

Analysis of Nitrate Levels in the South East Coastal Areas of Lake Tana using UV-Visible Spectrophotometer

Worku Kegne (Msc)¹
Begemedir College of Teacher's Education

Girma Kibatu Berihe(PhD)¹
College of Science, Department of Chemistry (Inorganic), Bahir Dar University, Ethiopia

Tadesse Mengistu Bediye(Msc)²
College of Science, Department of Chemistry (Inorganic), Debre Tabor University, Ethiopia

Abstract

Nitrogen compounds added to the terrestrial environment from agricultural sources impact fresh water ecosystems. Nitrate contamination resulting from deposition of nitrates onto soils and plants, with subsequent leaching out of the water shade may enhance the harmful processes of eutrophication in Lake Tana. The aim of this research is to analyze the level of nitrates in Lake Tana. The level of nitrate (NO_3^-) in samples from different sites within the Lake was determined in dry season with standard method using Uv-Visible spectrophotometer during March/April. Nitrate (NO_3^-) values for water samples in Lake Tana ranged from 0.24- 2.21 mg/L NO_3^- . The average nitrate concentrations of the different sites in mg/L Nitrate are as follows; Rib = 2.21 ± 0.21 , Gumara = 2.09 ± 0.26 , Gelda = 2.12 ± 0.20 , Mehal Zegie = 0.24 ± 0.12 , and Enfraz = 1.32 ± 0.17 . The value of nitrate (NO_3^-) was higher in the sites of east coastal river mouths of Lake Tana (Gumara, Gelda, and Rib). The southern part of the Lake has lower concentration of nitrates than those on the east coast. Agricultural practice in the east and urbanization in the south of the lake must have contributed for higher nitrate levels in these areas. Appropriate pollution control measures should be taken in our agricultural practices and urban waste disposal systems in the lake catchments though the levels encountered in this work for now are within the regulatory threshold set by EPA (45 mg/L NO_3^-).

Key words: Nitrate, Eutrophication, Met hemoglobin, Phenol disulphonopic acid.

1. Introduction

Lake Tana is a unique natural resource where the lives of half million people directly or indirectly depend and that is heavily utilized by riparian community. It has been used for transportation, drinking water supply, fishery, waste disposal, recreation and tourism. The lake is polluted by different contaminants: such as nitrate, phosphates and heavy metals etc which are obtained from the rapid growth of population, increased urbanization near to the lake, expansion of irrigation that more likely use different nitrogen containing fertilizers (urea and DAP) and in general the inflow of different rivers that consist these various agricultural by products and solid and liquid wastes from urban and rural areas. These processes may increase the concentration of nitrate ion in the Lake which subsequently affects the natural ecological system of the lake [1-4]. The Lake Tana environments are under growing stress from point and diffuse sources of pollution. Water pollution is a serious environmental problem in the world. It is the degradation of the quality of water that renders water unsuitable for its intended purpose. Anything which degrades the quality of water is termed as pollutant. Many surface and ground water are being polluted with different pollutants. Some pollutants are directly discharged from industrial effluents and municipal sewage, and others come from polluted runoff in urban and agricultural areas. Contaminants such as bacteria, viruses, heavy metals, nitrates and salts have found their way into water supplies as a result of inadequate treatment and disposal of waste industrial discharges, and over-use of limited water resources [5, 6]. Nitrate is one of the pollutants of groundwater and surface water is caused mostly by agricultural activity (including excess application of inorganic nitrogen containing fertilizer and manures), from waste water treatment and from the oxidation of nitrogenous waste products in human and animal excreta, including septic tanks [2, 7-10]. It can be endogenously reduced to nitrite, which can then undergo nitrosation reactions in the stomach with amines and amides to form a variety of N-nitroso compounds, most of which are highly carcinogenic [7, 9, 11, and 12]. And when the nitrate ion concentration exceeds about 45 mg /L NO_3^- it also promotes eutrophication and is toxic to fetuses and young of live stock and humans, as a result of runoff and discharge of sewage and certain industrial wastes. For these reasons, removal of nitrate and nitrite from water is a necessity. To limit the risk to human health from nitrate in drinking water, the World Health Organization (WHO) at a maximum acceptable concentration to be 45 mg /L NO_3^- [2,13]. Determination of nitrate ion is, therefore, very important in the ecosystems. The principles of Spectrophotometric determination is nitrate reacts with phenol disulphonic acid and produces a nitro derivative which in alkaline solution develops yellow color due to rearrangement of its structure. The color produced follows Beer's law and is

intensity proportional to the concentration of nitrate present in the sample. The present study thus focuses on the nitrate ion concentration levels in Lake Tana which is the home for many biological species and an invaluable resource for the people who depend on it using a UV-Visible spectrophotometer method.

2. Materials and Methods

Description of Study Area

Lake Tana is the largest fresh water situated in the north western high lands in Ethiopia. It has an area of 3200 Km² and it is a shallow lake with a mean and maximum depth of 8 m and 14 m respectively. It is located at 12°00' N and 37°15' E (approximate center of the lake). The assessment in this study was conducted only on some parts of Lake Tana which include river mouths and major tributaries in the southern and eastern part of the Lake, coastal areas next to Bahir Dar City in the South and Mehal Zegie. Out of more than 40 rivers feeding the lake Gilgel Abbay, Rib, Gumara, Gelda and Enfraz contribute much of the inflow are considered. The only surface water that drains the lake is the Blue Nile [1, 14, 15, 16]. Lake Tana area has warm temperature climate and have a mean annual temperature of 13.5 - 27.7 °C and the mean annual rain fall is about 1500 mm, of which 54 % falls in the months of July and August, when the rain fall can be 250- 300 mm per month. The seasonal rains cause the Lake Levels to fluctuate regularly with an average difference between the minimum, in May – June, and maximum is September – October of about 1.5 m [1].



Figure 1: The map of Lake Tana and location of sample site

Apparatus, materials and reagents

The apparatus, materials and reagents used in this study were: SANYO Sp-65 UV/Visible spectrophotometer (Gallenkamp, Made in UK), Hot plate, graduated pipettes (2, 5 and 10 mL), Fume hood, Analytical balance, Volumetric flask (25 to 1000 mL), water bath, Plastic funnel, Watch glass, Refrigerator, test tube, beaker (100 to 250 ml) and dissector, Measuring cylinder glassware, Ammonia solution (NH₄OH), doubly distilled water, hydrochloric acid (37% HCl), potassium nitrate (KNO₃), phenol (C₆H₅OH), concentrated sulfuric acid (98% H₂SO₄). All chemicals used are of analytical grade.

Procedure for water sample collection and determination of nitrates

The random sampling was used for collecting samples at the various stations randomly but decision from which site the samples collected were judged to include all possible sources for contaminants to emanate using judgmental sampling. Samples were collected in March and April from five different station of the Lake at shore based locations in Bahir Dar city Gelda, Gumara, Rib river mouth, Mehal Zegie and Enfraz river mouth. Samples were collected in plastic bottles which were cleaned thoroughly with detergent, rinse with 1N hydrochloric acid, followed with distilled water for prolonged time and collected samples were stored at 4 °C for a maximum holding time of 48 hours. Samples were acidified using 1N hydrochloric acid in order to prevent interference from hydroxide or carbonate concentration up to 1000 mg/L and then analyzed immediately for nitrate using UV-Visible spectrophotometer method.

Preparation of standard Nitrate- Nitrogen

For spectrophotometric determination of nitrate using UV-Visible spectrophotometer 5.0 g of potassium nitrate (KNO₃) was dried at 103-105 °C for 1 hr and stored in desiccators until it was cooled. 3.6107 g of potassium

nitrate (KNO₃) was dissolved in a 500 mL of distilled water in a flask to prepare standard stock solution, which was a concentration of 1000 ppm. It was closed, shaken vigorously and then labeled; 50 mL taken and again diluted using 500 mL volumetric flask up to mark with distilled water to get working standard solution that is 100 ppm. 0.1, 1, 2, 3 and 4 ppm standard solution were prepared by diluting 0.1, 1, 2, 3 and 4 mL of working standards with 100 mL distilled water to each flasks and filled up to mark [17].

Preparation of Phenol (1, 3) -Disulphonic acid

Phenoldisulphonic acid was prepared by dissolving 25 g of white phenol in 235 mL of concentrated sulfuric acid (H₂SO₄) was added and the solution was heated at 100 °C for 2 hours on water bath [17].

Sample preparation

A 5 mL of distilled water was pipette in to 150 mL beaker (blank). Then, 5 mL of sample was added to 150 ml beaker (sample volume) and was placed on a hotplate. Then, 2 mL of Phenoldisulphonic acid was added and the sides was washed down lightly, warmed on hotplate; removed and allowed to cool. 10 mL of concentrated ammonium hydroxide was then added carefully in fume hood. Samples were prepared in triplicates and brought to room temperature. It was added carefully to a 50 mL volumetric flask, washed, cleaned and made up to mark with distilled water. The absorbances were measured with the UV/Visible spectrophotometer at 410 nm [17]. The same procedure was followed for standards and absorbance readings were recorded. Finally, a standard graph was prepared according to the absorbance versus for the different concentrations of standards (table and figure).

Calculation: The analysis of nitrogen in different water sample is as mg /L NO₃⁻ -N, but it is also possible to express the concentration of nitrogen in terms of mg/L NO₃⁻ (nitrate). To convert the nitrate-nitrogen (mg/L NO₃⁻ -N) to nitrate (mg/L NO₃⁻) the conversion factors are used. The conversion factors (CF) for nitrate species are obtained by dividing the ionic mass of nitrate by the atomic mass of nitrogen .The nitrate concentration expressed in mg/L is equal to the concentration of nitrate –nitrogen multiplied by 4.43 constant number [17].

$$\text{Mathematically, CF for NO}_3^- = \frac{\text{ionic mass of nitrate (62)}}{\text{atomic mass of nitrogen (14)}} = 4.43$$

Nitrate ion concentration of the results from the experiment in mg/L NO₃⁻ is calculated using the following general formula: $\left(\frac{\text{corrected absorbance} - \text{intercepts from the calibration curve} \times 4.43}{\text{Sample volume(ml)}} \right)$

3. RESULTS AND DISCUSSION

Concentration of Nitrate ion in the Water Samples in Lake Tana

The amount of nitrate ion in seven different samples of the water of Lake Tana was determined using a calibration curve of the standard solution 0.1, 1, 2, 3 and 4 ppm.

Table 1: The absorbance of standard solution for UV/Visible spectrophotometer

Concentration of Standard Solution for Nitrate, ppm	Absorbance measured at 410 nm
0.1	0.015
1	0.028
2	0.041
3	0.041
4	0.061

For the establishment of method linearity various concentrations were prepared from secondary stock solution ranging from 0.1mg/l to 4mg/l and the samples were scanned in Sp65 UV- Visible spectrophotometer against blank. The calibration curve was obtained by plotting the absorbance versus the concentration data and was treated by linear regression analysis. The equation of the curve for nitrate obtained $Y = 0.0154 X + 0.01266$, the calibration curve was found to be linear in the aforementioned concentrations. The correlation coefficient (r) of determination was 0.99753 and is highly significant for the method.

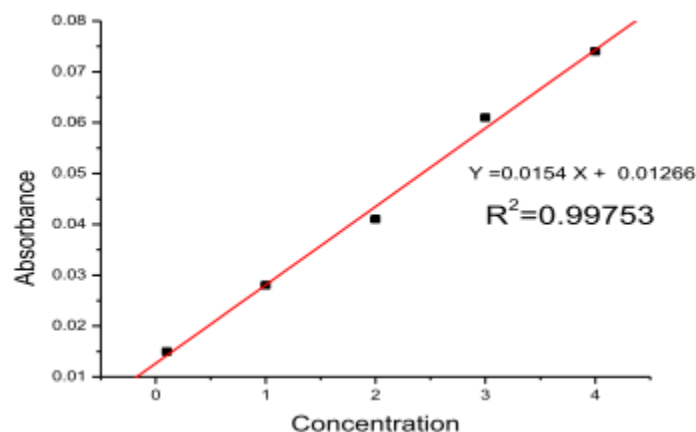


Figure 2: Calibration curve of the standard solution by UV/Visible spectrophotometer

Table 2: Optical and regression characteristics of UV-Vis Spectrophotometric method for nitrate

Parameter	Nitrate
Absorption maxima	410 nm
Linearity Range	0.1mg/l to 4mg/l
Regression equation(R)	$Y = 0.0154 X + 0.01266$
Correlation Coefficient	0.99753
Slope (A)	0.0154
Intercept (B)	0.01266

Table 3: Average nitrate level of estimated water samples of Lake Tana from different sites by UV-Vis spectrophotometric methods.

No	Sample sites code	Trial	Concentration (mg/L)	Mean \pm SD
1	Enfranz	1	1.267	1.32 \pm 0.17 ^b
		2	1.515	
		3	1.187	
2	Gumara	1	1.826	2.09 \pm 0.26 ^c
		2	2.107	
		3	2.339	
3	Gelda	1	1.931	2.12 \pm 0.20 ^c
		2	2.091	
		3	2.339	
4	Rib	1	2.428	2.21 \pm 0.21 ^c
		2	2.011	
		3	2.179	
5	Mehal Zegie	1	0.248	0.24 \pm 0.12 ^a
		2	0.106	
		3	0.354	

*Similar small letter superscripts indicate that there is no significant difference between stations values while different letters indicate the reverse is true.

The highest mean value of 2.21 \pm 0.21mg/l (around Rib) and 2.12 \pm 0.20 mg/l (Gelda) nitrate were obtained in the lake with an average value of 1.26 mg/l to the lake system (Table 3). In all observed sites the amounts of nitrate concentration at lake were by far below the permissible limit of WHO [18] for drinking aspects which is 10 mg/l. According to researchers high nitrate content (> 1 mg/l) is not conducive for aquatic life [19]. Nonetheless, in unpolluted waters the level of nitrate nitrogen is usually < 0.1 mg/l [20]. But value obtained in the present study may indicate pollution of the lake by the nutrient: this may be due to the application of fertilizers and high grazing area around the catchment and run-off from these sources than in the other sites of the lake. In line with this, literature described that increased population, agricultural practice, disposal of wastes (particularly from animal farming), changes in land use and fertilizers applications have had a great influence on the quality of water [21, 22].

Comparisons of Nitrate ion Level of Lake Tana with Other Related Data

Recently the contamination of fresh water with nitrate ion received the attention of many researchers in different countries because of its impact on human and animal health. But the origin, types, seasons of determination of

nitrate and pre analysis treatment method or in general the method of analysis used by these researchers were different and does not seem reasonable to compare, for a simple understanding the results of this study can be compared with the previous studies regardless of all the above differences.

Table 4: Comparison of the results of this work with the literature reported value

Sample sites	Other study		present study
	Concentration on NO ₃ ⁻ (mg/L)		Concentration on NO ₃ ⁻ (mg/L)
Rib, Gumara and Gelda	1.33	Ref.23	1.43-2.5
Mehal Zegie	0.14- 0.66	Ref.22	0.24- 0.60

4. CONCLUSIONS AND RECOMMENDATION

Human activities (examples agricultural practices, deforestation, wastewater discharge, deforestation, industrialization, fertilizer application and discharging of domestic sewages) have induced changes to the freshwater ecosystem bringing ecological imbalance in nature. The differences in concentration of nitrate levels in different sites of the Lake implied that the level of nitrates in the coastal areas depended on the availability of fertilizer intensive agricultural areas in the catchments; domestic wastes from urbanization and industrial effluents from industries. This study revealed contamination of the water body of Lake Tana by nitrates coming from different inflow rivers that consist different contaminants from agricultural areas, wastes from town and service industries. Therefore, developing programs on reduction of eutrophication into the lake through best management agricultural practices and effluent waste water treatment is needed.

Reference

- [1]. Goraw Goshu. Lake Tana water quality base line monitoring annual report, Ministry of water and energy. Tana and Beles integrated water resource development project Tana sub basin organization. Bahir Dar, Ethiopia, (2011), pp. 1-3, 11-12.
- [2]. N.Barrabe's, Jacinto Sâ. Catalytic nitrate removal from water, past, present, and future perspectives. Applied catalysis B: environmental, 104, (2011), pp. 1-5.
- [3]. M. Prosnansky, Y. Sakakibara, M. Kuroda. High- rate denitrification and SS rejection by bio film- electrode reactor (BER) combined with microfiltration. Water research, 36 (2002), pp. 4801-4802.
- [4]. S.Szekeres, Istvnkiss, T.B Tuvioa and M. Ines, M. Soares. Hydrogen dependent denitrification in a two-reactor bio- electro chemical system. Water Res., 35(3), (2001), pp. 715-716.
- [5]. Zeneb Yirgu. Accumulation of Certain Heavy Metals in Nile Tilapia (*oreochromis niloticus*) Fish Species Relative to Heavy Metal Concentrations in the Water of Lake Hawassa, (2011), pp.1-7.
- [6]. R. K Mohammad, T. Rmachar, M.Umamahesh. A study on chemical analysis of drinking water from some communities in Nandyal rural areas of Kurnool district, Andhra Pradesh, India. International journal of civil and structural engineering 2(1), (2011), pp. 351-352.
- [7]. World health organization (WHO). Nitrate and nitrite in drinking water.Back ground document for development of world health organization (WHO) guide line for drinking water quality. WHO, (2011), pp. 1-9.
- [8]. L. Ruiz, S. Abiven, P. Durand, C. Martin, F. Vertes and V. Beaujouan. Effect on nitrate concentration in stream water of agricultural practices in small catchments in Brittany: I. Annual nitrogen- budgets. Hydrology and earth system sciences, 6(3), (2002), pp. 497-498.
- [9]. X. Wang, L. Xing, T. Qin and M. Han. Simultaneous removal of nitrate and penta chloro phenol from simulated ground water using a biodenitrification reactor packed with corn cob, Environmental science pollut Res.,(2012), pp. 1-2.
- [10]. Y.H Liou, S.L. Lo, C.L. Lin, and W.H Kuan, S.C Weng. Chemical reduction of unbuffered nitrate solution using catalyzed and unanalyzed nanoscale iron particles. Journal of hazardous materials B127, (2005), pp. 102-105.
- [11]. R.B. Mohammad and P. Golabatoon. Determination of traces of nitrate in water samples using spectrophotometric method after its pre concentration on microcrystalline naphthalene. Fars Technological and Environmental Research Center, 34, 4, (2011), pp. 607-609.
- [12]. S. Pietro. Nitrate in vegetable: Toxicity, content, intake and electro chemical regulation. Journal of the science of food and agriculture, 86, (2006), pp.10-17.
- [13]. R. Adriana, M. Florica, S. Daniela, B. Georgeta, P. Stephen and S. Joop. Electrochemical determination of nitrate from water sample using Ag- doped zeolite modified expanded graphite composite electrode. Ovidus university annals of chemistry, 20(1), (2009), pp. 61-62.
- [14]. Y. Chebud and A. Melesse. Stage level, volume, and time- frequency information content of Lake Tana using stochastic and wavelet analysis methods. Hydrology and earth system science discussions, (2010), pp. 5526-5528.

- [15]. D.B. Oliver F. Einsle. Structure and function of cytochrome c nitrite reductase .Dissertation submitted to for the degree of doctor of natural Sciences, (1999), pp.11-24.
- [16]. Fitsum Merid. National Nile basin water quality monitoring base line report for Ethiopia.http://nile.riverawarenesskit.org/English/NRAK/Resources/Documentcentre/WQ_Baseline_report-Ethiopia, on May 8, (2013), pp. 11-13.
- [17]. R.C. Jagessar and L.Sooknundun. Determination of nitrate in waste water from nine selected areas of coastal Guyana via a spectrophotometric method. International journal of research and review in applied science, 7(2), (2011), pp. 203-206.
- [18]. WHO (2004) Guide line for drinking water quality, 3rd Ed. Recommendations. World Health Organization, Geneva.
- [19]. Murdoch, T., Cheo M. and O'Laughlin K.(2001) Stream keeper's field guide: Watershed inventory and stream monitoring methods.
- [20]. Chapman, D.(ed.) (1996). Water quality assessments: A guide to the use of Biota, sediments and water. Environmental monitoring. Second Edn.UNESCO, WHO, and UNEP. E and FN spon, London UK.
- [21]. H. Baalousha. Analysis of nitrate occurrence and distribution in ground water in Gaza strip using major ion chemistry. Global nest journal, 10(3), (2008), pp. 337-340.
- [22]. Hillary and Kipngetch. Nitrate anion levels in water from selected wells and points along Kimondi River, Nandi. African Journal of Pure and Applied Chemistry Vol. 6(13), pp. 224-228, November 2012.
- [23]. T. O. Imoobe and O. C Akoma. Assessment of Zooplankton Community Structure of the Bahir Dar Gulf of Lake Tana, Ethiopia. Ethiopian Journal of Environmental Studies and Management, 1(2), (2008), pp.26-28.