WOLKITE UNIVERSITY

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ASSESSMENT OF PHYSICOCHEMICAL PROPERTIES AND HEAVY METAL CONTAMINATION IN HORA HARSADE WATER, BISHOFTU, EAST SHOA ZONE, OROMIA, ETHIOPIA.

MSc. THESIS

NAOL ASSEFA

Sept, 2024

Wolkite, Ethiopia

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ASSESSMENT OF PHYSICOCHEMICAL PROPERTIES AND HEAVY METAL CONTAMINATION IN HORA HARSADE WATER, BISHOFTU, EAST SHOA ZONE, OROMIA, ETHIOPIA.

A Thesis Submitted to School of Graduate Studies, In Partial Fulfillment of the Requirement for the Degree of Master of Science in Chemistry

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APPROVAL SHEET

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We hereby certify that we have read and evaluated this thesis titled "Assessment of physicochemical properties and heavy metal contamination in Hora Harsade water, Bishoftu, East Shoa Zone, Oromia, Ethiopia." prepared under our guidance by Naol Assefa Tola. We recommend that the thesis shall be submitted as fulfilling the requirements for the award of a MSc. Degree in Chemistry.

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DEDICATION

This thesis manuscript is dedicated to all my family, for encouraging me with love dedicated partnership in the success of my life

DECLARATION

By my signature below, I declare and affirm that this Thesis is my own work. I have followed all ethical principles of scholarship in the preparation, data collection, data analysis and completion of this thesis. All scholarly matter that is included in the thesis has been recognition through citation. I affirm that I have cited and referenced all sources used in this document. Every serious effort has been made to avoid any plagiarism in the preparation of this thesis. This thesis is submitted in partial fulfillment of the requirement for a degree from the school of Graduate Studies at Wolkite University. The thesis is deposited in the Wolkite University Library and is made available to borrowers under the rules of the library. I solemnly declare that this thesis has not been submitted to any other institution anywhere for the award of any academic degree, diploma or certificate. Brief quotations from this Thesis may be used without special permission provided that accurate and complete acknowledgment of the source is made. Request for permission for extended quotations from, or reproduction of, this thesis in whole or in part may be granted by the Head of the School or Department or the Dean of the School of Graduate Studies when in his or her judgment the proposed use of the material is in the interest of scholarship. In all other instance, however, permission must be obtained from the author of the thesis.

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BIOGRAPHICAL SKETCH

The author was born from his father Assefa Tola and his mother Gadise Hordofa November 12, 1992 G.C in Kaso Abo kebele, Wacale District, North Shoa Zone of the Oromia regional state, Ethiopia. He started his education at Kaso Abo (1-4) and Nono Kore (5-8) elementary Regasa Wayesa Secondary School (9-10) and completed his senior secondary education at Regasa Wayesa preparatory School in Muke Turi town. Upon successful completion of his preparatory school studies, he then joined Ambo University in September, 2012 and graduated with BA Degree in Chemistry in June, 2015 G.C. He was then assigned by Ethiopian Ministry of Education as secondary school teacher on 2016 to Kersa Mallima district and take pedagogical science at Asosa University 2016-2018 G.C. He upgrades the education level recruited by the government sponsor to join Wolkite University in 2019 G.C in masters of Science in chemistry.

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ABBREVIATIONS AND ACRONYMS

APHA	American Public Health Association
BDL	Below Detection Limit
CDTA	Trans -1,2-Cyclo hexane Diamine Tetra Acetate
DO	Dissolved oxygen
EDTA	Ethylene Glycol Tetra Acetate
ESS	Ethiopia Socioeconomic Survey
EWSD	Ethiopia Water Sector Development
HRDO	High Range Dissolved Oxygen
ICP-OES	Inductively coupled plasma/optical emission spectrometry
IWRM	Integrated Water Resource Management
LOD	Limit of Detection
LOQ	Limit of Quantification
NDWQS	National Drinking Water Quality Standards
NSH	National Sanitation and Hygiene
RSD	Relative Standard Deviation
SD	Standard Deviation
SPPS	Statistical Package for Social Science
TDS	Total Dissolved Solid
TQWR	Tentative South African Target Water Quality Ranges
TSS	Total Suspended Solid
WAE	Water Aid Ethiopia
WHO	World Health Organization

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ABSTRACT

Hora is a type of ground natural mineral water which are used as a source of mineral supplement for livestock. It has the medicinal value to protect the animals from different diseases and useful for their health growth. The aim of this study was to assess Physicochemical Properties and Heavy Metal Contamination in Hora Harsade Water, Bishoftu, East Shoa Zone, Oromia, Ethiopia. The Hora water samples were analyzed for physicochemical parameters and heavy metal concentration using a DR/2400 UV-vis spectrophotometer, flame photometry and ICP-OES by following standard methods and laboratory procedures. The experimental procedures were set according to the international drinking water standards set by American Public Health Association (APHA). The study was carried in Winter, Spring and Summer, 2024. A total of 15 physicochemical properties and 5 heavy metal concentrations were analyzed in order to understand the characteristic and quality status of the Hora natural mineral water with temperature, pH, turbidity, electrical conductivity (EC), total dissolved solids (TDS), total suspended solids (TSS), Total solids (TS), Total Alkalinity (TA), Total hardness (TH), Dissolved solids (DO), Na, K, Ca, Mg, Chloride ion (Cl^-); and heavy metals like: Cu, Fe, Zn, Mn and Cr. The results were evaluated with national (NDWQS, 2013) and international (WHO, 2018) drinking water standard values for human and livestock. The recorded mean concentration of temperature 19.37±0.15 ^{0}C higher than 15 ^{0}C WHO, TSS (91.33±1.15 mg/L) which is above WHO (30 mg/L), Na (318.39±11.35 mg/L) is above 200 mg/L (NDWQS and WHO), and Mn (0.56±0.05 mg/L) which is above permissible limits of NDWQS (0.5 mg/L) and WHO (0.1 mg/L). All the rest listed above properties of water were observed within the recommended permissible limits of CES and WHO standards that agreed with domestic water quality level. Based on the current study result the Hora Harsadee spring water is suitable for domestic purposes after moderate treatment of temperature, TSS, Na & Mn. For more detail quality monitoring, other physicochemical, toxic metals and microbial analysis have to be done in order to have a broader picture of those spring water quantity.

Key Words: Hora Bishoftu, physicochemical parameters, heavy metals, water.

INTRODUCTION

1.1 Background of the Study

Water is one of the most important of all natural resources known on the earth. It is mainly used for drinking purposes which come from the surface and underground water sources. 97% water exists in the oceans which are not suitable for drinking purpose and 3% is fresh water. Of the 3% fresh water 2.97% is comprised of glaciers and ice caps and remaining little portion of 0.3% are available as a surface and groundwater for human use. High quality water is required for drinking purposes for better health (Tademe, 2019). Freshwater is already a limiting resource in many parts of the world. In the next century, it will become even more limiting due to increased population, urbanization and climate changes. Moreover, human beings depend on water for almost every developmental activity. Because of its importance, the pattern of human settlement throughout the history has often been determined by it is availability (Yilkal *etal.*, 2019).

In Ethiopia, the dominant source of drinking water used to supply major rural communities is from springs (Abdisa and Abebaw, 2014). Although there are no systematic and comprehensive water quality assessment programs in the country, there are increasing indications of water contamination problems in some parts of the country. The main causes of this pollution could be soil erosion, domestic waste from urban and rural areas and industrial wastes (Gebrekidan and Samuel, 2011; Abdisa and Abebaw, 2014).

Contaminants are substances that are dissolved in water and make it unfit for use. Some contaminants can be easily identified only by assessing the taste, odor and turbidity of the water because pure water remains tasteless, colorless and odorless. However, most cannot be easily detected and require testing to reveal whether or not water is contaminated. “Hora “is one of the natural mineral water. Mineral water has been used in human nutrition, especially in the different stages of life, during Physical activity and in the presence of some morbid conditions. The use of drinking mineral water as therapeutic and preventive remedies for many diseases affecting the respiratory tract, skin, liver, intestine,Gynecological apparatus and osteoarticular system has been demonstrated (Grassietal.,2002).

Most authors (Fioravanti etal., 2003;Petracciaetal., 2005) have suggested that thermal water is valid tool in the treatment of illnesses, such as functional dyspepsia, irritable bowel syndrome and functional disorders of the biliary tract, because carbonated water stimulates the secretion and motility of the digestive tract.

Furthermore, salt-rich mineral water enhances the conversion of cholesterol into bile acids and their subsequent secretion (Bertoni etal., 2002). The chemistry highly depends on the availability of mineralizing agents, such as temperature, CO_2 concentration, redox conditions and the type of adsorption complex. Mineral water contains different types of dissolved substances, namely minerals and other biological compounds. Spring mineral water has antioxidant, hypocholesterolaemic activity and may affect calcium metabolism (Albertini etal., 2007). For example, sulfurous mineral water was found to have antioxidant properties and a positive effect on the oxidative defense mechanism on both rabbits and rats, respectively. The oral intake of water containing calcium increases serum calcium and inhibits intact parathyroid hormone secretion (Cantalamessa and Nasuti, 2003).

In small concentrations, some heavy metals are nutritionally essential for animals' health. They are referred to as the trace elements. Examples include iron, copper, manganese, and zinc (Bánfalvi, 2011). To understand the importance of protecting water sources, one must begin with a basic understanding of where one's drinking water comes from. The main sources of drinking water are surface and ground water. Ground water is water that fills the open space or pore space, within the surface. Surface water is an open body of water, such as a river, stream, lake (Birhanu, 2007). Unfortunately, clean, pure and safe water only exists briefly in nature and is immediately polluted by prevailing environmental factors and human activities. Water from most sources is therefore unfit for immediate consumption without some sort of treatment (Omezuruike etal., 2008).

According to Tebbutt (1998), spring water is normally of good quality provided that it is derived from an aquifer and is not simply the discharge of a stream which has gone underground for a short distance. Therefore, it is important to maintain this good quality by protecting the spring and its surroundings from contamination by humans and animals (Abdisa and Abebaw, 2014). According to elder people's in Bishoftu city, the common water sources for drinking and other domestic uses is a naturally occurring springs the "Hora" water was used by livestock for drinking and other domestic purpose long time ago. So, people in this area use "Hora "water is still used as natural medicine to cure people and livestock with health problems, and it is observed that livestock always prefer to drink “Hora” water. So that it needs to be given special attention. The international water community continues to highlight good water quality as vital for securing the future of human and animals’ health. Thus, it is needed to emphasize the quality of water in the area under study since the communities are using water of untested quality for drinking and other domestic purposes.

1.2 Statement of the problem

Humans need water in many daily activities like drinking, washing, bathing, cooking etc. The quality of water usually described according to its physical, chemical and biological characteristics. It is necessary that the quality of drinking water should be checked at regular time interval before it is used for drinking, domestic, agricultural or industrial purpose, because due to use of contaminated drinking water, human population suffers from varied of water borne diseases. The availability of good quality water is an indispensable feature for preventing diseases and improving quality of life. Physicochemical parameters of water are important to determine the quality of drinking water (World Health Organization, 1996; Keshebo *etal*, 2015).In Ethiopia, the dominant source of drinking water used to supply major urban and rural communities is from wells and springs. People in rural area communities depend on spring water sources for drinking water, livestock, agriculture as well as other daily activities. The common water sources in Bishoftu rural area communities for drinking and other domestic uses is a naturally occurring springs.

The people living in the area always ride their cattle to the water, because the cattle infected by some diseases use the water as a medicine. There is no research conducted regarding why residents prefer to use the springs and to determine the levels of some heavy metal and physic-chemical properties in Hora Spring water sample in this area.

Thus, these observations have initiated us to explore the physicochemical properties and heavy metal concentration of the Hora Spring water. In the study area there are spring water. Among these spring water, Hora Spring water have a unique taste and livestock always prefer to drink “Hora” water. From the early time, peoples of this area use the Hora water as a medicine for treating the disease of animals. This initiated the researcher to assess the selected physicochemical characteristics and heavy metal concentrations in Hora Spring water in Bishoftu Hora Harsade.

1.3 Objectives of the study

1.3.1 General objective

Assessment of Physicochemical Properties and Heavy Metal Contamination in Hora Harsade Water, Bishoftu, East Shoa Zone, Oromia, Ethiopia.

1.3.2 Specific objective

a. To determine the concentration of selected heavy metals (Mn, Fe, Zn, Cu and Cr) in Hora harsade water.
b. To determine selected physical parameters (temperature, pH, turbidity, electrical conductivity, total dissolved solid, total suspended solid, total solid,) of the Hora Harsade water.
c. To determine selected chemical parameters (total alkalinity, Total hardness, dissolved oxygen, Na, K, Mg, Ca and Chloride Cl^-) of the Hora Harsade water.
d. To compare the result of this study with that of national and international drinking water standard values for human and livestock.

1.4 Significance of the study

This study is significant to all people living in the Bishoftu rural area. Frequent analysis of physicochemical properties and heavy metal concentration of water quality is the most sensitive way of assessing the hygienic conditions of water. Based on the finding, possible recommendations was suggested on the periodic water quality test and monitoring system and also to pinpoint important water contamination measures and to give base line information for further studies in the area selected.

2.LITERATURE REVIEW

2.1 Water Quality Supply

Worldwide, water is the most important natural resources of the ecosystem, having an important role for both drinking as well economic sectors. In the last century the availability and quality of surface or ground waters has been change, mainly due to urbanization, industrialization etc. The water quality can be assessed using physical, chemical and biological parameters, the harmful limits of those for human health being establish at international or national scale (WHO, EPA, CES) (Paiu and Breaban, 2014). Consequently, water quality can be defined by a range of variables which limits water use. Water quality is affected by a wide range of natural and human influences. The most important of the natural influences are geological and hydrological and climatic since these affect the quality of water viable (WHO, 2011). Throughout history, the quality of drinking water has been a factor in determining human welfare. It is clear that water pollution should be a concern of every citizen. Understanding the sources, interactions, and effects of water pollutant is essential for controlling pollutants in an environmentally safe and economically acceptable manner (Bizualem, 2017).

The quality of water, whether it is used for drinking, irrigation or recreational purposes, is significant for health in both developing and developed countries. In early days, water was primarily used for domestic needs like drinking, washing, bathing, cooking and etc. But due to industrial and urban development, requirement of water for these activities has increased along with domestic purpose (Bizualem, 2017). It is well known that water have played a crucial role in the growth and development of society. Urban growth, increased industrial activities, intensive farming and over use of fertilizers in agricultural productions are identified as major driving agents for degradation of water bodies.

2.2 Spring Water

A spring or seep occurs when groundwater emerges naturally on the earth’s surface by either gravity or artesian pressure. Springs have traditionally been used by allowing people and livestock direct access to the water and spring site. Springs commonly occur along hillsides and in low areas where porous soils or fractured rock formations allow water to flow onto the ground surface. Springs can occur at a single point or over a large area, called a seep. A slow hillside seep or trickle where no visible water flow is observed should not be considered a true spring.

Spring water is a system containing both the main course and the tributaries, carrying the one-way flow of important load of matter in liquefied and particulate phases from both natural and anthropogenic sources. Most springs will need some treatment before the water is considered harmless for drinking. Testing helps to regulate exactly how much treatment is necessary and may help to decide if other sources of water would be more economical (Lankford, 2018).

2.3 Uses of water

Water is the basic element of living things: they could not have appeared and could not survive without (Petraccia etal, 2006). The use of water includes drinking, washing and cleaning, transportation, providing hydroelectric power, irrigation and recreation. Living things need water to move nutrients in to their cells and to help them excrete wastes and toxins. Water is necessary in many chemical reactions and laboratory tests. Water is also necessary for many medical procedures, including dental treatments and dialysis. Clean water is an essential resource for drinking, irrigation, industry, transportation, fishing, support of biodiversity, and for absolute esthetic enjoyment (Morris *etal.*, 2003).

2.4 Heavy Metals: Sources, Properties, and Environmental Impact

The term heavy metal refers to metallic chemical elements that have relatively high density, toxic or poisonous at low concentration values. Heavy metal contamination is a major environmental concern due to the toxicity, carcinogenicity and mutagen city even at low concentration. They can cause damage to practically all organs of the body. The main sources of the heavy metal ions directly are food and water and indirectly, industrial activities. Drinking water is also an important source for heavy metals for humans (Ghaedi et al., 2005).

Heavy metals are elements with high atomic weights that are generally toxic in relatively low concentrations to plant and animal life. They tend to accumulate in the food chain. Living organisms require trace amounts of some heavy metals, including cobalt, copper, iron, manganese, molybdenum, vanadium, strontium, and zinc. Excessive levels of essential metals, however, can be detrimental to the organism. Nonessential heavy metals of particular because of their toxicity are cadmium, chromium, mercury, lead, arsenic, and antimony (Johns, 2011).

Copper (Cu)

Is both an essential nutrient, and a drinking water contaminant, but at high doses it has been shown to cause stomach and intestinal distress, liver and kidney damage and anemia. Cu in a drinking water supply usually arises from the corrosive action of water leaching Cu from Cu pipes in buildings. High concentrations can interfere with the intended domestic uses of the water. Staining of sanitary ware and laundry may occur at Cu concentrations above 1 mg/l. At levels above 5 mg/L, Cu also imparts a color and an undesirable bitter taste to water. Although Cu can give rise to taste, it should be acceptable at the health-based guideline value of 2 mg/L (Sokrab et al., 2010). The level of Cu regulation for drinking water standard values for humans is about 1.00 mg/L, and 1.5 mg/L is proposed for livestock water quality by WHO guide line (Tibebu et al., 2017). The guideline value of copper proposes by WHO in drinking water is to be 2 mg/L and the recommended EPA value is 1mg/L (Osman, 2021). At low concentration it may cause vomiting and nausea (Sokrab et al., 2010). The South African guideline for Cu in domestic water supply is < 1.0 mg/L.The TQWR for Cu in water for livestock watering is < 5 mg/L and the adverse chronic effect may occur at 1 to 10 mg/L Cu, depending on the livestock (Davies *et al.*, 2006).

Manganese (Mn)

Is one of the most abundant metals in the Earth crust, usually occurring together with iron (World Health Organization, 2004; Mezgebeetal., 2015). Manganese greensands are used in some locations for potable water treatment. Manganese is an essential element for humans and animals (Mezgebe *etal.*, 2015). Manganese occurs in over 100 common salts and mineral complexes that are widely distributed in rocks and soils. Manganese is generally present in natural surface water at concentrations below0.04 mg/L. It is regarded as one of the least toxic elements; toxicity in humans is usually the result of chronic inhalation of high concentrations of manganese in dust from industrial sources. At levels exceeding 0.15 mg/L, manganese stains plumbing fixtures and laundry and causes undesirable tastes in beverages. It may lead to the accumulation of microbial growths in the distribution system that could give rise to taste, odor, and turbidity problems in the distributed water (Edition, 2011). It does not occur in nature as the elemental metal, but is found in various salts and minerals, frequently along with iron compounds (Hedayati and Safahieh, 2012). The level of Mn regulation for drinking water standard values for humans is about 0.40 mg/L, and no health-based guide value is proposed for livestock water quality by WHO guide line (Tibebu, 2017).

Iron (Fe)

Iron s one of the most abundant heavy metals in Earth's crust. Its chief ores are the red-orange hematite (Fe_2O_3) and the black magnetite (Fe_3O_4). Fe contains both the +2 and +3 oxidation states (Csuros and Csuros, 2016). Fe is found in natural fresh waters at levels ranging from 0.5 to 50 mg/l. Fe may also be present in drinking waters a result of the use of Fe coagulants or the corrosion of steel and cast-iron pipes during water distribution. Fe is an essential element in human nutrition, particularly in the Fe(II) oxidation state (World Health Organization,2004).Iron is an essential and non-conservative trace element found in significant concentration in drinking water because of its abundance in the earth's crust (Gebrekidan and Samuel ,2011; Ezekweetal., 2017). The level of Feregulation for drinking water standard values for humans is about 0.40 mg/L, and no health-based guide value is proposed for livestock water quality by WHO guide line (Tibebu, 2017).

Zinc (Zn)

Zink is one of the most common elements in the earth's crust. It is also an essential element for all living things (Gyamfietal., 2012). Zinc is mostly found in some natural waters close to mining source. Zinc in drinking water is not a treat to health unless its level is very high. The diet is normally the principal source of Zn. Although levels of Zn in surface water and groundwater normally do not exceed 0.01mg/l, 0.05 mg/l, and 3mg/l respectively, concentrations in tap water can be much higher as a result of dissolution of Zn from pipes. It was considered that the derivation of a formal guideline value for Zn is not required. However, drinking water containing Zn at levels above 3 mg/L may not be acceptable to consumers (World Health Organization, 2004; Csuros and Csuros, 2016). Very high Concentrations may cause a bitter taste and opalescence in alkaline water (Gyamfietal, 2012). The level of Zn regulation for drinking water standard values for humans is about about 0.10 mg/L, and 24 mg/L is proposed for livestock water quality by WHO guide line (Tibebu, 2017).

Chromium (Cr)

Is widely distributed in Earth‟s crust. It occurs in minerals mostly as chrome iron ore, or chromite ($FeCr_2O_2$), in which it is present as Cr (III). In natural waters, dissolved Cr exists as either Cr^{3+}cations or in anions such as chromate ($CrO_4{}^{2-}$) and dichromate ($Cr_2O_7{}^{2-}$), where it is hexavalent with oxidation number +6. Though widely distributed in soils and plants, it generally is present at low concentrations in natural waters. Background levels in water typically range between 0.2 and 20μg/L, with an average of 1 μg/L (Johns, 2011). The level of Cr regulation for drinking water standard values for humans is about 0.05 mg/L, and 1.0 mg/L is proposed for livestock water quality by WHO and recommended EPA guide line (Tibebu *et al.*, 2017; Osman, 2021).

2.5 Physicochemical Properties of water

Physical and chemical parameters of drinking water quality are important not only in the assessment of the degree of pollution but also in the choice of the best source and the treatment needed. It gives an indication of water acceptability for human consumption which can be domestic, agricultural and industrial uses. The parameters must be taken in to consideration in the assessment of water quality such as source protection, treatment efficiency and reliability and protection, of the distribution network (WHO, 2011). Physical and chemical properties are parameters that do not identify particular chemical species but have used as an indicator of how water quality may affect water uses (Tadesse *et al.*, 2018). Selection of parameters for testing of water quality is solely depends upon for what purpose we are going to use that water and what extent we need its quality and purity.

Physical and chemical properties are factors that do not detect particular chemical species but are used as pointers of how water quality may affect water uses. These are temperature, electrical conductivity and hydrogen ion concentration (measured as pH), and (Huo etal., 2009; Hedayati and Safahieh, 2012).

2.5.1 Physical parameters

Some physical parameters of water may include: temperature, pH, turbidity, electrical conductivity, total solids, total suspended solids, total dissolved solids, etc.

Temperature of water

Is a significant biologically important factor, which plays a vital role in the metabolic activities of the organism. Cool water is generally more acceptable than warm water, and temperature will have an effect on the palatability of a number of other inorganic constituents and chemical contaminants that may affect taste. High water temperature enhances the growth of microorganisms and may increase problems related to taste, odor, color and corrosion

(Gopalkrushna,2011). The temperature regulation for drinking water standard values for humans is about 15^0C according to Canadian Ministry of Health, and 4.4-18.3^0C is for livestock water quality set by WHO guide line (Tibebu, 2017).

pH of water

The pH of most natural water falls within the range of 4 to 9. The majority of waters are slightly basic (i.e. generally over 7.0) because of the presence of carbonate and bicarbonates (Maitisk, 2004). The pH value is an indicator of the chemical state in which these compounds will be found and must be considered when establishing water quality standards. The pH of pure water at 25^oC is 7.0, but the pH of environmental waters is affected by dissolved $CO_2$and exposure to minerals (World Health Organization, 2004; Hedayati and Safahieh, 2012); Pradhan etal., 2011). The PH regulation for drinking water standard values is about 6.5-8.5 according to Ethiopian and WHO guideline for humans and for livestock water quality (Tibebu, 2017).

Turbidity

Turbidity is the cloudiness of water caused by a variety of particles and is another key parameter in drinking water analysis. It is also related to the content of diseases causing organisms in water, which may come from soil runoff (Rahmanian et al., 2015). The turbidity is one of the important physical parameters for water quality, defining the presence of suspended solids in water and causes the muddy or turbid appearance of water body. The consumption of high turbid water may cause a health risk, as excessive turbidity can protect pathogenic microorganisms from effects of disinfectants (Shigut et al., 2017). According to (Ameen., 2019) the higher levels of turbidity caused by suspended solid particles are due to fast transport pathway connecting potentially contaminated surface water with the aquifer. The low turbidity value is to indicate an absence of such contamination transport pathways. Turbidity is the cloudiness of water caused by a variety of particles and is another key parameter in drinking water analysis. It is also related to the content of diseases causing organisms in water, which may come from soil runoff. The standard recommended maximum turbidity limit set by WHO and National Drinking Water Quality Standard (NDWQS), for drinking water is 5 Nephelometric turbidity units (NTU) (Sokrab et al., 2010). For health purpose it should be less than 1 NTU. High turbidity in water hinders the disinfection of pathogenic microorganisms, thus it can cause health risk (Sokrab et al.,
2010; Tadesse *et al.*, 2018)

Electrical Conductivity (EC)

Is the measure of the capacity of water to transmit an electric current and depends upon the number of ions or charged species in the water (Maitisk, 2004; Gyamfi *etal.,* 2012; Tademe, 2019). The EC is the reciprocal of resistivity (R): EC = 1/R and is reported in millisiemens/cm (mS/cm) or mS/cm. It is related to the quantity of minerals present in water, but does not specify which element is present. High values of electrical conductivity mean that there are pollutants such as chloride, sodium (Ezekwe *etal.*, 2017). High values of conductance can be indicative of salinity problems but also are observed in eutrophic waterways where plant nutrients (fertilizer) are in greater abundance (Rodriguez *etal.* 2009; Chaabane *etal.*, 2017). No health-based guideline value is recommended by Ethiopian, and 1,500 mg/L according to WHO standard values for human respectively Soluble salt in drinking water have different effect on livestock for example, if the value is less than 1,000 mg/L, it is safe to drink and pose no health problems. If it is in between 1,000 and 2,999 mg/L, typically is safe to drink, may cause mild diarrhea; while 3,000–4,999 mg/L, cattle may initially refuse, may cause diarrhea and optimal performance not achieved due to lower water intake rates (Tibebu, 2017).

Table 1: Water classification based on electrical conductivity (Detay, 1997).

EC (μS/cm)	Mineralization
<1000	Very weakly mineralized water
1000-2000	weakly mineralized water
2000-4000	Slightly mineralized water
4000-6000	moderately mineralized water
6000-10000	Highly mineralized water
>10000	Excessively mineralized water

Total Dissolved Solid (TDS)

TDS, which is a measure of the salinity of groundwater, is also frequently used as a useful parameter for evaluating the quality of water and for classifying drinking and irrigation water. TDS is usually estimated by electrical conductivity (EC) and there is a strong relationship between EC and TDS. EC refers to the direct measure of TDS (Ameen., 2019). TDS to materials that is totally dissolved in water (WHO, 2004; Hadera., 2018). A large number of solids are found dissolved in natural waters, the common ones are carbonates, bicarbonates, chlorides, sulphates, phosphates, and nitrates of calcium, magnesium, sodium, potassium, iron, magnesium etc. In other words, TDS is simply the sum of the cations and anions concentration expressed in mg/L (Aly *et al.*, 2015). TDS can also be taken as an indicator for the general water quality because it directly affects the aesthetic value of the water by increasing turbidity. High concentrations of TDS limit the suitability of water as a drinking source and irrigation supply (Amanial *et al.*, 2015). The Recommended Standards for drinking water quality by EPA value is 200mg/L (Ameen., 2019). Taste problems in water often arise from the presence of high TDS levels with certain metals present, particularly iron, copper, manganese, and zinc (WHO, 2004; Hedayati and Safahieh, 2012); Pradhan *et al.,* 2011). According to WHO, the palatability of water with a TDS level of less than about 600 mg/L is generally considered to be good. Drinking water becomes significantly and increasingly unpalatable at TDS levels greater than about 1,000 mg/L. The amount of TDS for drinking water is No guideline values according to Ethiopia guide lines. But 1000 and 10000 mg/LWHO standard values of drinking water for human and for livestock respectively (Tibebu et al., 2017). The Potential health effects of TDS are undesirable taste, gastro-intestinal irritation, corrosion or incrustation (Tadesse *et al.*, 2018).

Table 2: Classification of water according to TDS (Selvam et al, 2012)

Water class	TDS (mg/L)
Fresh	<1000
Brackish	1000-10000
Saline	10,000-100,000
Brine	>100,000

Total suspended solid (TSS)

The movement and migration of total suspended solid (TSS) are the essential component of global material cycling and change. The spatial and temporal variation of TSS concentrations in estuaries and coasts are not only the issues of economic production activities closely related to estuarine coast, such as trade, transportation and fishery production, but also the focus of sustainable development of the human society, such as coastal zone planning and ports and waterways construction (Wang et al.,2018). According to national drinking water quality Standard (NDWQS), the maximum standard limit of TSS is 25mg/L (Popoola et al., 2019).

Total alkalinity (TA)

Alkalinity is a measure of its capacity to neutralize acid. That is, alkalinity is a measure of buffering acity of water. It is the sum of all the titrable bases. The major portion of alkalinity in natural waters is caused by hydroxide, carbonate, and bicarbonate. For practical purposes, alkalinity due to other materials in natural water is insignificant and may be ignored (Aly et al., 2015).There is no health based guideline value for alkalinity but it does contribute to the amount of total dissolved solids (TDS). Which has an esthetic guideline value of 400 mg/L. Levels between 30 and 400 mg/L are suitable for human drinking water, while no standard value was set for livestock both at national as well as international level (Tibebu et al., 2017). NO guideline value of total alkalinity proposed by WHO in drinking water is to be and the recommended EPA value is 11 <500mg/L (Osman, 2021). Alkalinity of water is not regarded as a pollutant so no limit is recommended by WHO for safe drinking water. High alkalinity values reflect high carbonate and bicarbonate ions and direct association between EC and alkalinity (Sokrab et al., 2010).

Table 3: Relationship between Hydroxide, Carbonate, and Bicarbonate alkalinities

Result of titration	OH^- alkalinity as $CaCO_3$	CO_3^{2-} alkalinity as $CaCO_3$	HCO_3^- alkalinity as $CaCO_3$
P=0	0	0	T
P<1/2T	0	2P	T-2P
P=1/2T	0	2P	0
P>1/2T	2P-T	2(T-P)	0
P=T	T	0	0

P=phenolphthalein alkalinity; T = Total alkalinity.

2.5.2 Chemical parameters

Total hardness (TH)

Hardness may be divided into two types, carbonate and non-carbonate. Carbonate hardness includes portions of Calcium and Magnesium, and certain number of bicarbonates. Non carbonate hardness is caused by the association of the hardness-causing cation with sulphate, chloride or nitrate. This type of hardness cannot be removed by boiling Hardness caused by Calcium and Magnesium is usually indicated by precipitation of soap scum and the need for excess use of soap to achieve cleaning. In some instances, consumers tolerate water hardness in excess of 500 mg/L (Pradhan and Pirasteh, 2011).

Hardness is a natural characteristic of water which can enhance its palatability and consumer acceptability for drinking purposes. Health studies in several countries in recent years indicate that mortality rates from heart diseases are lower in areas with hard water. Total hardness is taken to comprise the calcium and magnesium concentrations expressed as mg/L CaCO3. Total hardness is defined as the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate in mg/L (Osman, 2021). No health-based guideline value is recommended by Ethiopian and 400mg/L according to WHO standard for drinking water standard values for humans. No standard value was given national and international for livestock (Tibebu et al., 2017). NO guideline value of total hardness proposes by WHO in drinking water is to be and the recommended EPA value is <500mg/L (Osman, 2021).

Table 4: Different classification of water according to hardness (mg/L) guidelines for livestock (Edition, 2011)

Hardness (mg/L)	Water classification
0-60	soft
61-120	Moderately hard
121-180	Hard
181-350	Very hard
>350	Brakish

Dissolved oxygen (DO)

Dissolved oxygen is one of the most important parameters in assessing the quality of water, which is essential to maintain biotic forms in water. Oxygen content of water varies with temperature, salinity, turbulence, photosynthetic activity of algae and higher plants atmospheric pressure (Pandit et al., 2013). The amount of DO, which represents the concentration of chemical or biological compounds that can be oxidized and that might have pollution potential, can affect a sum of processes that include re-aeration, transport, photosynthesis, respiration, nitrification, and decay of organic matter. Low DO concentrations can lead to impaired fish development and maturation, increased fish mortality, and underwater habitat degradation (Iticescu et al., 2013). No health-based guideline value is recommended by Ethiopian and 4.5-7.5 according to WHO standard for drinking water standard values for humans. No standard value was given national and international for livestock (Tibebu et al., 2017). Dissolved oxygen in water the recommended limit of WHO (14mg/L) which doesn‟t makes it feasible for drinking (Sokrab et al., 2010).

Calcium (Ca)

Ca is an essential nutrient for plants and animals, essential for bone, nervous system, and cell development. Ca in food and water is essentially nontoxic. A number of studies suggest that water hardness protects against cardiovascular disease. One possible adverse effect from ingestion of high concentrations of Ca for long periods of time may be a greater risk of kidney stones. The presence of Ca in water decreases the toxicity of many metals to aquatic life. Thus, the presence of Ca in water is beneficial and no limits on Ca have been established for protection of human or aquatic health (Abdisa and Abebaw, 2014).

Calcium is found in bones and teeth, where it roles as a key structural elements. The remaining body calcium function in metabolism serving as a signal for vital physiological processes, including vascular contraction, blood clotting, muscle contraction and nerve transmission. Inadequate intakes of calcium have been associated with risks of osteoporosis, nephrolithiasis (kidney stone), colorectal cancer, hypertension and stroke, coronary artery disease, insulin resistance and obesity. However, no health guideline value proposed by WHO to Calcium in drinking water (Foster and Chilton, 2003).

Calcium is an important element for good health and levels between 20 and 30 mg/L are desirable in drinking water. Very high levels of calcium however, were produce scale and clog up water pipes. Calcium is one of the major elements responsible for water hardness. Water containing less than 60 mg/L of Ca is considered as soft water (Ezeldin, 2016). The amount of calcium for drinking water is 200 mg/L according to Ethiopia guide lines and WHO standard values of drinking water for human. But, the guideline WHO standard values of drinking water for cattle is 1000mg/L (Tibebu et al., 2017). NO guideline value of magnesium proposes by WHO in drinking water is to be and the recommended EPA value is ≤75mg/L (Osman, 2021)

Magnesium (Mg)

Mg is an essential nutrient for plants and animals, essential for bone and cell development. Mg in water is beneficial and no limits on Mg have been established for protection of human or aquatic health. There are no primary or secondary drinking water standards for Mg. Mg in drinking water may provide nutritional benefits for persons with Mg deficient diets (Abdisa and Abebaw, 2014).

Magnesium is an element that is critically involved in cardiac and vascular function. Small change in concentration has significant effect on cardiac excitability and on vascular tone, contractility, reactivity and growth. Increased concentration of extracellular magnesium cause vasodilation, improve blood flow, decrease resistance, increase capacitance function of peripheral, coronary, renal and cerebral arteries and attenuate agonist induced vasoconstriction, whereas decreased concentration causes contraction, potentiate agonist evoked vasoconstriction and increase vascular tone (WHO, 2009) . Low magnesium status has been implicated in hypertension, coronary heart disease, type 2 diabetes mellifluous and metabolic syndrome. The case–control studies showed that reduced cardiovascular mortality occurred at magnesium concentrations in water is above 10 mg/L. Increased intake of magnesium salts may cause a temporary adaptable change in bowel habits (diarrhea), but seldom causes hypomagnesaemia in persons with normal kidney function. However, above 250 mg/L of magnesium concentration in drinking-water can have a laxative effect (WHO, 2010). The Mg/Ca molar ratios lie mostly in the range 0.20– 1.84, indicating weathering of pure dolomite's; however, the highest value indicates for relatively impure higher Triassic dolomites. The amount of magnesium for drinking water is 50mg/L and 100mg/L according to Ethiopia guide lines and WHO standard values of drinking water for human respectively. But, No guideline WHO standard values of drinking water for cattle (Tibebu et al., 2017). NO guideline value of magnesium proposes by WHO in drinking water is to be and the recommended EPA value is ≥10mg/L (Osman, 2021).

Sodium (Na)

Sodium is a silver white metallic element and found in less quantity in water. Proper quantity of sodium in human body prevents many fatal diseases like kidney damages, hypertension, headache etc. The major source of Na were soap and detergent factory that uses caustic soda (NaOH) as a major raw material for soap manufacturing and sodium citrate and sodium silicate to produce liquid detergents; and naturally from sodium salts (e.g. sodium chloride). Sodium is a mineral found naturally in some drinking water. Too much sodium have identified as a risk factor for high blood pressure (Tadesse *et al*., 2018). It is a metallic element that is an important mineral for all living organisms. Almost all groundwater and surface water contains sodium (Ezekwe etal., 2017). Na is an important constituent for determining the quality of irrigation water. Most Na salts are readily soluble in water, but take no active part in chemical reactions. Na has large variations in its concentration in ground water (Pradhan *etal.*, 2011).

The levels of sodium salts in air are normally low in relation to those in food or water. It should be noted that some water softeners can add significantly to the sodium content of drinking water. No firm conclusions can be drawn concerning the possible association between sodium in drinking water and the occurrence of hypertension. Therefore, no health based guideline value is proposed. In most of the countries, majority of water supply bears less than 20 mg/L, while in some countries the sodium quantity in water exceeded from 250 mg/L (Meride and Ayenew, 2016). However, concentrations in excess of 200 mg/L may give rise to unacceptable taste (WHO, 2017).

Potassium (K)

Is occurs widely in the environment, including all natural waters. It can also occur in drinking water as a consequence of the use of $KMnO_4$ as an oxidant in water treatment. In some countries, KCl is being used in ion exchange for household water softening in place of, or mixed with, NaCl, so K ions would exchange with Ca and Mg ions. Possible replacement or partial replacement of Na salts with K salts for conditioning desalinated water has been suggested.

The latter seems to be an unlikely development at this stage, in view of the cost difference. Currently, there is no evidence that K levels in municipally treated drinking water, even water treated with $KMnO_4$, are likely to pose any risk for the health of consumers. It is not considered necessary to establish a health-based guideline value for K in drinking water (World Health Organization, 2004). The amount of potassium for drinking water is 5mg/L according to Ethiopia guide lines. But, No guideline WHO standard values of drinking water for human and for cattle (Tibebu, 2017).

Chlorides

Is normally the most dominant anion in water and it imparts salty taste to the water. Chlorides are widely distributed in nature, usually in the form of Na, K, and Ca salts (NaCl, KCl and $CaCl_2$), although many minerals contain small amounts of chloride as an impurity. Chloride is the most abundant anion in the human body and is essential to normal electrolyte balance of body fluids. Chlorides in water are more of a taste than a health concern, although high concentrations may be harmful to people with heart or kidney problems. There are no primary drinking water standards for chloride. The EPA secondary standard for chloride is 250 mg/l, based on adverse effect on taste (World Health Organization, 2004; Hedayati and Safahieh, 2012); Pradhanetal., 2011; Amanialetal., 2015). According to the USEPA guideline high level of Cl^- results eye/nose irritation; stomach discomfort and increase corrosive character of water (Amanial etal., 2015).The amount of chloride for drinking water is 30mg/L and 250mg/L according to Ethiopia and WHO standard values for human respectively. No guideline stated showing chloride content for cattle drinking water according to WHO guidelines (Tibebu, 2017).

2.1 Inductively coupled plasma/optical emission spectrometry (ICP-OES)

Inductively coupled plasma/optical emission spectrometry (ICP/OES) is a spectroscopic technique suitable for trace elements analysis in several types of samples. The technique is based on the unprompted emission of photons from atoms and ions that have been excited in a radiofrequency (RF) discharge. Samples are usually introduced into the plasma in liquid form; thus, solid samples require acid digestion prior to injection, while gas and liquid samples may be injected directly into the instrument. The sample solution is converted to an aerosol then sends into the Centre of the plasma which maintains high atomization temperature of around 10,000 K. As the plasma free atoms in the gaseous state are generated and adequate energy is often available to convert the atoms to ions then promote the ions to excited states. The ionic excited state species may then return to the ground state via emission of photons. Specific wavelength of the photons can be used to identify the elements and the number of photons is directly proportional to the concentration of the element in the sample (Figure 1). A variety of sample introduction methods are used in this technique such as nebulization, hydride generation (HG) for certain elements such as arsenic, selenium, and antimony, as well as electro thermal vaporization (ETV) and laser ablation.

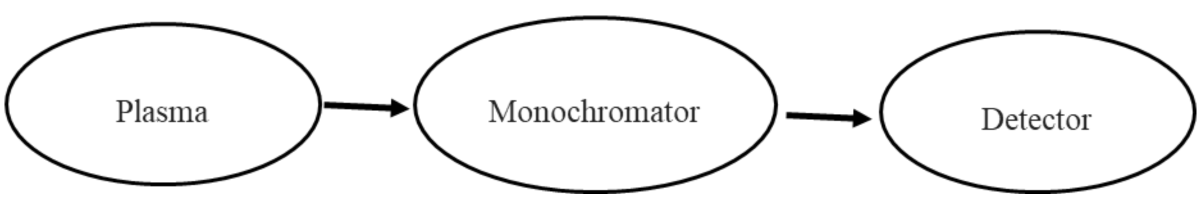

Figure 1: Basic ICP-OES

MATERIALS AND METHODS

1.5 Description of the Study Area

The study was conducted at Hora Harsade water in Celelake Sub-city Bishoftu City, Oromia, Ethiopia. Bishoftu City is one of the attractive City of Eastern Oromia. It is located in the East Showa Zone 40 km from Addis Ababa. The specific location is 8^0 44′ 4.74″ North latitude, 39^0 0′ 30.726″ East longitudes and sits at an elevation of 1920 m above sea level. According to the recent statistical data of the Bishoftu City statistical agency authority, the total population is 207,383 of 98,277 male and 109,106 female.

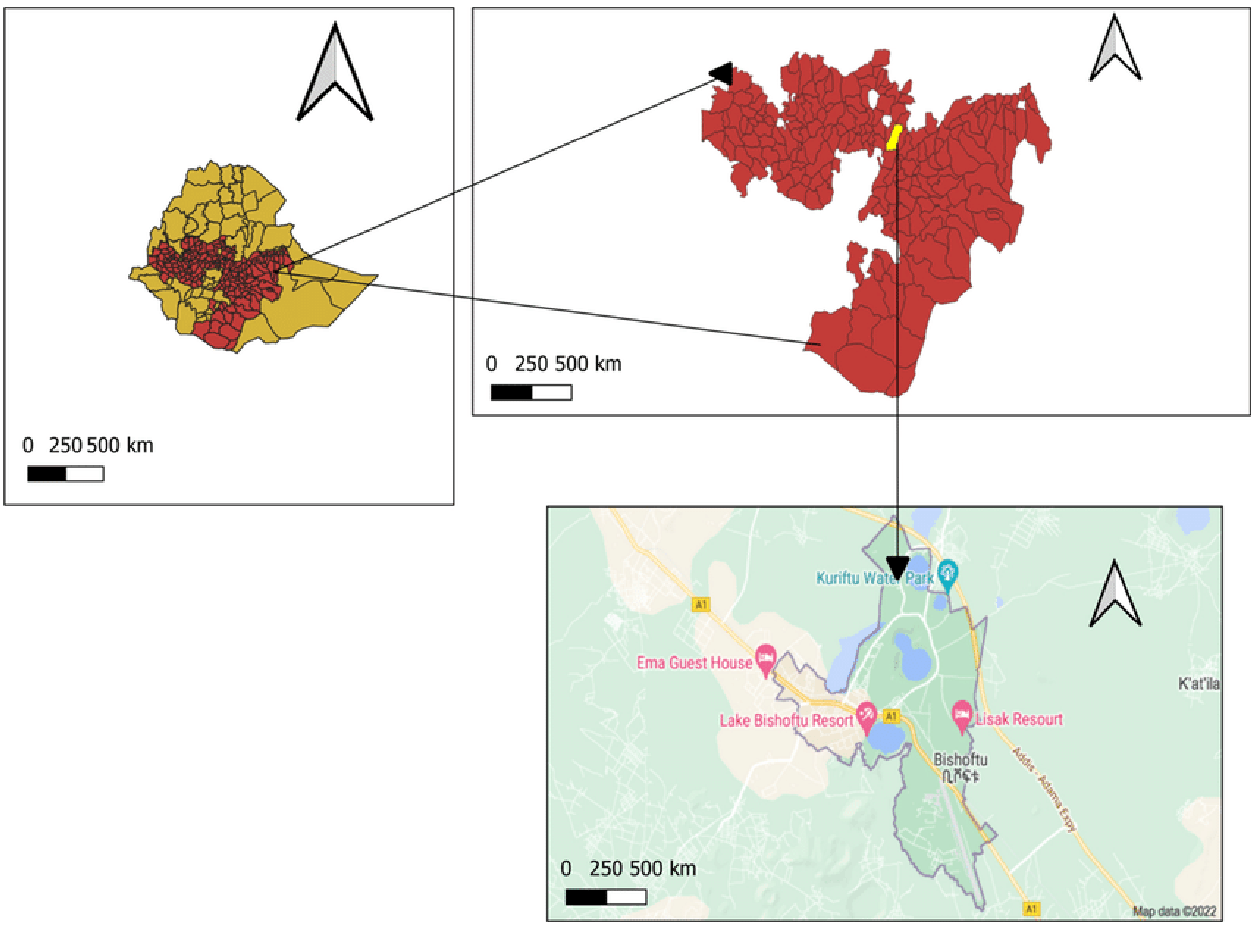

Figure 2: Location of maps of the study area

1.6 Experimental site

The data was analyzed in three separate seasons (Winter, Spring and Summer, 2024) and their values were determined in Bishoftu Hort Coop (Agricultural Research Center) Oromia, Ethiopia.

1.7 Materials

1.7.1 Instrument and Equipment

Table 5: Parameters and Analytical method used

Parameters	Units	Method used	Instrument
Temperature	^{o}C		Thermometer
pH			Portable digital pH meter
Turbidity	NTU		Portable Turbidity Meter
EC	µS/cm		TDS/ Conductivity meter
TDS	mg/L		TDS/ Conductivity meter
TSS	(mg/L)	Photometric	HANA Multi parameter
Total Hardness	mg/Las $CaCO_3$	Chlorophosphonazo	Spectrophotometer
Calcium	mg/L	Calmagnite colorimetric	Spectrophotometer
Magnesium	mg/L	Calmagnite colorimetric	Spectrophotometer
Potasium	mg/L	Tetra phenyl borate	Spectrophotometer
DO	mg/L	HRDO	Spectrophotometer
Total alkalinity	mg/Las $CaCO_3$	Titration	Digital Titrator
Chloride	mg/L	Mercuric thiocyanate	Spectrophotometer
Cu, Zn, Fe, Mn, Cr	(mg/L)		ICP-OES

One liter (1L) clean polyethylene bottles that has been washed with acid and deionzed water before sample collection was used as sample holder during sample collection. Label of bottles also used for identification. Ice-box was used for preservation during sample transportation. pH/temperature water proof meter and portable TDS/ Conductivity meter were used for temperature, pH and electrical conductivity, TDS measurements at site, respectively. Micropipettes or pipettes were used to prepare accurate concentration of standard solution. Volumetric flasks were also used to hold standard and sample solutions. Burettes were used during titration. Desiccator-with moisture indicating desiccant and evaporating dish will be used during TDS determination. AA-200DS analytical balance that is being calibrated with a known 100g mass was used for calibration of glassware and weighing of reagent. Portable turbidity meter (ZM-2002) was used for turbidity measurement. Inductively Coupled Plasma/Optical Emission Spectroscopy (ICP/OES) was used for determination of heavy metal contents (Na, Cu, Mn, Fe, Zn & Cr) and Portable DR/2400 Uv-Vis Spectrophotometer used for determination of other chemical parameters like DO, K, Ca, Mg, Total hardness (TH) and Chloride.Refrigerator was used to keep the digested sample until analysis. The concentration of sodium in the spring water samples was estimated by flame photometry. Measuring cylinder (10, 25, 50 and100 mL) and pippete was employed for measuring of volume of the sample solution, acid reagent and metal standard solution. Volumetric flask (25, 50,100, and 250 mL) was used for dilution of the sample and preparation of the sample. Fume hood was used to exhaust chemical fume. Whatman filter paper No.41 was used for the sample after digestion. Heating digester was employed to heat the digestion tube with programmed temperature. Different sized beakers, funnels, droppers, Poly ethylene bags, conical flask equipment was required during the study.

1.7.2 Chemical and reagent

All the chemicals and reagents used in this study were analytical graded. Distilled water was used for washing, all solution preparation and dilution purposes through the study. 1000 mg/L standard stock solutions including 1.0mL of HCl (37%), 0.5 mL H_2O_2 of (30%) solution, and 2 % HNO_3 (67-72%) for each metal (Fe, Cu, Zn, Mn, Cr and Na) were used for preparation of calibration standard and spiking the experiments. Buffer Solutions (pH 4.01±0.02, 7.00±0.02 and 10.01±0.02 at 25^0C) for calibration of pH meter. Potassium 1, 2 and 3 Reagent Pillow were used for determination of potassium. Chlorophosphanazono & CDTA reagent was used for determination of total hardness. A high range dissolved oxygen was used for determination of DO. Chlorophosphonazo Solution and CDTA Reagent for Ultra Low Range Hardness were used for examination of total hardness (TH), Phenolphthalein indicator, 0.02 N H_2SO_4 & Bromcresol indicator was used for the determination of total alkalinity (TA). Calcium and magnesium indicator solution, alkali solution, EDTA solution, EGTA solution was used for the determination of Calcium and magnesium. Mercuric Thiocyanate solution and ferric ion solution was used for the determination of chloride ion (Cl^-).

1.8 Methods

1.8.1 Water sample collection and pretreatment procedure

By known procedure (Tadesse *et al.*, 2018), the water samples were collected from Hora harsade spring water. Sample was drawn with the aid of bottles drawer into two same types of polyethylene bottles that were 1L for physicochemical parameters and 1L heavy metal concentration analysis by composite sampling technique, i.e., the samples were collected during the afternoon 12:00 -1:00 PM in pre cleaned polyethylene bottles from "Hora Harsade" in three separate seasons (Winter, Spring and Summer, 2024) and Composite sampling technique has applied according to sampling procedure described (Tadesse *et al.*, 2018). That was by combining portion of equal water volumes collected at a regular time interval in each single bottle. To avoid any kind of contamination during sampling extra care was taken and the bottles were previous washed by distilled water and soaked overnight with 5% HNO_3 solution (Rao & Mamatha, 2004). In-situ analysis was made for temperature, Electrical conductivity and pH. Then representative water samples were collected in selected materials and it was labeled accordingly.

1.8.2 Sample preparation and preservation procedure

The collected sample was stored for transport to laboratory in an insulated plastic box containing ice pacts (cool box) to maintain the temperature as close to 4 ^{0}C prior to analysis (APHA, 2017) and was transported to and analyzed at Bishoftu Hort Coop (Agricultural Research Center).

1.8.3 Sample digestion procedure

In this study, by following aqueous sample digestion procedures, about 100 mL of a well-mixed and acid preserved water sample from each sample was taken in separate 250 mL flasks and mixed with a mixture of 2.0 mL of HNO_3 (69-72%), 1.0mL of HCl (37%) and 0.5 mL H_2O_2 of (30%) solution. The samples were gently heated on hot plate under a fume hood to not more than 85^{o}C. After the digestion completed, and then evaporated on to the lowest possible volume (about 20 mL). This step takes about 2 to 3 hours for 100 mL aliquot with the rate of evaporation rapidly increasing as the sample volume approaches 20 mL. Vigorous boiling avoided preventing loss of the HCl- H_2O_2 a zeotrope. The flasks were covered with a watch glass to prevent sample contamination from the fume hood environment. The flasks were allowed cooling. Then, the digested samples were filtered through glass fiber filters prior to analysis. The filtrates transferred to 50 mL volumetric flasks and diluted to the mark with distilled water. The digested samples were preserved in refrigerator for analysis (Tadesse *et al.*, 2018).

1.9 Sample Analysis

1.9.1 Physicochemical analysis of water sample

By known procedure (Tadesse *et al.,* 2018), the measurement of physicochemical parameters such as temperature, pH, turbidity, electrical conductivity, total dissolved solid, total suspended solids, total solids, total alkalinity, dissolved oxygen, total hardness, chloride ion, sodium, potassium, calcium, and magnesium were carried out for Hora harsade spring water.

Physical analysis

Temperature: Water temperature was measured by known procedure (Tadesse *et al.,* 2018) in-situ, using Thermometer analyzer probe by dipping in water for about 2 to 3 minutes and has recorded in degree Celsius.

pH: Water pH was measured using a known procedure (Tadesse *et al.*, 2018) in-situ, using a portable digital pH-meter.

Turbidity: Turbidity was measured by known procedure (Tadesse *et al.,* 2018) in-situ, using a portable turbidity meter.

Electrical Conductivity (EC): Was measured by known procedure (Tadesse e*t al.*, 2018) using a combined portable microprocessor-based conductivity by shifting one of the four buttons of instrument. Before measuring the probes was rinsed with distilled water and purity of distilled water was checked. Then, the probe was immersed in beaker containing water sample and move up and down taped on the beaker to be free the electrodes from any bubbles. Then, the data was recorded.

Total dissolved solid (TDS): Was measured by known procedure (Tadesse *et al.,* 2018) using a TDS/ Conductivity meter by shifting one of the four buttons of instrument. Before measuring the probes was rinsed with distilled water and purity of distilled water was checked. Then, the probe was immersed in beaker containing water sample and move up and down taped on the beaker to be free the electrodes from any bubbles. Then, the data was recorded.

Total suspended solid (TSS): For total suspended solid, 500 mL of the sample was blended in a blender at high speed for two minutes. The blended sample was poured into a 600 mL beaker. The sample was stirred and 25 mL of the blended sample was poured immediately into a sample cell. A second sample was filled with 25 mL of the de ionized water. Gas bubbles in the water was removed by swirling or tapping the bottom of the cell on a table, and the blank was placed into the cell holder and touched zero, the display shows 0 mg/L suspended solids. The prepared sample was swirl to remove any gas bubbles and uniformly suspended any residue. The prepared sample was placed into the cell holder (APHA, 1999).

TS (mg/L) =TDS (mg/L) +TSS (mg/L) (APHA, 2017)

1.9.2 Chemical analysis

Total Alkalinity (TA): 50 mL of water sample was taken 200 mL beaker and 3 drops of phenolphthalein indicator was added. If no colour was produced, phenolphthalein alkalinity was zero. The 50 mL of the sample was titrated with 0.02N H_2SO_4 to pH 8.3 and phenolphthalein alkalinity was estimated (Equ. a) (phenolphthalein indicator was change color from pink to clear, at pH 8.3).

Phenolphthalein alkalinity (mg/L as $CaCO_3$) $= \frac{\mathbf{A1xNx50,000}}{\mathbf{V(\alpha)}}$------------------------Eqn, (a)

Where, A1=volume of H_2SO_4 used in mL.

N=Normality of acid used to titrate.

V= volume of sample used in mL

The same sample was used and 3 drops of bromcresol indicator was added. The 50mL of the sample was titrated with 0.02N H_2SO_4 to pH 4.5 and total alkalinity was estimated. (Bromcresol green color indicator was change blue to yellow at pH 4.5). Amount of acid used at this method was started from step1 (i,e A2) was used to react with the OH^- , CO_3^{2-} and HCO_3^- and its constitutes of total alkalinity (Equ. b).

Total alkalinity (in mg/L as $CaCO_3$) $= \frac{\mathbf{A2xNx50,000}}{\mathbf{V(b)}}$--------------------Eqn.(b)

Where, A2=volume of H_2SO_4 used in mL started from step1 ((i, e A2 >A1)

N=Normality of acid used to titrate.

V= volume of sample used in mL (APHA, 2017).

Dissolved oxygen (DO): Around sample cell was filled with 10 mL of sample (the blank). A blue ampule cap and a high range dissolved oxygen ACCUVAC ampule was filled with sample. The tip will be kept and immersed while the ampule fills completely. The ampule withheld with the tip pointing down and immediately placed the ampule into the ampule cap. The cap prevents contamination from atmospheric oxygen. The ampule was shaked for 30 seconds. A small amount of undissolved reagent was not affecting results. A two-minute reaction period was begun. This enables the oxygen that was degassed during aspiration to re-dissolved and reacted. The ampule was shaked for 30 seconds. The blank placed in the cell holder and touched zero, the display shows 0.0 mg/L oxygen. Then the ampule was placed into the cell holder. Approximately 30 seconds was waited for the air bubbles to disperse from the light path and by touching read results of oxygen was appeared in mg/L (USEPA, 2004).

Total hardness (TH): The cell and cell adapter was installed in the sample cell compartment and flush with 50mL of the ultra-pure water. A plastic multi path length was rinsed and the cap three times with water to be tested. The underside of the cap was done not allowed to come into contact with surfaces that may contaminate it. The plastic multi path length was filled to the 25mL mark with sample. The content of one chlorophosphanazono solution pillow was added to the sample cell. A small amount of solution may remain in the pillow. This will not affect results. 1mL of chlorophosphanazono solution may be used instead of the solution pillow. The cell and swirl to cap was mixed. The multi path length cell adapter was installed. The 25mm cell path length was used. The blank was placed into the cell adapter, touched zero, the display shows 0.0μg /L $CaCO_3$. The cell was removed from the instrument. One drop of CDTA reagent for ultra-low range hardness was added. The cell was cap and swilled to mix. The cell was placed into the multi path length cell adapter. The 25 mm cell path length was used touched read and the result was appeared in μg /L $CaCO_3$ (USEPA, 2004).

Potassium (K): 25 mL of the sample was filled with a graduated mixing cylinder. The content of one potassium 1 reagent pillow was added. The content of one potassium 2 reagent pillow was added and stopper and inverted in several times to mix. The content of one potassium 3 reagent pillow was added after the solution was cleared and stopper and shake for 30 seconds and reacts with sodium tetra phenyl borate to form potassium tetra phenyl borate, an insoluble white solid. The amount of turbidity produced is proportional to the potassium concentration. The time icon was touched. The solution from the cylinder was poured into a 25 mL of the sample cell. The second sample was filled with 25 mL of the sample. The blank was wiped and placed it into the cell holder, and touched zero. The display shows 0.0 mg/L K. The prepared sample was wiped and placed it into the cell holder within several minutes, and touched to read. The results of K were appeared in mg/L (USEPA, 2004).

Magnesium (Mg) and Calcium (Ca):100 mL of the sample was poured into 100 mL graduated mixing cylinder.1.0 mL calcium and magnesium indicator solution was added using a 1.0 mL of measuring dropper. The cylinder was stopped and inverted it several times. 1.0 mL of alkali solution for calcium and magnesium was added and tested using a 1.0 mL of measuring dropper. 25 mL of the solution was poured into each of the three, round sample cells, and one drops of 1mL of EDTA solution was added to the first cell swirl to mix. One drops of EGTA solution was added to the second cell and swirl to mix. The first cell was placed into the cell holder, and touched zero, the shows 0.00 mg/L $CaCO_3$. The second cell was placed into the cell holder and touched read. The result in mg/L magnesium as calcium carbonate was appeared. The cell was removed from the instrument and the result was recorded, and touched exit and touched zero. The display shows 0.00 ppm $CaCO_3$. The third cell was placed into the cell holder and touched read. The result in mg/L calcium as calcium carbonate was appeared (USEPA, 2004).

Analytical procedure for anion

Chloride ion (Cl^-): A round sample cell was filled with 25 mL of the sample (this was the prepared sample). Another sample was filled with 25 mL of the deionized water (this was the blank). 2.0 mL of the mercuric Thiocyanate solution was pipetted into each of the sample cell, and swirl to mix and to form mercuric chloride and liberate thiocyanate ion. Thiocyanate ions react with 1.030 mL of ferric ion solution into each of the sample, and swirled to mix and to form an orange ferric thiocyanate complex. The amount of this complex is proportional to the chloride concentration. The times icon was touched to ok and a two minutes reaction time was begun. Within five minute the blank was wiped and placed it into the cell holder and touched zero, the display shows 0.0 mg/L Chloride ion (Cl^-). The prepared sample was wiped and placed it into the cell holder and touched read and the results was appeared in mg/L Chloride ion (Cl^-) (USEPA, 2004).

1.9.3 Instrument calibration and heavy metal analysis procedure

1.9.4 Instrument calibration

In order to calibrate the instrument, standard metal solutions were prepared for each of the metals from an intermediate standard solution (100 mg/L), made by diluting 1000 mg/L of standard stock solution. After the digestion of blank solutions in triplicate (one using a mixture of 3 mL HNO_3 and 1 mL HCl for the wet digestion of the mixture of aqua-regia and 0.5 mL hydrogen peroxide for the digestion of the water samples), triplicate readings were obtained for each sample.

Heavy metal concentration analysis procedure

The concentration of heavy metals (Na, Zn, Fe, Cu, Cr, and Mn) in the water sample was determined by using ICP/OES. The concentration of sodium in the spring water samples was estimated by flame photometry. Standard used in establishing the heavy metals and sodium determination was prepared from standard 1000 mg/L stock solution. The intermediate solution (10 mg/L) of each metal has then freshly prepared by diluting the stock solution in 100 mL volumetric flask with de ionized water and working standard using de ionized water. Working standards of metal solution was prepared in 250 mL of volumetric flask by diluting with deionized water. The prepared standard solution in atomic absorption spectrometer following the standard as described. Immediately after calibration of the instrument, the sample solutions have aspired into ICP/OES instrument and direct reading of the metal concentration has recorded (APHA, 2017).

1.9.5 Analytical method validation

Method validation is the process of providing analytical method that is acceptable for its anticipated purpose. In order to validate the analytical method, the following method validation parameters such as limit of detection, limit of quantification, precision and accuracy.

Detection Limit

Detection limit is defined as the minimum concentration of a substance that can be detected or measured with 99% confidence that the analayte concentration is greater than zero and is determined from analysis of the sample in a given matrix containing the analyte. This is often taken as the signal of blank three times the standard deviation of the blank (Bard and Faulkner, 2001).

LOD = 3xSb: Where, Sb is standard deviation of the method blanks

Limit of quantification

Limit of quantification is the lowest concentration of the analyte that can be measured in the sample matrix at an acceptable level of precision and accuracy. Limit of quantification is the lowest limit for precise quantitative measurements. The quantification limit of each element is calculated as ten times the standard deviation of the blank (Ridgway *et al.*, 2007).

LOQ = 10xSb: Where, Sb is the standard deviation of the method blank

Linearity

Linearity measures how well a calibration curves follows a straight line; showing that response is proportional to the quantity of analyte. Regression equation established from a plot of absorbance readings of standards against their concentration was used to determine the concentration of sodium, potassium, iron, manganese, cupper, chromium, and Zink in triplicates. A common measure of linearity is the coefficient of determination (R^2). R^2 values that are closer to values of one indicate that there is strong relationship between the variables being represent a linear fit, whereas values closer to 0 indicate that there is no linear relationship.

Accuracy

The accuracy of analytical methods describes how the measured value closer to the true value. Spiking of the sample was digested in triplicate following the same procedure used for digestion of the sample. The resulting digest of the spiked samples was then analyzed for their respective metal contents using ICP/OES and percent recoveries were calculated.

$$\% \text{ Recovery}=\frac{\textbf{Conc in spiked sample} - \textbf{conc in unspikedsample}}{\textbf{added amount}}\text{x}100$$

By known method (Tadesse *et al.*, 2018), the acceptable ranges of percentage recovery for the studied metals were within 80–120% for metal analysis.

Precision

The precision of analytical method describes the closeness of individual measurement of an analyte when the procedure is applied repeatedly to multiple aliquots of a single homogeneous volume of sample matrix precision was expressed as the relative standard deviation (RSD) of the three replicate results and the spiked samples was then subjected to the same digestion procedure like the actual sample. The relative standard deviation (RSD) of the sample is obtained as:

$$\% \text{ RSD}= \frac{\textbf{Standard deviation}}{\textbf{mean}}\text{x}100$$

By known method Tadesse et al., 2018), Relative standard deviation is the parameter of choice for expressing precision in analytical sciences. The precision determined at each concentration level should not exceed 15% RSD.

Table 6: Instrument operation condition for ICP-OES

Element	Wavelength (nm)	Instrumental detection limit (mg/L)	Slit width (nm)	Current (mA)	Energy (EV)	Flame system
Na	589	0.002	0.5	7	100	Air/acetylene
Cu	324.8	0.007	1.2	2	75.4	Air/acetylene
Fe	248.3	0.03	0.2	7	71.6	Air/acetylene
Zn	213.5	0.0024	0.5	2	100	Air/acetylene
Mn	279.5	0.01	0.2	5	76	Air/acetylene
Cr	357.9	0.01	0.2	4	69.1	Air/acetylene

1.10 Pearson correlation

By known method (Abdisa and Abebaw, 2014), Physicochemical parameters and heavy metals correlation study in the samples in the Hora spring water was analyzed at P=0.05 and 0.01. When the correlation 1.0, there is complete dependency, if it is 0.0 there is no relationship, if it is negative, both are said to be correlated in opposite direction. However, if correlation is >0.5, it is said to be significant and less significant when <0.50.

1.11 Data analysis

The data were analyzed using SPSS software (version 21) and Microsoft Excel 2007. Descriptive data have generated for all variables and have presented (mean ± SD) of the triplicate measurements. The results of the physicochemical parameters analyzed and heavy metals concentration determined of the sampling site were compared with national and international drinking water standard values for human and livestock. The parameters have correlated against each other to determine their relationship using Pearson's correlation, Significance has considered at 95% confidence interval.

4. RESULTS AND DISCUSSION

4.1 Validation Results

4.1.1 Calibration Curves, Limit of Detection and Limit of Quantification

Table 7: Detection limit, Regression equation and Correlation coefficient of Hora Harsade spring water

Analyte	Detection limit		From calibration curve	
	LOD	LOQ	Regression equation	R^2(Correlation Coefficient)
Cu	0.0004	0.0013	Y=0.008x+0.002	0.984
Fe	0.0002	0.0007	Y=0.0084x+0.002	0.968
Zn	0.0004	0.0013	Y=0.015x+0.001	0.991
Mn	0.0003	0.0009	Y=0.015x+0.001	0.994
Na	0.0424	0.1412	Y=0.293x+0.04	0.984
Cr	0.01	0.0333	Y=0.008x+0.002	0.991

Table 7 shows, the calibration curve equation, the correlation coefficients, the limits of detection (LOD), and limits of quantification (LOQ) of the elements analyzed in the Hora Harsade sample. For all analyte, the analytical curves showed correlation coefficients (R^2) values higher than 0.968, indicating a good linear correlation between the analytical signal and the analyte concentration. From Table 7, the limit of detection (LOD) values for all the elements analyzed ranged from 0.0004– 0.0424 and the limit of quantification (LOQ) values for all the elements analyzed ranged from 0.0007 – 0.0333. The LOD and LOQ method obtained were low enough to detect the presence of elements interest at trace levels in the samples. In this study LOD< LOQ. This result indicates the method was verified and acceptable.

4.1.2 Accuracy, Precision and Percentage recoveries

The acceptable ranges of percentage recovery for the studied metals were within 80–120% for metal analysis (Tadesse *et al.,* 2018). This confirms that the results were good precision and accuracy. In this study, as shown in table 8, the validation results were made by the spiking experiments in which known quantities of the metals standard solution were added to the sample from sampling area for Hora Harsade sample and applied the whole procedure to the mixture (spiked samples) and calculated the percent recoveries. The obtained percentage recovery varied from 90.67 to 105.47 %, which was in the acceptable range. The high percentage recovery obtained from the study validates the accuracy and the reliability of the levels of metal concentration in this study.

Table 8: Percentage recoveries, Standard deviation (SD), and Relative Standard deviation (RSD) of heavy metals in Hora Harsade

Heavy metals and Na	Standard added	Unspiked/Original value			Spiked value			Recovery (%)
		Mean	SD	RSD	Mean	SD	RSD	
Na	1.5	326.54	2.26	0.69	327.95	0.49	0.15	93.78
Cu	0.03	0.12	0.01	9.04	0.15	0.01	4.08	94.44
Fe	0.5	0.68	0.02	3.12	1.15	0.06	4.98	94.93
Zn	0.075	0.20	0.03	16.77	0.27	0.01	4.49	90.67
Mn	0.05	0.64	0.06	9.78	0.69	0.07	10.79	105.47

4.2 Levels of Physicochemical Parameters of Water Sample

The physicochemical parameters directly related to the safety of the drinking water to human consumption, livestock and health concern. The physicochemical water quality parameters provide important information about the health of a water body. These parameters are used to find out the quality of water for drinking purpose. The main physicochemical parameters that were considered in the study include: temperature, pH, turbidity, electrical conductivity, total dissolved solid, total suspended solids, total solids, dissolved oxygen, total alkalinity, total hardness, chloride, calcium, magnesium, potassium, and sodium.

Temperature of water

The temperature in Hora Harsade sample was varies from 19.37± 0.15 (table 9). The esthetic objective for temperature of drinking water should be less than or equal to 15 ^{O}C. As it is adopted from the guidelines for Canadian drinking water. Cattle typically prefer drinking water at temperatures between 4.4 and 18.3^{O}C (Tibebu *et al.*, 2017). This range was also considered as above the maximum limit of temperature for drinking water specified by WHO which is 15 (^{O}C). But temperature is lower than the study conducted in Ambo town (27.33 to 40.83 ^{O}C) of Hora waters. When the temperature is more than 27 ^{O}C, water and feed intake rates often decrease, affecting animal productivity (WHO, 2006). The temperature in Hora Harsade sample was less than 27 ^{O}C. Therefore, have no affecting animal productivity. Higher water temperatures promote the growth of microorganisms in the water, which may increase the taste, odor, turbidity and cause corrosion problems and also it decreases the solubility of gas in the water (Sekhar, 2020). Pearson mean correlation shows temperature was positively correlated with turbidity (r = 0.866), EC (r = 0.866), TDS (r = 0.756), TSS (r = 0.945), TS (r = 0.982), TA (r = 0.866),DO (r = 1.00), TH (r = 0.655), Cl (r = 1.00), K (r = 0.50), Fe (r = 0.564) and the other temperature with (pH, Na, Mg, Ca, Cu, Mn & Zn) are negative correlation (Table 10)

Table 9: The physicochemical parameters in Hora Harsade

Parameters	N	Mean	SD	Mean±SD	NDWQS, 2013	WHO, 2018
Temp (^{0}C)	3	19.37	0.15	19.37±0.15	<25	15
pH units	3	7.03	0.06	7.03±0.06	6.5 to 8.5	6.5 to 8.6
Turb. (NTU)	3	3.10	0.10	3.100±0.100	5	5
EC (µS/cm)	3	232.00	2.00	232±2.000	1000	1000
TDS (mg/L)	3	154.67	1.53	154.67±1.53	500	400
TSS (mg/L)	3	91.33	1.15	91.33±1.15	25	
TS (mg/L)	3	246.00	1.73	246.000±1.73		
TA (mg/L)	3	28.00	1.73	28.000±1.73	250	250
DO (mg/L)	3	1.47	0.12	1.47±0.12	5.0 to 7.0	5.0 to 7.0
TH (as $CaCO_3$ mg/L)	3	2.44	0.09	2.44±0.09	300	300
Cl (mg/L)	3	1.83	0.06	1.83±0.06	250	250
Na (mg/L)	3	318.39	11.35	318.39±11.35	150	200
K (mg/L)	3	4.77	0.06	4.77±0.06	5	
Ca (mg/L)	3	0.35	0.04	0.35±0.04	75	75
Mg (mg/L)	3	1.38	0.03	1.38±0.03	50	50

pH of water

The pH reading in Hora Harsade sample was 7.03 ± 0.06 (Table 9). They were within the national and WHO water quality guidelines of permissible range of 6.5–8.5 for natural water bodies. The pH values were also within the range of water quality guideline for livestock (Tibebu *et al.*, 2017). The pH of most natural water falls within the range of 4 to 9. The majority of waters are slightly basic (i.e. generally over 7.0) because of the presence of carbonate and bicarbonates ((Aly *et al.*, 2015). Pearson mean correlation shows pH was positively correlated with TH (r = 0.327), Na (r = 0.572), K (r = 0.500), Ca (r = 0.904), Mg (r = 0.918), Cu (r = 1.000), Fe (r = 0.434) and the other pH with(EC, TDS, TSS, TS, DO,TH, Cl^- , and Mn) are negative correlation and pH with turbidity (r = 0.000), TA (r = 0.000). Therefore, there is no relationship (Table 10).

Turbidity

Turbidity is the cloudiness of water caused by a variety of particles and is another key parameter in drinking water analysis. It is also related to the content of diseases causing organisms in water, which may come from soil runoff (Rahmanian et al., 2015). The measured turbidity value in Hora Harsade sample was 3.10 ± 0.10 (Table 9). The standard recommended maximum turbidity limit, set by WHO and National Drinking Water Quality Standard (NDWQS), for drinking water is 5 (NTU).The consumption of high turbid water may cause a health risk, as excessive turbidity can protect pathogenic microorganisms from effects of disinfectants (Shigut et al., 2017). The results were below the WHO guidelines and National Drinking Water Quality Standard (NDWQS), for drinking water for quality indicating that no palatability problem concerned with turbidity of the studied waters.

Pearson mean correlation shows turbidity was positively correlated with EC(r = 0.500), TDS(r = 0.327), TSS(r = 0.982), TS(r = 0.756), TA(r = 1.000), DO (r = 0.866), TH(r = 0.945), Cl^- (r = 0.866), K (r = 0.866), Fe (r = 0.901) and the other turbidity with (Na, Ca, Mg, Mn and Zn), negative correlation. Turbidity with Cu(r = 0.000) (Table 10).

Electrical conductivity (EC)

The concentration of electrical conductivity in Hora Harsade sample was varies from 232.00 ± 2.00 (Table 9), which is below the Ethiopian guideline (1,000 μS/cm) and WHO (1,500μS/cm) (Tibebu et al., 2017). The Electrical conductivity for the water of Hora Harsade was less than 1000 μS/cm), can be classified according to (in Table 1) as very weakly mineralized water. High values of electrical conductivity mean that there are pollutants such as chloride, sodium (Ezekwe et al., 2017). High values of conductance can be indicative of salinity problems but also are observed in eutrophic waterways where plant nutrients (fertilizer) are in greater abundance (Rodriguez et al., 2009; Chaabane et al., 2017). The current study gave the results below the guidelines for drinking water quality. Soluble salt in drinking water have different effect on livestock, if the value is less than 1,000 µS/cm, it is safe to drink and pose no health problems. Therefore, no issues concerned with EC if the waters to be used for drinking. Pearson mean correlation shows EC was positively correlated with TDS (r = 0.982), TSS (r = 0.655), TS (r = 0.945), TA (r = 0.500), DO (r = 0.866), TH (r = 0.189), Cl^- (r = 0.866), Fe (r = 0.075) and the other EC with (Na, Mg, Ca, Cu, Mn & Zn), negative correlation. EC with K(r = 0.000) (Table 10).

Total dissolved solid (TDS)

The concentration of total dissolved solid in Hora Harsade sample was varies from 154.67 ± 1.53 (Table 9). According to WHO, the palatability of water with a TDS level of less than about 600 mg/L is generally considered to be good. Drinking water becomes significantly and increasingly unpalatable at TDS levels greater than about 1,000 mg/L. To date no health-based guideline for TDS has been proposed in Ethiopia, However, 1,000 mg/L for humans and 10,000 mg/L for livestock are the recommended values. The TDS value was also found to be in the range of water quality guideline for livestock respectively (Tibebu et al., 2017). High concentrations of TDS limit the suitability of water as a drinking source and irrigation supply (Amanial *et al.*, 2015). The TDS for the water of Hora Harsade were less than (1000 mg/L), can be classified according to (in Table 2) as fresh water. Taste problems in water often arise from the presence of high TDS levels with certain metals present, particularly iron, copper, manganese, and zinc (WHO, 2004; Hedayati and Safahieh ,2012); Pradhan *et al.*, 2011). The results were below the WHO guidelines for drinking water quality indicating that no palatability problem concerned with TDS of the studied waters.

Pearson mean correlation shows TDS was positively correlated with TSS (r = 0.500), TS (r = 0.866), TA (r = 0.327), DO (r = 0.756), Cl^- (r = 0.756), Mn (r = 0.075) and the other TDS with (Na, K, Mg, Ca, Cu, Fe & Zn), negative correlation. TDS with TH(r = 0.000) (Table 10).

Total suspended solid (TSS)

The spatial and temporal variation of TSS concentrations in estuaries and coasts are not only the issues of economic production activities closely related to estuarine coast, such as trade, transportation and fishery production, but also the focus of sustainable development of the human society, such as coastal zone planning and ports and waterways construction (Wang *et al.*, 2018). The concentration of total suspended solid in Hora Harsade sample was varies from 91.33

± 1.15 which is higher than 30 mg/L (WHO, 2018) and 25 mg/L (NDWQS, 2013) (Table 9). According to national drinking water quality Standard (NDWQS), the maximum standard limit of TSS is 25 mg/L (Popoola *et al.,* 2019). The results were above national drinking water quality Standard. This is because the sample in these areas had no filtration systems, thus no removing all the suspended particles such as silt, clay, and other inorganic particles. High suspended solids in drinking water or wastewater can have both environmental effects and effects on human health. When it comes to water quality, high TSS may decrease water's natural dissolved oxygen levels and increase water temperature. Pearson mean correlation shows TSS was positively correlated with TS (r = 0.866), TA (r = 0.982), DO (r = 0.945), TH (r = 0.866), Cl^- (r = 0.945), K(r = 0.756), Fe (r = 0.803) and the other TSS with (Na, Mg, Ca, Cu, Mn & Zn), negative correlation (Table 10).

Table 10: Correlation between physicochemical parameters of the Hora Harsade

Par.	Temp	pH	Turb	EC	TDS	TSS	TS	TA	DO	TH	Cl	Na	K	Ca	Mg
Temp	1														
pH	-0.5	1													
Turb	0.866	0	1												
EC	0.866	-0.866	0.5	1											
TDS	0.756	-0.945	0.327	0.98	1										
TSS	0.945	-0.189	0.982	0.66	0.5	1									
TS	0.982	-0.655	0.756	0.95	0.866	0.87	1								
TA	0.866	0.001	1.000**	0.5	0.327	0.98	0.76	1							
DO	1.000**	-0.5	0.866	0.87	0.756	0.95	0.98	0.87	1						
TH	0.655	0.327	0.945	0.19	0.002	0.87	0.5	0.95	0.655	1					
Cl	1.000**	-0.5	0.866	0.87	0.756	0.95	0.98	0.87	1.000*	0.655	1				
Na	-0.996	0.572	-0.821	-0.91	-0.81	-0.91	-0.99	-0.82	-0.996	-0.59	-1	1			
K	0.5	0.5	0.866	0.001	-0.19	0.76	0.33	0.87	0.5	0.982	0.5	-0.43	1		
Ca	-0.822	0.904	-0.427	-1	-0.99	-0.59	-0.92	-0.43	-0.822	-0.11	-0.82	0.87	0.08	1	
Mg	-0.803	0.918	-0.397	-0.99	-1	-0.56	-0.9	-0.4	-0.803	-0.08	-0.8	0.85	0.12	.999*	1

** Correlation is significant at the 99% level.

* Correlation is significant at the 95% level.

Total alkalinity (TA)

The major portion of alkalinity in natural waters is caused by hydroxide, carbonate, and bicarbonate. Alkalinity due to other materials in natural water is insignificant and may be ignored (Aly et al., 2015). The obtained TA values are due to Bromcresol alkalinity (at about pH 4.5) because the phenolphthalein alkalinity which is expected at about pH 8.3 in the site is zero. According to the standard method (in Table 3), when pH = 0 the OH^-alkalinity and $CO_3{}^{2-}$ alkalinity are zero while $HCO_3{}^-$ alkalinity is equal with TA. Therefore, the observed alkalinity is possibly due to $HCO_3{}^-$ from dissolved CO_2. The concentration of total alkalinity in Hora Harsade sample was varies from 28 ± 1.73 (Table 9). There is no health-based guideline value for alkalinity but it does contribute to the amount of total dissolved solids (TDS). Which has an esthetic guideline value of 400 mg/L. Levels between 30 and 400 mg/L are suitable for human drinking water, while no standard value was set for livestock both at national as well as international level (Tibebu et al., 2017). Therefore, the Hora Harsade was not affected for human based on total alkalinity. Pearson mean correlation shows TA was positively correlated with DO (r = 0.866), TH(r = 0.945), Cl^- (r = 0.866), K(r = 0.866), Fe(r = 0.901) and the other TA with (Na, Mg, Ca, Mn&Zn) are negative correlation. TA with Cu(r = 0.000) (Table 10).

Total hardness (TH)

The concentration of total hardness in Hora Harsade sample was varies from 2.44 ± 0.09 (Table 9). No health-based guideline value is recommended by Ethiopian and 400 mg/L according to WHO for drinking water standard values for humans (Tibebu et al., 2017). The results were below the WHO guidelines for drinking water standard values for humans. This hardness might be as the result of limestone and magnesium terrain crossed by water. Hardness of water does not pose a health risk but can cause esthetic problems. In some 40 instances, consumers tolerate water hardness in excess of 500 mg/L (Pradhan and Pirasteh, 2011). The classification of Hora Harsade according to hardness (mg/L) guidelines for livestock given (in Table 4) is soft water. Pearson mean correlation shows TH was positively correlated with Cl^- (r = 0.655), K(r = 0.982), Cu (r = 0.327), Fe (r = 0.993) and the other TH with (Na, Mg, Ca, Mn & Zn) are negative correlation (Table 10).

Dissolved oxygen (DO)

Dissolved oxygen is one of the most important parameters in assessing the quality of water, which is essential to maintain biotic forms in water (Pandit *et al.*, 2013) and is one of the most vital indicators of water quality. High DO levels improve the taste of drinking water, but this can couse corrosion in water pipes. The concentration of dissolved oxygen in Hora Harsade sample was varies from 1.47± 0.12 (Table 9). No health-based guideline value is recommended by Ethiopian and 5.0 to 7.0 according to WHO standard for drinking water standard values for humans and no standard value was given national and international for livestock (Tibebu et al., 2017). But the values are below WHO standard for drinking water standard values for humans. Low DO concentrations can lead to impaired fish development and maturation, increased fish mortality, and underwater habitat degradation (Iticescu and Topa, 2013). Additionally, the low DO levels below 5.0 mg/L stress aquatic life and creates hypoxic conditions. Pearson mean correlation shows DO was positively correlated with TH(r = 0.655), Cl^- (r = 1.000), K(r = 0.500), Fe (r = 0.564) and the other DO with (Na, Mg, Ca, Cu, Mn & Zn) are negative correlation (Table 10).

Sodium (Na)

Almost all groundwater and surface water contain sodium (Ezekwe et al., 2017). Most Na salts are readily soluble in water, but take no active part in chemical reactions. Sodium has large variations in its concentration in ground water (Pradhan et al., 2011). Sodium is an essential nutrient needed by the human body for a number of functions such as muscle and nerve function (Ameen., 2019; Sokrab et al., 2010). The concentration of Sodium in Hora Harsade sample was varies from 318.39 ± 11.35 (Table 9). The amount of sodium for drinking water is 150 mg/L and 200 mg/L according to Ethiopia and WHO standard values for human respectively. No guideline stated showing sodium content for cattle drinking water according to WHO guidelines (Tibebu et al., 2017). The values are above the maximum value recommended by Ethiopian guideline WHO standard values for human respectively. The recommended EPA value of sodium in drinking water is <200 mg/L (Osman, 2021). The values are above the maximum value recommended EPA. An excess of sodium more than 200 mg/L in drinking water may cause a salty taste (Ezeldin., 2016). “Hora Harsade” spring water sample was an excess of sodium more than 200 mg/L. Therefore, may cause a salty taste. Sodium has large variations in its concentration in ground water (Pradhan et al., 2011). The taste threshold concentration of sodium in water depends on the associated anion and the temperature of the solution. According to (Rao and Nageswararao, 2013) the dissolution of tablet salt or halite is cited as a source of both Sodium and Chloride in natural water. If the concentration of Sodium exceeds Chloride concentration the sample under consideration suggesting that additional sources of Sodium is present. Therefore, the possible source of high concentration of Sodium in the analyzed water samples is the dissolution of tablet salt. Additionally, excessive sodium in drinking water can produce an increase in blood pressure as a person ages. This can eventually lead to the development of hypertension in people with a family history of the disease. Pearson mean correlation shows Na was positively correlated with Ca(r = 0.867), Mg(r = 0.851), Cu(r = 0.572), Mn (r = 0.526), Zn(r = 0.698) and the other Na with (K &Fe) are negative correlation (Table 10).

Potassium (K)

Is occurs widely in the environment, including all natural waters. It can also occur in drinking water as a consequence of the use of potassium permanganate as an oxidant in water treatment (WHO, 2004). The concentration of Potassium in Hora Harsade sample was varies from 4.77 ± 0.06 (Table 9), which is below the Ethiopian guideline (5 mg/L). To date health-based guideline for potassium has been proposed in Ethiopia, and no health-based guideline was proposed by WHO for human and live stocks (Tibebu *et al.*, 2017). The values are below the maximum value recommended by Ethiopian guideline for drinking water quality indicating no health risks concerned with potassium at levels found in these waters. Pearson mean correlation shows K was positively correlated with Ca (r = 0.082), Mg(r = 0.115), Cu(r = 0.500), Fe(r = 0.997) and the other K with (Mn & Zn) are negative correlation (Table 10).

Magnesium (Mg)

Magnesium in drinking water may provide nutritional benefits for persons with Magnesium deficient diets (Abdisa and Abebaw, 2014). The concentration of Magnesium in Hora Harsade sample was varying from 1.38 ± 0.03 (Table 9). The Mg/Ca ratio for Hora Harsade spring water was 3.92. The molar ratios lie mostly in the range 0.20–1.84, indicating weathering of pure dolomites; however, the highest value indicates for relatively impure higher triassic dolomites. The amount of magnesium for drinking water is 50mg/L and 100mg/L according to Ethiopia guide lines and WHO standard values of drinking water for human respectively. But, no health-based guideline value was proposed by WHO for cattle (Tibebu et al., 2017). The values are below the maximum value recommended by Ethiopian guideline and WHO standard values of drinking water quality for human. Low magnesium status has been implicated in hypertension, coronary heart disease, type 2 diabetes mellitus and metabolic syndrome. The case–control studies showed that reduced cardiovascular mortality occurred at magnesium concentrations in water is above 10 mg/L having affected human health through long time consumption (WHO, 2010). But value found in Hora Harsade was less than the recommended concentration level that reduced cardiovascular mortality. Small change in concentration has significant effect on cardiac excitability and on vascular tone, contractility, reactivity and growth (WHO, 2009). So the Hora Harsade has no affect human health through long time consumption. Pearson mean correlation shows Mg was positively correlated with Cu (r = 0.918), Fe (r = 0.040), Zn (r = 0.217) and Mg with Mn (r = 0.000) (Table 10).

Calcium (Ca)

Calcium in water is essentially nontoxic. The presence of Ca in water decreases the toxicity of many metals to aquatic life (Abdisa and Abebaw, 2014). The concentration of calcium in Hora Harsade sample was varies from 0.35 ± 0.04 (Table 9). The amount of calcium for drinking water is 200 mg/L according to Ethiopia guide lines and WHO standard values of drinking water for human. But, the guideline WHO standard values of drinking water for cattle is 1000 mg/L (Tibebu et al., 2017). The values are below the maximum value recommended by Ethiopian guideline and WHO standard values of drinking water quality for human, and livestock. Calcium is an important element for good health and levels between 20 and 30 mg/L are desirable in drinking water. A very high level of calcium, however, was produce scale and clog up water pipes. Calcium is one of the major elements responsible for water hardness. Water containing less than 60 mg/L of Ca is considered as soft water (Ezeldin, 2016). The values are below less than 60 mg/L of Calcium. So, Hora Harsade is considered as soft water. Therefore, no issues concerned with calcium if the waters to be used for drinking. Pearson mean correlation shows Ca was positively correlated with Mg(r = 0.999), Cu (r = 0.904), Mn (r = 0.033), Fe (r = 0.077), Zn (r = 0.249) (Table 10).

Chloride (Cl^-)

Is normally the most dominant anion in water and it imparts salty taste to the water. Chlorides are widely distributed in nature, usually in the form of (NaCl, KCl and $CaCl_2$), although many minerals contain small amounts of chloride as an impurity. Chloride is the most abundant anion in the human body and is essential to normal electrolyte balance of body fluids. Chlorides in water are more of a taste than a health concern, although high concentrations may be harmful to people with heart or kidney problems. There are no primary drinking water standards for chloride. The EPA secondary standard for chloride is 250 mg/L, based on adverse effect on taste (WHO, 2004; Hedayati and Safahieh, 2012); Pradhan *et al.,* 2011; Amanial *et al.,* 2015).

The concentration of Hora Harsade sample was varies from 1.83 ± 0.06 (Table 9). The amount of chloride for drinking water is 30 mg/L and 250 mg/L according to Ethiopia and WHO standard values for human respectively. No guideline stated showing chloride content for cattle drinking water according to WHO guidelines (Tibebu *et al.,* 2017). The values are below the maximum value set by WHO for drinking water standard values for humans and below recommended by EPA guideline for drinking water standard values. Chlorides in water are more of a taste than a health concern, although high concentrations may be harmful to people with heart or kidney problems. Therefore, the Hora Harsade has no affect human health concerned with chloride if the waters to be used for drinking through long time consumption. Pearson mean correlation shows $Cl^-$was positively correlated with K(r = 0.500) and Fe (r = 0.564) and the other Cl^- with (Na, Mg, Ca, Cu, Mn & Zn) are negative correlation (Table 10).

4.3 Results of the Levels of selected heavy metals concentration.

The measured levels of heavy metal elements in this study (Cu, Mn, Fe, Zn and Cr) were determined by using ICP-OES in the Hora Harsade sample. Results are expressed as mean ± SD triplicate analyses.

Copper (Cu)

Is both an essential nutrient, and a drinking water contaminant, but at high doses it has been shown to cause stomach and intestinal distress, liver and kidney damage and anemia. Cu in a drinking water supply usually arises from the corrosive action of water leaching Cu from Cu pipes in buildings. High concentrations can interfere with the intended domestic uses of the water. At levels above 5 mg/L, Cu also imparts a color and an undesirable bitter taste to water (Sokrab et al., 2010). Copper was the 3^{rd} accumulated heavy metal element next to iron determined in the Hora Harsade sample studied in this work. The concentration of Cu determined in Hora Harsade sample was 0.09 ± 0.01 (in Table 11).

The level of Cu regulation for drinking water standard values for humans is about 1.00 mg/L, and 1.5 mg/L is proposed for livestock water quality by WHO guide line (Tibebu et al., 2017). The guideline value of copper proposes by WHO in drinking water is to be 2 mg/L and the recommended EPA value is 1mg/L (Osman, 2021). The values are below guideline value of copper proposes by WHO for drinking water standard values for humans and for livestock ,also below recommended by EPA guideline values in drinking water. The South African guideline for Cu in domestic water supply is < 1.0 mg/L. The value obtained for Hora Harsade is low, thus Cu is not supposed to be a problem for domestic use. The TQWR for Cu in water for livestock watering is < 5 mg/L and the adverse chronic effect may occur at 1 to 10 mg/L Cu, depending on the livestock. Cu in waters of the Hora Harsade did not exceed this level; therefore Cu will not be a problem if used for livestock (Davies et al., 2006). Pearson mean correlation shows Cu was positively correlated with Fe (r = 0.434), and the other Cu with (Mn & Zn), negative correlation (Table 12).

Manganese (Mn)

Is one of the most abundant metals in the Earth crust, usually occurring together with iron (WHO, 2004). Manganese is an essential element for humans and animals (Mezgebe *et al.*, 2015). Manganese was the 1st accumulated heavy metal element determined in the Hora Harsade sample studied in this work. The concentration of Mn determined in Hora Harsade sample was 0.56 ± 0.05 (Table 11). The level of Mn regulation for drinking water standard values for humans is about 0.40 mg/L, and no health-based guide value is proposed for livestock water quality by WHO guide line (Tibebu et al., 2017; Osman, 2021). The recommended EPA value is <0.1mg/L (Osman, 2021). The values are above the maximum value recommended by WHO standard values of drinking water quality and the recommended EPA value for human. Because it does not occur in nature as the elemental metal, but is found in various salts and minerals; frequently along with iron compounds. This observation could be due to groundwater contact with dissolved soil, rock and minerals of manganese (Popoola et al., 2019). At levels exceeding 0.15 mg/L, manganese stains plumbing fixtures and laundry and causes undesirable tastes in beverages. It may lead to the accumulation of microbial growths in the distribution system that could give rise to taste, odor, and turbidity problems in the distributed water (Edition, 2011). Health effects in case of elevated amount of Mn are apathy, irritability, headache, insomnia, gastrointestinal irritation and respiratory diseases (Sokrab et al., 2010). Therefore, the Hora Harsade has affected human health concerned with manganese. Pearson mean correlation shows Mn was positively correlated with Zn (r =0.976) and negatively correlated with Fe (r =-0.999) (Table 12).

Table 11: Levels of selected heavy metals concentration (mg/L) in Hora Harsade

Metals	N	Mean	SD	Mean± SD	NDWQS, 2013	WHO
Cu	3	0.09	0.01	0.09±0.01	2	2
Mn	3	0.56	0.05	0.56±0.05	0.5	0.1
Fe	3	0.19	0.02	0.19±.02	0.3	0.3
Zn	3	0.05	0.01	0.05±.05	5	5
Cr	3	BDL	BDL	BDL	0.003	0.003

Iron (Fe)

Iron is one of the most abundant heavy metals in Earth‟s crust. Its chief ores are the red-orange hematite (Fe_2O_3) and the black magnetite (Fe_3O_4) (Tadesse et al., 2018). Fe is found in natural waters at levels ranging from 0.5 to 50 mg/L. Iron may also be present in drinking waters a result of the corrosion of steel and cast-iron pipes during water distribution. Iron is an essential element in human nutrition, particularly in the Fe (II) oxidation state. Fe may affect acceptability of drinking water (WHO, 2004). Iron was the 2nd accumulated heavy metal element determined in the Hora Harsade sample studied in this work. The concentration varies from 0.19 ± 0.02 (Table 11).

The level of Fe regulation for drinking water standard values for humans is about 0.40 mg/L, and no health based guide value is proposed for livestock water quality by WHO guide line (Tibebu et al., 2017) and the recommended EPA value is <0.3mg/L for drinking water standard values (Osman, 2021). The values are below the maximum value by WHO for drinking water standard values for humans and below recommended by EPA guideline.

The shortage of iron causes disease called "anemia"" and prolonged consumption of drinking water with high concentration of iron may lead to liver disease called as Haermosiderosis (Gebrekidan and Samuel, 2011; Ezekwe et al., 2017). Therefore, the Hora Harsade have no affect human health concerned with iron if the water to be used for drinking through long time consumption. Pearson mean correlation shows Fe was negatively correlated with Zn (r = -0.967) (Table 12).

Table 12: Correlation between heavy metals of the Hora Harsade

Parameters	Cu	Mn	Fe	Zn
Cu	1			
Mn	-0.4	1		
Fe	0.434	-0.999*	1	
Zn	0.19	0.976	-0.97	1

** Correlation is significant at the 99% level.

* Correlation is significant at the 95% level.

Zinc (Zn)

Zinc is mostly found in some natural waters close to mining source. Zinc in drinking water is not a treat to health unless its level is very high. Although levels of Zn in surface water and groundwater normally do not exceed 0.01 mg/L, 0.05 mg/L, and 3 mg/L respectively. However, drinking water containing Zn at levels above 3 mg/L may not be acceptable to consumers (WHO, 2004; Ali and Khan, 2018). Zinc was the least of all the heavy metal elements determined in this study. The concentration of zinc determined in Hora Harsade sample was 0.05 ± 0.01 (Table 11). The level of Zn regulation for drinking water standard values for humans is about 0.10 mg/L, and 24 mg/L is proposed for livestock water quality by WHO guide line (Tibebu et al., 2017). The recommended EPA value is <3mg/L (Osman, 2021). The values are below the maximum value set by WHO for drinking water standard values for humans and livestock also, below recommended by EPA guideline. Therefore, the Hora Harsade has acceptable for human health and livestock concerned with zinc if the water to be used for drinking through long time consumption. The South African guidelines for Zn in domestic water supply is < 3 mg/L , hence adverse effect was not be expected by using water from hora spring water for domestic purpose. Also the TWQR levels of Zn in water for livestock watering is 20 mg/L. therefore water from Hora Harsade can be utilized for livestock watering since the range obtained was much lower than the TWQR values (Davies et al., 2006).

Chromium (Cr)

Is widely distributed in Earth’s crust. In natural waters, dissolved Cr exists as either Cr^{3+}cations or in anions such as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$), where it is hexavalent with oxidation number +6. Though widely distributed in soils and plants, it generally is present at low concentrations in natural waters. The level of Cr regulation for drinking water standard values for humans is about 0.05 mg/L, and 1.0 mg/L is proposed for livestock water quality by WHO guide line (Tibebu *et al.*, 2017; Osman, 2021). Chromium was below detection limit (BDL) in the Hora Harsade sample studied in this work (Table 11). The concentration of Cr can result from industrial and mining processes. Around the Hora Harsade there is no any industry. So, the concentration of chromium is not detected. Cr was not detected in the Hora Harsade may be due to the capacity of ICP-OES.

Generally, the mean concentration of the metals in the studied Hora Harsade, varied in the order of Na > K > Mg >Mn > Ca > Fe>Cu>Zn.

5. CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Water is life. Hence, the quality of drinking water must be monitored accordingly. In this study, water sample from HoraHarsade spring water was analyzed for characterization of Physicochemical Properties and Heavy Metal Contamination of spring drinking water sample in Bishoftu, East showa zone, Oromia, Ethiopia. The results of water quality of the spring water show significant relations amongst the measured properties of water. Comparison of the Hora Harsade parameters with that of national (NDWQS, 2013) and international (WHO, 2018) drinking water standard values for human and livestock. The values obtained in the current study were within both the guideline values except for temperature (19.37±0.15 ^{0}C), TSS (91.33±1.15 mg/L), Na (318.39±11.35 mg/L), Mn (0.56±0.05 mg/L) respectively higher than 15 ^{0}C, 25 & 30 mg/L, 200 mg/L, 0.5 & 0.1 mg/L standards set by (NDWQS, 2013) and (WHO, 2018); and the value of DO (1.47±0.12 mg/L) was lower than the ranges 5.0 to 7.0 mg/L of NDWQS and WHO for drinking water standard values for humans and for livestock. According to the findings, the Hora harsade spring water sample site is potable after moderate treatment of temperature, TSS, DO, Na, & Mn. In general, the spring drinking water qualities from the Hora harsade is safe for drinking according to the analysis of the present study.

5.2 Recommendations

Based on the present study, the following recommendations were given for concerned bodies.

The Hora spring water needs further treatment to minimize or reduce the amount of temperature which may decrease water feed intake rates affecting animal productivity; TSS may decrease water's natural DO levels and increase water temperature; Sodium which may develop a salty taste and can produce an increase in blood pressure as a person age; Manganese may stains plumbing fixtures and laundry which causes undesirable tastes in beverages and may lead to the accumulation of microbial growths in the distribution system that could give rise to taste, odor and turbidity problems in the distributed water. Additionally, the content of dissolved oxygen in Hora sample should need to maximize to the standard limit for drinking water which may cause stress aquatic life and creates hypoxic conditions.

- ❖ The study was conducted within period of three seasons. It may lack comprehensiveness. Further studies should be conducted in different seasons considering other water quality parameters such as physical, chemical and bacteriological properties before using for drinking, domestic and other sensitive purposes.
- ❖ The study was taken as the starting material for the interested body/group for further analysis of physicochemical quality parameters and other parameters by sophisticated equipment and standardized laboratory in order to have a broader picture of that Hora Spring water.

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APPENDIXES

Appendix 1: The measured values of physicochemical parameters in Hora Harsade, Bishoftu City in selected three seasons

Parameters	22-Dec-23	11-Mar-24	12-Jun-24
Temp (^{0}C)	19.5	19.2	19.4
pH units	7.03	6.97	7.08
Turb. (NTU)	3.1	3.2	3
EC (µS/cm)	232	230	234
TDS (mg/L)	156	155	153
TSS (mg/L)	92	90	92
TS (mg/L)	248	245	245
TA (mg/L)	29	29	26
DO (mg/L)	1.37	1.44	1.6
TH (as $CaCO_3$ mg/L)	2.4	2.38	2.55
Cl (mg/L)	1.8	1.9	1.8
Na (mg/L)	319.5	306.52	329.14
K (mg/L)	4.7	4.8	4.8
Ca (mg/L)	0.3	0.38	0.37
Mg (mg/L)	1.39	1.35	1.4

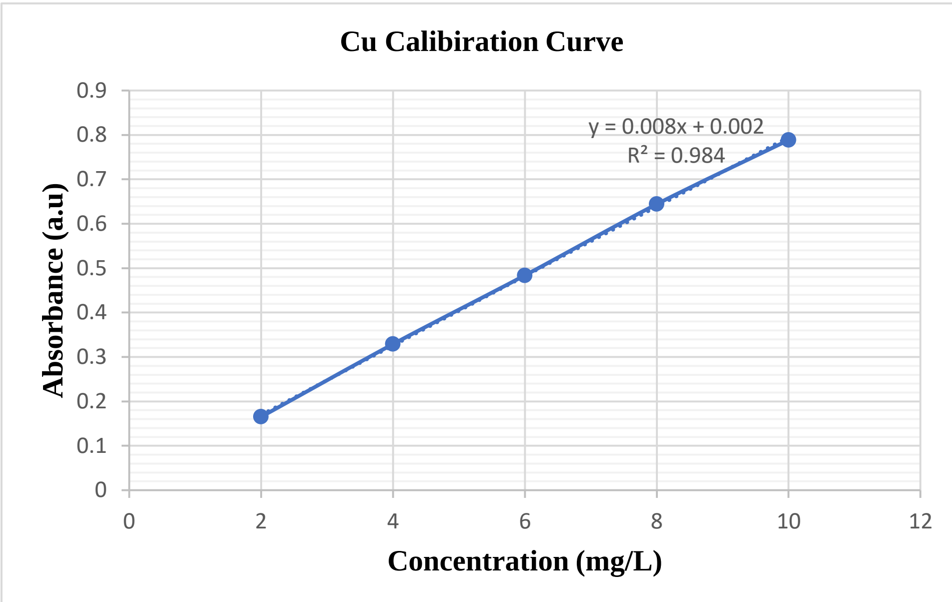
Appendix 2: Measured values for calibrations of sodium and heavy metals concentration in the three selected season

Heavy metals & Na	Standard added	Un spiked/Original value			Spiked value		
		22-Dec-23	11-Mar-24	12-Jun-24	22-Dec-23	11-Mar-24	12-Jun-24
Na	1.5	327.12	328.46	324.05	328.15	327.39	328.31
Cu	0.03	0.107	0.127	0.124	0.142	0.147	0.154
Fe	0.5	0.662	0.67	0.702	1.13	1.11	1.218
Zn	0.075	0.17	0.238	0.201	0.279	0.257	0.277
Mn	0.05	0.599	0.6088	0.712	0.65	0.649	0.779

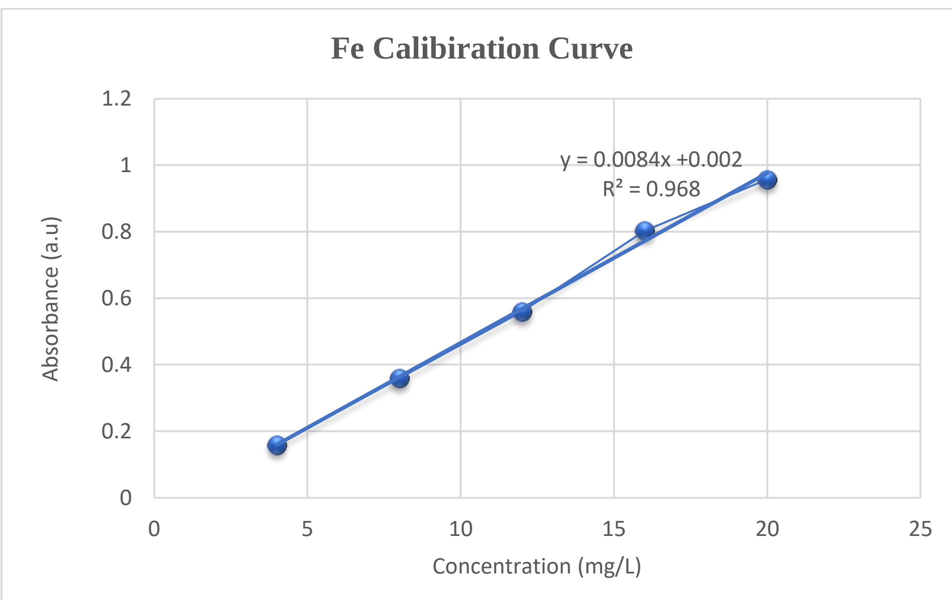
Appendix 3: Measured Levels of selected heavy metals concentrations in Hora Harsade, Bishoftu city in the selected three seasons.

Heavy metals	22-Dec-23	11-Mar-24	12-Jun-24
Cu	0.1	0.08	0.09
Mn	0.59	0.59	0.5
Fe	0.18	0.19	0.21
Zn	0.05	0.05	0.04
Cr	BDL	BDL	BDL

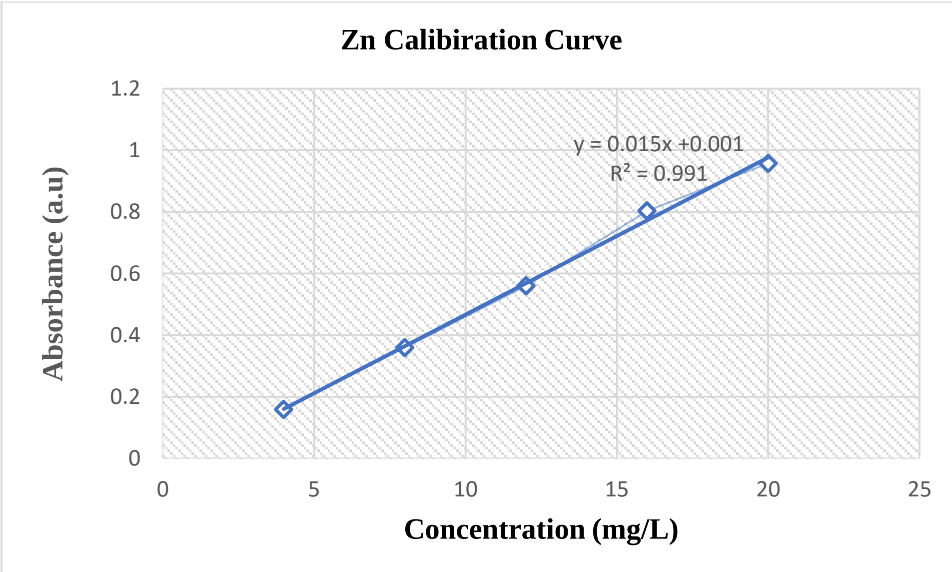
Appendix 4: Plot of Absorbance versus Concentration for Cu



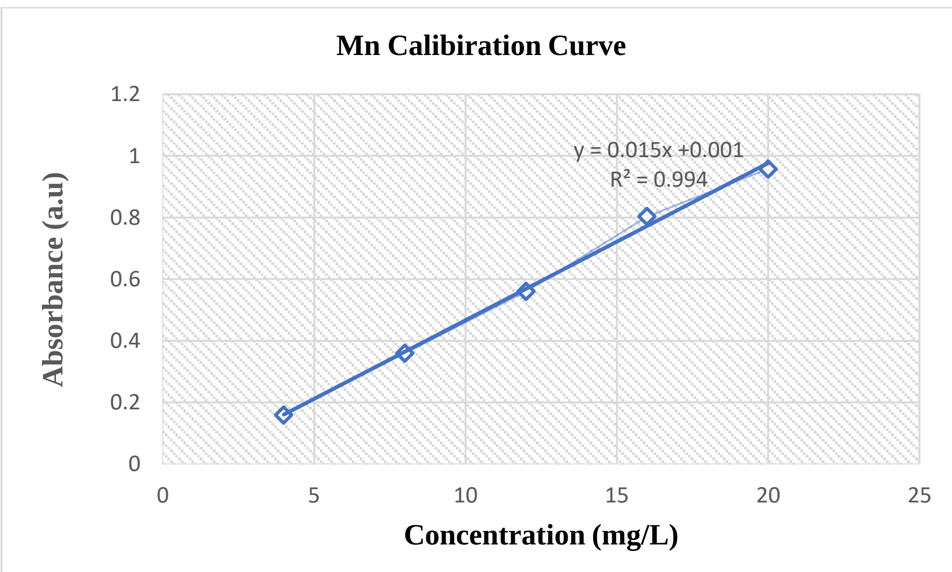
Appendix 5: Plot of Absorbance versus concentration for Fe



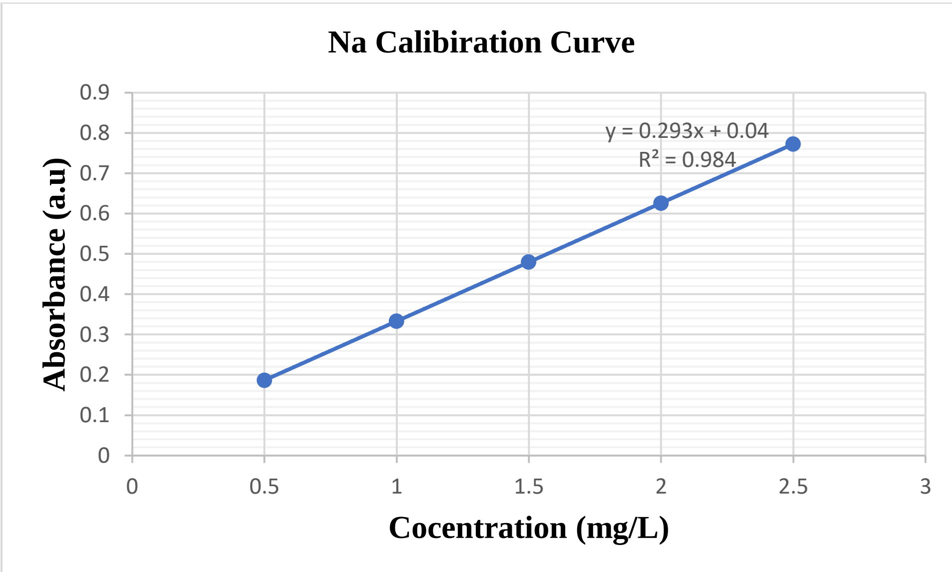
Appendix 6: Plot of Absorbance versus Concentration for Zn



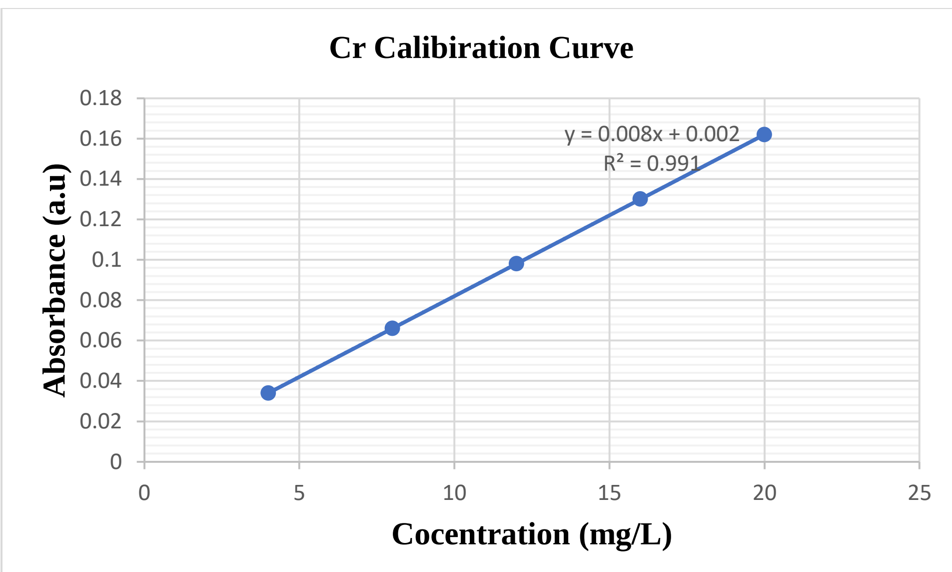
Appendix 7: Plot of Absorbance versus Concentration for Mn



Appendix 8: Plot of Absorbance versus Concentration for Na



Appendix 9: Plot of Absorbance versus Concentration for Cr



Appendix 10: List of figures or instruments

Figure 3: (3a) DR/2400 Portable Spectrophotometer (3b) Conductivity/TDS meter