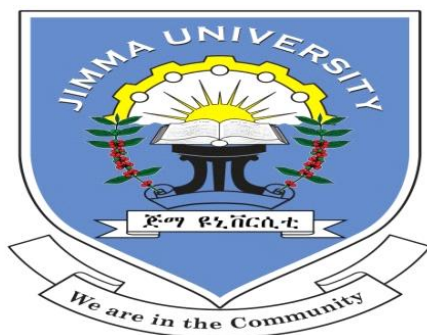


JIMMA UNIVERSITY SCHOOL OF GRADUATE STUDIES

COLLEGE OF NATURAL SCIENCES

DEPARTMENT OF CHEMISTRY



**PHYSICO-CHEMICAL STUDY OF DIFFERENT WATER SOURCE AROUND
YAYO WOREDA, I/A/BOOR ZONE, OROMIA REGION, ETHIOPIA.**

OCTOBER, 2017

JIMMA, ETHIOPIA

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ETHIOPIA.**

**M. Sc THESIS SUBMITTED TO THE SCHOOL OF GRADUATE
STUDIES, JIMMA UNIVERSITY, COLLEGE OF NATURAL
SCIENCE, CHEMISTRY DEPARTMENT IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF
THE MASTERS OF SCIENCE (M. Sc) IN CHEMISTRY
(ANALYTICAL).**

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Acronyms/Abbreviation

NTU - Nephelometric Turbidity Unit

BIS - Bureau of Indian Standards

WHO - World Health Organization

SON - standards organization of Nigeria

DO - Dissolved oxygen

TDS - Total dissolved solid

EC - Electrical conductivity

TA -Total Alkalinity

TH- Total hardness

COD - Chemical oxygen demand

ANOVA- Analysis of Variance

ICP-OES-Inductive coupled plasma- optical emission spectrometry

TISAB- Total ion strengths adjustment buffer

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Abstract

Spring and ground water is a major source of water for drinking and domestic use. The availability of good quality water is an indispensable feature for preventing diseases and improving quality of life. Therefore, this study was to determine some physico-chemical parameters different water samples (spring, tap and well water) and which was collected from different eight sample site in Yayu Woreda including Yayu town, Geci, and Bondawo. It is necessary to know details about different physico-chemical parameters such as, temperature, hardness, pH, chloride, alkalinity that are used as measures of water quality. Physico-chemical parameters such as pH, temperature, DO and EC were measured in the field. Nitrate and phosphate of the water samples were determined using Spectrophotometer and heavy metal determined by ICP-OES. Chloride, Total hardness, total alkalinity and COD were also determined by titration method. The mean average physico-chemical and the metals in water samples were in range; DO (1.89 ± 0.21 to 6.72 ± 0.35 mg/L), turbidity (1.40 ± 0.04 to 60.57 ± 2.27 NTU), total alkalinity (40.00 ± 0.50 to 99.92 ± 0.63 mg/L), total hardness (101.67 ± 2.89 to 401.67 ± 1.53 mg/L), Cl (143.18 ± 1.39 to 247.85 ± 0.98 mg/L), TDS (34.80 ± 1.07 to 262.47 ± 1.95 mg/L), NO_3^- (0.022 ± 0.01 to 0.114 ± 0.00 mg/L), PO_4^{3-} (1.04 ± 0.01 to 3.79 ± 0.02 mg/l), COD (8.00 ± 8.00 to 26.67 ± 12.12 mg/L) F^- (0.42 ± 0.01 to 0.48 ± 0.02 mg/L), Fe (0.257 ± 0.0010 to 1.244 ± 0.0400 mg/L), Cu (0.061 ± 0.0010 to 0.065 ± 0.0001 mg/L), Zn (0.065 ± 0.0001 to 0.182 ± 0.0005 mg/l), Cd (0.004 ± 0.0000 to 0.005 ± 0.0011 mg/l) and Pb (0.028 ± 0.0012 to 0.039 ± 0.2800 mg/l). This study revealed that the physico-chemical variables such as temperature, TDS, EC, pH, fluoride, phosphate, nitrate, total hardness, chloride, total alkalinity, COD and heavy metal (Cu, Zn, Cd and Pb) were lie within the permissible limit recommended by WHO guide line values. The level of concentration of Fe was above maximum allowable limit recommended by WHO guide line values.

Keyword: Physico-chemical parameters, Water quality, Heavy metal, Yayu water sources

1. Introduction

1.1. Background of the study

Water is essential for life on earth. Because of its importance, the pattern of human settlement throughout history has often been determined by its availability [1]. Next to oxygen, water is the most important substance for human existence [2]. Human existence mainly depends on fresh water supply which is less than 1% of the water available on earth [3]. Ground or spring water represents an important source of drinking water and its quality is currently threatened by a combination of over-abstraction and microbiological and chemical contamination [4]. In addition to the process of desertification, pollution is also reducing the volume of safe drinking water. Drinking water is water pure enough to be consumed or used with low risk of immediate or long term harm. In most developed countries water supplied to households, commercial and industry is all of drinking water standard even though only a very small proportion is actually consumed in food preparation [5]. But the majority of the population in developing countries is not adequately supplied with potable water and is thus compelled to use water from sources like shallow wells, boreholes, springs and streams that render the water unsafe for domestic and drinking purposes due to high possibilities of contamination [6, 7]. In order to ensure a safe public health, water supply for human consumption must be free from pathogens, free from chemical toxins and must be physically clear and appealing to taste [8]. It is also important that water for domestic, agricultural or industrial uses should not be acidic or alkaline than is required by standards for the purpose.

Water plays an important role in the world economy, as it functions as a solvent for a wide variety of chemical substances, industrial cooling, transportation and agriculture. More than 70% of freshwater is consumed for agriculture [9]. Safe drinking water is a human birthright as much as its birthright for clean air. In fact, in most of the developing African and Asian countries, even in relatively advanced countries such as India; safe drinking water is not easily available. Of the 6 billion people on earth, more than one billion lack accesses to safe drinking water and, about 2.5 billion do not have access to adequate sanitation services [10].

Although 70 percent of our globe is covered by water, yet freshwater covers only 3 percent of the earth's surface and much of it is salt contaminated or lies frozen in the Antarctic and Greenland polar ice [11]. Freshwater that is available for human consumption comes from rivers, lakes and subsurface aquifers. These sources account for only one percent of the entire water on the earth. Six billion people depend on this supply and a significant portion of the world's population is facing water shortages. Today, 31 countries representing 2.8 billion people, including China, India, Kenya, Ethiopia, Nigeria and Peru confront chronic water problems. Within an eneration the world's population will climb to an estimated 8 billion people. Yet, the amount of water will remain the same [11]. The challenge is as clear and compelling as pristine water cascading down a mountain stream. Therefore, we must find new and equitable ways of saving, using and recycling the water that we have [12].

Contaminants such as bacteria, heavy metals, nitrates and salt have found their way into water supplies due to inadequate treatment and disposal of waste from human and livestock, industrial discharges, and over-use of limited water resources [13]. Even if no sources of anthropogenic contamination exist, natural sources are also equally potential to contribute higher levels of some metals and other chemicals that can harm human health. This is highlighted recently in Bangladesh where natural levels of arsenic in groundwater were found to be causing harmful effects on the population [14].

In Ethiopia, the dominant source of drinking water used to supply major urban and rural communities is from wells, rivers, lakes and springs [15]. Even though, 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 major causes of this contamination could be soil erosion, domestic waste from urban and rural areas and industrial wastes [16].

The use of physic-chemical properties of water to assess water quality gives a good impression of the status, productivity and sustainability of such water body [17]. The evaluation of potable water supplies for coliform bacteria is important in determining the sanitary quality of drinking water [18].

The primary concerns are the effects of these domestic and agricultural wastes on the water quality and aquatic life and maintenance. Water quality monitoring is of immense

importance to activity involving the use of water bodies in the management of fisheries, water supply, pollution, sewage reservoir and impoundment. It involves the assessment of physicochemical parameters of water bodies, which is a function expressed as pollution parameters. Impacted changes in the water quality are reflected in the biotic community structure, with the most vulnerable dying. While the most sensitive species act as indicators of pollution [19]. The healthy aquatic ecosystem is depended on the physicochemical and biological characteristics. The quality of water in any ecosystem provides significant information about the available resources for supporting life in that ecosystem. Good quality of water resources affects on physicochemical parameters and biological characteristics. To asses that monitoring of these parameters is essential to identify magnitude and source of any pollution load [20].

There are no reports so far in the literature on the study of physic-chemical parameters and heavy metal contents of municipal tap water, spring and well water supply in Yayu Woreda of Ethiopia. The proposed study of physico-chemical and metals analysis is expected to deliver a base line data on the levels of metals in municipal tap water, spring and well water supply of Yayu Woreda. For this reason, due emphasis is given to the determination of the levels of physico-chemical and heavy metals present in drinking water. Therefore, determination of level of metals in the municipal different source of water is very important to ensure individuals health status. Furthermore, the result of this study may help for regular monitoring and control of water used for drinking to prevent excessive contamination, above permissible level, of the municipal water by the metals. Based on this finding the local expertise and concerned bodies will try to manage the normal level of physico-chemical and metals depending on the reported result under this study.

1.2. Statement of the problem

Water sources, which is used for domestic and drinking purposes and provide to social and economic benefits as a result of tourism and recreation. The quality of water in any ecosystem provides significant information about the available resources for supporting life in that ecosystem. Good quality of water resources affect on a large number of physico-chemical parameters and biological characteristics. Analysis of water quality in

water sources is vital to assess the current status of the water sources providing that the surrounding community to use for different purpose. There are no reports so far in the literature on the study of physico-chemical parameters and heavy metal contents of municipal tap water supply in Yayu Woreda of Ethiopia and public waste disposal and the effect of this waste site on water pollution has not yet been assessed. The present study is formulated to determine the potability of the spring water, tap water and well water by assessing the level of some physicochemical parameters (pH, DO, EC, TDS, EC, TA, TH, and COD) which justifies the quality of a drinking water. Therefore this study was attempted to answer the following basic research questions:-

- To what extent does the physicochemical parameters affects various sources of drinking water in the study area?
- Which of the parameters is highly concentrated around the study area and its effects?
- Is there a significant difference in the physical and chemical parameters of drinking water in the study area?

1.3. Objectives of the study

1.3.1. General objectives

The main objective of this study is to assess physicochemical parameters of different water sources (spring, well and tap water).

1.3.2. Specific objective

1. To determine selected physical- chemical characteristics such as temperature, turbidity, pH, EC, TDS, DO, nitrate, phosphate, Cl^- , F^- , COD, alkalinity and hardness of Yayu Woreda drinking water source.
2. To compare content physico-chemical parameters between different water sources and with international standards.
3. To determine content of some heavy metals such as Fe, Cu, Zn, Cd and Pb in Yayu Woreda drinking water source.

4. To recommend the use of those spring, well and tap water for drinking and domestic purposes based on the data obtained

1. 4. Significance

Access to quality water and seek of unpolluted environment is the need of all citizens and concern of government. Urbanization and population growth is one of the factors for the discharge of uncontrolled wastes into the environment. Especially, in developing countries lack of waste management system and poor remedial strategies makes the problem series. A suitable environment is necessary for any organism, since life depends upon the continuance of a proper exchange of essential substances and energies between the organism and its surroundings. So, the study which was carried out on the physicochemical analysis of different sources drinking water of Yayo Woreda Oromia Regional state. Therefore, the finding obtained from this study was help to know how much the area is affected by physicochemical parameter and this study can serve as an indicator for other researchers so as to study the details of these and other of the study area and this study of significant is giving information on the level of contamination and the use of the water for different purposes.

2. Literature review

2.1. Water quality

The availability of good quality drinking water is extremely important for prevention of diseases and for improving the quality of life for humans. Pure water does not exist in nature. Water in its natural form contains living / non-living, soluble / insoluble, organic / inorganic components and its quality keeps on changing from time to time and place to place. The contamination of water is directly linked to the contamination of our environment. Potable water is derived either from surface water (rivers, lakes, streams, ponds etc). However, water from either source is rarely fit for drinking. It becomes important to measure the quality of drinking water on regular basis to sufficiently support human health and to match BIS (Bureau of Indian Standards) as well as WHO (World Health Organization) standards [21].

The principal objectives of municipal water are the production and the distribution of safe water that is fit for human consumption [22]. A good knowledge of the chemical qualities of raw water is necessary so as to guide its suitability for use. Thus, regular physico-chemical analysis of water at source must be carried out to determine or check the effectiveness of treatment process.

Water is very essential for the survival of life. Of the total water present on the planet, only 1% is fresh water which is available for various domestic purposes like drinking, cooking etc. However, the amount of total fresh water available is rapidly decreasing due to industrialization and other anthropogenic activities, all the water bodies including groundwater are being polluted more than ever before. Disposal of sewage, garbage and hazardous industrial effluents directly into the water bodies, be it rivers, streams or lakes, has posed a serious threat to the aquatic life. Such activities are not only harmful for life but also destroy the aesthetics of the total environment. Therefore there is an urgent need to conserve this precious Natural Resource [23].

2.2. Physicochemical parameters

2.2.1. PH

The pH of natural water can provide important information about many chemical and biological processes and provides indirect correlations to a number of different impairments. The pH is the measurement of the acid/base activity in solution; specifically it is the negative common logarithm of the activity/concentration of hydrogen ions;

$$\text{PH} = -\log [\text{H}^+]$$

In natural waters, the pH scale runs from 0 to 14. A pH value of 7 is neutral; a pH less than 7 is acidic and greater than 7 represents base saturation or alkalinity.

Pure water free of dissolved gases will naturally become ionized; $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$

The actual number of water molecules that will ionize is relatively very small with the amount of hydrogen ions $[\text{H}^+]$ being equal to the amount hydroxide ion $[\text{OH}^-]$. At room temperature the concentration of $[\text{H}^+]$ in pure water will be 1×10^{-7} moles per liter. A pH of 7 is neutral because the $-\log(1 \times 10^{-7})$ is 7 by definition.

In unpolluted or pure waters, the pH is governed by the exchange of carbon dioxide with the atmosphere. Carbon dioxide is soluble in water and the amount of CO_2 that will dissolve in the water will be a function of temperature and the concentration of CO_2 in the air. As the gaseous CO_2 becomes aqueous, the CO_2 will be converted into H_2CO_3 which will acidify the water to a pH of about 6. If any alkaline earth metals such as sodium are present, the carbonates and bicarbonate formed from the solubilization of CO_2 will interact with sodium increasing the alkalinity shifting the pH up over 7 [24].

Lower values in pH are indicative of high acidity, which can be caused by the deposition of acid forming substances in precipitation. A high organic content will tend to decrease the pH because of the carbonate chemistry. As microorganisms break down organic material, the by product will be CO_2 that will dissolve and equilibrate with the water forming carbonic acid (H_2CO_3) [24].

Most metals will become more soluble in water as the pH decreases. For example, sulfur in the atmosphere from the burning of coal will create acid rain. The acid rain will dissolve metals such as copper, lead, zinc and cadmium as the rain runs off of manmade structures and into bodies of water. The excesses of dissolved metals in solution will negatively affect the health of the aquatic organisms [24].

The alkalinity of natural waters is controlled by the concentration of hydroxide and represented by a pH greater than 7. This is usually an indication of the amount of carbonates, and bicarbonates that shift the equilibrium producing $[\text{OH}^-]$. Other contributors to an alkaline pH include boron, phosphorous, nitrogen containing compounds and potassium

Changes in pH can be indicative of an industrial pollutant, photosynthesis or the respiration of algae that is feeding on a contaminant. Most ecosystems are sensitive to changes in pH and the monitoring of pH has been incorporated into the environmental laws of most industrialized countries.

pH is typically monitored for assessments of aquatic ecosystem health, recreational waters, irrigation sources and discharges, live stock, drinking water sources, industrial discharges, intakes, and storm water runoff [24].

2.2.2. Dissolved Oxygen

Dissolved oxygen (DO) is essential to all forms of aquatic life including the organisms that break down man-made pollutants. Oxygen is soluble in water and the oxygen that is dissolved in water will equilibrate with the oxygen in atmosphere. Oxygen tends to be less soluble as temperature increases. The DO of fresh water at sea level will range from 15 mg/l at 0 °C to 8mg/l at 25 °C. Concentrations of unpolluted fresh water will be close to 10 mg/l.

In general, the concentration of dissolved oxygen will be the result of biological activity. Photosynthesis of some aquatic plants will increase the DO during day light hours and the DO levels will fall during the night time hours. In natural waters, man-made contamination, or natural organic material will be consumed by microorganisms. As this microbial activity increases, oxygen will be consumed out of the water by the organisms

to facilitate their digestion process. The water that is near the sediment will be depleted of oxygen for this reason.

In waters contaminated with fertilizers, suspended material, or petroleum waste, microorganisms such as bacteria will break down the contaminants. The oxygen will be consumed and the water will become anaerobic. Typically DO levels less than 2 mg/l will kill fish [24].

DO is an important for many chemical and biological processes taking place in water. Dissolved oxygen in water can decrease due to microbial activity, respiratory and organic decay. Dissolved oxygen value is an indicative of pollution in water and depicts an inverse relationship with water temperature [21].

2.2.3. Total Hardness

Water hardness is caused by the polyvalent metallic ions dissolved in water. In fresh water these are primarily calcium and magnesium although other metals such as iron, strontium and manganese contribute to the extent that appreciable concentrations are present. Hardness commonly is reported as an equivalent concentration of calcium carbonate (CaCO_3). The concept of hardness comes from water supply practice. It is measured by soap requirements for adequate lather formation and as an indicator of the rate of scale formation in hot water heaters and low pressure boilers [25].

The most desirable range of hardness is between 80 and 100 mg/L. A total hardness of less than 80 mg/L may result in corrosive water, while hardness above 100 mg/L may result in the need for more soap during bathing and laundering. Excessive hardness may also lead to scale deposits in pipes, heaters, and boilers [26]. Temporary hardness which can be treated just by boiling is caused by a combination of calcium/magnesium ions and bicarbonate ions in the water. In contrast, permanent hardness is hardness that cannot be removed by boiling. It is usually caused by the presence of calcium and magnesium sulfates and/or chlorides in the water, which become more soluble as the temperature rises. The measurement for water hardness ranges described as by Water Quality Association is given in Table 1 below.

Table 1 The measurement for hardness by water quality association [37].

Hardness Level	mg/L or ppm
Soft	less than 17.1
Slightly Hard	17.1 to 60
Moderately Hard	60 to 120
Hard	120 to 180
Very Hard	180 and above

2.2.4. Electrical Conductivity

Electrical conductivity in natural waters is the normalized measure of the water's ability to conduct electric current. This is mostly influenced by dissolved salts such as sodium chloride and potassium chloride. The common unit for electrical conductivity is Siemens per meter (S/m). Most freshwater sources will range between 0.001 to 0.1 S/m. The source of EC may be an abundance of dissolved salts due to poor irrigation management, minerals from rain water runoff, or other discharges. EC is also the measure of the water quality parameter "Total Dissolved Solids" (TDS) or salinity. At about 0.3 S/m is the point at which the health of some crops and fresh water aquatic organisms will be affected by the salinity. Field measurements of EC reflect the amount of total dissolved solids (TDS) in natural waters. The relationship between TDS and EC can be described by the equation;

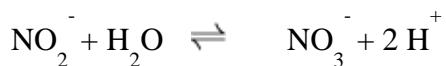
$$\text{TDS (mg/L)} \approx \text{EC (mS/cm)} \times 640$$

Salinity refers to the presence of dissolved inorganic ions such as Mg^{++} , Ca^{++} , K^+ , Na^+ , Cl^- , SO_4^{4-} , HCO_3^- and CO_3^{2-} in the aqueous solution or soil matrix. The salinity is quantified as the total concentration of soluble salts and is expressed in terms of electrical conductivity. When salts such as sodium chloride are in their solid form, they exist as crystals. Within the salt crystal, the sodium and the chlorine atoms are joined together in what is called an ionic chemical bond. An ionic chemical bond holds the atoms tightly together because the sodium atom will give up an electron to the chlorine thus ionizing

the atoms. If an atom like sodium gives up an electron, it is said to be a positively charged ion (also called a cation). If an atom such as chlorine receives an electron, it is said to be a negatively charged ion (also called an anion and is given the suffix ide, like chloride). The sodium and the chloride ions comfortably arrange themselves into a stacked like configuration called a crystal lattice. The sodium chloride crystal lattice has a zero net charge [25].

2.2.5. Nitrate

Nitrate ion is the common form of nitrogen in natural waters. Nitrite (NO_2^-) will oxidize into nitrate after entering an aerobic regime.



Similarly, plants and microorganisms will reduce nitrate into nitrite but nitrite ion will quickly oxidizes back into nitrate once it reenters the water. Natural sources of nitrate are igneous rock, plant decay and animal debris. Nitrate levels over 5 mg/L in natural waters normally indicates man made pollution, 200 mg/L is an extreme level. Man made sources of include, fertilizers, livestock, urban runoff, septic tanks, and waste water discharges. In general, nitrates are less toxic to people than ammonia or nitrite however at high levels nitrate will become toxic especially to infants. Methemoglobinemia is nitrate poisoning where high levels of nitrate enter in hemoglobin will oxidize the ferric iron II into ferrous iron III inhibiting the blood's ability to carry oxygen.(water parameter) In adults it is less effective due to nitrate metabolizing triglycerides present at higher concentration [21].

In the environment, nitrate will become toxic to fish at about 30 mg/L. Nitrate pollution will cause eutrophication of a stream where algae and aquatic plant growth will consume the oxygen and increase the TSS of the water. Eutrophication is usually the result of nitrate and phosphate contamination and is a significant reduction of water quality.

Nitrate can exist naturally in groundwater but can increase dramatically on irrigated lands if the irrigation operation is not managed properly. Groundwater contaminated with nitrate can contaminate sources of drinking water in wells, and will contaminate the surface water as the ground water recharges streams and lakes. As more land is converted

into agricultural land and as urban areas expand, nitrate monitoring is an important tool in accessing locating and mitigating man made sources of nitrate [24].

2.2.6. Alkalinity

Alkalinity is a measure of the buffering capacity of the water, and since pH has a direct effect. On organisms as well as an indirect effect on the toxicity of certain other pollutants in the water, the buffering capacity is important to water quality. Examples of commonly occurring materials in natural waters that increase the alkalinity are carbonates, bicarbonates, phosphates and hydroxides.

The alkalinity of water used for municipal water supplies is important because it affects the amounts of chemicals that need to be added to accomplish calculation, softening and control of corrosion in distribution systems. The alkalinity of water assists in the neutralization of excess acid produced during the addition of such materials as aluminum sulfate during chemical coagulation. Waters having sufficient alkalinity do not have to be supplemented with artificially added materials to increase the alkalinity.

Excessive alkalinity can cause problems for swimmers by altering the pH of the lacrimal fluid around the eye, causing irritation. For industrial water supplies, high alkalinity can be damaging to industries involved in food production, especially those in which acidity accounts for flavor and stability, such as the carbonated beverages. In other instances, alkalinity is desirable because water with a high alkalinity is much less corrosive.

The effect of alkalinity in water used for irrigation may be important in some instances because it may indirectly increase the relative proportion of sodium in soil water [25].

To maintain a fairly constant pH in a water body, a higher alkalinity is preferable. High alkalinity means that the water body has the ability to neutralize acidic pollution from rainfall or basic inputs from waste water [28]. Poorly-buffered water will have a low or very low alkalinity and will be susceptible to pH reduction by, for example, "acid rain"[27].

2.2.7. Total dissolved solids

Dissolved solids and total dissolved solids are terms generally associated with freshwater systems and consist of inorganic salts, small amounts of organic matter, and dissolved

materials. The principal inorganic anions dissolved in water include the carbonates, chlorides, sulfates, and nitrates (principally in ground waters); the principal cations are sodium, potassium, calcium, and magnesium.

Excess dissolved solids are objectionable in drinking water because of possible physiological effects, unpalatable mineral tastes, and higher costs because of corrosion or the necessity for additional treatment. The physiological effects directly related dissolved solids include laxative effects principally from sodium sulfate and magnesium sulfate and the adverse effect of sodium on certain patients afflicted with cardiac disease and women with toxemia associated with pregnancy [25, 29].

2.2.8. Temperature

Many aquatic organisms are sensitive to changes in water temperature. Temperature is an important water quality parameter and is relatively easy to measure. Water bodies will naturally show changes in temperature seasonally and daily; however, man made changes to stream water temperature will affect fish's ability to reproduce. Many lake and rivers will exhibit vertical temperature gradients as the sun will warm the upper water while deeper water will remain cooler.

Fish friendly dams will have selective water releases where the temperature of the stream can be controlled by the water depth of release. In the summer, the water could be released from the bottom of the dam and in the winter the water is released from the top. This selective release will mitigate the impact the dam will have on the water temperature [25].

Some streams will increase in temperature as the stream water moves down stream through urban, industrial and agricultural areas. A stream in forested head waters will be at a suitable temperature for the native aquatic life. As the stream meanders through pasture land, the riparian vegetation will not be abundant enough to effectively shade the stream. Once the stream makes in to urban area, the stream may become channeled to make room for housing. Removing the natural meander from a stream will increase the velocity of the water which will cause erosion further degrading the quality of the water. Impervious structures such as parking lots, roads and buildings will prevent the infiltration of rainwater into the groundwater. Instead of being fed from cool

groundwater, the stream will receive run off after rain events further degrading the quality of the water and increasing the temperature.

Environmental policies require the monitoring of stream water temperature. In most urban and industrial locations, environmental permits are required to help minimize the temperature loading to streams [25].

2.2.9. Turbidity

Turbidity or Total Suspend Solids (TSS) is the material in water that affects the transparency or light scattering of the water. The measurement unit used to describe turbidity is Nephelometric Turbidity Unit (NTU). The range for natural water is 1 to 2000 NTU.

TSS is typically composed of fine clay or silt particles, plankton, organic compounds, inorganic compounds or other microorganisms. These suspended particles range in size from 10 nm to 0.1 mm although in standardized laboratory tests, TSS is defined as the material that cannot pass through a 45 μm diameter filter. TSS as well as TDS can be influenced by changes in pH. Changes in the pH will cause some of the solutes to precipitate or will affect the solubility of the suspended mater. The manmade sources of TSS include erosion, storm water runoff, industrial discharges, microorganisms, and eutrophication. Many fish species are sensitive to prolonged exposure to TSS and monitoring of TSS is an important criteria for assessing the quality of water [25].

Turbidity can indicate that water may be contaminated with pathogens presenting human health concerns [30].

2.2.10. Phosphate

Phosphates will form salts with sodium and calcium and fall out of solution to accumulate in the sediment. Phosphates ions in natural waters will exist in solution in its ionized form, as salts, in organic form or as a particulate species. Higher concentrations rarely occur, because after it enters a water system, it will be rapidly up taken by plants. Phosphorous is an essential nutrient to living organisms. In unpolluted waters, phosphorous can enter a water system from the weathering of phosphorous baring rocks and minerals. In areas of high volcanic activity, phosphorous may be naturally abundant in the soils. Man made sources of phosphate in the environment include domestic and

industrial discharges, agricultural runoff where fertilizers are used, and changes in land use in areas where phosphorous is naturally abundant in the soil. [24]

In general, phosphates are not very toxic to people or other living organisms. Like nitrogen containing compounds, the main environmental impact associated with phosphate pollution is eutrophication. High levels of phosphorus will be quickly consumed by plant and microorganisms, impairing the water by depleting the dissolved oxygen and increasing the turbidities. These impairments will kill or harm fish and other aquatic organisms [24].

2.2.11. Chloride

Chloride anions are usually present in natural waters. High chloride content may indicate pollution by sewage or industrial wastes or by the intrusion of seawater or saline water into a freshwater body or aquifer. A salty taste in water depends on the ions with which the chlorides are associated. With sodium ions the taste is detectable at about 250 mg/ l Cl^- , but with calcium or magnesium the taste may be undetectable at 1,000 mg/ l high chloride content has a corrosive effect on metal pipes and structures and is harmful to most trees and plants [24].

Chloride is very common and occurs in human, animal and industrial wastes. The differential permeability of clay is considered to be a major factor in the behavior and composition of saline water resources associated with fine-grained sediments. However, the most common type of water in which chloride dominates have high sodium content [31]. High chloride content has also a corrosive effect on metal pipes and structures and is harmful to most trees and plants [32].

2.2.12. Chemical oxygen demand

The chemical oxygen demand (COD) is the amount of oxygen consumed by organic matter from boiling acid potassium dichromate solution. It provides a measure of the oxygen equivalent of that portion of the organic matter in a water sample that is susceptible to oxidation under the conditions of the test. It is an important and rapidly

measured variable for characterizing water bodies, sewage, industrial wastes and treatment plant effluents. [32].

In the absence of a catalyst, however, the method fails to include some organic compounds, such as acetic acid, that are biologically available to the aquatic organisms but does include some biological compounds, such as cellulose, that are not part of the immediate biochemical demand on the available oxygen of the receiving water. With certain wastes containing toxic substances, COD or a total organic carbon determination may be the only method for determining the organic load. It should be noted that the COD is not a measure of organic carbon, although the same chemical reactions are involved. Where wastes contain only readily available organic bacterial nutrients and no toxic matter, the results can be used to obtain an approximate estimate of the ultimate carbonaceous BOD values.

The use of exactly the same technique each time is important because only a part of the organic matter is included, the proportion depending on the chemical oxidant used, the structure of the organic compounds and the manipulative procedure. The dichromate method has been selected as a reference method for the COD determination because it has advantages over other oxidants owing to its oxidizing power, its applicability to a wide variety of samples and its ease of manipulation. The test will have most value for monitoring and control of effluents and receiving waters after correlation with other variables has been established [32].

2.2.13. Fluoride

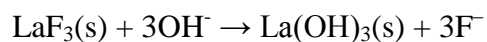
Fluorides come naturally into water by dissolving minerals that contain fluor, such as *fluorite* (CaF_2), the most common fluor mineral, *apatite* ($\text{Ca}_5(\text{Cl},\text{F},\text{OH})(\text{PO}_4)_3$), *cryolite* (Na_3AlF_6). Amphibole minerals, such as hornblende and some sorts of mica can contain fluor that partially replaces hydroxide ion. Rocks rich in alkali metals have a larger content of fluoride than other volcanic rocks. Fresh volcanic ash, as well as the ash of the other sediments can contribute to fluor content increasing in surface waters. Mixed minerals $\text{NaMgAl}(\text{F},\text{OH})_6\cdot\text{H}_2\text{O}$ and $\text{Al}_2(\text{F},\text{OH})_6\cdot\text{H}_2\text{O}$ and are rare, but can contribute to the fluoride content increasing while rinsing with water. According to values for the dissolving result of calcium fluoride in water, where activity of calcium ion is 0.001

mol/dm³ concentration of fluoride ions is 3.1 mg/dm³. Total concentration of fluoride ions will be somewhat higher, which depends on ion strength and complexing effects, and it will be higher in waters where the concentration of Ca²⁺ ion is smaller (that is, in waters with low hardness) [33].

The main source of fluor intake is drinking water and food, and secondary are stomatology prophylactic preparations. To date there are not reliable data about minimal daily nutritive requirements for fluor. Fluoride ion in traces in drinking water helps in growth and development of healthy, resistant teeth and bones. In many researches it was determined that fluorides are efficient in prevention of dental caries. Teeth enamel is mostly made of mineral hydroxyapatite. Hydroxyapatite contains hydroxide ion, which fiercely attacks acids (results of bacteria in mouth where they are feeding with sugar), as a difference from much weaker basis, fluoride-ion in fluoroapatite [34]. Fluoride selective electrode is very sensitive, and temperature range of electrode goes from 0 to 50°C. For potentiometric analysis of fluoride ion, in commercial usage, there are mostly used electrodes with homogenic membrane made from fluoride lanthana (LaF₃), which was first suggested by Frant and Ross [35].

Fluoride selective electrode is very selective to fluoride ions, but at the same time, in a certain amount, it is selective to hydroxide ion. Adjustment of pH value with buffer is necessary because fluoride and hydroxide ions have the same electricity and similar ion radius, so hydroxide ions can interfere in the measurement of the fluoride selective electrode. In acid solutions hydrofluoric is formed, to which the fluoride selective electrode is not sensitive. In that way, with solution pH values decreasing, the activity of fluoride ion in solution also decreases, so the measurement will not be reliable.

On the other hand, in highly base solutions a thin layer of La(OH)₃ is formed on the surface of the sensor part:



A simple and widely used method uses a fluoride ion selective electrode. This electrode in combination with a suitable reference electrode forms an electrochemical cell whose electrical potential is a function of fluoride ion concentration. To minimize the effects of varying ionic strength and interference from other ions, a buffer referred to as a total ionic strength adjusting buffer (TISAB) is added to all standards and the sample(s). The

electrode is calibrated using a series of known concentrations of fluoride. The voltage of each solution is measured, and this voltage plotted as a function of concentration. The response of the sample is obtained in a similar manner and the concentration is then determined from the calibration curve.

2.3. Heavy Metal and their Toxicity

Heavy metals are elements having atomic weights between 6.5 and 200.6 and a specific gravity more than 5.0 [36]. Some heavy metals are toxic or carcinogenic, and are not biodegradable and tend to accumulate in living organisms [37]. When natural water bodies are contaminated with wastewater containing higher concentration of heavy metals, it affects aquatic life and is destructive to the environment. Bioaccumulations of heavy metals in the body through food chain lead to a variety of incurable diseases when people drink the water or eat the food contaminated by heavy metals [38]. Some heavy metals *viz.* copper, iron, and zinc are required in trace amount by living organisms. However, they can be detrimental to the organism when they are in excessive level. Non-essential heavy metals of particular concern to surface water systems are cadmium, and lead, [36].

Lead: Lead is considered as one of the most dangerously toxic heavy metals because it is ubiquitous metal which is present everywhere including homes, soil, work place, foods and water [39]. The main sources of pollution of natural water by lead are lead pipes, mines and effluent of many industries such as those producing batteries, automobiles, metal sheets garages or paint. Lead may enter the atmosphere during mining, smelting, refining, manufacturing processes and by the use of lead products. Lead intake occurs from the 10 consumption of whisky, fruit juices, food stored in lead containers, cosmetics, cigarettes and motor vehicle exhaust [40]. Lead may occur in drinking water either by contamination of the source water used by the water system, or by corrosion of lead plumbing. The WHO guideline about drinking water for human consumption states that the maximum allowed lead concentration in drinking water should not exceed 0.015mg/L and some precautions can be taken to lower lead content in drinking water [41].

Cadmium: Cadmium is a highly toxic heavy metal, considered carcinogen. Its harmful action is similar to the effect of lead and it can be released in drinking water by zinc and iron pipes. Zinc always contains a small amount of cadmium [42]. Cadmium occurs naturally in zinc, lead, copper and other ores which act as source to ground and surface waters. Cadmium can be released in drinking water from the corrosion of some galvanized plumbing and water main pipe material [42].

3. Material and Method

3.1. Instrument and Apparatus

Hatch Digital conductivity meter 4600, DO meter, PC 300 pH meter, mercury thermometer (0-100⁰C), photometer 7100, PerkinElmer Optima 8000 ICP-OES, HI1315 F combination electrode, ice bag, refrigerator, stand flask, mechanical shaker, Polyethylene bottle, analytical balance was used during the experiment.

3.2. Chemicals

All reagents in the analysis is analytical grade. Nitric acid (HNO₃ 69%, LOBA CHEMIE, India), Hydrogen peroxide (H₂O₂ 30%), China H4 EDTA 99%, Hydrochloric acid (HCl 36%, LOBA CHEMIE, India), Sulfuric acid (H₂SO₄ 98%, LOBA CHEMIE, India), Sodium Oxalate (Na₂C₂O₄ 99%, China), Potassium permanganate (KMnO₄, India), Copper sulfate (CuSO₄), Ammonia (NH₃), Potassium dichromate (K₂Cr₂O₇ 99%), methyl orange, Potassium iodide (KI), Ammonium chloride (NH₄Cl), Ammonium hydroxide (NH₄OH) , Calcium carbonate (CaCO₃), Sodium carbonate (Na₂CO₃), EBT , was used. Distilled, de-ionized and double distilled water was used for cleaning and dilution purposes.

3.3. Study area

In this study, different water sources samples was collected from Yayu water sources and its surrounding areas of Yayu town, I/A/Bor zone, Oromia Region which is located at 08⁰, 20.830'N 035⁰, 50.079'E about 528 km away in southwestern part of Addis Abeba, Ethiopia.

Table 2. GPS location of study area

Code	Source Name	GPS location of sampling point		Elevation (m)
		Latitude(N)	Longitude (E)	
T-01	Wobo Tap water	08 ⁰ 20.544'	035 ⁰ 48.449'	1577
S-02	Shewa beri spring water	08 ⁰ 20.618'	035 ⁰ 49. 639'	1625
W-03	Wobo well water	08 ⁰ 20.540'	035 ⁰ 48.947'	1607
S-04	Aba Faji spring water	08 ⁰ 20.436'	035 ⁰ 49.514'	1607
S-05	Geci spring water	08 ⁰ 21.676'	035 ⁰ 52.363'	1471
W-06	Bus station well water	08 ⁰ 20.512'	035 ⁰ 49.028'	1619
W-07	Geci well water	08 ⁰ 20.830'	035 ⁰ 50.079'	1682
T-08	Bondawo Tap water	08 ⁰ 21.201'	035 ⁰ 50.332'	1608

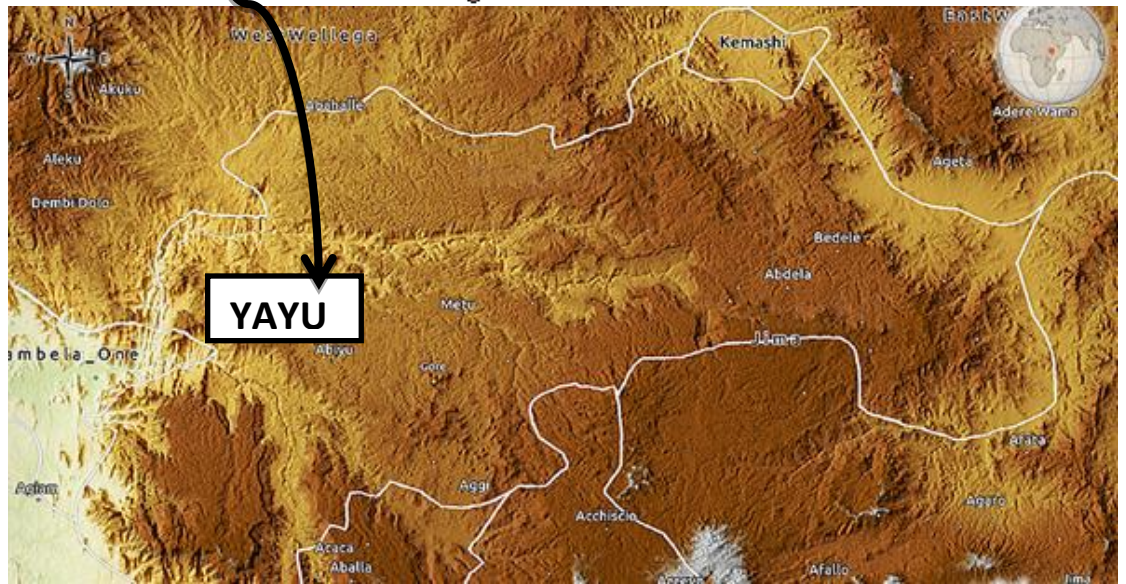
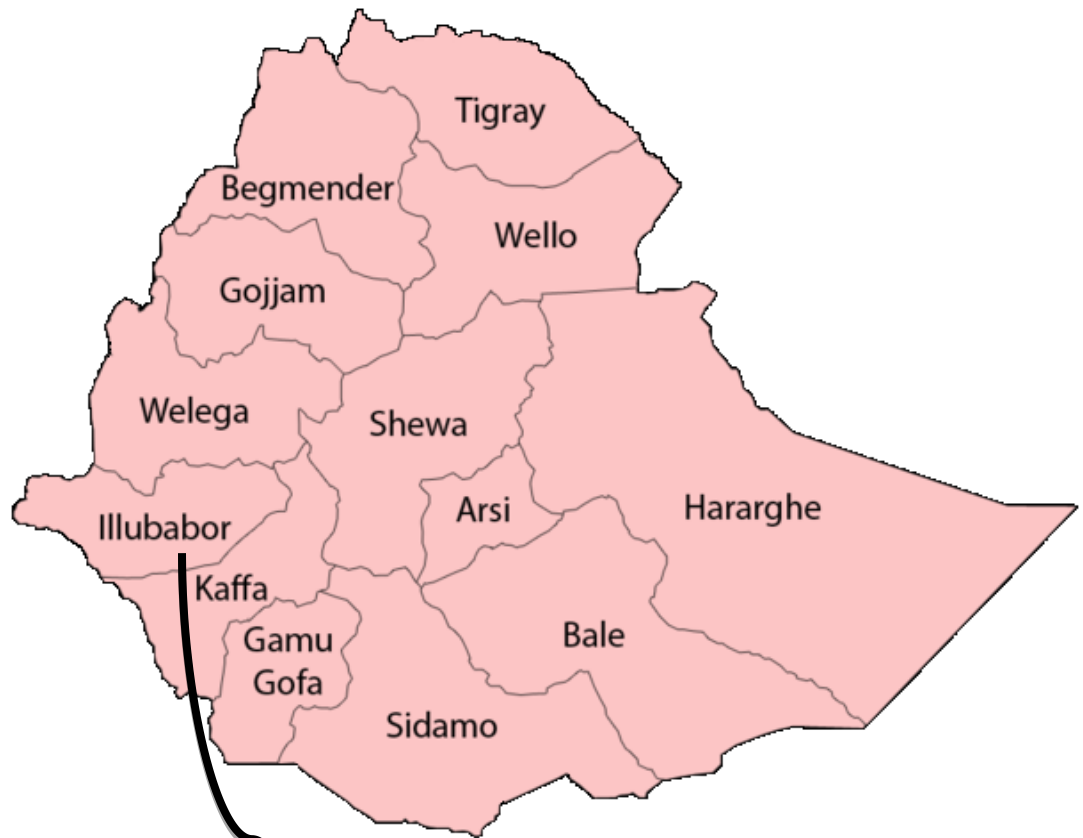


Figure 1. Map of Ilubabor shows sample location Yayu [43]

3.4. Samples and sampling techniques

Spring, well, and tap water samples were collected from eight different Stations in the Morning Hours between 6:00 to 9:00 am, in one liters capacity polythene bottles separately, without any air bubbles and prior to the collection, the polythene bottles were previous washed and soaked overnight with 5% HNO₃ solution. To avoid any kind of contamination during sampling extra care was taken and the bottles were rinsed several times with the water being collected or filled and every precautionary measure was taken. Finally the water samples collected 1 L of the sample was acidified with 5 ml concentrated HNO₃ (Analytical grade).were kept in refrigerator (4°C).

3.5. Methodology of the experiment

Standard methods were used for determining of chemical and physical characteristics of the water samples. Samples were analyzed for the following physicochemical properties: pH, temperature, conductivity, turbidity, total dissolved solids (TDS), total hardness, total dissolved oxygen (DO), chemical oxygen demand (COD), total alkalinity, nitrate, chloride, and phosphate, using standard techniques. P^H, turbidity, temperature and electrical conductivity were determined using P^H meter, turbidity meter, thermometer, and conductivity meter, respectively. Total hardness, total alkalinity, and chloride, was determined by titration. Total dissolved solids, Nitrate, phosphate, chemical oxygen demand; total dissolved oxygen was determined by TDS meter, Spectrophotometric method, DO meter method respectively and Estimation of various Physico-chemical Parameters like Water Temperature, conductivity, dissolved oxygen and pH was recorded at the time of Sample Collection, by using Thermometer, conductivity meter, DO and Digital pH Meter. While other Parameters Such as, TDS, Hardness, Chlorides, Fluorides, Alkalinity, Phosphate and Nitrate was determined by TDS meter, titration, ion selective electrode, and Spectrophotometric method.

3.6 procedures

Digital pH meter was used to determine the pH of samples after calibrating with two different buffer solutions (4.0 and 7.0 pH values) [7].

A Hatch conductivity meter 4600 was used to determine the conductivity of the samples. An electrode connected to a meter was immersed into the sample of water so that the water covered a sensitized electrode. Values on the display kept varying until a stabilized value was obtained and recorded.

Determination of alkalinity procedure primary standard solution of 0.1 M Na_2CO_3 is provided and secondary standard solutions of HCl and water sample are provided. Standardize of HCl solution by primary standard Na_2CO_3 solution. Pipette out 10ml of Na_2CO_3 solution in conical flask add 2 drops of methyl orange indicator, fill up the burette with 0.1 M HCl solution and titrate till the color of the solution changes from yellow to red [44]. For determination of total hardness procedure take out 20 ml of the field sample by pipette and fill conical flask and add 2 ml of ammonia buffer, So that the P^{H} was maintained between 9 and 10 and 2 drops of EBT indicator turns to win red in color. Fill the burette with 0.1 EDTA and titrate the contents against EDTA solution, continues the titration till the color changes to steel blue and then calculate the total hardness [45]. Determination of chloride procedure dilute sample water by pipette 20 ml sample into 100 ml volumetric flask and making it up to the mark with distilled water and pipette a 10 ml aliquot of dilute sample water in to conical flask and add about 50 ml distilled water and 1 ml of chromate indicator and titrate the sample with 0.1 M silver nitrate solution. The end point of the titration is identified as the appearance of a red-brown color of silver chromate. [46]

Determination of Chemical Oxygen Demand (COD) was determined according to the method reported by Rand and Taras (1975). Ten milliliter of the sample was taken in a 100 ml bottle then 5 ml of conc. H_2SO_4 was added and about 1g of copper sulphate (CuSO_4) also added. Then 3 ml of prepared N/40 KMnO_4 solution was added and the bottle was immersed in boiling water for 30min while keeping the surface of the boiling water at the higher level than the surface of the sample. Then 3 ml prepared N/40 sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) was added and immediately titrated with N/40 potassium permanganate (KMnO_4) until violet color appeared then repeated for the blank separately under same condition using 10 ml of distilled water instead of 10 ml of sample. Then,

$$\text{COD as mg O}_2/\text{L} = \frac{(\text{B}-\text{A}) \frac{1}{40} \times 8000}{\text{ml of sample}}$$

Where: A = ml of KMnO_4 used for sample.

B = ml of KMnO_4 used for blank.

$1/40$ = molarity of KMnO_4 .

8000 = milliequivalent weight of oxygen \times 1000 ml/L.

Determination of fluoride using ion selective electrode procedure buffer solution, pH 5.0 to 5.5: To approximately 500 mL of distilled water in a 1 liter beaker add 57 mL of glacial acetic acid, 58 g of sodium chloride and 4 g of EDTA. Stir to dissolve and cool to room temperature. Adjust the pH of this solution to between 5.0 and 5.5 using 5N sodium hydroxide (about 150 mL will be required). Transfer solution to a 1 liter volumetric flask and dilute to the mark with distilled water. Sodium hydroxide, 5N: Dissolve 200 g sodium hydroxide (solid) or 400 g of 50% sodium hydroxide solution in distilled water cool and dilute to 1 liter. Note: This is used only to adjust the pH of the buffer solution. Prepare a series of at least five calibration standards covering the range of 0.1 mg/L F^- to 10 mg/L by pipetting appropriate amounts of the fluoride stock solution into 100.00 mL volumetric flasks. Add 50 mL of the TISAB solution, then dilute to the mark with deionized water. Unless the standards are immediately analyzed, store in polyethylene containers. You may need to make an intermediate concentration of fluoride, from which your calibration standard can be prepared. This process is described as “serial dilution”. Pipet 25.00 mL of the unknown into a 50.00 mL volumetric flask and mark it to dilute with TISAB. If it is necessary to store the sample transfer it to a polyethylene container. After measuring all of the calibration solutions and the sample(s), prepare a calibration curve by plotting the relative mV vs. the log of the concentration of the standards. Read the concentration of the unknown sample from the calibration curve. From this data calculate the mg/L (ppm) fluoride ion in the water sample. [47]

3.7 Digestion of Water Samples

EPA 3005A method was used for digesting the water samples [48]. Typically, 50 ml of sample was mixed with 1mL concentrated HNO_3 , 2.5mL concentrated HCl and drop of H_2O_2 and heated on a hot plate until the volume was reduced to about 15mL. The solution was filtered and finally diluted to 50 ml using de ionized water. The concentrations of heavy metals were determined using ICP-OES.

3.8 Method validation

3.8.1 Instrument calibration

Calibration curves were prepared to determine the concentration of heavy metals in tap, spring and well water samples under investigation are presented in table 2. The working standard solutions of each metal were prepared from intermediate standard solutions of the respective metals. The correlation coefficients of the calibration curve for each of the metals are presented in Table 2.

Table 3. Results of correlation coefficient, intercept and slop from the calibration curves for heavy metal and fluoride.

Metal	intercept	slop	R ²
Fe	0.06	1E + 06	0.999
Cu	-0.005	87412	0.998
Zn	0.34	47780	0.999
Cd	0.06	88072	0.999
Pb	0.04	73626	0.999
F ⁻	2.07	61.76	0.999

3.9. Method detection limit and Limit of quantification

Method detection limit is defined as the minimum concentration of analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero [49]. In other words, it is the lowest analyte concentration that can be distinguished from statistical fluctuations in a blank, which usually correspond to three times the standard deviation of the blank δ blank where δ standard deviation of the blanks and added the mean of the blanks [49].

Five blank samples were digested following the same procedure as the samples and each of the blank samples was analyzed for the selected heavy metals (Fe, Cu, Zn, Cd and Pb) and fluoride concentrations inductive coupled plasma – optimized emission spectrometry and ion selective electrode respectively. The standard deviations for each metal were

calculated from the five blank measurements and the mean to determine method detection limit of the instrument [50].

Limit of detection (LoD) is based on the standard deviation of the response and the slope.

The detection limit (LoD) may be expressed as: $MDL = 3.3 \sigma/S$

Where σ = the standard deviation of the response (peak height, peak area etc.)

S = the slope of the calibration curve

- The slope S may be estimated from the calibration curve of the analyte.
- For this purpose the “blank + 3 δ ” approach will usually suffice.
- δ = standard deviation of sample blank or fortified sample blank value.

Limit of quantification (LoQ) based on the standard deviation of the response and the slope.

The quantitation limit (QL) may be expressed as: $QL = 10 \sigma/S$

Where σ = the standard deviation of the response (peak height, peak area etc.)

S = the slope of the calibration curve

- The slope S may be estimated from the calibration curve of the analyte.
- For this purpose the “blank + 5 δ , 6 δ or 10 δ ” approach will usually suffice.
- δ = standard deviation of sample blank or fortified sample blank value

Table 4. Method detection limits for municipal tap, spring and well water samples

Metal	IDL(mg/L)	MDL(mg/L)	LoQ
Fe	0.0046	0.1090	0.1580
Cu	0.0097	0.0450	0.0520
Zn	0.0059	0.0750	0.0780
Cd	0.0027	0.0028	0.0031
Pb	0.0042	0.0187	0.0249
F ⁻	–	0.4094	0.4120

IDL = Instrument detection limit; MDL = Method detection limit and LoD= Limit of quantification

3.10. Recovery Test

The efficiency of the digestion procedure used for digesting the water samples was estimated using recovery test and also the validity for water sample was checked by carrying out spiking. The percentage recoveries were calculated by using the following formula given below [51].

$$\text{Percent recovery} = \frac{C - C_0}{C_A} \times 100$$

Where: C- Concentration of the spiked sample

C₀- Concentration of non-spiked sample

C_A- Concentration of metal added

4 Results and Discussions

4.1 Physico-chemical parameters

Table 5.The results of P^H and temprature(⁰C)

Code	Types of sample water	pH	Temperature(⁰ C)
T-01	Wobo tap water	6.80	19
S-02	Shewa bari spring water	6.50	22
W-03	Wobo well water	7.05	23
S-04	Aba Faji spring water	6.98	21
S-05	Geci spring water	7.25	21
W-06	Buss station well water	7.79	24
W-07	Geci well water	8.24	20
T-08	Bondawo tap water	7.80	19

pH

The pH is a measure of the hydrogen ion concentration in water (Table 4). The pH value of water indicates whether the water is acidic or alkaline. Drinking water with pH 6.5 to 8.5 is generally considered satisfactory. In this study, the concentration of hydrogen ion (pH) ranges between 6.50 to 8.24 and the minimum value recording at site Shewa beri spring water and the maximum value recorded at site Geci well water. The fluctuations may be due to low rates of decomposition and good amount of calcium carbonates and magnesium in the area. All the water samples analyzed have concentration within the safe limit of 6.5 to 8.5 standard set by the WHO and SON.

Temperature: Basically important for its effect on other properties. Temperature readings were made on-site immediately before sedimentation of water at each sampling site [52]. The value for spring, tap and well water temperatures were range “between” 19 to 24. The minimum level recorded at the site of Wobo tap water and Bondawo tap water and the maximum level recording at the site of Buss station well water. The values reported in this work are within the range recommended by WHO which is 30°C.

Table 6. Mean and standard deviation values of various physico-chemical properties of spring water and tap water sample (n=3)

Types	Spring water			Tap water	
	S-02	S-04	S-05	T-01	T-08
physicochemical properties	Mean \pm SD	Mean \pm SD	Mean \pm SD	Mean \pm SD	Mean \pm SD
EC	166.99 \pm 0.01	127.56 \pm 0.79	460.60 \pm 0.85	161.18 \pm 0.43	109.88 \pm 0.52
NTU	1.41 \pm 0.05	1.69 \pm 0.06	1.62 \pm 0.06	1.61 \pm 0.04	1.40 \pm 0.04
TA	79.92 \pm 0.42	89.75 \pm 0.66	49.83 \pm 0.29	99.92 \pm 0.63	50.00 \pm 0.00
TH	299.67 \pm 0.58	299.67 \pm 1.32	299.50 \pm 0.87	101.67 \pm 2.89	401.67 \pm 1.53
Cl ⁻	143.18 \pm 1.39	174.54 \pm 2.71	247.85 \pm 0.98	178.09 \pm 1.02	230.75 \pm 1.78
TDS	139.13 \pm 0.99	133.67 \pm 2.08	113.33 \pm 2.52	34.80 \pm 1.07	124.03 \pm 1.54
DO	3.37 \pm 0.03	1.89 \pm 0.21	3.5 \pm 0.50	4.32 \pm 0.05	4.70 \pm 0.30
NO ₃ ⁻	0.025 \pm 0.00	0.046 \pm 0.00	0.022 \pm 0.00	0.04 \pm 0.01	0.025 \pm 0.00
PO ₄ ³⁻	1.50 \pm 0.026	1.15 \pm 0.01	1.55 \pm 0.01	1.04 \pm 0.01	3.79 \pm 0.02
COD	13.33 \pm 2.31	12.00 \pm 4.00	26.67 \pm 6.11	24.00 \pm 4.00	24.00 \pm 4.00
F ⁻	0.48 \pm 0.02	0.45 \pm 0.02	0.48 \pm 0.02	0.43 \pm 0.02	0.44 \pm 0.02

SD= Standard deviation, S-02 =Shewa Bari spring water, S-04= Aba Faji spring water, S-05= Geci spring water, T-01= Wobo tap water and T-08= Bondawo tap water

Table 7. Mean and standard deviation values of various physico-chemical properties of well water sample (n=3)

Types physicochemical properties	Well water		
	W-03	W-06	W-07
	Mean \pm SD	Mean \pm SD	Mean \pm SD
EC	464.50 \pm 0.71	498.08 \pm 0.60	91.04 \pm 0.35
NTU	1.61 \pm 0.06	1.51 \pm 0.25	60.57 \pm 2.27
TA	60.00 \pm 0.50	40.00 \pm 0.50	70.00 \pm 0.00
TH	201.67 \pm 2.63	201.17 \pm 1.26	400.00 \pm 0.00
Cl ⁻	181.05 \pm 3.55	177.50 \pm 3.55	246.73 \pm 1.78
TDS	123.47 \pm 0.45	193.00 \pm 2.00	262.47 \pm 1.95
DO	4.32 \pm 0.35	6.72 \pm 0.35	5.32 \pm 0.25
NO ₃ ⁻	0.138 \pm 0.001	0.028 \pm 0.001	0.114 \pm 0.001
PO ₄ ³⁻	1.45 \pm 0.01	2.41 \pm 0.01	1.75 \pm 0.01
COD	18.00 \pm 2.00	22.67 \pm 2.30	8.00 \pm 8.00
F ⁻	0.43 \pm 0.01	0.48 \pm 0.02	0.42 \pm 0.01

W-03= Wobo well water, W-06= Buss station well water and W-07= Geci well water

Electrical conductivity (EC)

It is known that EC is a measure of the ability of aqueous solution to carry an electric current that depends on the presence and total concentration of ions, their mobility and valance and on the temperature [53]. The EC is a valuable measure of the amount of metal ions dissolved in wastewater and water.

In present study, the values of EC in all sampling points were ranged from 91.04 \pm 0.35 to 498.08 \pm 0.60 μ S. The minimum value EC is recorded at site Geci well water and the maximum value recorded at site Buss station well water. The electrical conductivity values shows fluctuations and may be due to the contamination from domestic sewage and inorganic fertilizer inputs [54] and also may be due to bicarbonate and calcium ions present in the rocks there and Very large variations in the electric conductivity may be attributed to variation to total dissolved solids.

The values obtained in all sampling sites were within the standard value of WHO drinking water quality which is 500 μ S. So they are good for use.

Turbidity (NTU)

The turbidity of water sample recorded from 1.40 \pm 0.04 to 60.57 \pm 2.27 NTU. The maximum value of 60.57 \pm 2.27 NTU was recorded at Geci well water site, it may be due to human activities and the rain fall since it is open well water, decrease in the water level and presence of suspended particulate matter and minimum value of 1.40 \pm 0.04 NTU at Bondawo tap water. These maximum results indicate that, it may be due to the presence of colloidal and suspended matter (such as clay, silt, finely divided organic and inorganic matter, plankton, and other microscopic organisms). The added presence of turbidity increases the apparent, but not the true colour of water. The values obtained in all sapling sites were within permissible limit of WHO drinking water quality which is 5 NTU except Geci well water sample.

Total alkalinity

Alkalinity of water is defined as the ionic concentration, which can neutralize the hydrogen ions. In the present study the total of the S-02, S-04 and S-05 were 79.92 \pm 0.42 mg/L, 89.75 \pm 0.66 mg/L and 49.83 \pm 0.29 mg/L respectively for spring water, T-01 and T-08 were 99.92 \pm 0.63 mg/L and 50.00 \pm 0.00 mg/L respectively and W-03, W-06 and W-07 were 60.00 \pm 0.50 mg/L, 40.00 \pm 0.50 mg/L and 70.00 \pm 0.00 mg/L respectively for each sample values and the minimum concentration level was 40.00 \pm 0.50 mg/L recording at the site Buss station well water and the maximum concentration level were 99.92 \pm 0.63 mg/L recorded at site Bondawo tap water. Total alkalinity may be due to bicarbonates of calcium and magnesium in the tap water and the variations are significant at P<0.05.

According to ISI and WHO the permissible limit for alkalinity in drinking water is 200 mg/L. Therefore, the value of total alkalinity content in all sampling points have been found to as compared to desired limit value, it is permissible limit.

Total hardness

Total hardness of water mainly depends upon the amount of calcium and magnesium salts or both. The permissible limits of total hardness in potable water ranged within 500 mg/L as given by WHO for drinking water. In the present study the values of total

hardness in all sampling sites ranged from 101.67 ± 2.89 to 401.67 ± 1.53 mg/L. the minimum value recorded Wobo tap water and maximum value recording at Bondawo tap water. The higher values of calcium and magnesium are in the rocks and the variations are significant at $P < 0.05$. Wobo tap water moderately hard and all the rest are very hard. The water quality analysis showed the hardness values of the spring water, tap water and well water sample were within permissible limit and is safe for drinking and other domestic uses.

Chloride (Cl⁻)

Cl⁻ is normally the most dominant anion in water and it imparts salty taste to the water. The permissible limit of chloride in drinking water is 250 mg/L as given by WHO and SON. In present study, the results of chlorides in all sampling sites, S-02, S-04 and S-05 were 143.18 ± 1.39 mg/L, 174.54 ± 2.71 mg/L and 247.85 ± 0.98 mg/L respectively for spring water samples, T-01 and T-08 were 178.09 ± 1.02 mg/L and 230.75 ± 1.78 mg/L respectively for tap water and W-03, W-06 and W-07 were 181.05 ± 3.55 mg/L, 177.50 ± 3.55 mg/L and 246.73 ± 1.78 mg/L respectively for well water and the variations are significant at $P < 0.05$. The chloride level recorded in the entire sampling points of the spring water, ground water and tap water were the permissible levels of chloride for safe drinking water set by WHO (250 mg/L) and SON (250 mg/L). Therefore thus studied samples of spring water, tap water and well water are safe for drinking and other domestic uses.

Total dissolved solids (TDS)

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 [55]

In the present study, the concentrations of TDS in all sampling sites were ranged from 34.80 ± 1.07 mg/L to 262.47 ± 1.95 mg/L. These values were within the standard limits of drinking water quality set by WHO (500 mg/L) and SON (500 mg/L) and the variations are significant at $P < 0.05$. Thus a low level of TDS contents of the spring water, well water and tap water allows the water for drinking and other domestic uses.

Total dissolved oxygen

The measured values of total dissolved oxygen in all sampling sites S-02, S-04 and S-05 were 3.37 ± 0.03 mg/L, 1.89 ± 0.21 mg/L and 3.5 ± 0.50 mg/L respectively for spring water, T-01 and T-08 were 4.32 ± 0.05 mg/L and 4.70 ± 0.30 mg/L respectively for tap water and W-03, W-06 and W-07 were 4.32 ± 0.35 mg/L, 6.72 ± 0.35 mg/L and 5.32 ± 0.25 mg/L respectively for well water. The fluctuation in the DO value - the variation may be difference in water temperature [54]. The large value of DO which is 6.72 ± 0.35 mg/L was recorded Wobo well water and higher values of DO in case of W-03 may be due also to the greater photosynthetic activity as compared to all the rest water samples. All water samples with in permissible limit of the maximum standard values of DO in drinking water set by WHO which is 7 mg/L.

Nitrates (NO_3^-)

Follett RF et al. [56] stated that low levels of nitrogen (in the form of nitrate) are normal in groundwater and surface water. However, elevated nitrate caused by human activity is a pollutant in the water. Nitrate enters ground or spring water from many sources, including nitrogen-rich geologic deposits, wild-animal wastes, precipitation, septic system drainage, feedlot drainage, dairy and poultry production, municipal and industrial waste, and fertilizer.

In the present study the levels of nitrate in all the sampling sites S-02, S-04 and S-05 were 0.025 ± 0.001 mg/L, 0.046 ± 0.001 mg/L and 0.022 ± 0.001 mg/L respectively for spring water, T-01 and T-08 were 0.040 ± 0.010 mg/L and 0.025 ± 0.001 mg/L respectively for tap water and W-03, W-06 and W-07 were 0.138 ± 0.001 mg/L, 0.028 ± 0.001 mg/L and 0.114 ± 0.001 mg/L respectively for well water. The fluctuations in the nitrate nitrogen values or the higher concentration of nitrogen compounds in water may be due to domestic sewage which enters into the ground water through leeching from soil and the variations are significant at $P < 0.05$. All these values were found within the prescribed limit value of WHO which is 5 mg/L. It shows the water is safe in terms of its NO_3^- content for drinking and other domestic uses.

Phosphate (PO_4^-)

In the present study the levels of phosphate in all the sampling sites S-02, S-04 and S-05 were 1.50 ± 0.026 mg/L, 1.15 ± 0.01 mg/L and 1.55 ± 0.01 mg/L respectively for spring

water, T-01 and T-08 were 1.04 ± 0.01 mg/L and 3.79 ± 0.02 mg/L respectively for tap water and W-03, W-06 and W-07 were 1.45 ± 0.01 mg/L, 2.41 ± 0.01 mg/L and 1.75 ± 0.01 mg/L respectively for well water. The value of phosphate fluctuates from 1.04 ± 0.01 mg/l to 3.79 ± 0.02 mg/l. The maximum value (3.79 ± 0.02 mg/l) was recorded in water sample Bondawo site and the variations are significant at $P < 0.05$. All these values were found within the prescribed limit value of WHO which is 6.5 mg/L which shows the water is safe in terms of its PO_4^{3-} content for drinking and other domestic uses.

Chemical oxygen demand (COD)

The measured values of COD in all sampling sites S-02, S-04 and S-05 were 13.33 ± 2.31 mg/L, 12.00 ± 4.00 mg/L and 26.67 ± 6.11 mg/L respectively for spring water, T-01 and T-08 were 24.00 ± 4.00 mg/L and 24.00 ± 4.00 mg/L respectively for tap water and W-03, W-06 and W-07 were 18.00 ± 2.00 mg/L, 22.67 ± 2.30 mg/L and 8.00 ± 8.00 mg/L respectively for well water. The large value of COD which is 26.67 ± 6.11 mg/L was permissible limit of the maximum standard values of COD in drinking water set by WHO which is 250 mg/L.

Fluoride (F^-)

The measured values of F^- ion in all sampling sites S-02, S-04 and S-05 were 0.48 ± 0.02 mg/L, 0.45 ± 0.02 mg/L and 0.48 ± 0.02 mg/L respectively for spring water, T-01 and T-08 were 0.43 ± 0.02 mg/L and 0.44 ± 0.02 mg/L respectively for tap water and W-03, W-06 and W-07 were 0.43 ± 0.01 mg/L, 0.48 ± 0.02 mg/L and 0.42 ± 0.01 mg/L respectively for well water. The large value of F^- which is 0.48 ± 0.02 mg/L was permissible limit of the maximum standard values of F^- in drinking water set by WHO and SON which is 1.5 mg/L. The high concentration of fluoride as recorded may be attributed to the presence of both organic and inorganic compounds containing fluoride in water such as hydrofluoric acid (HF), sodium fluoride (NaF) and uranium hexafluoride (UF_6) [57]. High values of F^- in drinking water also results in Fluorosis, skeletal tissue (bones and teeth) morbidity [58]. The recovery test is calculating using blank (standard solution) which gives 89%.

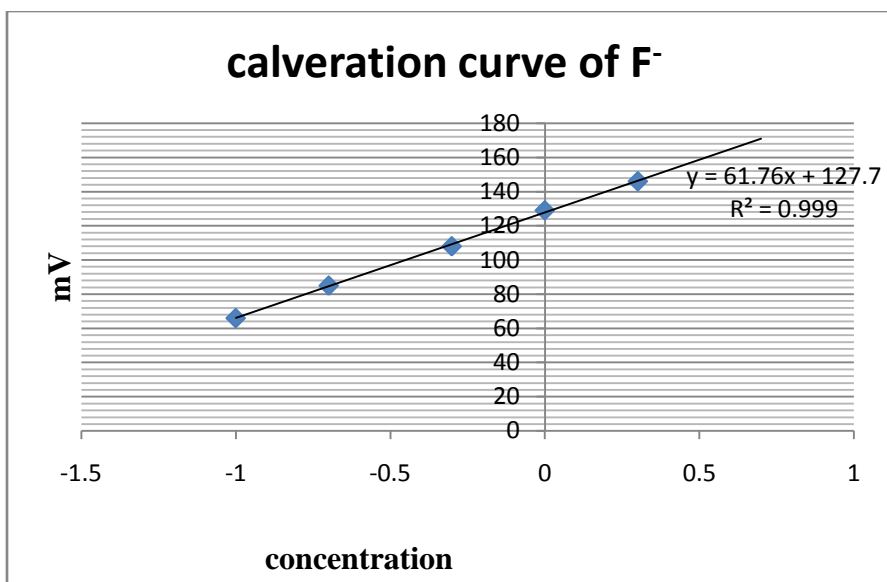


Figure 2. Calibration curves of ion selective electrode for F^- using mV vs the log of the standards concentration

4.2 Heavy metal analysis of the different drinking water source samples.

Drinking Water Standard

Metals such as iron, copper, zinc, Cadmium and Lead present in water beyond some specific maximum allowable concentrations are considered toxic for human consumption. The maximum allowable concentrations for Fe, Cu, Zn, Cd and Pb are 0.3, 1, 3, 0.03 and 0.05 mg/L respectively of these elements (WHO; 1996 2006-2008).

Table 7 and 8 shows vital information on the contents of heavy metals in the sampled spring, tap and well water in Yayo. The concentration of iron (Fe) in the spring, tap and well water ranged between 0.257 ± 0.0010 mg/L to 0.332 ± 0.000 mg/L, 0.279 ± 0.0400 mg/L to 0.576 ± 0.0058 mg/L and 0.385 ± 0.0024 mg/L to 1.244 ± 0.0400 in mg/L respectively and in all water sample site the minimum value recorded at Geci spring water and the maximum value recorded at Geci well water. Fe content in the sampled spring, tap and well water is within WHO maximum permissible limit of 0.3mgL^{-1} . The low concentration of Fe means water from those water sources does not have the potentials of staining laundering as well as disrupt the human system. High level of iron in water has been associated with vomiting and cardiac problems. Aba Faji spring water, Bondawo tap water and all well water the samples results showed higher concentrations

which are all above WHO maximum acceptable contaminant levels in drinking water 0.30 mg/l. In drinking water supplies, Iron (II) salts are unstable and are precipitate as insoluble Iron (III) hydroxide which settles out as a rust-coloured sludge which can promote bacterial growth.

Copper is an essential substance to human life, but in high doses it can cause anemia, liver and kidney damage, and stomach and intestinal irritation. Copper occurs in drinking water from copper pipes, as well as from additives designed to control algal growth. In this study the concentration of S-02, S-04, S-05, T-01, T-08, W-03, W-06 and W-07 were 0.061 ± 0.0010 mg/L, 0.062 ± 0.0001 mg/L, 0.065 ± 0.0001 mg/L, 0.061 ± 0.0005 mg/L, 0.064 ± 0.0001 mg/L, 0.061 ± 0.0001 mg/L, 0.062 ± 0.0001 mg/L and 0.065 ± 0.0001 mg/L respectively. Spring water, tap water and well water all concentration of copper permissible limit of WHO maximum allowable concentration 1ppm in drinking water standard. Therefore spring water, tap water and well water allows the water for drinking and domestic uses. Zinc is considered non-toxic, but excess amount can cause system dysfunctions that result in impairment of growth and reproduction. The clinical signs of zinc have been reported to include vomiting, diarrhea, bloody urine, icterus (yellow mucus membrane), liver failure, kidney failure and anemia [59, 60]. Zinc (Zn) content in the Yayu different drinking water samples source were S-02, S-04, S-05, T-01, T-08, W-03, W-06 and W-07 are 0.350 ± 0.0080 mg/L, 0.182 ± 0.0005 mg/L, 0.216 ± 0.0001 mg/L, 0.216 ± 0.0010 mg/L, 0.301 ± 0.0015 mg/L, 0.350 ± 0.0008 mg/L, 0.277 ± 0.0013 mg/L and 0.127 ± 0.0004 mg/L respectively. All are within WHO maximum allowable of 3.0 mg/L for drinking water. This indicates that water from the sampled water contain the right proportion of Zn which is an essential plant and human nutrient element. The low concentration further implies the Yayu different drinking water sources do not have caustic taste, hence ideal for consumption and other domestic uses.

From the result obtained cadmium concentration Yayu different drinking water source samples were S-02, S-04, S-05, T-01, T-08, W-03, W-06 and W-07 was recorded 0.005 ± 0.0010 mg/L, 0.005 ± 0.0011 mg/L, 0.004 ± 0.0000 mg/L, 0.005 ± 0.0008 mg/L, 0.005 ± 0.0000 mg/L, 0.005 ± 0.0010 mg/L, 0.004 ± 0.0001 mg/L and 0.004 ± 0.0001 mg/L respectively and the data analysis for cadmium, all the samples showed detectable levels

of cadmium and with all the samples having concentrations below the Maximum acceptable concentration for drinking water 0.03 mg/L (WHO).

Lead is the most toxic of the heavy metals. Its inorganic forms are absorbed through ingestion by food, water and inhalation [61]. In humans exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. High levels of exposure may result in toxic biochemical effects in humans which in turn cause problems in the synthesis of hemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system [60, 62]. In this study the concentration of lead in S-02, S-04, S-05, T-01, T-08, W-03, W-06 and W-08 were recorded 0.033 ± 0.0008 mg/L, 0.028 ± 0.0012 mg/L, 0.031 ± 0.0310 mg/L, 0.033 ± 0.0002 mg/L, 0.033 ± 0.0009 mg/L, 0.037 ± 0.0011 mg/L, 0.031 ± 0.0004 mg/L and 0.039 ± 0.2800 mg/L respectively and the entire samples are permissible limit with WHO maximum allowable concentration of drinking water 0.05 mg/L. Therefore all the samples use for drinking and domestic uses.

Table 8. Mean and standard deviation scores of the metal concentration in spring and tap water samples (n=3)

Sample	Analyte	Spring water			Tap water	
		S-02	S-04	S-05	T-01	T-08
		Mean \pm SD	Mean \pm SD	Mean \pm SD	Mean \pm SD	Mean \pm SD
Non-spike sample	Fe	0.279 ± 0.0011	0.332 ± 0.0007	0.257 ± 0.0010	0.279 ± 0.0400	0.576 ± 0.0058
	Cu	0.061 ± 0.0010	0.062 ± 0.0001	0.065 ± 0.0001	0.061 ± 0.0005	0.064 ± 0.0001
	Zn	0.350 ± 0.0080	0.182 ± 0.0005	0.216 ± 0.0001	0.216 ± 0.0010	0.301 ± 0.0015
	Cd	0.005 ± 0.0010	0.005 ± 0.0011	0.004 ± 0.0000	0.005 ± 0.0008	0.005 ± 0.0000
	Pb	0.033 ± 0.0008	0.028 ± 0.0012	0.031 ± 0.0310	0.033 ± 0.0002	0.033 ± 0.0009
Spike sample	Fe	2.007 ± 0.0300	2.534 ± 0.0040	2.108 ± 0.0200	1.960 ± 0.0060	2.380 ± 0.0300
	Cu	2.183 ± 0.0100	1.746 ± 0.0200	2.188 ± 0.0300	1.872 ± 0.0040	2.319 ± 0.0200
	Zn	2.498 ± 0.0300	2.597 ± 0.0020	2.561 ± 0.0090	1.747 ± 0.0020	2.319 ± 0.0200
	Cd	0.266 ± 0.0030	0.166 ± 0.0060	0.165 ± 0.0020	0.177 ± 0.0010	0.186 ± 0.0020
	Pb	0.248 ± 0.0030	0.276 ± 0.0006	0.245 ± 0.0006	0.211 ± 0.0020	0.224 ± 0.0000

Table 9. Mean and standard deviation scores of the metal concentration in well water samples (n=3)

Sample	Analyte	Well water		
		W-03	W-06	W-07
		Mean \pm SD	Mean \pm SD	Mean \pm SD
Non-spike sample	Fe	0.385 \pm 0.0024	0.689 \pm 0.0043	1.244 \pm 0.0400
	Cu	0.061 \pm 0.0001	0.062 \pm 0.0001	0.065 \pm 0.0001
	Zn	0.350 \pm 0.0008	0.277 \pm 0.0013	0.127 \pm 0.0004
	Cd	0.005 \pm 0.0010	0.004 \pm 0.0001	0.004 \pm 0.0001
	Pb	0.037 \pm 0.0011	0.031 \pm 0.0004	0.039 \pm 0.2800
Spike sample	Fe	1.946 \pm 0.0030	2.643 \pm 0.0060	2.775 \pm 0.0080
	Cu	2.259 \pm 0.0090	1.742 \pm 0.0090	2.345 \pm 0.0600
	Zn	2.494 \pm 0.0100	1.775 \pm 0.0010	2.499 \pm 0.0200
	Cd	0.179 \pm 0.0020	0.164 \pm 0.0000	0.184 \pm 0.0040
	Pb	0.255 \pm 0.0030	0.276 \pm 0.0000	0.280 \pm 0.0000

Pearson correlation of physic-chemical parameters and metals in different drinking water source sample

To correlate the effect the concentration of both physic-chemical parameters and metals on the other concentration of physic-chemical parameters and metal in different drinking water source samples, the Pearson correlation matrices using correlation coefficient for the samples used [49]. The correlation coefficients are given in appendix 2 and 3 for physico-chemical parameters and metals respectively. It was found that there is positive correlation of EC with DO, NO₃⁻ and F⁻, NTU with TA, TH, TDS, DO and COD, TH with DO, Cl⁻, PO₄³⁻ and F⁻, NO₃⁻ with PO₄³⁻ and F⁻ and PO₄⁻ with F⁻ for physico-chemical parameters and it has positive correlation of Fe with Cu and Pb, Zn with Cd and Pb and Cd with Pb. It also has negative correlation EC with NTU, TA, TH, TDS, Cl⁻, PO₄⁻ and COD, NTU with NO₃⁻ and PO₄⁻, TA with TH, TDS, DO, Cl⁻, NO₃⁻ and PO₄⁻, TH with

DO, TDS with NO_3^- , DO with NO_3^- and COD, Cl^- with COD, NO_3^- with COD and PO_4^- with COD for physico-chemical parameters and it has negative correlation Fe with Zn and Cd, Cu with Zn and Cd for metals.

Analysis of variance (ANOVA)

Results obtained from the laboratory analysis were represented using tables and averages, while analysis of variance (ANOVA) for significant variation in water quality among the sampled Yayu water source was determined using ANOVA one way for Windows. Physico-chemical parameters and trace elements analysed were Fe, Cu, Zn, Cd and Pb. Analysis of variance (ANOVA) is a widely used method to compare means. The one way ANOVA can compare the mean of more than two groups of samples. The variation in sample mean of the analyte was tested by using ANOVA. The ANOVA result (Appendix 4 and 5) showed that there exist statistically significant differences 95% confidence level in mean concentration of all physic-chemical parameters and metals except Cd and Pb which is expected from variation in experimental procedure.

Percentage Recovery

The lowest standard on the calibration curve should be accepted as the limit of quantification if the analyte response is at least five times the response compared to the blank response and if the analyte response is identifiable, discrete, and reproducible with a precision of 20% and accuracy of 75 to 125% [63]. The efficiency and accuracy of the optimized methods were evaluated by analyzing the digests of spiked samples. 0.2 ppm for Pb and Cd and 2 ppm for Fe, Cu and Zn were taken from stock solution of each metal and spiked was 0.25 mL and 2.5 mL respectively to Erlenmeyer flask containing 50 mL water sample. The recoveries of metals in the spiked water samples were average 77% to 122%. Generally, good recoveries were obtained for all metals, (particularly in spring, tap and well of S-02, S-04, S-05, T-01, T-08, W-03, W-06 and W-07 water for metals like (Fe, Cu, Zn, Cd and Pb) except the recovery of cadmium in S-02. This error may be due to personal error or instrumental error. Each determination was carried out at least three times in order to ensure precision.

5. Conclusion and recommendation

5.1. Conclusion

In these study physico-chemical parameters such as pH, temperature, EC, turbidity, total alkalinity, total hardness, TDS, Cl^- , NO_3^- , PO_4^{3-} , COD, F^- and heavy metals (Fe, Cu, Zn, Cd, and Pb) of the spring water, tap water and well water were measured. And from the experimental data it was found that the concentration of Fe was higher than the permissible levels of Fe for safe drinking water set by WHO in Aba Faji spring water, Bondawo tap water and all well water site. But all the rest parameters were found within the safe limit drinking water quality standards and are found to be safe for drinking and other domestic purposes at the physicochemical level. Analysis of physicochemical parameters and metals in the drinking water is very important as the water used for various purposes by the community which has health implication. The present study revealed that wet digestion was a reliable method for quantitative determination of metals in the water samples. The result of recovery test was found in the acceptable range for the analyzed metals, except cadmium. However, it is also important to investigate other potential water contaminations such as chemicals, microbial and radiological materials for a longer period of time, in order to assess the overall of the spring water, tap water and well water quality.

Statistical analysis indicated that there were significant differences in the levels of all physico-chemical parameters and most metals (Fe, Cu and Zn) within the analyzed water samples ($P < 0.05$). While, other metals (Pb and Cd) are not significant between their means ($P = 0.05$). The variation in the level of some metals for the studied samples which could be mainly arose from erosion, contribute appreciable amounts of certain minerals, natural mineral sources in the studied area or the studied area might contains higher concentration of mineral nutrient in the water and soil.

5.2. Recommendation

This study, recommends the government and other responsible authorities to introduce relevant drinking water treatment techniques which can reduce the current levels of physico-chemical parameters (turbidity) and heavy metal (Fe), to the accepted level current results indicate that there concentration are above limit guideline. In addition to this, the responsible authorities should replace the iron pipe by plastic pipes unless the concentration of heavy metal may increases above accepted level from time to time.

Finally further studies should focus on the possibility to determine the levels physico-chemical parameters and heavy metals and the authenticity of Ethiopian municipal tap water taking into account of increased number of samples and additional parameters like BOD, sulfate, mercury, arsenic, manganese, etc

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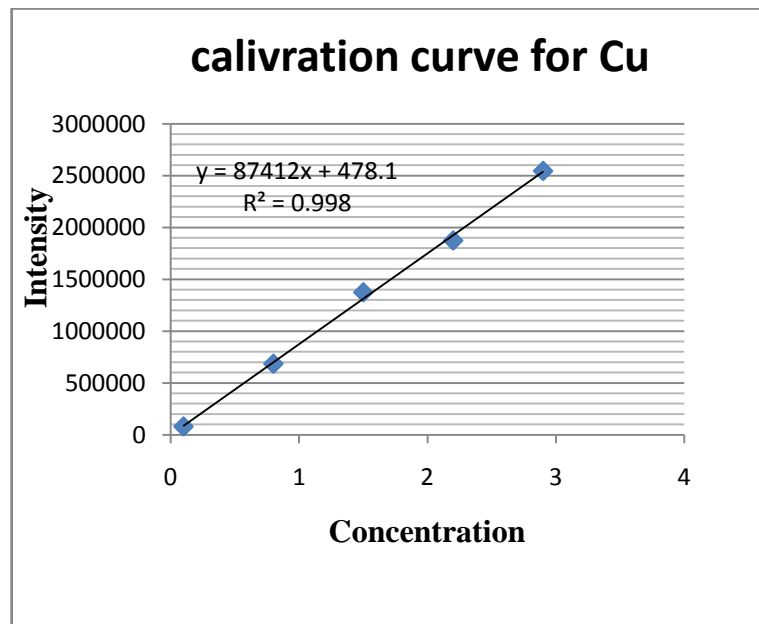
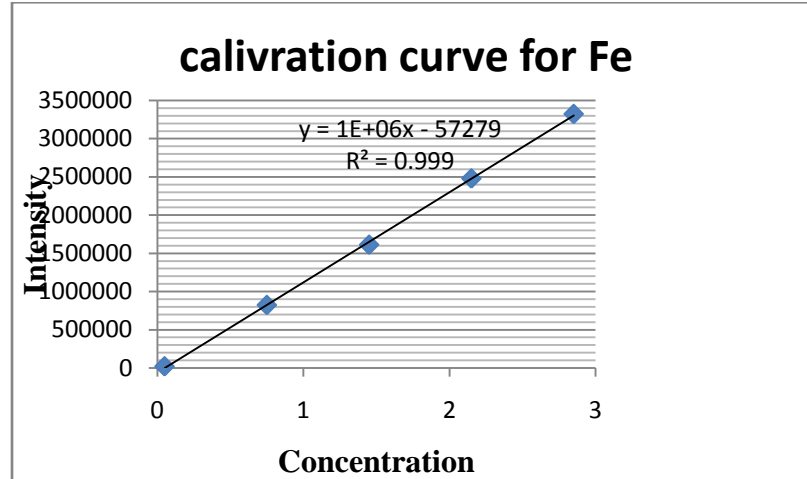
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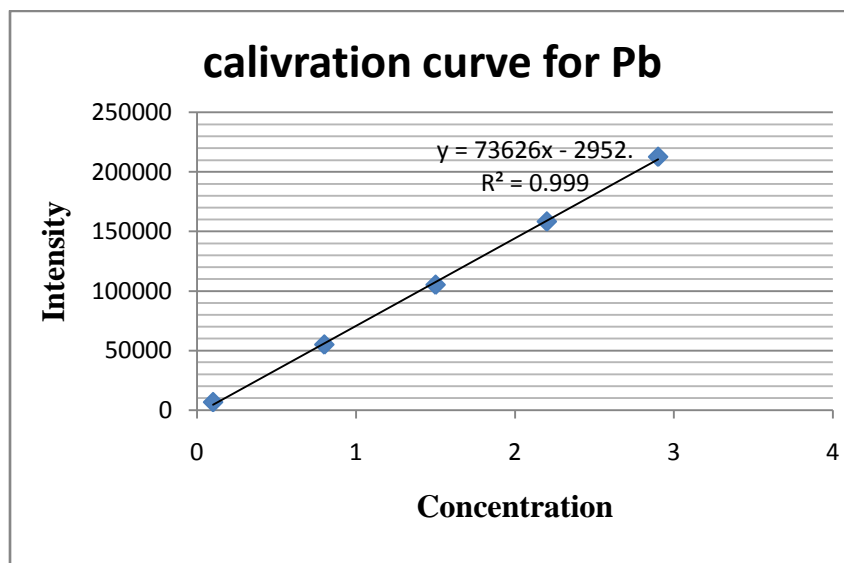
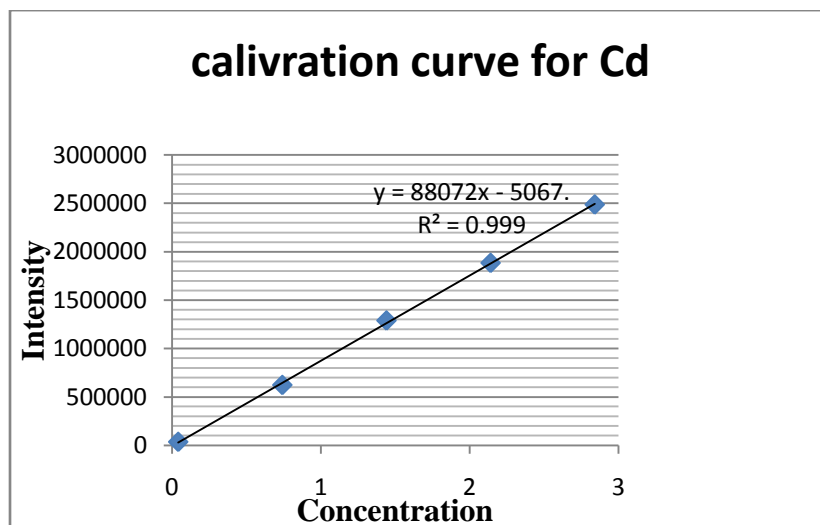
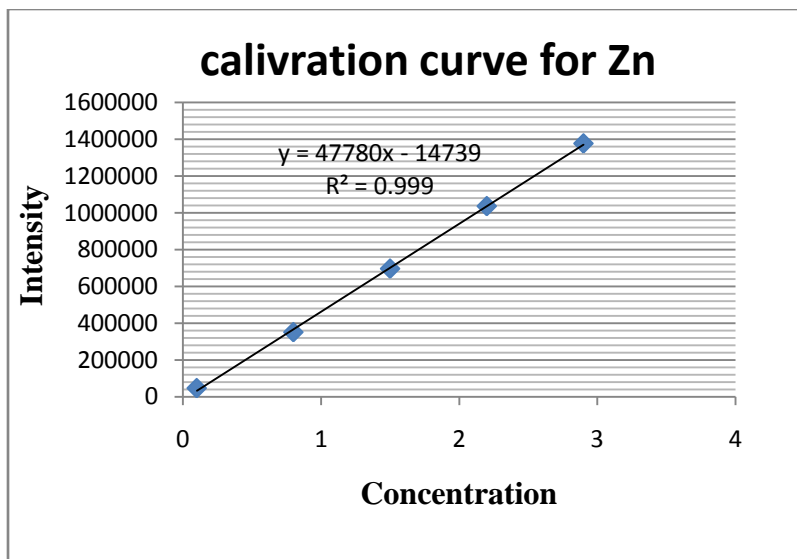
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Appendix

Appendix 1: Calibration Curves of heavy metals for tap, spring and well water samples





Appendix 2. Person correlation coefficient among physico-chemical parameters of Yayu different source of drinking water samples

	EC	NTU	TA	TH	TDS	DO	Cl ⁻	NO ₃ ⁻	PO ₄ ³⁻	COD	F ⁻
EC	1										
NTU	-0.37901	1									
TA	-0.62844	0.05083	1								
TH	-0.43396	0.48566	-0.29596	1							
TDS	-0.03747	0.74996	-0.39464	0.59103	1						
DO	0.32824	0.29489	-0.57263	-0.10380	0.42834	1					
Cl ⁻	-0.02707	0.51210	-0.43197	0.56093	0.31349	0.20503	1				
NO ₃ ⁻	0.23107	-0.29408	-0.57317	0.36249	-0.19913	-0.02912	0.58664	1			
PO ₄ ³⁻	-0.06908	-0.03962	-0.65990	0.50891	0.22162	0.47405	0.37219	0.52264	1		
COD	-0.56140	0.58796	0.71403	0.11462	0.23310	-0.35045	-0.07402	-0.49869	-0.64864	1	
F ⁻	0.40660	-0.33841	-0.36897	0.11790	0.15405	-0.19213	-0.02665	0.34992	0.01198	-0.18254	1

Appendix 3. Person correlation coefficient among metals in Yayu different source of drinking water samples

	Fe	Cu	Zn	Cd	Pb
Fe	1				
Cu	0.64283	1			
Zn	-0.46947	-0.53199	1		
Cd	-0.61476	-0.48795	0.58685	1	
Pb	0.60298	0.12474	0.00694	0.10899	1

Appendix 4. ANOVA between and within in of heavy metal drinking water from different source of samples at 95% confidence level

Metal	Source of variation	Degree of freedom	F _{calculated}	P-value
Fe	Between samples	7	833.857	0.000
	Within samples	16		
	Total	23		
Cu	Between samples	7	57.252	0.000
	Within samples	16		
	Total	23		
Zn	Between samples	7	2,221.218	0.000
	Within samples	16		
	Total	23		
Cd	Between samples	7	1.661	0.189
	Within samples	16		
	Total	23		
Pb	Between samples	7	0.004	1.000
	Within samples	16		
	Total	23		

Appendix 5. ANOVA between and within physico-chemical in drinking water from different source of samples at 95% confidence level

Physico-chemical	Source of variation	Degree of freedom	C _{calculated}	P-value
EC	Between	7	277,598.953	0.000
	Within	16		
	Total	23		
Turbidity	Between	7	1,997.427	0.000
	Within	16		
	Total	23		
TA	Between	7	6,752.891	0.000
	Within	16		
	Total	23		
TH	Between	7	11,570.495	0.000
	Within	16		
	Total	23		
Cl ⁻	Between samples	7	847.914	0.000
	Within samples	16		
	Total	23		
TDS	Between samples	7	4,460.326	0.000
	Within samples	16		
	Total	23		
DO	Between samples	7	70.851	0.000
	Within samples	16		
	Total	27		
NO ₃ ⁻	Between samples	7	458.003	0.000
	Within samples	16		
	Total	23		
PO ₄ ³⁻	Between samples	7	11,461.166	0.000
	Within samples	16		
	Total	23		
COD	Between samples	7	10.309	0.000
	Within samples	16		
	Total	23		
F	Between	7	5.918	0.002
	Within	16		
	Total	23		