africa with the highest levels of water resources, including surface water. Surface water, however, is impacted by a number of causes [1]. Although the exact causes of the principal pollutants that influence Ethiopian lakes and rivers are unknown, they appear to include the movement of sediment, siltation, industrial discharge from a few companies and mining operations, runoff from agricultural areas, and home sewages [1-4].

The quality of water and the associated biological communities can be impacted by anthropogenic factors include modifications to land usage and the handling of agricultural chemicals in lake water sheds [5], which can result in a reduction in the availability of various goods and ecological services.

A lake in the Ethiopian Rift valley influenced by anthropogenic and natural activities is Lake Ziway [6]. An increase in large-scale investment initiatives, such as horticulture and irrigation-based agricultural development activities, unplanned use of agrochemicals, domestic waste influents from Ziway/Batu town, and rivers like the Meki

Rivers in Meki town (about 30 km far from Ziway) that flow into Lake Ziway carry contaminated discharge from industrial and domestic sources, are currently putting pressure on Lake Ziway [7-10]. Numerous researches have been published on the physicochemical properties, trace metal concentrations and pesticide pollution in Lake Ziway [11]. While heavy metals are naturally present in the earth, human-caused activities cause them to concentrate. Heavy metal poisoning of water has serious consequences because it could poison both terrestrial and aquatic life [12]. The studies of heavy metals show that in traces in water sources and still be very toxic and impose serious health problems to humans and other ecosystems, because the toxicity level of a metal depends on factors such as the organisms which are exposed to it, its nature, its biological role and the period at which the organisms are exposed to the metal [9, 13-15]. Investigating the current concentrations of a few specific heavy metals and physicochemical properties in Lake Ziway water as a result of point- and nonpoint-influencer discharges was the major goal of this study. A variety of water sample characteristics, including pH, temperature, conductivity, total hardness, total dissolved solids (TDS), magnesium and calcium hardness, nitrate, sulfate, phosphate, and heavy metals like Cu, Zn, Mn, Pb, Ni, and Cr, were examined.

2. Materials and Methods

2.1. Description of Study Area

In terms of location, Lake Ziway is situated in the Ethiopian Rift Valley at an elevation of 1636 meters above sea level, between 7° 5" and 8° 8" N and 38° 40" and 38° 56 E". The Lake is located at about 160 km in South of Addis Ababa, the capital city of Ethiopia, on the left side of Addis to Hawassa road. Ziway is the shallowest lake in the rift valley, with maximum and mean depths of 8.95 m and 2.5 m, respectively. It is the fourth largest lake in Ethiopia, with an open water area of 434 km^2 and a shoreline length of 137 km.
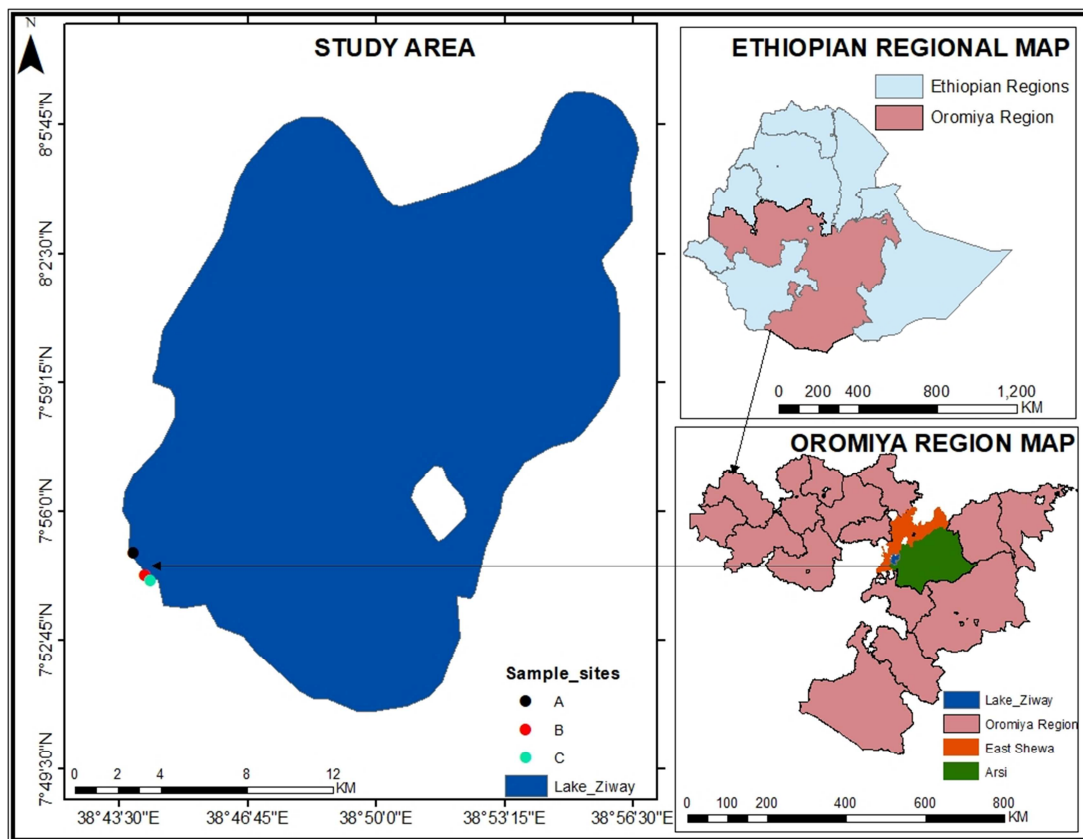

Figure 1. The map of study area.

It has a maximum length of 32 km and maximum width of 20 km. The Lake is fed by two major rivers, Meki from North West and Katar from East, and has one outflow in the South, Bulbula River which flows into Lake Abiyata. Lake Ziway is bordered and hence controlled by three districts belonging to two administrative Zones of Oromia regional state.

While Arsi zone's Ziway Dugda district (Habura town) borders the Lake in the eastern to south-eastern part, East Shoa Zone's Dugda (Meki town) and Adami Tullu Jiddo Kombolcha (A/T/J/K, Ziway/ Batu town) districts border the Lake in the north-western and western to south-western parts, respectively.

2.2. Instruments

Palin test photo meter, (model 7100 wagtech) Atomic Absorption Spectrophotometer, AAS (Model 210VPG, buck scientific) and filter paper (Whitman N0-42) were used to analyze samples.

2.3. Chemical and Reagents Used

All of the reagents utilized in the analysis were of the analytical variety. 69-70% HNO_3, 37% HCl, buffer solution of p^H 4, 7 and 10, de-ionized water, 1000 mg/L in 2% HNO_3 stock solution of Pb, Cr and Ni (BDH chemicals Ltds-UK) obtaned from certified manufacturer for palintest.

2.4. Sample Collection

Sample A (Site A) is a water sample taken from the Ziway town influent discharges, Sample B (Site B) is a sample taken from a floriculture field, and Sample C (Site C) is a sample taken from Lake Ziway. Three samples were randomly chosen from each of the above sites, and the samples were then collected and stored in plastic until preparation and analysis.

2.5. Sample Preparation

A flame atomic absorption spectrophotometer (FAAS) was used in the chemistry lab at Hawassa University to measure the levels of heavy metals (Ni, Cr, and Pb) in water samples.

Standards produced from standard 1000 mg/L stock solution were utilized to establish the analytical curve for the measurement of heavy metals. De-ionized water was used to dilute the stock solution in a 100 mL volumetric flask and working standards to make the intermediate solution (10 mg/L) for each metal. In a 50 mL volumetric flask, working standards of metal solutions were prepared by dilution with deionized water. 50 mL of measured water sample were placed in a clean conical flask along with 1 mL of 70% HNO_3 and 2 mL of 37% HCl. On a hot plate, the sample's contents were heated to a clear solution and a volume of approximately 15 mL at 95°C. The mixture was then filtered using Whatman N_0-2 filter paper in 50 mL volumetric flask and filled to the labeled mark. Then the solution was stored at 4°C until FAAS analysis. Digestion of reagent blank sample was also performed in parallel with the sample keeping all the digestion the same. For analysis of root sample three reagent blank samples were prepared for each. All digested blank were stored in refrigerator until analysis. The solution of the digested blank sample used to determine the concentration of each element by FAAS.

2.6. Method Validation

2.6.1. Evaluation of Analytical Precision, Accuracy, Recovery Test and Quality Control

The process of demonstrating that an analytical technique is appropriate for its intended use, in accordance with quality assurance protocols, and that steps were taken to assure the reliability of the result is known as method validation. Throughout the investigation, deionized water and analytical-grade chemicals were used. The instrument readings were adjusted using reagent blank determinations. A recovery study was conducted by spiking and analyzing samples with varying concentrations of standard solutions of the metals in order to validate the analytical procedure.

Precision is an analytical procedure has usually expressed as the variance, relative standard deviation and percentage relative standard deviation of a series of measurements. In this study, the precision of the results was evaluated by percentage relative standard deviation of the results of three samples (N=3) and triplicate readings for each sample giving nine measurements for a given bulk sample.

Accuracy of analytical method has evaluated in terms of percent recovery by either the assay of known added amount of analyte in the sample or as the difference between the mean and the accepted true value together with the confidence intervals. In this study, the analytical accuracy of the procedures was determined by spiking experiment. The spiked sample were prepared by adding 1 mg/L solution containing 1 mg/L each heavy metal has added to the blank sample. The resulted spiked samples have digested, diluted and analyzed for total heavy metals.

2.6.2. Data Analysis

Microsoft Excel 2010 was used to examine the data. For each variable, descriptive data have been created and are shown as means and standard deviations (SD). The findings of the physical-chemical parameter analyses and the heavy metal concentrations found at all three sampling locations were compared to the WHO surface water guidelines and classified as acceptable or unsuitable. One-way ANOVA was used to assess the average data variations between the three sites.

3. Results and Discussion

3.1. Method Detection Limits

Three duplicates of the blank (de-ionized water) spiked with the target analyte were used to estimate the method detection limit (MDL) of the analytical method for each analyte. The calculated values indicate the analyte's measured minimum concentration, and they were reported with 99% certainty that the analyte concentration was higher than zero (Table 1).

Table 1. *Instrument detection limit (IDL) and method of detection of limit (MDL).*

Element	Cu	Zn	Mn	Cr	Ni	Pb
IDL	0.001	0.002	0.001	0.014	0.001	0.002
MDL	0.003	0.006	0.003	0.04	0.003	0.006

3.2. Recovery Tests

The analytical method's precision and accuracy were calculated in terms of relative standard deviation and percent recovery (Table 2). Recovery and relative standard deviation (RSD) both fell within the acceptable / necessary range of 80–120% and 20%, respectively [10]. The recovery % was computed as follows:

$$\% \text{ recovery} = \frac{F-I}{A} \, x \, 100$$

Where F = Spiked sample concentration; I = Unpicked sample concentration; A = concentration of Analyze added to the spiked port.

Recovery values in the above range are acceptable for environmental investigations and the digestion procedure has believed to remove metals fractions associated with carbonates, sulphides, soluble salts, organic matter and Fe-Mn oxide phase [5].

According to the standard, 80-120% recovery and ≤20% RSD can have used as starting for assessment of accuracy and precision [16] unless other criteria are provided by a chosen laboratory. Therefore, the percentage recovery values have found between the lowest 79.9% to and highest 99.9% and except for lead at all sites were within the required criteria. In addition, the RSD value is below for the entire standard limit (Table 4) except for Pb & Mn at site C. This confirms that the method has provided results within the required levels of accuracy and precision.

Table 2. Recovery test results for concentration of metals.

Heavy metal	Concentration in (mg/L)			
	unpicked blank	amount added	Spiked sample	% recovery
Cr	0.0014	2	2.0014	99.8
Pb	0.001	2	2.001	79.9
Ni	0.003	2	2.003	97.7

Table 3. The working standard concentrations and correlation coefficients of the metals.

Metals	Concentration of standard solution, mg/L	R^2
Cr	2.00, 1.00, 0.50	0.9999
Pb	1.50, 1.00, 0.50	0.9998
Ni	2.00, 1.00, 0.50	0.9995

3.3. Physicochemical Characteristics of Water Samples

Table 4. The mean ± SD of physicochemical parameters of each water samples.

Parameters	Site A	% RSD	Site B	% RSD	Site C	% RSD
pH	7.47 ± 0.05	0.66	7.57±0.045	0.59	7.45±0.049	0.66
EC	600 ± 4	0.66	565.3±11.5	2.00	744±4	0.50
TDS	300± 2	0.66	276±1.5	0.50	372±2	0.50
Turbidity	137.3 ± 1.5	1.10	12.3±0.5	4.00	18.8±0.2	1.10
TH	185± 5.5	3.00	18.7±7.4	4.70	55.7±2	3.40
NH_3	2.18 ± 0.02	0.9	0.08±0.01	0.50	0.1±0.01	10
NO_2	1.3 ± 0.01	0.76	0.26±0.01	7.60	0.42±0.01	2.30
NO_3^-	24.2 ± 0.3	1.20	2.97±0.06	2.00	3±0.02	0.66
PO_4^{3-}	13.4 ± 0.4	3.00	0.28±0.1	3.50	0.84±0.07	8.00
SO_4^{2-}	48 ± 1	2.00	2.5±1.3	52.00	12±1	8.30
DO	1.8 ±0.1	5.60	2.86±0.06	2.00	2.3±0.1	4.30
COD	2.3 ± 0.1	4.30	576.7±4	0.70	592±7.2	1.20
BOD	307 ± 4.6	1.50	261.7±25.5	9.70	280.7±55.5	1.90

Except for Turb (NTU) and EC (µS/cm), all units are in mg/L, Site A= surface runoff from Ziway town, Site B = Influent discharge from floriculture farm, Site C= water sample of Lake Ziway. In this study, the turbidity value ranged from the minimum value 12.3 NTU at site B to the maximum value 137.3 NTU at site A. Turbidity does not have direct health effect. However, it affects the water treatment system and decrease intensity. The variation in total hardness observed in the three water samples site A, B & C. The minimum value of total hardness recorded at site B (18.7 mg/L) and maximum value at site "A" (185 mg/L). These values are in range of standard limit of WHO (2008).
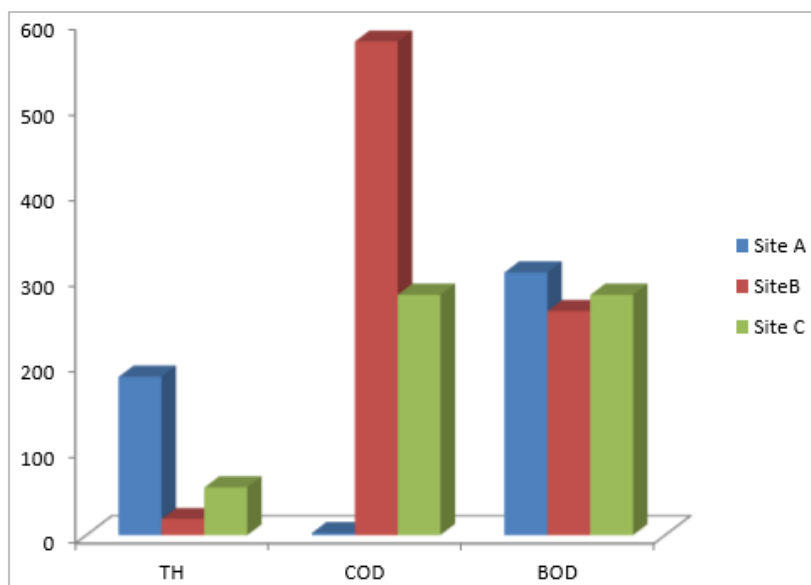
The higher value recorded at site A may be due to influent discharges of urban runoff which contains high concentration of magnesium &calcium ions 12 mg/L and 110 mg/L respectively.

The value of pH ranged from 7.45 site C to 7.57 site B. COD is the amount of oxygen required to carry out oxidation of organ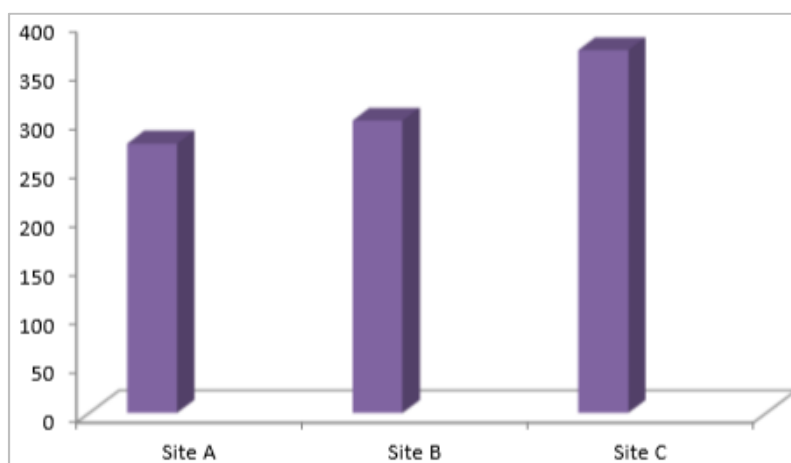ic waste by using strong oxidizing agent [17]. The water sample found to have COD minimum values 2.3 mg/L (site B) and maximum value 292.3 mg/L (site C) and was under state recommended value by WHO. Different studies indicated that the value of DO for the Lakes of Ethiopia is in permissible set by WHO in the range of 4.5 to 7.5mg/L [18]. Lake Ziway has the lowest DO value from the other Ethiopian Lakes [3]. The present studies also similar with this finding in which the value ranges from 1.8 mg/L to 3 mg/L at site A and site C respectively.

The highest concentration value of electrical conductivity recorded were probably associated with the discharge from dissolved substance from domestic waste, municipal effluent discharged from resident community and waste substance from the market in the town. The mean concentration values of electrical conductivity of water samples varied significantly among the sampling sites. Since, the conductivity of the water is a function of the number of charged ion in solution; it is another measure of dissolved materials [19]. The electrical conductivity values at each site
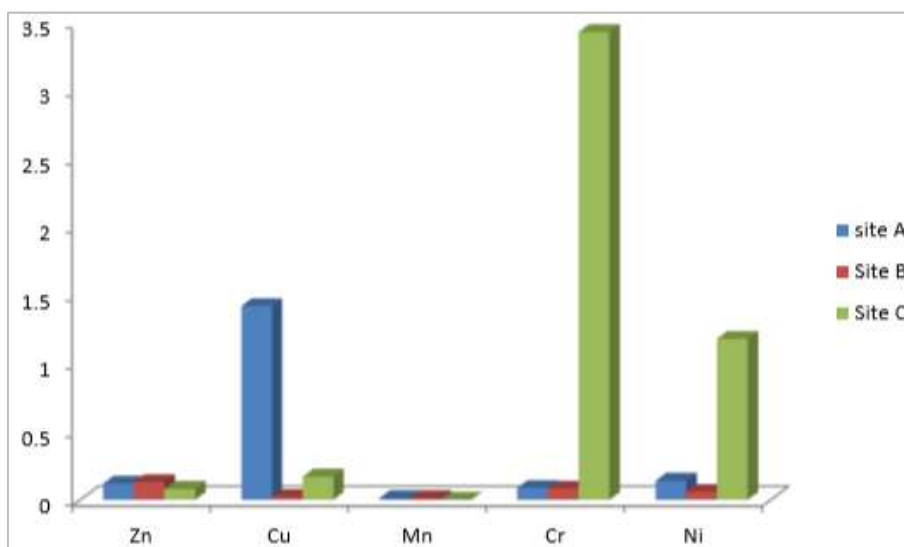
differ significantly from each other (site B differ from sites A   and C, Site B differ from site C) (Table 4).

Figure 2. *Variation of TH, COD and BOD concentration in each water sample for three sites.*

Figure 3. *Variation of EC in each site water samples.*

Figure 4. *Variation of Cu, Zn, Mn, Cr and Ni concentrations in three site water sample.*

This indicates that the amounts of dissolved ion responsible for the conductivity in the three sites are not the same due to their different in the potential sources of pollution [20]. The electrical conductivity values usually give an estimate of the presence of certain ions in water such as carbonate, bicarbonates, chloride, sulphate, nitrate, sodium, potassium, calcium, magnesium, all of which carry an electrical charge [13]. The presence of these chemical constituents gives water the ability to conduct electricity. This is a clear indication of the river water contains high quantity of dissolved ionic salts that might not be safe both to humans and other domestic animal [8].

The highest concentration of chromium recorded at site C was 3.43 mg/L. When this value compared with standard guide line, all values are above permissible limits. These sources of chromium might be pesticides and fertilizers contamination. The concentration of Chromium at site A was 0.089 mg/L. The sources of contamination may be corrosion of chromium metal alloys that are discharged to surface water runoff during rain fall and also from engine and vehicle body wear.

4. Conclusion

The two influent discharges, surface runoff from Ziway town and flower farm waste water that discharged to the Lake, were found to have an impact on the Lake according to a study of the quality of the water of Lake Ziway near the flower industry farm site. Most metrics, including nitrites, nitrate, phosphate, and sulfate, as well as total hardness, total dissolved solids, electrical conductivity, pH, dissolved oxygen, and biochemical and chemical oxygen demands, were consequently found in the lake.

According to the study's findings, the WHO guideline for surface water quality for aquatic life indicates that DO indicates below allowed levels and PO_4^{3-} indicates over permissible limits. Because the influent discharges contain measurable levels of trace metals like Cu, Mn, Zn, Cr, Ni, and Pb, the study's findings suggest that pesticides and fertilizer pollution from flower farms are some heavy metals pollutant sources in this lake location.

This investigation also showed that, at a specific moment in the study, there was an accumulation of various heavy metals, particularly chromium and nickel that were beyond the permitted limits (in Lake Ziway). The Lake's water is poisoned since these heavy metals are present in significant concentrations. Fishing may therefore increase the amount of metal that enters the food chain through eating fish by causing bioaccumulation on fish. Because of this, Lake Ziway's water cannot be used for agriculture, drinking, or aquatic life without some physical and chemical treatment. Therefore, it is anticipated that this finding will serve as a warning so that a comparable study can be conducted.

Conflict of Interest

The authors of this work declare that they have no financial or other conflicts of interest.

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