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DEPARTMENT OF CHEMISTRY

M.Sc. THESIS ON:

PHYSICO-CHEMICAL ANALYSIS AND DETRMINATION OF THE LEVEL OF SOME SELECTED HEAVY METALS IN WELL-WATERS FROM BENJA TOWN,AND SURROUNDING KEBELES, JIMMA, ETHIOPIA

BY:

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JIMMA, ETHIOPIA

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A RESEARCH SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES JIMMA UNIVERSITY, COLLEGE OF NATURAL SCIENCES DEPARTMENT OF CHEMISTRY IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

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Declarations

This is to certify that this thesis entitled: Physico-chemical and selected heavy metal analysis of well-water from Benja and surrounding Keeble's, Jimma zone, southwest Ethiopia, submitted to School of Graduate Studies, Department of Chemistry in partial fulfillment for the requirements of Master of Science Degree in Chemistry. I Jalata Kumsa hereby declare that this M.Sc. thesis is my original work and has not been presented for a degree in any other University and that all source of materials used for the thesis have been duly acknowledged.

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List of Abbreviations

AAS	Atomic Absorption Spectroscopy
APHA	American Public Health Agency
APHA	American Public Health Association
CMP	Community Managed Project
DL	Detection Limit
DO	Dissolved Oxygen
ESA	Ethiopian Standard Agency
EC	Electrical Conductivity
FAAS	Flame Atomic Absorption spectroscopy
LCS	Laboratory Control Sample
MAL	Maximum Admissible Limit
MPL	Maximum Permissible Limit
NGL	No Guide Line
NTU	Nephelometricturbidity Unity
RSD	Relative Standard Deviation
TDS	Total Dissolved Solid
TSS	Total Suspended Solid
USEPA	United State Environmental Pollution Agency
UV-Vis	Ultraviolent-Visible
WHO	World Health Organization

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ABSTRACT

The study was conducted in Benja Town and surrounding kebeles, Jimma Zone, Oromia Regional State, southwestern Ethiopia aiming to assess the qualities of the well-waters in case of hand dug well, deep well, hand pump well and shallow well, in which the people of the village used for drinking as well as for some other activities. Five well-water samples were collected from Benja town and seven surrounding kebeles.Physicochemical parameters, includin g temperature, Electrical conductivity, TDS, DO, Turbidity were measured on site by using portable multi meter. Whereas, nitrate and phosphate were determined by spectro-photometer (model). And the level of heavy metals in the sample was analyzed by FAAS. The mean average results of the physicochemical parameter analyzed were ranges from: Temperature (20.43±0.42 to 25.20±0.10^{0}C), pH(6.68±0.04 to 8.78±0.01),EC(218.33±0.58 to1306.67±0.58μs/cm), TDS(161.00±1.00 to 650.67±0.58mg/L),DO (2.12±0.09to 5.60±0.51mg/L), PO_4^{3-} (0.02±0.01to 0.47±0.02mg/L), NO_3^-(2.42±0.02 to8.28±0.01mg/L),and that of heavy metals were in the range of Pb (0.274±0.001to 0.275±0.001), Mn (0.152±0.004to 3.7±0.194), Fe (0.145±0.001to 0.344±0.043), Cd (0.75±0.081to 1.27±0.021) and Cr(0.334±0.002to 0.336±0.0004)in mg/L.And Site W1 and W2 recorded high value of all parameter One-way ANOVA test ($p \leq 0.05$) showed that all measured vary significantly across location. Based on the finding of this study, some of the water samples for some physicochemical parameters and most heavy metals were above the EWQG and WHO guideline for drinking water and hence needs further treatment..

***Keywords**:Physicochemical analysis, Heavy metals, Well water, FAAS*

1. INTRODUCTION

1.1 Background of the study

Water is one of the most important resources that are needed for the life of both animals and plants. Our planet contains about 1.388×10^{15} m^3 of water. Of this, 97.3% is salty oceanic water, 2.7% is fresh water, 0.61% is underground water and 0.09% of water is that of lakes and rivers. From 2.7% of fresh water about 2.04% is found in polar ice and glaciers [1]. Human settlement and availability of fresh water have positive correlation, since ancient time, human settlements are following the availability of fresh water, such as along the rivers, lakes, streams and etc. for their consumption, use and sustainability. As a result water that is found near the sites of human settlements are vulnerable to many pollutants. Because people release different wastes and pollutants into the water bodies that cause water had borne diseases. It has been reported that, in developing countries 80% of the people's illness is related to water borne diseases and more than 5 million people die due to water borne diseases per a year. [2, 3].

On the other hand, nowadays, different industrial wastes and chemicals also appear as the major sources of pollutants to the water bodies and thus became a threat to human's health as well as the survival of most plants lives, aquatic organisms and wildlife [4]. The most common water pollutants include heavy metals, phosphates, nitrates, fertilizers and other soluble materials [5]. These water pollutants enter in to the water system through floods, erosion, percolation, leeching, deposition, decomposition and etc via biotic and a biotic factors.

The sources of fresh water which is needed for the human consumptions are usually river, lakes and underground water and this estimated to be about one percent of the earth water. Despite of the scarcity of fresh water, safe and pure drinking water is not available for most of peoples of the world especially for developing countries [2]. Now days, supplying fresh water with adequate quality and quantity, for the community are becoming a headache to national and international organizations; UNCEF, FAO, WHO and other NGOs to succeed GTP and sustainable development. More recently, to address the safe water for the community, the technology has been applied for domestic water supply from ground water. A number of international NGOs, including Practical Foundation, World Vision and, CMP introduced and developed this technology in Ethiopia in over 76 districts. Of 76 Nono Beneja district of Jimma zone is one, incorporated under CMP project as Co-WASH integrated with national and regional water and energy bureau of Ethiopia. In these district the project have contributed its part for the supply of safe water supply for the local community and drilled more than 20 wells (deep tube well. Hand dug well with hand pump, and shallow wells) starting from 2017 in which the project will end in 2020.

Regardless of any adaptations, the community of Nono Benja district uses the drilled wells for domestic water supply, including drinking**.** To ensure sustainable provision of good quality water to the population and attain The Ethiopian planned target 985%„of drinking water supply to the community in the Second Growth and Transformation National plan (2015/16–2019/20). However, quality did not give similar attention. As a result, continuous monitoring and evaluation of trace metals and its physicochemical properties is essential [6]. The results of the study are expected to be useful to planners, researchers, policy makers and decision makers involved in the monitoring and regulation of water quality especially Oromia regional water and energy Bureau, CMP project as COWASH whereby the quality status of underground water will be known with certainty and applicable recommendations given.

Pollutants can enter into the underground water by leaching through soils and aquifers in unpredictable ways. Generally, well-water could be contaminated any time, even after many months pollutants enter the underground water [8]. Heavy metals normally occurring in nature are not harmful to our environment because they are only present in very small amounts [9]. However, if the levels of these metals and physico-chemical parameters are higher than the recommended limits, their roles may change to a negative impact on the environment and health of human being.

Therefore, in this study analysis of physicochemical and heavy metal properties of different well-water and tap water were carried out. The finding was evaluating of the water quality and suitability for drinking and compares the values with the national and international standards

1.2. Statement of the problem

Water is one of the most important natural resources needed for the life of both animals and plants. Ideally, the water resources that are used by mankind should be pure and free from different contaminants, for safety and health of human beings. Approximately, two thirds of the world's populations obtain water supply from ponds, wells, springs, rivers, rains etc [10]. But these water sources are vulnerable to different pollutants such as heavy metals Hg, Pb, Cd, Ni, Cu and Cr, which are toxic to human beings [11]. In Ethiopia, the main source of water supply for both urban and rural communities is the underground water which accounts to 70% of the total water supply of the nation [12]. Water quality is considered as a big issue in many areas of developing countries. In terms of surface contamination, ground water is less vulnerable and valuable than surface water for portability of water, but due to the geology of the soil of well water and different activities done by human beings, this water is contaminated. Even though, tap water is available for the community of Benja town starting from past decades, which is constructed by the integration of Oromia regional water and energy Bureau, and CMP project as COWASH .from deep well source to pipe distribution systems, the residents of the town are not using this tap water because of its unpleasant taste. The community of Benja and the surrounding kebele has less access to a spring , river and other source of water, these was due to the geographical and land nature of the area, most of the water source are seasonal and will dry during dry season and emerge with rain. Hence they are using Hand dug well, shallow well, and deep well for their need of water for drinking; domestic and other activities. So far there was no reported literature available on the subject showing the water quality of the study area. Therefore, it is crucial to analyze the physicochemical parameters and level of heavy metals of the well water from different source available in the study area for water quality.

1.3. Objectives of the study

1.3.1. General objective

The main objective of this study was to evaluate the physicochemical parameters as well as the levels of some selected heavy metals in well-water of Benja town and the surrounding Keeble, Jimma Zone, southwest Ethiopia.

1.3.2. Specific objectives

- To determine physicochemical parameters like temperature, TDS DO, EC,pH.Phosphate, nitrate, of well-water of the sample under study
- To determine the concentration of (Cd, Cr, Pb, Mn, and Fe)in well-water .
- To compare the obtained results for the quality of water parameters with the international and national standards as well as to reported literature values.

1.4. Significant of the study

The finding of this study could be used as a secondary source of information for further study and also needed to understand the quality of the water which may affect the human healthy and the health of the ecosystem as well and also help ground water management for effectiveness. Furthermore it may provide some information which parameter is within the guideline of the WHO water quality standard and which parameter is above or below the guide line of WHO water quality standard.

The finding of the study may also be used as a base line resource for other researchers who intended to carry out further investigation on the well-water and may use as a secondary source of information for further study

2. REVIEW OF RELATED LITERATURE

2.1. Ground water

Groundwater is one of the major sources of water and provides the rural, urban, and industrial and irrigation water needs of about two billion people around the world [17] Being considered as the purest forms of water available in nature comprising of 97 percent of the world's readily accessible freshwater. Major part of the world like the Indian populace depends upon freshwater supplies from open wells, ponds, bore wells and natural springs. It mostly originates when rain infiltrates through the soil into subsurface aquifers and hence said to be purer than surface water. Groundwater is believed to be naturally clear, tasteless and odorless unless it is contaminated. Although considered as safe, some groundwater sources are generally susceptible to physicochemical contamination due to their low depth [18]. If groundwater contains high amount of various ions and salts, using it would affect the health of the water users .There are various ways of contaminating groundwater such as use of fertilizers in agriculture and effluent from sewerage systems seeping through the ground to the water bearing rocks[18]. During passage through the ground, water dissolves minerals in rocks, collect suspended particulate matter particularly those of organic sources as well which contributes to ground water contamination[19].

Ethiopia's development is seriously influenced by complex water resources legacy and lack of access to clean water and management of the water resources. Clean water supply and appropriate sanitation are the most essential components for healthy life. The provision of drinking water with adequate sanitation facilities to both the rural and the rapidly expanding urban populations can reduce mortality rates that come from water borne and other water related diseases such as cholera, diarrhea and malaria [17].Although, there are diversified water resources in the country, large proportion of the population does not get access to clean drinking water. As a result, poor hygiene, cholera outbreak, dehydration and high child mortality are observed throughout the nation.

Ethiopia, the major sources of drinking water, for the vast majority of the rural population and residents of many small towns are unprotected surface waters (such as springs, ponds and rivers) as well as underground water (hand dug wells and hand pump well-water) [19, 20]. The health risks of the water obtained from such sources are significant as they are exposed to the earlier mentioned contaminations sources [20]. Use of contaminated drinking water may cause adverse health effects over prolonged periods of exposure. Therefore, determination of the level of water contaminants, such as heavy metals, that have cumulative toxic effect on the users' should be continually monitored [18].

2.2. Ground water hydro geochemistry

Groundwater constitutes a variety of chemical in varying concentrations depending on the geology of the area and the human activities carried out in the area. The soluble constituents in groundwater come from the minerals contained in the soils and rocks with a very small part of it coming from the atmosphere and surface water sources. About 95% of the ions in most groundwater are represented by major cations and anions; these cat ions include ions like sodium, potassium, calcium and magnesium and the anions like fluoride, chloride, sulfate, bicarbonate and nitrate. When these ionic species interact in the water, they tend to contribute to the salinity and hence mineralization of the water which eventually results to an increase in the total dissolved solids [21].

2.3. Ground water contamination

Ground water contamination has become one of the main environmental issues today and it has been reported to have contributed to serious health problems among many users. Ground water contamination can result from natural substances or anthropogenic activities that can cause disturbance of the natural materials or add contaminants to the existing ones[22]. Water can be contaminated by natural and anthropogenic sources and thus the physical and chemical properties of the water may vary over time and by location. These contaminants include different naturally occurring chemicals and anthropogenic chemicals emerging from industry, human dwellings and agricultural farmlands. Chemicals used in water treatment such as pesticides which are used in water for public health purpose;cyanbacterial toxins and other contaminants derived from biological sources are also so urces of water contaminants [23].

2.4. **Natural substances**

The nature of the natural contaminants in groundwater depends on the geological materials through which the water moves to the aquifer. As the water moves through the rocks and soils down to the aquifers, it may be influenced by the rock constituents and ends up having a wide range of minerals some of which may be in high concentrations. The effect of these natural sources of contamination of groundwater quality depends on the type of contaminants and its levels in water. The occurrence of contaminants in water is hazardous to human health and a threat to human life but their occurrence in the levels within the permissible limit is considered to be harmless to human health [27].

2.5. Anthropogenic activity

The safety of groundwater is also affected by the nature of the human activities in the area. For instance agricultural activities cause ground water contamination through various ways of which common examples include spillage of fertilizers and pesticides during handling, washing of pesticides sprayers or other application equipment containing the chemicals near the shallow wells and application of organic manure to the soil like animal waste. Economic activities like industrial processes and transport also contribute to ground water contamination through leakage and spillage of chemical substances that get through the aquifers through leaching. Domestic waste is also of great concern as the release of such waste near the wells can result to leaching of the waste which contaminates the ground water[27].

2.6. Types well water

A number of global technology options are available for improved rural water supply systems. However, not all can be applied everywhere. In most rural parts of Ethiopia, the common choices are boreholes equipped with hand pumps or motorized pumps; hand dug wells (with hand pumps), shallow wells (with hand pump), and developed springs. This operation and maintenance management guideline focuses on these three types of technological options.

2.6.1. Hand Dug Well

The traditional method of obtaining groundwater in rural areas is still the most common by means of hand-dug wells. However, because they are dug by hand their use is restricted to suitable types of ground, such as clays, sands, gravels and mixed soils where only small boulders are encountered. Hand-dug wells provide a cheap, low-technology solution to the challenges of rural water supply. It is excavated and lined by human labor, generally by entering the well with a variety of hand tools. Depths of hand-dug wells range from 5 meters deep, to over 20 meters. It is impractical to excavate a well which is less than a meter in diameter; an excavation of about 1.5 meters in diameter provides adequate working space for the diggers and will allow a final internal diameter of about 1.2 meters after the well has been lined. Hand Dug Wells can be lined, unlined or a combination. In all wells, however, at least the top 3 meters should be lined to prevent (potentially dirty) surface water seeping in.

Figure 1: Photo of Traditional Hand Dug Well fitted with rope Pumps

2.6.2. **Shallow Well**

This system is an advanced type of hand-dug well which is constructed in accessible area by a medium drilling rig which can reach greater depth than hand-digging. The major advantage of using shallow wells over hand-dug wells is: 1) they can be reaching up to 75 meters depth, 2) they are not risky during the dry season, and 3) they cannot be polluted easily. Shallow drilled wells are wells which have been drilled with drilling machine and lined with PVC or steel casing. This type of wells could be fitted with Village Level Operation and Maintenance .type hand pumps and the diameter of the wells is usually 4 to 6 inch. Cleaning of such well is not done manually but with the use of pumps, surging and or bailing. Thus it requires drilling machine, pumps and accessories and trained personnel. To this effect cleaning and developing of such well is done by drilling company or by the Regional Water Bureaus. Therefore, when there is a need to do such work the Water Sanitation and Hygiene Committee .should contact the WWO. Regarding the maintenance of the well head and the hand pump it is identical with the hand dug well. However, if the well is fitted with pumps such as Indian Mark II a tripod, chain block and pipe clamp is required for maintenance of the pump as one should remove all the riser pipes. Hence, it should only be done by qualified technician.

2.6.3. Hand pump well

A typical hand pump well and hand dug well is presented in Figure 2.

Figure 2. Selected Picture illustrating Hand pump and Hand dug well in the study area.

2.7. Analysis of the physico-chemical parameters of water

Physicochemical parameter study is very important to get information about the quality of water. We can compare results of different physicochemical parameter values with standard values. It is very essential and important to test the water before it is used for drinking, domestic, agricultural or industrial purpose. Physical and chemical properties are parameters that do not identify particular chemical species but are used as indicators of how water quality may affect water uses. These are Temperature, electrical conductivity, total dissolved solids, chemical oxygen demand, hydrogen ion concentration (measured as pH), alkalinity, hardness, and sodium adsorption ratio [25]. Water must be tested with different physic-chemical parameters. Selection of parameters for testing of water is solely depends upon for what purpose we are going to use that water and what extent we need its quality and purity. Water does contain different types of floating, dissolved, suspended and microbiological as well as bacteriological impurities. For obtaining more and more quality and purity water, it should be tested for its trace metal, heavy metal contents and organic i.e. pesticide residue. It is obvious that drinking water should pass these entire tests and it should content required amount of mineral level. Only in the developed countries all these criteria are strictly monitored. Due to very low concentration of heavy metal and organic pesticide impurities present in water it need highly sophisticated analytical instruments and well trained manpower. Following different physic chemical parameters are tested regularly for monitoring quality of water [24].

2.7.1. Temperature

Parameter like temperature will be determined in the field due to their unstable nature. Water temperature is one of the controlling factors for the dynamics of aquatic environments; because it interferes in the organism's metabolism, influencing the reproduction, accelerating their actions' speed and increasing the degradation rate of organic matter [24]. Cool water is generally more palatable than warm water, and temperature will have an impact on the acceptability 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 [26]. The variation in river water temperature usually depends on the geographic location, season, sampling time and temperature of wastewater discharges entering the stream [27].

2.7.2. Electrical conductivity

Electrical conductivity (EC) is the measure of the ability of water to conduct an electric current and depends upon the number of ions or charged particles in the water. EC determinations are useful in aquatic studies because it provides a direct measurement of dissolved ionic matter in the water. Low values are characteristic of high-quality, low-nutrient waters. 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. Very high values are good indicators of possible polluted sites. The main reason behind fluctuation of mean EC values in is dumping of huge volumes of toxic wastes into the river and city's many of industrial units and sewerage lines and agro-industries [28]. Conductivity often is used to estimate the amount of TDS rather than measuring each dissolved constituent separately [29].The EC increases going down river apparently due to the accumulation of domestic and sewage wastewater and also to the enrichment of electrolytes from mineralization or weathering of sediment [30

2.7.3. pH

pH is most important in determining the corrosive nature of water. Lower the pH value, higher is the corrosive nature of water. pH will positively have correlated with electrical conductance and total alkalinity [31]. The reduced rate of photosynthetic activity the assimilation of carbon dioxide and bicarbonates which are ultimately responsible for increase in pH, the low oxygen values coincided with high temperature during the summer seasons. Various factors bring about changes the pH of water. The higher pH values observed suggests that carbon dioxide, carbonate bicarbonate equilibrium is affected more due to change in physicochemical condition [32]. The pH of pure water at $25^{o}C$ is 7.0, but the pH of environmental waters is affected by dissolved CO_2 and exposure to minerals [24].

2.7.4. Total Dissolved Solids

Total dissolved solids indicate the salinity behavior of river water. The composition of solids present in a natural body of water mainly depends upon the nature of the bedrocks and the soil developed from it. The term total dissolved solid (TDS) refer to materials that are completely dissolved in water and the physicochemical factors, which govern the chemistry of salts in water, may also influence the composition [24]. Dissolved solids in natural waters may consist of carbonates, bicarbonates, chlorides, sulfates, phosphates, nitrates, magnesium, sodium, iron, manganese and other substances. Determination of the "solids" content is important for both aesthetic and practical reasons; drinking water with high solids content can have a disagreeable palatability. 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 1000 mg/L. Taste problems in water often arise from the presence of high TDS levels with certain metals present, particularly iron, copper, manganese, and zinc. The increase in values of TDS indicates pollution by extraneous sources. The high amount of dissolved, suspended and total solids of samples adversely affects the quality of running water and it is unsuitable for any other purpose irrigation and drinking [24].

2.7.5. Phosphate

Increase in concentration of phosphate indicates that there is mixing of industrial effluents, sewage water and waste water in the river water. Higher concentration of Phosphates leads to eutrophication and this result in deficiency of dissolved oxygen (DO) which kills fishes and other aquatic fauna. Toxicity of PO_4^{3-} in humans includes impaired renal function, rhabdomyolysis and tumorlysis Syndrome. Sewage, detergent use and fertilizer runoff are common sources. Phosphorus is also a constituent of animal wastes [24]. Compounds containing phosphorus that are of interest to water quality include Orthophosphates (all contain PO_4^{3-}), tri sodium phosphate (Na_3PO_4), disodium phosphate (Na_2HPO_4), monosodium phosphate (NaH_2PO_4), and ((NH_4)2HPO4). Orthophosphates are soluble and are considered the only biologically available form. To measure total phosphate, all forms of phosphate are chemically converted to orthophosphates or hydrated forms [25].

Orthophosphate, which could exist as H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, is the only source of phosphorus (P) for plants and micro-organisms [37]. Naturally, phosphorus occurs at low concentrations and is essential for all forms of life [38]. Presence of large amount of phosphorus in the water indicates nutrient status, organic enrichment and may also be the quality of the water. It enters into water systems through weathering of rock and decomposition of organic matters. The phosphorus content of water system may also be increased due to different reasons including, discharge of sewage or detergents, urban and rural runoff containing fertilizers, discharging animals and plants matter [37, 39].

Though, phosphorus is essential nutrient, it may cause different problems in the water ecosystem if its concentration is higher than certain concentration limits. These problems include algal blooms, and the loss of species diversity [37, 38]. Abundant plant growth such as algal blooms leads to increased pH, turbidity and also the production of toxins and bad odor of the water [38]. As has been reported, algal blooms, occurs in water when the concentration of phosphorous is in the range of 0.01 to 0.1 mg/L [39,38].

Quantitative determination of orthophosphate and nitrate can be carried out by various analytical methods. Orthophosphate can be analyzed by flame photometer, amino acid method, Molybdovanadate method and stannous chloride method [40]. For example, in a Molybdovanadate method, in acidic medium, orthophosphate reacts with ammonium molybdate and results in the formation of molybdophosphoric acid. The obtained molybdophosphoric acid further reduced to molybdenum blue by reacting with reducing agent such as stannous chloride or ascorbic acid. The developed molybdenum blue color is then spectrophotometrically measured at a certain wave length that gives maximum absorbance, particularly at 690 or 880 nm

2.7.6. Nitrate

Nitrate is attributed mainly to anthropogenic activities such as runoff water from agricultural lands, discharge of household and municipal sewage from the market place and other effluents containing nitrogen specie. High nitrate concentrations in domestic water supplies can be toxic to human life. Nitrate is used mainly in inorganic fertilizers. In soil, fertilizers containing inorganic nitrogen and wastes containing organic nitrogen are first decomposed to give ammonia, which is then oxidized to nitrite and nitrate. Most natural water is deficient in nitrate having a concentration usually below 5 mg/L, but certain polluted surface water and ground water may have substantially higher quantities. Drinking water standards for nitrate are strict because the nitrates can be reduced to nitrites, which oxidize iron in blood hemoglobin from ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}). The resulting compound, called met hemoglobin, cannot carry oxygen. The resulting oxygen deficiency is called methemoglobinemia. It is especially dangerous in infants (blue baby syndrome) because of their small total blood volume.

Nitrate (NO_3^-) is another essential nutrient and usually originated from the breakdown of nitrogen containing compounds [40]. Nitrate may be found naturally in the soil. Thus, flowing water picks NO_3^- up from the soil. The types of soil and the amount of water moving through the soil also play a role in NO_3^- levels in water bodies. Nitrate is a well-known contaminant of water ecosystem. It enters the underground water through leaching and thus can reduce the quality of water [41]. Nitrate is also determined by several analytical methods including spectrophotometric methods, phenol disulphonic acid (PDA) method and ion exchange chromatography with specific ion electrodes [37, 42] For instance, flame photometer has been reported for quantitative determination of NO_3^- and phosphate concentrations in water .

2.8. Sources of trace heavy metals

Heavy metals can be released to the environment from both natural (for instance mineralogy of the soil) and anthropogenic sources (such as industrial, mining, smelting and processing activities) [43]. Others sources such as mineralogy of the soil, deposition of combustion particles from the atmosphere, deposition of traffic related particles, agricultural wastes, sewage sludge and fossil fuel combustion were also reported as the sources of trace metals contaminants [44]. Pollution may also originate from specific sources such as pipe, agricultural fields where fertilizers or pesticides are used, from dumpsite wastes, parking lots, gardens, and roads [45, 46]. In addition, car batteries, canned fruit/juices, cigarette ash, kitchen utensils, glassware, refineries, smelters, meats, paint, cookware, shampoos, etc. were also reported as possible sources of these trace metals.

It has been reported that elements such as Zn, Fe, Mn and Al originate from natural sources whereas Pb, Cu and Cd were anthropogenic origin[47]. Surface treated wood and industrial preservative treated wood were also reported as the sources of the metals such as As, Cr, Pb, Cu and Zn [48]. Agrochemicals such as organic fertilizers or solid manures were suggested as a source of Zn and Cu pollution [48, 49]. Untreated waste water is also one of the sources of trace metals pollution and thus, metals such as Pb, Cr and Ni are reported to be from such sources [49]. Chromium is a naturally occurring element present in water, sediments, rocks, soils, plants, biota, animals, and volcanic emissions [60].

Trace metals can enter into water bodies directly or indirectly from the surrounding environment, i.e., soil and air. Depending on its pH and organic matter contents, metals may exist in the soil either in soluble form3 or being adsorbed to the soil particles. The sorption ability of trace metals in the soil increased with increasing soil pH. On the other hand, soil samples with alkaline pH and high organic matter contents accumulated higher concentrations of trace metals. Therefore, at acidic pH metals are more soluble and thus, their leach ability into underground water increases [50, 51].

2.9. Toxicity and role of trace metals

Water pollution by heavy metals has become a question of considerable public and scientific concerns because of their toxicity to human health and biological systems. They exist in water as colloidal, particulate and dissolved substances [52]. Most trace metals are essential to human beings below certain concentration levels. For example; Co, Cu, Mn, Mo and Zn are needed at low contraction levels in many enzymes.. Fe is used to prevent anemia and to transport oxygen in the body of humans, whereas, Zn is used in more than 100 enzymatic reactions as a cofactor, and other activities [53]. However, some trace heavy metals such as Pb, Hg, As, Cd and Cr, have been classified as potentially toxic substance to human beings. Because they are indestructible, non-biodegradable and have ability to bind with biologically important function groups such as sulfhydryl groups of proteins and amines which disrupt normal functioning of enzymes [54]. Moreover, nutritionally essential elements may also have toxic effects on living organisms when their concentration exceeds certain levels [55].

In general, the potential toxicity of trace heavy metals is widely different due to their unique chemical and physical properties. For example, a study conducted on Brine Shrimp Artemia showed that the toxicity of trace metals decreases in the order of Pb, Cd, Cu, Ni, Zn, Fe, and Mn [57]. This order cannot be merely generalized for other organisms although it provides information about trends of the metals toxicity. The risk for toxicity depends on the frequency, intensity, and duration of contact with the contaminant along with the exposure route; and the inherent toxic potential of the metal itself [56].

Table 1. Summary of some major source and health effect of selected heavy metals

Sr.no	Pollutants	Major source	Effect of human health	Water quality guideline	
				ESA(mg/L) (2010)	WHO (mg/L) (2008)
1	Mn	Domestic waste, industrial effluent, atmospheric dust and decomposition of plant material.	Mn deficiency in females causes are diced maternal carrying for her young The +7 oxidation numberMn oxidize manganese and/or other organic matter	0.5	0.5
2	Fe	Erosion ofminerals from rocks and soil,corrosion of pipeline,sewage from metallurgical,dying	Increase the free radical production, which is responsible for degenerative diseases and ageing	0.3	0.3
3	Pb	Paint, pesticide, lead storage batteries, crystal glass, preparation fertilizers	Cognitive impairment in children, cause blood and brain disorder, peripheral neuropathy in adults, developmental delay, decrease in hemoglobin production,	0.01	0.01
4	Cd	Rock,coal, petroleum, paint, pigments,electroplating, batteries production	Cd appears to accumulate with age, especially in the kidney and it is considered also as a cancer and cardiovascular diseases, fragile bones and damage to lungs, liver and blood	0.003	0.003
5	Cr	Chromium arises from industrial sources and/or agriculture activities at the studied areas. Metal plating	For public health problems of cardiovascular disease, impaired glucose tolerance, elevated circulating insulin levels, and elevated serum cholesterol.	0.05mg/L	0.05mg/L

2.10. Analytical methods for analysis of heavy metals

Quantitative determination of heavy metals in water and other matrices can be carried out by various analytical methods including colorimetric, ultraviolet visible spectroscopy (UV-Vis) [58], ion exchange chromatography with UV-Vis detector (IEC/UV-Vis) [59], graphite furnace atomic absorption spectroscopy (GFAAS), inductively coupled plasma-mass spectrometry (ICP-MS) [60], flame atomic absorption spectrometry (FAAS) [61], inductively coupled atomic emission spectrometry (IC-AES) [62].

Table 2. Drinking water quality parameters with maximumadmissible limit set by different national and international organizations

No	Parameter	WHO(2015)	ESA	USEPA, 2008
1	Temperature	15-20 ^{o}c	❖ NM	❖ NM
2	EC	250µs/cm	250 µs/cm	2500 µs/cm
3	pH	6.5-8.5	6.5- 8.5	6.5 -8.5
4	Dissolved oxygen	8 mg/L		
6	TDS	1000mg/L	1000mg/L	500 mg/L
7	Nitrate	50mg/L	50mg/L	10 mg/L
8	Phosphate	5mg/L	-	NM
9	Mn	400 µg/L	400 µg/L	50 µg/L
10	Fe	200 µg/L	200 µg/L	300 µg/L
11	Pb	10 µg/L	10 µg/L	15 µg/L
12	Cd	3 µg/L	3 µg/L	5 µg/L
13	Cr	50 µg/L	50 µg/L	100 µg/L

NM: not mentioned

3. MATERIALS AND METHODS

3.1.Description of the study area

The study was conducted in Benja Village, Nono Benja District,Jimma Zone, Oromia Regional State (Fig. 2). It is one of the 21 Districts found in Jimma Administrative Zone, with the population of 87,945 of which 44,412 are males and 43,533 are females. The District is located to the North of Jimma town at the distance of 157 kilo meters, and altitude ranges from 1,700 to 1,850 meters above sea level. The District is found at 37’57:15 longitude and 8’ 47:57 latitude and the mean annual temperature is 15 to 24 degree Celsius.

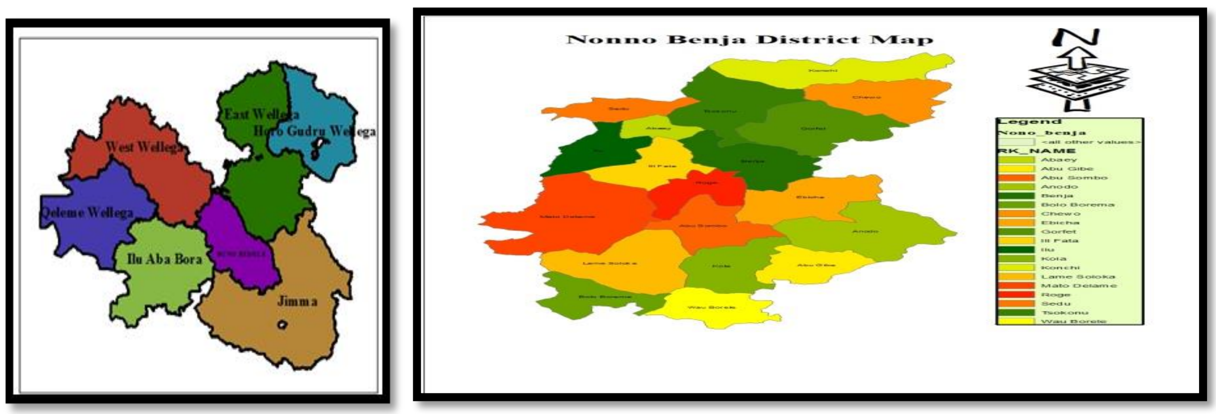

Figure 3. Map of Nono Benja District with the specific sampling sites of the well waters and map of west Oromia

3.2. Chemicals and reagents

All chemicals and reagents used for this study are analytical grade. Commercially available 1000mg/L standard solution of (Cd, Cr, Pb, Mn,and Fe were obtained from (Merck, Germany). 37%, HCl, and 67% HNO_3, (sigma-Aldrich, England) were used for extraction and sample digestion. Phosphate (PhosVer® chemical reagent, Germany) and Nitrate (Nitra Ver®5 nitrate reagent chemical, Germany), and distilled water was used throughout this work for preparation of solutions and cleaning of glass wares.

3.3. Instruments and Apparatus

Laboratory equipment's and apparatus such as Polyethylene bottles, Ice-box, and glass wares were used as per necessary. Portable multi-meter 900P (Bante instruments, UK), photometer (Model DR2800, Hach, Japan), Micro-wave digestion with top wove control unit model-912A743(Company, Germany), Flame Atomic Absorption Spectroscopy(FFAAS NOVAA400P analytic jena, GERMANY**)** were used.

3.4. Sample collection, preservation and sampling technique

The well-water samples were collected from Benja town and six surrounding kebels, namely (Ilfata,Gurifat,Dokonu, Benja Badiyya, abbayi and Roge) purposively during the month of October, 2019. The samples were taken during the morning before it was disturbed and in the evening after much fetching activity has taken place on the wells, and mixed together utilizing polyethylene bottles previously cleaned by soaking in 10% HNO_3 for 24 h after washing with non-ionic detergent and were rinsed with distilled water prior to usage and taken as representative for each sample. The deep well sample was collected on two sites from elevated reservoir and at house hold level. The collected sample was labeled as from the selected well of the kebeles, Hand dug well from (Ilfata(**HDW1**) and Gurifat(**HDW2**)), Hand pump well from (Dokonu(**HPW3**) and Benja badiya(**HPW4**)), Shallow well from (Abbayi(**SW6**) and Roge(**SW7**)) and Deep well from Benja town(**DW5**)respectively. Physicochemical parameters like Temperature, pH, Conductivity, TDS and DO were analyzed onsite using portable multi meter (900P). In the filed the polyethylene bottle were rinsed at list three times with the water the water to be sampled prior to sampling and 2 % nitric acid were added to sample and subsequently stored at room temperature until analysis to reduce change of the physicochemical properties of the metals and deposition on the containers[63].

Table 3. Table showing the Specific sampling locations of the well-water sample collected from Nono Benja District, Jimma Zone, Oromia Regional State, and southwest Ethiopia.

Sampling Sites	Altitude (m)	North-direction	East- direction
Hand dug well (W_1)	1720	N- $08^0$72.064'	E-$037^0$09.625'
Hand dug well (W_2)	1754	N-$08^0$72.191'	E-$037^0$09.476'
Hand pump Well(W_3)	1725	N-$08^0$71.006'	E-$037^0$10.004'
Hand pump Well(W4)	1716	N-$08^0$70.799'	E-$037^0$09.628'
Deep well (W_5)	1755	N-$078^0$72.156'	E- $037^0$08568'
Shallow Well(W_6)	1850	N-$08^0$71.155'	E-$037^0$10.808'
Shallow Well(W_7)	1724	N-$08^0$69.948'	E-$037^0$09.970'

3.5. Procedure for physicochemical analysis

The physicochemical parameters such as, Temperature, Electrical conductivity, Dissolved oxygen and pH were measured onsite. These parameters were measured by portable multi meter 900P initially calibrated using known standard buffer solution with a pH value of 4, and 10 following the procedures given on the instruction manual. The electrode was removed from the buffer solution and rinsed with distilled water and dried by gently blotting with a soft tissue paper. Finally, the electrode was immersed in the containers containing water sample and the reading was recorded directly from the screen of the multi-meter. The portable multi-meter has been calibrated before and after taking measurements prior to each site of samplings.

3.5.1. Sample preparation procedure for NO_3^- , $PO_4^{3-}$by photometer

Nitrate: -A sample cell was filled with 10mLof sample. The Nitrate reagent powder pillow was added to the cell. Then sample cell was closed and shacked vigorously to dissolve the solid. The reaction time required 2 min and yellow color were developed due to the presence of nitrate. Then the instrument was calibrated by blank to (0.00mg/L NO_3^-). Reading of nitrate was done by using photometer in mg/L[65].

Phosphate: -A sample cell was filled with 10mL of sample. Phosphate Reagent Powder Pillow was added to the cell. A blue color was developed due to the presence of phosphorus is in the sample. Then sample cell was closed and Shacked vigorously for 10 seconds. A 2-minute reaction time was required. Then the instrument was calibrated by blank to (0.00 mg/L PO_4^{3-}). The result was taken from the photometer in mg/L [65].

3.6. Sample preparation procedure for heavy metal analysis using FAAS

3.6.1. Digestion of water samples for Heavy metal determination

Digestion of the water samples were done in triplicates using concentrated nitric acid (Analytical Grade) according to method described by [64]: 20mL of water sample were taken in to 100mLof digesting tube (Analytical Jena). To this water sample, 8mLof 3:1 ratio of nitric acid and hydrochloric acid were added. The solution was then digested in microwave digestion by adjusting temperature from 150-180 °Cfor boiling water and 50°C for cooling for total 30 minutes. Then, the digested and cooled sample solution was filtered with qualitative filter paper 20-25µ pore size of 0.9 cm inserted in a 100mLpore filtration glass. A blank solution had been similarly prepared and made ready for analysis of heavy metals using atomic absorption spectroscopy.

3.7. Solution preparation

3.7.1. Working Standard solution preparation

Analytical grade stock standard solutions containing 1000 mg L^{-1} of (Mn,Cd, Cr, Fe, and Pb)purchased from(Merck, Germany) were used for preparation of working standards solution. The working solution for each selected heavy metal were prepared freshly from intermediate standard solution (20mg/L) which was prepared by diluting stock standard solution (1000mg/L).Five standard calibrating solutions were prepared from the previously prepared 20 mg/L of working standards solution by serial dilution of each metal stock solution.

3.7.2. Calibration of Instrument

Calibration was done by preparing working standard solutions of known and certified standard chemical within working range of instruments for six points of calibration curve for each metal. By following the read out device (computer) the working standards, the FAAS constructs a suitable calibration curve of response /absorbance verses concentration. The FAAS was used suitable graph and determined concentrations of unknown analyte (Appendix 8) showings the absorbance versus concentration has constructed through direct analysis of five-point calibration standards at specified wavelength of the analytes. The calibration curve shows good correlation coefficient (R^2) greater than the minimum acceptance value 0.995 [40]. This shows that there was a good linear relationship between the concentration and instrument responses. Instrument was calibrated for each selected heavy metals using five series of their standard –calibration before qualitative determination of them in the sample. The calibration curve for were plotted as function of Absorbance verses concentration of the standard solution as showed in the table below. The linearity for calibration line for Mn, Fe, Pb, Cd and Cr showed correlation coefficient (r^2) of 0.997, 0.998, 0.998, 0.998, 0.999, respectively which are greater than or nearly the minimum acceptance value of 0.995[12]

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Table 4. Table of working standard solution concentration Calibration curve Regression equation and correlation coefficient for each metal analyzed.

Metal	**Concentration standard (mg/L)**	**Regression equation**	**Regression coefficient limit(r^2)**
Mn	0.2 ,0.4, 0.6, 0.8, 1.0, 1.2	Y=0.1383x+0.0802	0.997
Fe	0.1,0.5,1.0,1.5, 2.0, 2.5	Y=0.634x-0.058	0.997
Pb	0.5, 1.0, 1.5 ,2.0 2.5	Y=0.036x-0.0094	0.998
Cd	0.2 , 0.4, 0.6 ,0.8, 1.0, 1.2	Y=0.478x+0.046	0.998
Cr	0.2 ,0.4 ,0.6, 0.8, 1.0	Y=0.067x-0.012	0.997

Therefore, the calibration curve was showed that there was linearity between the instrument response and prepared concentration which indicating the best working condition of the instrument. The calibration curves are given in Appendix [7]

3.8. Limit of detection and Limit of quantification

The Limit of detection and Limit of quantification for the analysis of metal using FAAS in water for each selected heavy metal were determined experimentally by running blank samples and their values here given in the Table 6. This was done to determine whether the blank sample contributes measurable quantities of the metal to be analyzed or contamination is introduced during digestion.

Table 5.IDL, LOD and LOQ (mg/L) of the methods

Metal	IDL	LOD	LOQ
Mn	1×10^{-4}	0.006	0.02
Fe	3×10^{-4}	0.003	0.013
Pb	3×10^{-4}	0.006	0.02
Cd	7.5×10^{-3}	0.005	0.016
Cr	5×10^{-4}	0.002	0.007

3.9. Heavy metals analysis procedures

The data qualities obtained from FAAS for heavy metal analyses are highly affected by the calibration curve and standard solution prepared procedures. The calibration curve was established from five series working standard solution. The working solution for each selected heavy metals (Mn, Fe, Pb, Cd, Cr) were prepared freshly from intermediate standard solution (20mg/L) which was prepared by diluting stock standard solution (1000mg/L). After the instrument was calibrated; the sample solution aspired Flame Atomic Absorption and absorbance of the sample was recorded. Then, the concentration of selected heavy metals was obtained from the measured absorbance. The calibration curve (Appendix [7]) showing Absorbance verses concentrated through direct analysis of six-point calibration standard at specific wave length of the analyte. The calibration curve shows good correlation (R^2) greater than minimum acceptance value 0.995 [12]. This shows that there was a good linear relation between the concentration and instrument responses.

3.10. Method validation

3.10.1 Determination of method detection limit

Method detection limits is defined as the minimum concentration of analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. Method detection limit for heavy metal may vary with wavelength selected and the spectrometer configuration and operation conditions. Methods of detection Limit for water sample analysis will be determined using reagent water blank with (HNO_3/HCl) that will be digested in the same condition as the sample. The method detection limit of each element has obtained by multiplying the standard deviation of the reading blank by three

MDL= 3δ blank

Where δ blank is standard deviation of the blank reading

3.10.2 Determination of limits of quantization (LOQ)

Limit of quantification (LOQ) – is the lowest concentration level at which measurement is quantitatively meaningful.

LOQ = 10δblank

3.10.2. Precision and recovery Studies

The analytical method precision will be assessed in terms of relative standard deviation (RSD) and standard deviations (SD) among measurements.

$$RSD = \frac{SD}{\bar{x}} X100$$

where, RSD =Relative standard deviation, SD=standard deviation, $\bar{x}$ = mean value

Accuracy of analytical method has evaluated in terms of percent recovery by either the assay of Known added amount of analyte in the sample or as the difference between the mean and the accepted true value together with the confidence intervals. In this study, the analytical accuracy of the procedures was determined by spiking experiment. The resulted spiked samples was digested, diluted and analyzed for total heavy metals. The percentage recovery of each data was calculated as

$$\mathbf{R} = \frac{mean\ spiked\ value - unspiked\ value}{standard\ of\ spike\ added} \times \mathbf{100}$$ where, R= Percent of recovery

3.10.3.Data Analysis

Result of water sample analysis were compared against standard set by WHO, ESA and the obtained data were analyzed using SPSS software (version25) and Microsoft Excel 2016. Descriptive data have generated for all variables and presented as means ± standard deviation ($\bar{x}$± SD). The mean variations in data between the five sites have analyzed using One-way ANOVA. The parameters have correlated against each other to determine their relationship using Pearson’s correlation. Significance has considered at 95% confidence interval. Data was generated, organized and summarized using appropriate methods. Analysis was done using simple descriptive statistics assisted by Microsoft Excel. And SPSS

4. RESULTS AND DISCUSSION

4.1. Physicochemical parameters result of well water sample under study

Water quality refers to the physical, chemical and biological characteristics of water. It is a measure of the condition of water relative to the requirements of one or more biotic species and or to any human need. Hence physicochemical parameter study is very important to get exact idea about the quality of water and to compare results of different physicochemical parameter values with standard values. The physicochemical characteristics of water samples from eight different well water sample at the study site are presented in Table 7.

Table 6. Physico-chemical parameters of well water sample from Benja and surrounding kebels (Mean ± SD, n=3)

Information of the samples			Parameters						
Sample site	Sources	Sample Code	Temperature (°C)	pH	TDS (mg/L)	DO (mg/L)	EC (μs/cm)	PO_4^{3-} (mg/L)	NO_3^- (mg/L)
Benja town	Deep well	W1	25.20 ± 0.10	8.78 ±0.01	650.67 ± 0.58	5.24± 0.02	1306. ± 0.58	0.03±0.01	3.12±0.12
Benja twon	Deep well	W2	24.40 ± 0.26	8.68 ± 0.07	651.67 ± 0.58	5.60± 0.51	1302.67 ± 1.52	0.22± 0.01	3.13±0.02
Ilfata	HDW1	W3	23.63 ± 0.25	8.50 ± 0.05	553.37 ± 1.15	4.65± 0.02	763.33 ± 0.58	0.05± 0.01	4.45±0.03
Gurifat	HDW2	W4	20.43 ± 0.42	6.76 ± 0.08	161.00 ± 1.00	4.35± 0.04	453.00± 1.00	0.07±0.01	2.42±0.02
Dokonu	HPW3	W5	22.96 ± 0.11	7.62 ± 0.03	535.67 ± 0.58	2.12± 0.09	461.33± 1.15	0.02±0.01	3.94±0.01
Benja badiya	SPW4	W6	22.10 ± 0.20	7.75 ± 0.03	250.00 ± 1.00	4.20± 0.01	416.00± 1.00	0.41± 0.02	4.23±0.02
Abbayi	SH6	W7	21.90 ± 0.20	7.75 ± 0.03	295.33 ± 0.58	3.84± 0.03	575.33± 1.15	0.25±0.03	3.25±0.03
Roge	SH7	W8	23.43 ± 0.21	6.68 ± 0.04	178.00 ± 1.00	3.53± 0.02	218.33± 0.58	0.47±0.02	8.28±0.01
WHO Standard (2010)			-	6.5 – 8.5	1000	8	250	5	50

4.1.1 Temperature

Temperature measurements are very useful in understanding the trend of physical, chemical and biological activities which are enhanced/ retarded by the variation of temperature The present Investigation reveals that the temperature of the well waters varied from a minimum of 20.43°C of the site of W4 well water to maximum of 25.20°Cat W1 (reservoir) .. One-way ANOVA test ($p \leq 0.05$) showed that the temperatures varied significantly among the well water sites. Temperature of the well water is highly correlated with TDS (r= 0.788) and (r=0.706). In Table 9, water temperature at siteW1 (reservoir) was higher than the other sampled well waters .This might be the attribute to the fact that the site W1 (reservoir) is located relatively in the head of water, which have more shade and located at higher altitude and no foreign wastes and daily discharged to it.

4.1.2 pH

pHis an index of the amount of hydrogen in (H^+) that are in a substance. The pH scale measured with respect to neutral substances as reference. Substances with a pH higher than 7.0 (7.1-14.0)are considered alkaline or basic. Substance with a pH less than 7.0(0-6.9) are considered as acidic. According to the WHO, the minimum and maximum allowable PH ranges from 6.5 to 8.5for potable water. There is no health risks related to consuming slightly acidic or basic water.PH values of water in the study area. The pH values study area ranges from 8.78 site (W1) to 6.68(W8) as It is indicated in table (9) the pH was weakly alkaline in the entire sites except in (W8) The higher pH value observed suggest that carbon dioxide,carbonate,bicarbonate equilibrium has affected more due to change in physicochemical condition **..**

4.1.3Electrical Conductivity

Pure water is not a good conductor of electric current rather a good insulator. Increase in ions concentration enhances the electrical conductivity of water. Generally, the amount of dissolved solids in water determines the electrical conductivity. Electrical conductivity (EC) is actually measures the ionic process of a solution that enables it to transmit current In the study area EC value ranges from 1306µS/cm-218.33 µS/cm the well waters sampled W1 ,and W2 was found to be more conductor than the others. High conductivity of water sample implies that there are a number of cations and anions in the ground and surface water, and is an indication for the saltiness of the water. These results clearly indicate that water in study areas was considerably ionized and has the higher-level of ionic concentration activity due to excessive dissolve solids. Thus, it is a fine conductor of electric current.

4.1.4 Total dissolved solids

In drinking water, total dissolved solids are primarily made up of inorganic salts with small concentrations of organic matter. Contributory ions are mainly carbonate, bicarbonate, chloride sulphate, nitrate, potassium, calcium and magnesium. Major contribution to total dissolved solids in water is due to natural contact with rocks and soil. . The observed mean total dissolved solid concentration in well water currently measured varied between a minimum mean values of 161.00 ± 1.00 mg/L (siteW4) to a maximum mean values of 651.67 ± 0.58 mg/L (site W2). The mean total dissolved solid values varied significantly ($p \leq 0.05$) among the selected sites of the river. The dissolved salt present in the water, affect its aesthetic value as well as its physicochemical properties. High content of dissolved solid elements, affect the density of water, influences osmoregulation of freshwater in organisms, reduces solubility of gases (like oxygen) and utility of water for drinking, irrigation

4.1.5Dissolved oxygen

The Dissolved oxygen (DO)was observed in all sampling sites. They vary within a range of (5.60 to2.12 mg/L) (Table;9). The low levels of DO were observed in the well-water sampled from W5 (2.12± 0.09 mg/L). The possible reason for these lower concentrations might be due to the high rate of oxygen consumption by ox disable matter and the higher level of nutrient load. Higher values of DO was detected in well-water sampled from W2 (5.65± 0.51 mg/L) and W1 (5.24 ± 0.02 mg/L). These observed results were due to the capacity of water to hold oxygen. Literature values reported that the concentration of DO below 5 mg/L may adversely affect the functioning and survival of biological communities and below 2 mg/L may also lead to the death of most fish. Therefore, since the observed concentrations DO were below these resent studies they could affect the functioning and survival of biological communities

4.1.6 Nitrate

Nitrate represents the most oxidized form of nitrogen and the product of oxidation of nitrogenous matters and its concentration may depend on the nitrification and de-nitrification activities of microorganisms. Nitrate mean concentration range from a minimum of 2.42± 0.02 mg/L (site W4) to a maximum of 8.28 ± 0.01 mg/L (site W8). The values in all the sites were below the permissible limit of WHO and EDWQ (50 mg/L).

4.1.7 Phosphate

Phosphate was estimated from all eight samples. The lowest phosphate means concentration value of (0.002±0.001) was observed at W5 and the highest phosphate value were observed at W8,W6(0.47±0.02 mg/L), (0.41±0.02mg/L) respectively. The highest phosphate values indicate that the farmers along the higher farm land use fertilizers, which has potential of being leached or washed in the river. In this study, the maximum mean concentration of phosphate was recorded at W8 due to discharge from fertilizers runoff, detergent use, domestic waste and biological process .High levels of both phosphates and nitrates can lead to Eutrophication, which increases algal growth and ultimately reduces dissolved oxygen in the water and the common source of phosphate and nitrate which were increased activity of washing, detergent use, fertilizer runoff, and wastes from Agro-industry [11**].** On way ANOVA test ($p \leq 0.05$) show that the phosphate varied significantly among the eight sample sites. The comparison with the WHO standard and Ethiopian standard, the mean concentration of the phosphate in the well sample sites were below permissible limit. This indicates that in the cause of phosphate the well water is not polluted in all site.

4.2. Analysis of heavy metals in water samples

The mean concentration of selected heavy metals (Mn, Fe, Pb, Cd, Cr) in water samples were presented in Table 8.

4.3. The mean variation of heavy metals by using one-way ANOVA

In the present study, significant variations have indicated by the concentration of the metals with higher concentration shown in . (Table 8) contains the results of the laboratory analysis conducted on the well water samples from Benja Village and their detail discussions have given in the following section.

Table 7. Concentration of heave metal (mg/L), mean ± SD (n=3)in well water from Benja and surrounding kebeles.

Parameter	**Site**	**Mean ± SD**	**Drinking water standard**		
			WHO	ESA	USEPA
Mn	W1	3.70±0.19	0.50mg/L	0.50 mg/L	0.50mg/L
	W2	2.36±0.09			
	W3	0.32±0.02			
	W4	0.152±0.004			
	W5	BDL			
Fe	W1	0.344±0.043	0.30mg/L	0.30mg/L	0.30mg/L
	W2	0.145±0.0002			
	W3	0.145±0.001			
	W4	0.245±0.025			
	W5	0.280±0.006			
Pb	W1	0.275±0.001	0.01mg/L	0.01mg/L	0.015mg/L
	W2	0.274±0.0005			
	W3	0.274±0.0001			
	W4	0.275±0.0001			
	W5	0.274±0.001			
Cd	W1	1.27±0.021	0.003mg/L	0.003mg/L	0.003mg/L
	W2	0.75±0.081			
	W3	BDL			
	W4	BDL			
	W5	BDL			
Cr	W1	0.336±0.0004	0.05mg/L	0.05mg/L	0.05mg/L
	W2	0.335±0.0002			
	W3	0.346±0.002			
	W4	0.344±0.002			
	W5	0.334±0.002			

W1=Reservoir W3=Hand dug W4= Hand pump

W2=House hold (composite) W5=Shallow

4.3.1 Lead (Pb)

Lead is regarded as highly hazardous for plants, animals and particularly for microorganisms. Long-term exposure to lead can result in a buildup of lead in the body and severe symptoms. These include anemia, pale skin, a decrease handgrip strength, abdominal pain, nausea, vomiting and paralysis of the wrist joint. Prolonged exposure may also result in kidney damage. If the nervous system is affected, usually due to very high exposure, the resulting effects include severe headache, coma, delirium and death. Continued exposure can lead to decreased fertility and/or increased chance of miscarriage or birth defects [68].The highest Pb concentration was observed in well-water of W_1 (0.275 ± 0.001 mg/L) and the lowest were observed in well-water of W2, W3, W5(0.274 mg/L). The Pb concentrations observed in all well-water sampling sites were found to be above the WHO, EU and USEPA guideline value (Table.12) These high concentrations might be due to some anthropogenic origin that were released by the surrounding communities. In addition to these, the five sampled well-water used old Pb pumps for pumping the water from underground. The composition of groundwater is dependent on natural factors (geological, topographical, meteorological, hydrological and biological) in the drainage basin which could poison and a possible human carcinogen..[35]

4.3.2 Chromium (Cr)

The Cr concentrations were observed in all well-water sampling sites. These concentrations ranged from 0.334 ± 0.002 mg/L to 0.346 ± 0.00 mg/L (Table 12). All these Cr concentrations detected in all well-water sampling sites were above WHO set by ES (0.05mg/L) W1 (0.336 ± 0.0004 mg/L), W2 (0.335 ± 0.002 mg/L), W3 (0.346 ± 0.002 mg/L) W4 (0.344± 0.002 mg/L) and W5(0.334±0.002)mg/L.

4.3.3 Cadmium

The mean concentration of Cadmium in the study area was minimum 0.75±0.081 mg/L (site W2) and maximum 1.27±0.021 mg/L at site W1. The concentration Cd values recorded fromtwo sites are much more than the recommended.(0.003mg/L)set by the WHO and the Ethiopian Standards. Sample W1,and sample W2, hence the deep well water was polluted. Cd in W3, W4, W5is not detected by instrument. in case of Cd. One-way ANOVA ($p \leq 0.05$) Cd is a poisonous metal and can cause serious health problems even if ingested in small amounts. Acute exposure in the other sampling well water sites are below detection limit . Cd can cause nausea, vomiting, diarrhea, muscle cramps, salivation, sensory disturbances, liver injury, convulsions, shock, and renal failure.

Long-term exposure to low levels of Cd in air, food, and water leads to a build-up of Cd in the kidneys and possible kidney disease. Other potential long-term effects are fragile bones and damage to lungs, liver, and blood [9].

4.3.4 Manganese

The mean concentrations of Mn for the five (5) considered sampling stations are recorded on Table 12 showing values that ranged between 0.152-3.7 mg/l. The mean concentrations in W1 and W2 sampling sites were found to be higher than the recommended limit (0.5 mg/l) for Mn in drinking water the other sampling stations sites W3 (0.323) W4(0.152) are below the limits. The higher levels will imply health hazard that could result in Mn related illnesses like neurological damage and motor disturbances. All the sampling stations were also found to record Mn mean concentrations that were significantly different $P<0.05$. The excess heavy metal load was attributed to the discharge of industrial effluents, municipal wastes, geology of river bed and catchment area Constant assessment of manganese to control its discharge.

4.3.5 Iron (Fe)

Mean iron concentration of the well water ranges from minimum value of 0.145±0.0002 mg/L (site W2) to the maximum value of 0.344±0.043 mg/L (site W1). When compared with maximum permissible limit of WHO and ESA guideline, Fe concentration in the entire sites was above the maximum acceptable limit (0.1mg/L). This probably due to iron tendency to form complex ligands (compounds) with anions and iron in lower oxidations easily soluble and could settle on the water bed. Statistical ANOVA result ($P<0.05$) The earth's core has believed to consist largely of a metallic iron-nickel alloy. Studies from other parts of the world documented Fe to have considerable effects on alveolar epithelial cell. Even though allowed limit is necessary for normal human health, higher concentrations are associated with stomach and intestinal corrosion, leading to bleeding and shock development. The shortage of iron causes diseases called “anemia” and prolonged consumption of drinking water with high concentration of iron may lead to liver disease called ashaermosiderosis.

4.4. Correlations

Table 8. Correlation between physico-chemical parameters and heavy metals among the selected sites of Well water from Benja and surrounding kebeles

	Tem	pH	TDS	DO	EC	PO_4^{3-}	NO_3^-
Tem	1						
pH	.708**	1					
TDS	.788**	.890**	1				
DO	0.378	.570**	0.345	1			
EC	.694**	.871**	.836**	.742**	1		
PO_4^{3-}	-.442*	-0.112	-.473*	-0.054	-0.353	1	
NO_3^-	0.19	-.430*	-0.343	-0.333	-.506*	-0.067	1

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).

Correlation between physic-chemical parameters

Pearson correlation coefficient was used examine the relationship between the various physic-chemical parameters in the water sample from all the sample sites. Table 9 shows the correlation matrix of the relation between the physico-chemical parameter concentrations of river water samples. In previous study reported at high correlation coefficient (near +1 or -1) means good relationship between two variable and its concentration around zero means no relation between them at significant level of 0.05%l it can be strong correlated , If r>0.7, whereas r value between 0.5 and 0.7 shows moderate correlation between two different parameters. Therefore, Pearson correlation coefficient matrixes among the determined physico chemical parameter are present in Table (9). There was strong correlation between the TDS, pH(r=.890), TDS,Temp.(r=.788) pH,Temp (r=.788). ,EC,pH(r=.871) EC,TDS(r=.836) EC,DO(r=.742). And there was moderate correlation between, E.C,Temp. (r=.694), DO pH,(r=.570) and weak correlation between NO_3^-, Temp (r=0.19) DO, Tem (r=0.378),DO,TDS(r=0.345) respectively.

Table .9 Correlation between measured metals

	Mn	Fe	Cr	Pb	Cd
Mn	1				
Fe	-0.403	1			
Cr	-0.127	0.43	1		
Pb	-.574*	0.48	-0.014	1	*
Cd	.985**	-0.465	-0.087	-.580*	1

Pearson correlation coefficient matrix among the selected heavy metal is present in Table (13) significant correlation between the heavy metals Cd and Mn(r=0.985) Cr with Fe (r=0.43),Pb with Fe(0.48) could indicate the same or similar source input Pearson correlation coefficient was used to examine the relation between the various heavy metal in the water from all sample site. Table 13 shows the correlation matrix of the relation between heavy metal concentration of well water sample [64] reported at high concentration coefficient (near+ or -1) means good relationship between the two variable and its concentration around zero means no relationship between them at significant level of 0.05% level, it can be strong correlated , If r$>$ 0.7, whereas, r value between 0.5 and 0.7 show moderate correlation between two different parameter

4.5. Evaluation method performance

In this study the precision of the results was evaluated by standard deviation and relative standard deviation of the result of triplicate samples with triplicate measurement of each sample were used for the analysis of heavy metals and physicochemical parameter. The precision of the analytical method has the method of detection calculated interims of relative standard deviation.

It can be seen in Table 8 that the values of relative standard deviation (%RSD) are less 9% for all mean concentration of fortified matrix and triplicate samples. All of these values are below 15% (Table 8). This shows that the precision of the result obtained in all methods is acceptable [12**]**

Accuracy of the analytical methods has calculated percent of recovery. The percent calculated values have given in Table 7**.** The recovery was within standard (80-120%) [12**].**The recovery values in the above range are acceptable.

Therefore, the percentage recovery values have found between the lowest 86 % to and highest 96.5% and all were within the required criteria. In addition, the RSD value is all below the standard limit Table7. This confirms that the method has provided results within the required levels of accuracy and precision

Table 10 . Mean percent recovery, Standard deviation and relative standard deviation of heavy metal

Name metal	Site	Mean spiked value (mg/L)	Amount of sample added	Unspiked value (mg/L)	Recovery
Cd	W1	3.028	2	0.037	87.7%
	W2	3.1005		0.050	93.3%
	W3	1.5329		BDL*	
	W4	1.4487		BDL*	
	W5	1.500		BDL*	
Cr	W1	2.158	2	0.310433	92.4%
	W2	2.2394		0.361323	93.9%
	W3	2.200		0.361323	91.9%
	W4	2.089		0.310433	88.9%
	W5	2.221		0.361323	93%
Pb	W1	1.99	2	0.263617	86.4%
	W2	2.059		0.263617	89.8%
	W3	2.034		0.285417	87.5%
	W4	2.055		0.285403	88.4%
	W5	2.038		0.285403	87.6%
Fe	W1	1.908	2	0.134 04	88.7%
	W2	1.926		0.11032	90.8%
	W3	2.214		0.489917	86.4%
	W4	2.023		0.217082	90.3%
	W5	2.1035		0.2289 44	93.7%
Mn	W1	5.652	2	2.7898	93.1%
	W2	5.3976		3.466859	96.5 %
	W3	1.9204		0.198602	86%
	W4	2.168		0.323933	92.2%
	W5	1.9385		0.152808	89.2%

BDL*- Below detection limit

5. CONCLUSION AND RECOMMENDATION

5.1 .Conclusion

In this study physico-chemical parameters such as Temperature, Turbidity, TDS, EC, DO, pH, NO_3^-, PO_4^{3-} and heavy metals (Fe, Mn,Pb, Cd and Cr) in different well water sample were investigated. From the finding, physico-chemical parameters such as pH determination in water sample of W1 and W2 showed that the ground water sample was found to be basic similarly; higher electrical conductivity was recorded in most water samples, which is an indication for high salinity. As a result, these samples were above the recommended value of EWQG and WHO guide line for drinking water quality. However, the concentration of dissolved oxygen in most ground water samples is below the WHO guideline while the rest measured physicochemical parameters are within the WHO guideline and other standards. The results showed that the amount of Iron, Lead, Manganese, Chromium and Cadmium in(reservoir and house to house sample)found in ground water samples were quiet higher than the level set by EWQG and WHO guide line. The selected acid digestion procedure for the sample was found efficient for all of the metals. It was evaluated through the recovery experiment and good percentage recoveries were obtained for all of the metals investigated. Based on the finding of this study, some of the water samples for some physicochemical parameters and heavy metals were above the EWQG and WHO guideline for drinking water and hence needs further treatment.

5.2 Recommendation

- Based on the finding of this study, the following recommendations are forwarded.
  - Awareness creation to the community of the study site could help them to manage some water contaminants.
  - Further studies based on seasonal variation have to be conducted to know the source of common pollutants of the water source and to suggest possible scientific solution for the community of the study site
  - The concerned government, Oromia Water and Energy Bureau, Non-Governmental Organizations as well as the surrounding communities should discuss together for the improvement of the water quality of the study site.

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Appendix 1. Mean ± SD values for Metal Analysis

Report

sampling site		Mn	Fe	Cr	Pb	Cd
One	Mean	3.700651	.145438	.336152	.275173	1.274287
	N	3	3	3	3	3
	Std. Deviation	.1941536	.0008126	.0004747	.0011490	.0218930
Two	Mean	2.358159	.145836	.335719	.274807	.754243
	N	3	3	3	3	3
	Std. Deviation	1.9121958	.0002094	.0002759	.0005140	.08180805
Three	Mean	.323933	.344673	.336152	.274440	-.181112
	N	3	3	3	3	3
	Std. Deviation	.0191305	.0436031	.0004747	.0001211	.0112766
four	Mean	.152808	.245584	.334619	.275173	-.199169
	N	3	3	3	3	3
	Std. Deviation	.0041746	.0257023	.0021812	.0011490	.0174136
five	Mean	-.584719	.280419	.334619	.274507	-.204586
	N	3	3	3	3	3
	Std. Deviation	.0083492	.0068059	.0021812	.0000057	.0031276
Total	Mean	1.190166	.232390	.335452	.274820	.288732
	N	15	15	15	15	15
	Std. Deviation	1.7991976	.0826520	.0013991	.0007229	.7076572

Appendix 2: One- way ANOVA test Result forMetal Analysis

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
Mn	Between Groups	37.930	4	9.483	12.833	.001
	Within Groups	7.389	10	.739		
	Total	45.320	14			
Fe	Between Groups	.090	4	.023	43.324	.000
	Within Groups	.005	10	.001		
	Total	.096	14			
Cr	Between Groups	.000	4	.000	.911	.494
	Within Groups	.000	10	.000		
	Total	.000	14			
Pb	Between Groups	.000	4	.000	.633	.651
	Within Groups	.000	10	.000		
	Total	.000	14			
Cd	Between Groups	5.671	4	1.418	10.577	.001
	Within Groups	1.340	10	.134		
	Total	7.011	14			

Appendix 3- Correlation parameters some metal analysis

Correlations

		Mn	Fe	Cr	Pb	Cd
Mn	Pearson Correlation	1	-.403	-.127	-.574*	.985**
	Sig. (2-tailed)		.136	.653	.025	.000
	N	15	15	15	15	15
Fe	Pearson Correlation	-.403	1	.430	.480	-.465
	Sig. (2-tailed)	.136		.109	.070	.081
	N	15	15	15	15	15
Cr	Pearson Correlation	-.127	.430	1	-.014	-.087
	Sig. (2-tailed)	.653	.109		.962	.758
	N	15	15	15	15	15
Pb	Pearson Correlation	-.574*	.480	-.014	1	-.580*
	Sig. (2-tailed)	.025	.070	.962		.023
	N	15	15	15	15	15
Cd	Pearson Correlation	.985**	-.465	-.087	-.580*	1
	Sig. (2-tailed)	.000	.081	.758	.023	
	N	15	15	15	15	15

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed

Appendix 4: One- way ANOVA test Result for all parameters among the water sample sites

Report

Sampling site		TDS	EC	DO	PH	TEM	N03	P04
0ne	Mean	608.33333	313.00000	2.59333	7.08000	22.06667	22.23667	.02833
	N	3	3	3	3	3	3	3
	Std. Deviation	.577350	1.000000	.005774	.010000	.404145	.499032	.007638
two	Mean	577.33333	296.66667	3.85000	8.02000	25.66667	3.19000	.02233
	N	3	3	3	3	3	3	3
	Std. Deviation	1.527525	1.527525	.010000	.010000	.416333	.096437	.002517
three	Mean	617.66667	337.66667	1.51000	7.26333	21.73333	4.56000	.05233
	N	3	3	3	3	3	3	3
	Std. Deviation	1.154701	1.154701	.010000	.005774	.305505	.208087	.002082
four	Mean	627.66667	991.00000	2.98000	8.04000	21.20000	3.41667	.07900
	N	3	3	3	3	3	3	3
	Std. Deviation	1.527525	1.000000	.010000	.010000	.264575	.015275	.001000
five	Mean	601.00000	79.00000	3.44133	6.98000	24.76667	3.94000	.02267
	N	3	3	3	3	3	3	3
	Std. Deviation	1.000000	1.000000	.012055	.010000	.251661	.010000	.001528
Total	Mean	606.40000	403.46667	2.87493	7.47667	23.08667	7.46867	.04093
	N	15	15	15	15	15	15	15
	Std. Deviation	17.699072	318.836695	.831341	.477129	1.868103	7.661583	.022986

Appendix 5- Correlation parameters some selected ground water

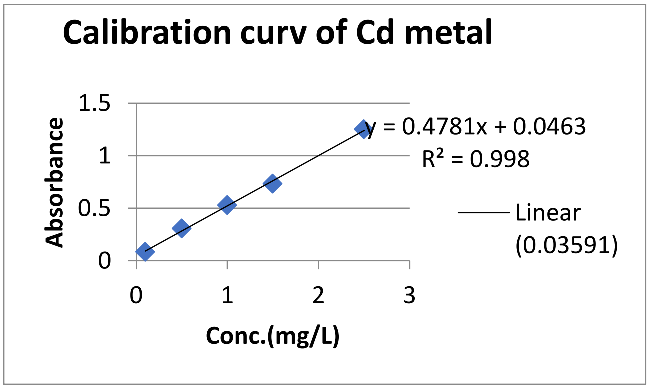
Correlations

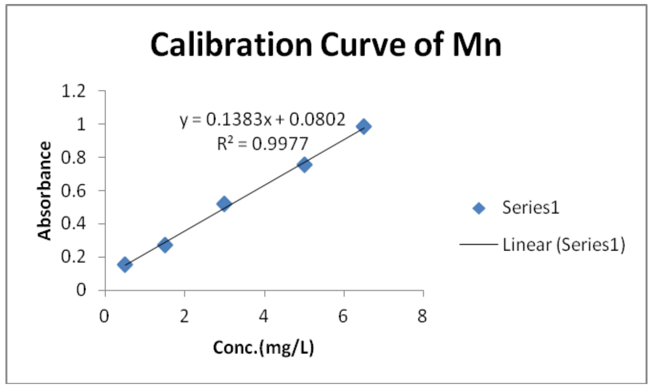
		TDS	EC	DO	PH	TEM	N03	P04
TDS	Pearson Correlation	1	.624**	-.656**	-.109	-.911**	.084	.817**
	Sig. (1-tailed)		.006	.004	.350	.000	.383	.000
	N	15	15	15	15	15	15	15
EC	Pearson Correlation	.624**	1	-.090	.682**	-.629**	-.169	.897**
	Sig. (1-tailed)	.006		.375	.003	.006	.274	.000
	N	15	15	15	15	15	15	15
DO	Pearson Correlation	-.656**	-.090	1	.384	.746**	-.228	-.409
	Sig. (1-tailed)	.004	.375		.079	.001	.207	.065
	N	15	15	15	15	15	15	15
PH	Pearson Correlation	-.109	.682**	.384	1	.049	-.475*	.448*
	Sig. (1-tailed)	.350	.003	.079		.432	.037	.047
	N	15	15	15	15	15	15	15
TEM	Pearson Correlation	-.911**	-.629**	.746**	.049	1	-.307	-.755**
	Sig. (1-tailed)	.000	.006	.001	.432		.132	.001
	N	15	15	15	15	15	15	15
N03	Pearson Correlation	.084	-.169	-.228	-.475*	-.307	1	-.278
	Sig. (1-tailed)	.383	.274	.207	.037	.132		.158
	N	15	15	15	15	15	15	15
P04	Pearson Correlation	.817**	.897**	-.409	.448*	-.755**	-.278	1
	Sig. (1-tailed)	.000	.000	.065	.047	.001	.158	
	N	15	15	15	15	15	15	15

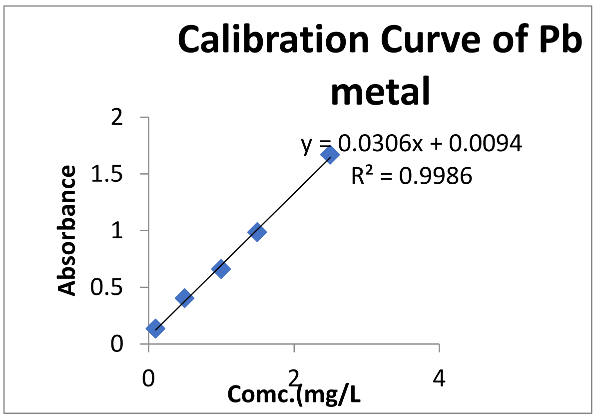
**. Correlation is significant at the 0.01 level (1-tailed).

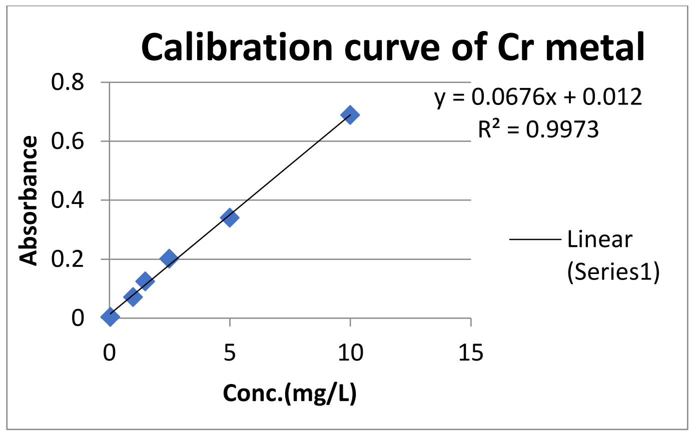
*. Correlation is significant at the 0.05 level (1-tailed).

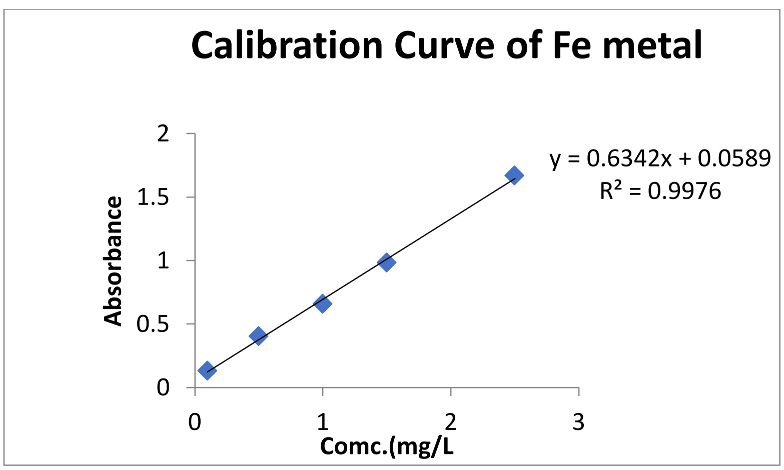
Appendix -6 FAAS standard calibration graph for Heavy Metal











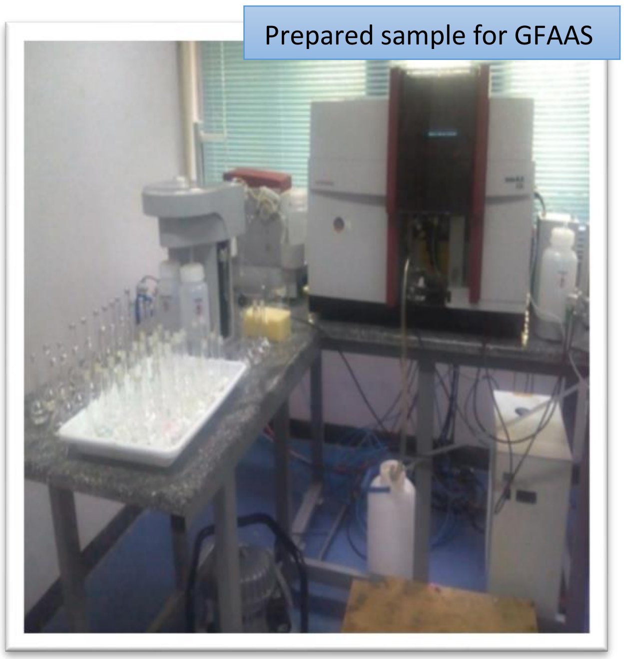


Image showing laboratory analysis