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INVESTIGATION OF PHYSICOCHEMICAL PROPERTIES AND THE LEVELS OF SELECTED HEAVY METALS IN WELL, TAP AND RIVER WATERS OF BANTU TOWN, SOUTH WEST SHOA, ETHIOPIA.

BY: TARIKU DUGASA

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BY: TARIKU DUGASA

Advisors: ABERA GURE (PhD)

Co- Advisor: FEYISA WADAJO (M.Sc.)

A THESIS SUBMITTED TO COLLEGE OF NATURAL SCIENCE, JIMMA UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY.

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Advisor	**Signature**	**Date**
Abera Gure (PhD)	----------------------	-----------------------

Assoc.Prof. on Analytical chemistry

Department of Chemistry

College of Natural Sciences,

Jimma University

Co-Advisor	**Signature**	**Date**
Mr. Feyisa Wadajo	-------------------------	---------------------------

Department of Chemistry

College of Natural Sciences,

Jimma University

External examiner	Signature	Date
------------------------	-------------------------	---------------------------

Department of Chemistry

College of Natural Sciences,

Jimma University

Internal examiner	Signature	Date
Fekadu Melak	-------------------------	---------------------------

Department of Chemistry

College of Natural Sciences,

Jimma University

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ABBREVIATIONS

AAS:	Atomic Absorption Spectroscopy
APHA:	American public health association
ASV:	Anodic striping voltammetry
BDL:	Bellow detection limit of the method
DO:	Dissolved oxygen
EC:	Electrical conductivity
ECM:	Electrochemical Methods
EPA:	Environmental Protection Authority
ES:	Ethiopian drinking water quality standard
FAAS:	Flame Atomic Absorption Spectroscopy
ISO:	International standard organization
MPL:	Maximum permissible limit
MDL:	Method detection limit
NTU:	Nephelometric Turbidity Unity
PEPB:	Poly ethylene plastic bottles
pH:	Power of concentration of hydrogen ion
SD:	Standard deviation
TDS:	Total dissolved solids
WHO:	World Health Organization

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ABSTRACT

In this study, physicochemical parameters and concentrations of selected heavy metals in hand-dug sand well, river, well and tap waters of Bantu town, Ethiopia were investigated. Totally, 9 water samples (2 from hand-dug sand, 2 from river, 3 from well, 1 from tanker and 1 from resident home tap) were collected for the analysis. Physicochemical parameters such as temperatures, pH, electrical conductivity, total dissolved solids, dissolved oxygen and turbidity were determined onsite by portable multi parameter. Other parameters like nitrite nitrate, sulphate, and phosphate were determined by palintest photometer and concentrations of selected heavy metals (Cd, Cr, Cu and Pb) were determined by flame atomic absorption spectroscopy. The obtained results demonstrated electrical conductivity ranging from 182.30 – 919.90 µs/cm, turbidity from 1.15 – 11.95 NTU, dissolved oxygen from 2.70 – 6.10 mg/L, pH from 6.91 – 8.34, temperature from 18.80 – 23.80 ^{0}C, total dissolved solid from 88.40 – 470.60 mg/L, nitrite from 0.01 – 0.02 mg/L, nitrate from 3.88 – 33.72 mg/L, sulphate from 22 – 37.88 mg/L, and phosphate from 0.10 – 0.59 mg/L. Concentrations of Pb under the study area were 0.004 - 0.33 mg/L. The results show that, except the dissolved oxygen, electrical conductivity, turbidity and concentration of Pb, all the parameters fulfill the minimum and maximum permissible limit for drinking water guidelines of WHO, US EPA and ES.

Key Terms: - *Tap water, Sand water, Well water, River water, Physicochemical, Heavy metals, FAAS, Photometer*

1. INTRODUCTION

Water is the most abundant substance on the earth's surface and it is essential for the survival of all known forms of life [1]. Access to safe drinking water is essential to human health [2]. Water plays an essential role for drinking purposes, sanitary uses and industrial processes. In Ethiopia, the dominant sources of drinking water for urban and rural communities are from well, river and spring waters [3, 4].

Improper disposal of many common products can pollute drinking water. Pollution of heavy metals in aquatic environment is a growing problem worldwide and currently it has reached on alarming rate. Some heavy metals originates from anthropogenic activities like draining of sewerage, mining, industrial production, smelting operation, dumping of hospital wastes and recreational activities. Conversely, metals also occur in small amounts naturally and may enter into aquatic system through leaching of rocks and soils. The major causes of this contamination could be agricultural activities, metal corrosion, soil erosion of metal ions and etc. [5-7].

Heavy metals in water occur only in trace levels but more toxic to the human. Toxicity can result from any of the heavy metals but some metals are considered by the Agency for toxic substances and disease registry in the top 20 hazardous list. The mechanism of toxicity for heavy metals can be explained by their ability to interact with nuclear proteins and DNA, causing oxidative deterioration of biological macromolecules. Heavy metals like copper (Cu) are the essential trace elements but show toxicity if present in excess amounts in drinking water. It is suspected for the production of free radical in our body which can cause mitochondrial damage, DNA breakage, and neuronal injury. Lead (Pb) has the ability to replace calcium (Ca) in bone. Cadmium (Cd) is extremely toxic even in low concentrations, and will bio-accumulate in organisms and in human body biochemically it can replaces zinc (Zn) [8, 3, 9].

Heavy metals are known to cause a wide variety of diseases. Some of these include damaged mental and central nervous function, badly effect vital organs such as kidneys and liver, muscle weakness, the long-term exposure of these metals result in physical, muscular, and neurological degenerative processes that cause brain disorder, even death [9].

Physicochemical parameter study is very important to get idea about the quality of drinking waters. Good quality of water resources depends on a large number of physicochemical parameters. Thus there is a need to look for some useful indicators, both chemical and physical, which can be used to monitor the quality of drinking water [2, 9].

Because of rapid urbanization, intense agricultural practice, over uses of chemicals, draining of sewerage, water system is at high risk. In developing countries like Ethiopia, people use untreated drinking water from different sources. For instance, the resident of Bantu town, southwest Shoa zone, Oromia regional state, Ethiopia use tap water, well water, hand-dug sand water, and river waters for drinking.

The aim of this study was to determine physicochemical parameters such as pH, dissolved oxygen, electrical conductivity, turbidity, temperature, total dissolved solid, nitrite, nitrate, sulphate, phosphate and the concentrations of selected heavy metal including Cd, Cr, Cu and Pb in river, well, hand-dug sand and tap waters of Bantu town, Ethiopia. The obtained results were compared with national and international guidelines for drinking water to evaluate whether the water safe for drinking or not.

1.1 Statement of the Problem

Residents' of Bantu town and its surrounding, southwest Shoa, Ethiopia, use tap, hand-dug sand, well and river waters for drinking and other purposes. Although, the source was not well protected, tap water has been administrated to the community after some treatments. It is surrounded by intensified agricultural activities that use fertilizer and pesticides. It also receives effluent discharges from surrounding communities. It is distributed to the resident homes, using galvanized pipes and metal fittings, which may also leak heavy metals like Pb, Cu and Cd to the water. In addition, the people of the area also use well water for drinking. Because the tap water is obtained only when electric power is present. In the town, totally 3 well water are available and commonly used for drinking and other purposes. People of the area said that the well waters have suspended matters, bad test and consume long time to get it. As a result some residents prefer river water than well water for drinking and other purposes.

In the area, river water is located in the catchment basin with intense human activities and characterized by deforestation, overgrazing, and traditional farming along the river bank, which leads to erosion and siltation into water bodies. The rivers also used for vehicle washing which could also lead to its pollution. The river water is expected to be polluted by agrochemicals, and waste discharges from the surrounding community. Generally, presence of pollutant in water system could affect its physicochemical properties and the levels of heavy metals. Uses of polluted waters affect human health and aquatic organisms. Therefore, investigation of the physicochemical parameters and the levels of selected heavy metals in river, hand-dug sand, well, and tap water of the area is important, to know whether the water is safe or not.

1.2 Objectives of the study

1.2.1 General objective

The main objective of this study is to determine the physicochemical characteristics and the levels of selected heavy metals in well, tap, hand-dug sand and river water samples of Bantu town, South west Shoa, Ethiopia.

1.2.2 Specific objectives

The specific objectives of this study:-

- To determine the physicochemical parameters such as pH, EC, DO, TDS, turbidity, temperature, nitrite, nitrate, sulphate and phosphate of river, tap and well drinking water of Bantu town.
- To determine the levels of selected heavy metals Pb, Cr, Cu and Cd in well, tap and river drinking water of Bantu town.
- To compare the levels of selected heavy metal ions in well, tap and river waters analyzed in this study.
- To compare the quality of water with the recommendable values of international and national standards of drinking water quality.

1.3 Significance of the study

The finding of the study could be used to provide adequate information about the physicochemical parameters and the levels of the studied heavy metals in river, well and tap waters of the study area. It also provides scientific evidences for governmental and non-governmental organization that work in the areas to provide pure water for community. It could also be used as base line information on the quality of the water of the area for other researcher. The result of this study will also assist the relevant industries and authorities in designing appropriate preventive measure to ensure that the water quality is improve.

2. LITERATURE REVIEW

2.1 Drinking water

Water is essential to sustain life, and a satisfactory (adequate, safe and accessible) supply must be available to all [2]. Next to air, water is human kind most important substance [1]. In Ethiopia, well water, spring water, surface water, lake and tap water are the common water supply source used in both urban and rural areas for different purposes [4]. The presence of toxic chemicals in drinking water may risk human health among which cancer and chronic illness are worth mentioning. Epidemiological studies have demonstrated a strong relationship between the prevalence of several diseases in humans, particularly cardiovascular diseases, kidney, related disorders, and various forms of cancer and the presence of many metals such as cadmium, mercury and lead [10].

2.1.1 Well water

Well water is a resource found under the earth's surface that is untreated. Well drillers drill down to the aquifers, which is an underground layer of permeable rock containing water. Then, a pump system is installed to carry the water up from the ground [11]. Most wells water comes from rain and melting snow soaking into the ground. Water fills the spaces between rocks and soils, making an aquifer. Since ground water is essentially rain that has moved through the soil and into an aquifer, it can absorb a lot of other things along the way. Ground water its depth from the surface, quality for drinking water and chance of being polluted varies from place to place. The amount of new water flowing in to the area also affects ground water quality. Ground water may contain some natural impurities or contaminants, even with no human activity or pollution. Natural contaminants can come from many conditions in the watershed or in the ground. Water moving through underground rocks and soils may pick up heavy metals [12]. The quality of the well water is constantly changing, and the best way to protect the peoples is to have well tested. The EPA recommends that well water must be tested at least once a year [11].

2.1.2 Tap water

Tap water is drinking water that comes from an indoor tap or spigot. It is part of a larger indoor plumbing system that requires a complex supportive infrastructure, including a stable water source, piping, and water filtration to keep the water safe. The primary advantage to indoor plumbing, of course, is that it makes water readily accessible for cooking, washing, cleaning, and drinking, but it is also often designed with water safety in mind. Water safety can be controlled at a source like a reservoir or well, at a water treatment plant along the way, or at the house, depending on the type of plumbing system involved. There are a number of ways to force water to the tap, including using a water pump to push water through the plumbing, or using a pressurized water system, such as the system used by many cities to maintain water pressure, ensuring that as soon as the tap is opened, water will flow out. The safety of this water can be compromised by any number of things. In some regions, water purification systems are insufficient, allowing potential pathogens and other forms of contamination into the supply. In other regions, water may become contaminated somewhere along the way to the tap, as might be the case when a sewer pipe bursts, allowing dirt and other contaminants into lines used to supply water to homes, or when home pipes become corroded, adding metals and other materials to the water [12].

2.1.3 River water (surface water)

Surface waters could be regarded as including all inland waters permanently or intermittently occurring on the Earth surface as rivers, temporary streams, lakes, reservoirs and bogs. Natural water flows moving under the force of gravity along their channels and fed by surface and underground runoff are called rivers. Rivers can be divided into mountain, which have rapid flows and narrow valleys, or lowland rivers, which have slower flows and wider, often terraced, valleys. The rivers of Polar Regions and high mountain areas can be mainly supplied by glacier melting. Rivers are classified according to their topographic/morphological features and their hydrological regime. These in turn are influenced by climate, soils, relief, heavy metals, anthropogenic activities and vegetation [13].

2.2 Source of heavy metals in drinking water

Heavy metals are metallic elements which have high atomic weight and have much high density at least 5 times than that of water. Trace amounts of metals are common in water, and these are normally not harmful to our health. In fact, some metals are essential to sustain life. Calcium, magnesium, potassium, and sodium must be present for normal body functions. Cobalt, copper, iron, manganese, molybdenum, selenium, and zinc are needed at low levels as catalysts for enzyme activities [14, 10].

The earth's crust is one of the major sources of heavy metals .Weathering of rocks and leaching of soils, aerosol particles from the atmosphere and anthropogenic activities could be among the several ways through which heavy metals enter into the aquatic system. Dramatically rising urbanization and industrialization have intensified the levels of heavy metals in drinking water supplies. Drinking water containing high levels of these essential metals, or toxic metals such as aluminum, arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver, may be hazardous to our health. Metals in our water supply may occur naturally or may be the result of contamination. Naturally occurring metals are dissolved in drinking water when it comes into contact with rock or soil material [14].

Most chemicals generated from industrial, agricultural and other human activities will eventually end up in our water ways which may there after affect our drinking water there by posing a great danger to human lives in small amount also. These dangerous chemicals enter the rivers, lakes and underground water which supply our drinking water. The heavy metals in drinking water that are linked most often to human poisoning are lead, iron, cadmium, copper, zinc, chromium and etc. They cannot be degraded or destroyed and toxic or poisonous at low concentrations. [15].

2.3. Analysis of heavy metals

Many instrumental analytical methods may be employed to measure the concentration level of heavy metals in various samples. The most predominant techniques are atomic absorption spectrometry (AAS), atomic emission or fluorescence spectrometry (AES/AFS), inductively coupled plasma mass spectrometry (ICP-MS), electrochemical method (ECM) and etc. [16]. Quantization is accomplished by comparison with standards prepared from pure elements or compounds that are irradiated and measured under the same conditions as the samples [17]. However, out of these available analytical techniques for metal ion analysis in drinking water samples, AAS method has been selected and due to its wide applicability for metal ion analysis in drinking water samples, the low capital cost and simplicity of operation.

2.4 Physicochemical parameters of water

Physicochemical parameter study is very important to get idea about the quality of drinking water and we can compare results of different physicochemical parameters with standard values. It is very essential to test the water before used for drinking purpose. Physicochemical 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, turbidity, electrical conductivity, total dissolved solids, hydrogen ion concentration and dissolved oxygen [18].

Water does contain different types of floating, dissolved, suspended, microbiological and bacteriological impurities. In assessing the quality of drinking water, consumers rely principally upon their senses. Microbial, chemical and physical constituents of water may affect the appearance, odor or taste of the water and the consumer will evaluate the quality and acceptability of the water on the basis of these criteria. Although these constituents may have no direct health effects, but drinking water should be free of tastes and odors [2]. Table 1 shows Water quality parameters used for testing quality of water and their sources as well as potential health effect [19].

Table1: Water quality parameters used for testing quality of water and their sources of and potential health effect [19].

Parameters	Sources	Potential health effects
pH	Different dissolved gases and solid.	Bitter test, corrosion, affects mucus membrane.
Temperature	Chemical reaction, hot waste water	Influence chemical, biochemical, biological of aquatic system, effect on solubility of essential gases.
EC	Due to different dissolved solid (salts).	High conductivity increases corrosive nature of water.
TDS	From the Presence all dissolved salt.	Influence the composition, undesirable taste, gastro-intestinal irritation, corrosion, or incrustation.
Turbidity	Soil runoff	Higher level indicates the presence of disease causing organisms like bacteria, viruses, and parasites.
DO	Due to dissolved oxygen gas.	Very high levels of dissolved oxygen may exacerbate corrosion of metal pipes
Nitrite	NH_3 compounds	Form nitrosamine's – carcinogenic.
Nitrate	Run off fertilizers	Taste affect; gastro-intestinal irritation.
Sulphate	Due to dissolved metal sulphate	Taste affect; gastro-intestinal irritation.
Phosphate	Waste water from detergent effluent, rocks	Stimulate microbial growth, algal growth.
Cu	Agro chemicals,	Liver and kidney damage; digestive disturbances.
Cd	Storage battery	Kidney damage.
Cr	Paints	Liver, kidney and lung damage.
Pd	Car washing, metal pipes,	Brain, nerve and kidney damage; digestive disturbance

2.4.1 Turbidity

Turbidity in water is caused by suspended particles or colloidal matter that obstructs light transmission through the water. It may be caused by inorganic or organic matter or a combination of the two [2]. It has no health effects. However, turbidity can interfere with disinfection and provide a medium for microbial growth. High turbidity may indicate the presence of disease causing organisms. These organisms include bacteria, viruses, and parasites that can cause symptoms such as nausea, cramps, diarrhea, and associated headaches [5]. High turbidity reduces light penetration; therefore, it impairs photosynthesis of submerged vegetation and algae. Turbidity interferes with the disinfection of drinking water and is aesthetically unpleasant [19]. In all procedures in which disinfection is used, the turbidity must always be low preferably lower than 1 NTU. It is recommended that, for water to be disinfected, the turbidity should be less than 5 NTU [2].

2.4.2 Total dissolved solid

The term total dissolved solid refer to materials that are completely dissolved in water and which govern the chemistry of salts in water, may also influence the composition [20]. Dissolved solids in natural waters may consist of carbonates, bicarbonates, chlorides, sulfates, phosphates, nitrates, magnesium, sodium, iron, manganese and other substances. Total dissolved solid is an important parameter in evaluating the suitability of water for irrigation, since the solid might clog both pores and components of water distribution system.

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, and reduces solubility of gases (like oxygen) and utility of water for drinking purposes. According WHO standards, the maximum permissible level is 1,000 mg/L and greater than 1200 mg/L may be objectionable to consumers and could have impacts for those who need to limit their daily salt intake example severely hypertensive, diabetic, and renal dialysis patient. High concentration of total dissolved solid also reduces water clarity and lead to an increase in water temperature [19].

2.4.3 Temperature

Temperature is an important in controlling the rate of all chemical reaction and biological reactions. 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 there actions' speed and increasing the degradation rate of organic matter. 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 [2].

2.4.4 Electrical conductivity

Electrical conductivity 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 (μs/cm). This is influenced by dissolved salts such as sodium chloride, potassium chloride and etc. In general, the amount of dissolved solids in water concludes that the electrical conductivity. According to WHO standards, EC value of drinking water quality should not exceeded 500 μs/cm. Low values are characteristic of high quality of the waters. High values of conductance can be indicative of salinity problems but also are observed in eutrophic water ways where plant nutrients or 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 water [20].

2.4.5 pH

pH is a measure of the hydrogen ion concentration or activity of an aqueous solution. This value ranges from pH 0 to 14. In general, water with a pH of 7 is considered neutral while lower than this referred acidic and a pH greater than 7 known as basic. pH is most important in determining the corrosive nature of water. Lower the pH value higher is the corrosive nature of water. Various factors bring about changes the pH of water. According to WHO standards, optimum pH required will vary in different supplies according to the composition of the drinking water and the nature of the construction materials used in the distribution system, but it is usually in the range 6.5 – 8.5 [17, 21].

2.4.6 Dissolved oxygen

All living organisms depend upon oxygen to maintain the metabolic processes that produce energy for growth and reproduction. The dissolved oxygen content of water is influenced by the source, raw water temperature, treatment and chemical or biological processes taking place in the distribution system. Depletion of dissolved oxygen in water supplies can encourage the microbial reduction of nitrate to nitrite and sulfate to sulfide. It can also cause an increase in the concentration of ferrous iron in solution, with subsequent discoloration at the tap when the water is aerated. There is no WHO guidance level for DO standards were ever issued by the Health authority, mainly due to the lack of toxicity. However, very high levels of dissolved oxygen may exacerbate corrosion of metal pipes [2]. Dissolved oxygen is best measured directly in the water using a calibrated dissolved oxygen sensor. This sensor can measure the amount of dissolved oxygen directly in the water as mg/L or as a percent dissolved oxygen (% DO). Water at lower temperatures should have higher mg/L of dissolved oxygen and higher % DO while warmer, polluted waters will have lower mg/L and % DO. Healthy water should generally have dissolved oxygen concentrations between 6.5 - 8 mg/L and between about 80 - 120 % [22].

2.4.7 Sulfates

Sulfates occur naturally in many waters. Sulfates are introduced into treated waters by the use of such chemicals as aluminum sulfate, sodium bisulfate and sulphuric acid. The presence of high levels of sulphate can be undesirable for a number of reasons. In industrial waters containing sulphate localized corrosion of iron, steel and aluminum in plant and pipe work can occur through the action of sulphate reducing bacteria. These bacteria, which generate sulfides, cause a characteristic pitting of the metal surface.

High sulphate levels can also cause damage to concrete and cement based materials through the formation of calcium sulpho aluminate. This causes expansion and crumbling of the cement. It can affect concrete structures and pipes in water distribution systems carrying sulfate bearing ground waters; and can attack grouting in tiled swimming pools using sodium bisulfate for pH adjustment [46]. No health-based guideline is proposed for sulfate. However, because of the gastrointestinal effects resulting from ingestion of drinking water containing high sulfate levels, it is recommended that health authorities be notified of sources of drinking water that contain sulfate concentrations in excess of 500 mg/L. The presence of sulfate in drinking water may also cause noticeable taste and may contribute to the corrosion of distribution systems [2].

2.4.8 Phosphates

Phosphates are extensively used in detergent formulations and washing powders. Phosphates also find widespread application in the food processing industry and in industrial water treatment processes. Agricultural fertilizers normally contain phosphate minerals and phosphates also arise from the breakdown of plant materials and in animal wastes. Phosphates can therefore enter water courses through a variety of routes particularly domestic and industrial effluents and run-off from agricultural land. Whilst phosphates are not generally considered harmful for human consumption, they do exhibit a complex effect on the natural environment. In particular phosphates are associated with eutrophication of water and with rapid unwanted plant growth in rivers and lakes [46].

2.4.9 Nitrate

Nitrate is found naturally in the environment and is an important plant nutrient. It is present at varying concentrations in all plants and is a part of the nitrogen cycle. Nitrate can reach both surface water and ground water as a consequence of agricultural activity (including excess application of inorganic nitrogenous fertilizers and manures), from waste water disposal and from oxidation of nitrogenous waste products in human and animal excreta, including septic tanks. Surface water nitrate concentrations can change rapidly owing to surface run off fertilizer and de nitrification by bacteria, but ground water concentrations generally show relatively slow changes. Some ground waters may also have nitrate contamination as a consequence of leaching from natural vegetation.

Nitrate has been frequently studied, and there have been suggestions of carcinogenic activity, but only at very high doses. The guideline value for nitrate of 50 mg/L as nitrate is based on epidemiological evidence for methaemoglobinaemia in infants, which results from short-term exposure and, consequently, other parts of the population [2].

2.4.10 Nitrite

Nitrite is a versatile chemical agent which has found numerous applications ranging from dye manufacture to food preservation. Nitrites enter water supplies from the breakdown of natural vegetation, the use of chemical fertilizers in modern agriculture and from the oxidation of nitrogen compounds in sewage effluents and industrial wastes. It produces carcinogenic nitrosamines in the human body through its reaction with amines or amides. Nitrite is one of the pollutants found in the atmosphere and natural water and is an important intermediate in biological nitrogen cycle. Traces of nitrite in drinking water may lead to mathemeglobmenia in infants and with long term exposure is a possible cancer risk. Similarly nitrite is harmful to fish and other forms of aquatic life and the nitrite level must be carefully controlled in water used for fish farms and aquariums. The nitrite test is also applied for pollution control in waste waters, and for the monitoring of drinking water [46]. The WHO guideline value for nitrite is 3 mg/L as nitrite [2].

2.5 Roles of heavy metals in the environment

Heavy metals are released into the environment through natural process and anthropogenic activities. Industrial processes generate wastes, which are mostly discharged into the environment. Poorly treated domestic and agricultural waste water contains high concentrations of metals, which are often discharged into the environment. The sources of drinking water e.g., surface waters; ground water and sea water are likely to be polluted by heavy metals [23]. Most chemicals generated from industrial, agricultural and other human activities will eventually end up in our water ways which may there after affect our drinking water thereby posing a great danger to human lives [24]. The heavy metals in drinking water linked most often to human poisoning are lead, iron, cadmium copper, zinc, chromium and etc. [5].

2.5.1 Lead

Lead is a naturally occurring element that people have used almost since the beginning of civilization. It is a very soft, blue-gray, has no characteristic test or smell. Because it is so soft, lead is usually alloyed with other elements and it forms a variety of interesting and beautiful minerals, all of which are heavy due to their lead content. The major uses of lead and its compounds are storage batteries, pigments, ammunition, solders, paints, plumbing, cable covering, bearings, and caulking. A variety of human activities have spread widely throughout the environment, such as leaded gasoline which in the mid-20th century became a significant cause of lead poisoning, especially in children. Lead has no known nutritional and physiological function and it is toxic and harmful even in small amounts for organisms. Guideline value of

WHO standards (2011) the permissible limit in drinking water for lead is ≤ 0.01 mg/L. It impend the synthesis of hemi and accumulates within the red cells as well as the bones to give rise to anemia, headache, dizziness, and damage to the digestive and nervous systems [2, 23 - 27].

Most of the lead we take is removed from our bodies in urine; however, as exposure to lead is cumulative over time, there is still risk of buildup, particularly in children. High concentration of lead in the body can cause death or permanent damage to the central nervous system, the brain, and kidneys [28].

Lead in the environment arises from both natural and anthropogenic sources. In the old days, lead is widely used in water distribution system as lead pipe and it was banned after the discovery of health problems caused by it, but lead pipe may still exist in older water distribution system nowadays. Exposure can occur through drinking water, food, air, soil and dust from old paint containing lead [29]. The Environmental Protection Agency (EPA) estimates that nearly 20% of human exposure to lead occurs through contaminated drinking water [30]. Lead is rarely present in tap water as a result of its dissolution from natural sources; rather, its presence is primarily from corrosive water effects on household plumbing systems containing lead in pipes, solder, fittings or the service connections to homes [2].

2.5.2 Cadmium

Cadmium derives its toxicological properties from its chemical similarity to zinc. Cadmium is bio persistent and, once absorbed by an organism, remains resident for many years although it is eventually excreted. In humans, long-term exposure is associated with renal dysfunction. High exposure can lead to obstructive lung disease and has been linked to lung cancer. Cadmium may also produce bone defects (osteomalacia, osteoporosis) in humans and animals. In addition, the metal can be linked to increased blood pressure and effects on the myocardium in animals [31].

Cadmium compounds are widely used in batteries. It is released to the environment in waste water, and diffuse pollution is caused by contamination from fertilizers and local air pollution. Cadmium occurs naturally in zinc, lead, copper and other ores which act as source to ground and surface waters. It can be released in drinking water from the corrosion of some galvanized plumbing and water main pipe material [8]. Contamination in drinking water may also be caused by impurities in the zinc of galvanized pipes, solders and some metal fittings. Guideline value of WHO standards (2011) the permissible limit in drinking water for cadmium is ≤0.003 mg/L [2].

Cadmium accumulates primarily in the kidneys and has a long biological half-life in humans of 10 - 35 years. There is evidence that cadmium is carcinogenic by the inhalation route, and it has classified as cadmium and cadmium compounds probably carcinogenic to humans. However, there is no evidence indicating its essentiality to humans [2]. On the other hand, cadmium is generally classified as toxic trace element. It is found in very low concentration in most rocks, as well as in coal and petroleum and often in combination with zinc. Geologic deposits of cadmium can serve as sources to groundwater and surface water, especially when in contact with soft, acidic waters [17]. In low doses, cadmium can produce coughing, headaches, and vomiting. In larger doses, cadmium can accumulate in the liver and kidneys, and can replace calcium in bones, leading to painful bone disorders to coma and to a renal failure [32]. Cadmium is a severe pulmonary and gastrointestinal irritant, which can be fatal if inhaled or ingested. After acute ingestion, symptoms such as abdominal pain, burning sensation, nausea, salivation, muscle cramps, vertigo, shock, loss of consciousness and convulsions usually appear within 15 to 30 minutes [15].

2.5.3 Chromium

Chromium occurs in both natural deposits, as well as in manufacturing processes such as electroplating and pigment factories. It can enter ground water through erosion, mining waste, and industrial waste. Chromium is used in metal alloys and pigments for paints, cement, paper, rubber and other materials. Chromium metal (Cr) occurs naturally in the environment and has both beneficial and potential to human risks. Cr exists in many oxidation states with Cr (III) and Cr (VI) being the primary existing oxidation states in the environment. Trivalent Chromium is an essential nutrient for maintaining lipid, insulin, and glucose metabolism and its deficiency may lead to diabetes [33]. The trivalent form is relatively non-toxic and is regarded as an essential trace element, whilst Cr (VI) is of relatively high toxicity and has been shown to be a carcinogen in animal studies. Unlike Cr (III), Cr (VI) is more mobile and is often found in potable waters [34].

In addition to naturally occurring Cr (VI), various industries, including metal plating, leather tanning, metallurgy, panting, and stainless steel production industries, utilize chromic acid or other forms of Cr (VI) [35, 36]. This heavy metal contaminant is also found in inks, pigments, fungicides, soils, tobacco smoke, effluents and paints [37, 38]. Exposure to Cr (VI) in an aerosol form has been shown to cause chronic ulcers, dermatitis, and even lung cancer [39]. Low level exposure can irritate the skin and cause ulceration. Long-term exposure can cause kidney and liver damage, and damage too circulatory and nerve tissue [31]. All hexavalent chromium compounds are strong oxidizing agents and potentially carcinogenic. Hence, chromates are regulated in the environment and are a primary drinking water contaminant [39]. Guideline value of WHO standards (2011) the permissible limit in drinking water for total chromium is ≤ 0.05 mg/L [2].

2.5.4 Copper

Copper, Cu is a transition element with atomic number 29 and molar mass 63.546 with its ions commonly exist in cuprous (Cu^{+}) and cupric (Cu^{2+}) form. Copper is both an essential nutrient and a drinking-water contaminant. It is used to make pipes, valves and fittings and is present in alloys and coatings. It can be found in most of the water such as underground water, surface water, and tap water and occurs naturally in rock, soil, sediment, and air. Copper compounds are also used as an agricultural pesticide, and to control algae in lakes and reservoirs [3, 40].

Copper is an essential element for human in order to maintain enzyme system in body and plays an important role in center nervous system development. However, only less than 3% of copper intakes are excreted through urine per day thus excessive copper intake for long period of time will caused several health issue. Ingesting large amounts of copper compounds can cause death by nervous system, liver and kidney failure [2, 5].

Drinking water may contain higher levels of a dissolved form of copper. High levels of copper occur if corrosive water comes in contact with copper plumbing and copper containing fixtures in the water distribution system. The level of copper in drinking water increases with the corrosively of the water and the length of time it remains in contact with the plumbing. Immediate effects from drinking water which contains elevated levels of copper include vomiting, diarrhea, stomach cramps and nausea. Contamination of drinking water with high level of copper may lead to chronic anemia [41]. High concentrations can interfere with the intended domestic uses of the water. Staining of sanitary ware and laundry may occur at copper concentrations above 1 mg/l. At levels above 5 mg/l, copper also imparts a colour and an undesirable bitter taste to water. Although copper can give rise to taste, it should be acceptable at the health-based guideline value of 2 mg/L [2].

3. MATERIALS AND METHODS

3.1 Study areas

The study was conducted in Bantu Town, Tole district, Southwest Shoa zone, Oromia regional state, Ethiopia. It was established in 1928 E.C and it is located at 82 km in the southwest from Addis Ababa, the capital city of Ethiopia. It is situated at 2159 - 2202 elevation, 951781- 952847 northing and 429500 - 431053 easting. It occupies an area of 6066 km² with total population of about 10255. The study was conducted on well, tap, hand-dug sand and river waters which are available in the radius of 1 km from the center of the town. Figure 1 is the Map of Bantu town showing the sites of study area which was obtained by GPS and GIS software 10.1.

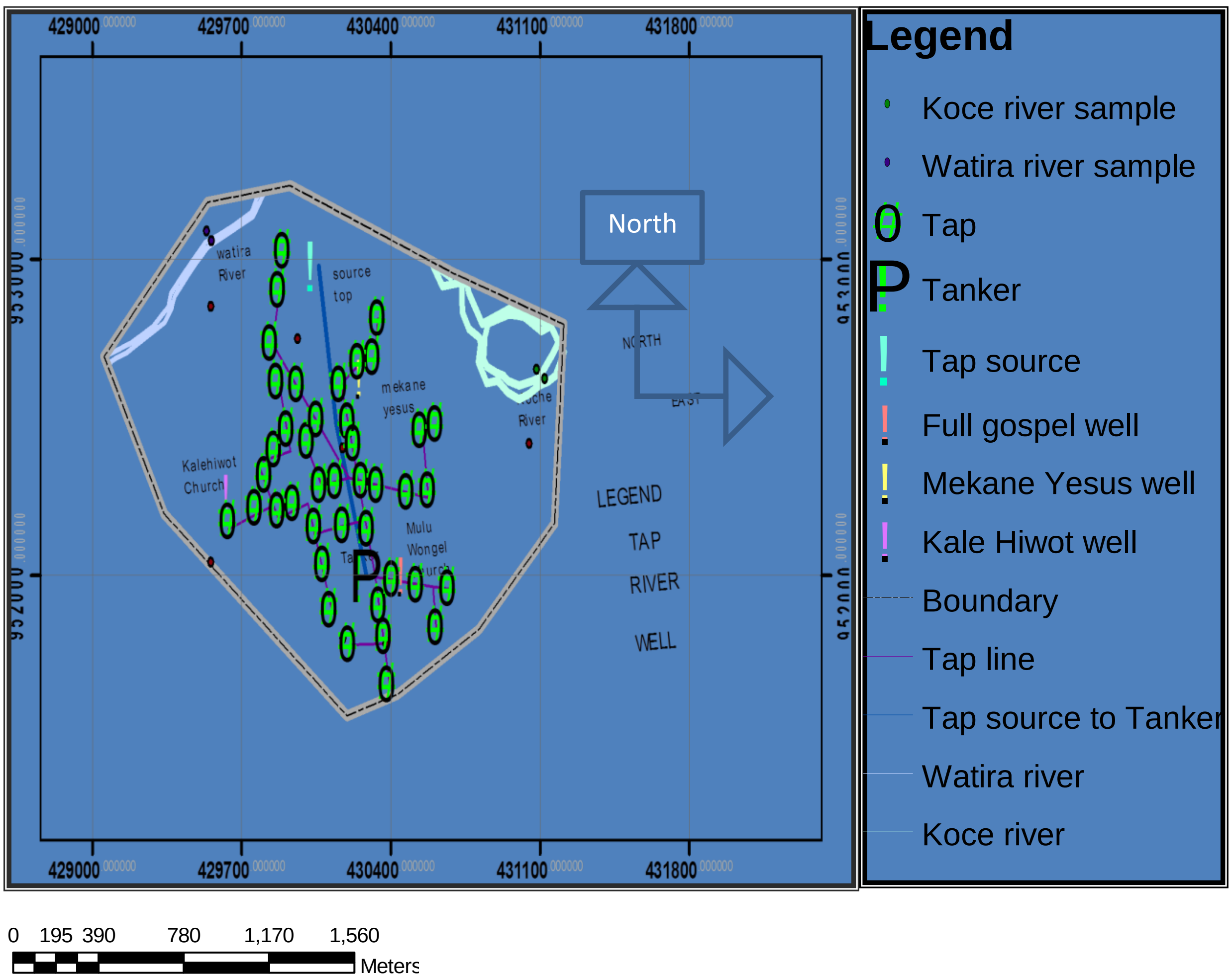

Figure1: Map of Bantu town showing the sites of study area of Tole district developed from GPS and GIS software 10.1.

3.2 Sampling and sampling strategies

Water samples were collected according to the procedure described in literatures of [8, 42. 43]. The samples were collected in 1 L plastic bottles. Prior to sampling, the bottles were thoroughly washed with phosphate free detergent and then soaked in 10% nitric acid overnight. Finally, the bottles were repeatedly rinsed with distilled water and subjected to drying. Before taking the sample, the bottle was rinsed three times with the water to be sampled.

Totally, 9 water samples including 4 river water samples (2 samples from hand-dug sand water along the river bank, and 2 from the main river), 3 well waters, 1 from tanker of tap water and 1 tap water from residents' home were collected in the radius of 1 km from the center of the town. River and hand-dug sand water samples were collected from two different rivers Kura Luku (Koce River) and Qursiti (Watira river water) and along their banks, which are available at the east and west of the town. Each water sample collected from river water was during bright early in the morning day. From each river, hand-dug sand water sample was at about 2 m distance from the site where the river sample was taken.

Well water samples were collected from Goda Jimata (Mekane Yesus church), Doro Manaka (Full Gospel church) and Katila (Kale Hiwot church) which are located at north, close proximity, and west of the center of the town, respectively. Tap water samples were taken from the tanker or reservoir and residents homes. To get representative tap water samples, 40 resident homes water randomly selected in all direction of the town. After collecting samples from all direction, they were mixed and a composite sample 1 L was taken for subsequent analysis.

Tap and well water samples were taken after running the water for more than 5 min. River and hand-dag sand water samples were collected by direct immersion of sampling bottles. All samples were collected in the morning before 9:00 am. Immediately after sample collection, 3 mL of nitric acids was added to reduce adsorption of metals onto the walls of the plastic bottles. All sample bottles were tagged properly, labeled to indicate date of sampling and the sampling site. These samples were subsequently stored at 4°C for as short a time as possible before analysis to minimize physiochemical changes and transported to Arba Minch University Chemistry Department laboratory and treated for heavy metals analysis.

3.3 Chemicals and reagents

Analytical graded chemical reagent and solvent were used. Concentrated HNO_3 (69-72%), concentrated HCl (36 – 40%), stock standard solutions containing 1000 mg/L, Cr, Cd, Cu and Pb (Merck KGaA 64271 Darmstadt Germany), chemical reagents like nitricol tablet, nitratest powder, phosphate LR tablet, sulphate turb tablet and distilled water were used.

3.4 Instruments and apparatus

Flame atomic absorption spectroscopy (FAAS) (Buck Scientific Model 210VGP AAS, East Norwalk, USA) equipped with deuterium ark background corrector hollow cathode lamps for each respective heavy metal and air acetylene flame was used for analysis of the metals. Bante portable multi parameter (900P), international portable turbidity meter (model wag- WT 3020), photometer (wag tech 710) and plastic bottles were used during analysis.

3.5 Physiochemical analysis.

Physicochemical parameters such as temperature, electrical conductivity, dissolved oxygen, total dissolved solid, pH and turbidity of the waters were measured at the sites [44]. 500 mL of water sample was added to 1000 mL of beaker [24]. To measure temperature, electrical conductivity, pH, DO and total dissolved solid of water samples, 500 mL water was taken into 1 L beaker. Then, portable multi parameter was dipped into the water until the stable value was observed. Turbidity of water samples was also measured by portable turbidity meter. For each parameter, triplicate measurements were carried out in the morning before 9:00 am.

Anions analysis procedures

Anions such as nitrite (NO_2^-), nitrate (NO_3^-), sulfate (SO_4^{2-}) and phosphate (PO_4^{3-}) were determined by palintest photometer at their respective wavelength using palintest reagents.

Nitrite

In acidic solution NO_2^- react with sulphanilic acid to form a diazonium salt, which in turn reacts with N-(1-naphthyl)-ethylene diamine di hydrochloride to form a reddish dye. The palintest nitricol method features a single tablet reagent containing both of these reagents in an acidic formulation. The test is simply carried out by adding a tablet to a sample of the water under the test. The intensity of the colour produced in the test is proportional to the nitrite concentration and is measured using a palintest photometer [46].

Accordingly, to measure the NO_2^-, 10 mL water was taken in to a test tube. Then, a nitricol tablet was crashed and added, to the water and subjected to dissolve. The resulting solution was kept stand for 10 min to allow the full colour development. 10 mL sample that has not been reacted with any reagent was used as a blank was taken in to another test tube. Then, after calibrating the instrument using sample that has not been reacted with any reagent water, the concentration of NO_2^- of the prepared sample was directly recorded.

Nitrate

To determine NO_3^- by the palintest nitratest method, it should be first reduced to NO_2^-; the resulting nitrite is then determined by a diazonium reaction to form a reddish dye. The reduction stage is carried out using zinc-based nitratest powder, and nitratest tablet which aids rapid flocculation after the one minute contact period. After reduction, its determination follows similar procedure to that of to NO_2^- [46].

Sulphate

The palintest test was employed for the determination of SO_4^{2-} of water samples. The method involves use of a single tablet reagent containing barium chloride in a slightly acidic formulation. Barium salts react with SO_4^{2-} to form insoluble barium sulphate. The formation of the insoluble SO_4^{2-} was observed by formation of turbid solution. The degree of turbidity is proportional to the SO_4^{2-} concentration and is measured using a palintest photometer [46].

Accordingly, to measure SO_4^{2-}, 10 mL of water sample was taken into test tube. Then, a sulphate turb tablet was crushed, added and mixed to dissolve. Then, the resulting solution was allowed to stand for 5 min. In another test tube, 10 mL sample that has not been reacted with any reagent was taken to calibrate the photometer reading. Finally, after calibrating the instrument using sample that has not been reacted with any reagent water, the concentrations of SO_4^{2-} in the samples were directly recorded.

Phosphate

Palintest phosphate method was used for the determination of PO_4^{3-} concentration. In the method, in acidic media PO_4^{3-} reacts with ammonium molybdate to form phospho-molybdic acid.

This resulting compound is reduced by ascorbic acid to form intensely coloured 'molybdenum blue' complex. A catalyst is incorporated to ensure complete and rapid colour development, and an inhibitor is used to prevent interference from silica. The reagents are provided in the form of two tablets for maximum convenience. The test is simply carried out by adding one of each tablet to a sample of the water. The intensity of the colour produced in the test is proportional to the phosphate concentration, and is measured using a palintest photometer [46].

Accordingly, to measure PO_4^{3-} by the method, 10 mL water sample was taken into test tube. Then, two phosphate tablets was crushed, added and mixed to dissolve. The resulting solution was then allowed to stand for 10 min for full colour development. After calibrating the instrument with blank sample that has not been reacted with any reagent, the concentrations of PO_4^{3-} water samples were directly recorded.

3.6 Digestion of Water Samples for Metal Analysis

Water samples were digested using concentrated nitric acid and concentrated HCl as has been mentioned in literature [42]. Accordingly, 50 mL water was taken into 1L beaker. Then, after addition of 1 mL Conc. HNO_3 and 0.5 mL conc. HCl, the beaker was covered with watch glass and placed on hot plate at approximately 85 °C until its volume was reduced to about 20 mL. Then, after cooling for 30 min, the digested was reconstituted to with deionized water to 50 mL. Finally, the resulting solution was filtered using Whatman 0.42 filter paper and preserved in refrigerator for until it was analyzed. Each water sample was digested in triplicate and each digest was analyzed in triplicate. Blank samples were also prepared by the same procedure.

3.7 Laboratory Analysis

Stock standard solutions containing 1000 mg/L of Pb, Cd, Cu and Cr were used for preparation of series of solutions for construction of calibration curves. For all metals series of solutions were containing 0.1, 0.5, 1.0, 1.5, 2.5 and 3.5 mg/L were prepared from the stock solutions by serial dilutions in distilled water and used. After constructing calibration curves, the concentrations of the heavy metals in water samples were analyzed at their specific wavelength. The obtained calibration curves are presented in Appendix 3.

3.8 Method validation

The analytical characteristics of the method used for analysis concentrations of heavy metals were evaluated in terms of the linearity of the calibration curves, repeatability precisions, recovery (accuracy) study, determination of limits of detection (LOD) and quantifications (LOQ).

3.8.1 Precision

The precision of an analytical procedure has usually expressed as the variance, relative standard deviation and percentage relative standard deviation of replicate measurements. In this study, the precision of the method was investigated in terms of standard deviations (SD) of replicate analysis.

3.8.2 Accuracy

Accuracy of analytical method has evaluated in terms of percent recovery (%R) 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 accuracy of the method was determined by spiking 1.5 mg/L each heavy metal in to the water samples. The %R was then determined by the following formula.

$$\%R = [(C_{sp} - C_{usp})/C_s] \times 100$$

Where C_{sp}, C_{usp} and C_s are concentrations of the heavy metal in spiked sample, unspiked sample and spiked (added) the sample, respectively

3.8.3 Limit of detection

Method detection limit (LOD) is the minimum concentration of analyte that can be detected, measured and reported with 99% confidence that the analyte concentration is greater than zero [48]. LOD of the method was determined by digesting three blank reagent (deionized) water and determining each blank sample seven times. The LOD of each element was then determined by the following formula [49].

$$LOD = X_b + 3S_b$$

Where X_b is the mean concentration of the blank and S_b is the standard deviation of the blank.

3.8.4 Limit of quantification

LOQ is the lowest concentration of an analyte in a sample that can be determined with acceptable precision and accuracy under the stated conditions of test. LOQ of each analyte was obtained by the following formula [49].

$$LOQ = X_b + 10S_b$$

3.9. Data analysis

Data were analyzed using SPSS software (version 21) and Microsoft Excel 2010. Descriptive data were generated for all variables and presented as mean and standard deviation of replicate measurements. One way ANOVA ($p \leq 0.05$) was used to analysis of the variation of data.

4. RESULT AND DISCUSSION

4.1. Physicochemical parameters of the water samples

The obtained physicochemical parameters of 9 water samples were presented in Table 2. The studied parameters were also compared with the WHO, US EPA, ES - 261 and interpreted in accordance with the result obtained from analysis with the maximum WHO permissible limits. The results of physicochemical parameters were presented in Table 2.

Table2: Physicochemical parameters of tap, well, river and hand-dug sand well water samples (mean ± SD) and statistical P- values (n = 9).

Parameter	Water samples									
	TW (T)	**TW (H)**	**GDJWW**	**DMWW**	**KWW**	**KRW**	**WRW**	**KHDSWW**	**WHDSWW**	**p-value**
Temp (^oC)	20.50 ± 0.40	20.00 ± 1.20	22.50 ± 0.30	21.60 ± 0.20	20.20 ± 0.30	22.40 ± 1.00	23.50 ± 0.30	19.90 ± 1.10	20.20 ± 0.01	0.00
EC (µS/cm)	824.00 ± 20.30	766.90 ± 50.90	686.00 ± 12.50	910.00 ± 9.90	577.00 ± 10.60	186.00 ± 3.70	192.20 ± 4.80	287.70 ± 3.50	367.30 ± 12.20	0.00
TDS (mg/L)	423.0 ± 4.60	382.40 ± 27.80	344.0 ± 5.30	466.00 ± 4.60	290.0 ± 2.50	90.40 ± 2.00	93.50 ± 3.40	136.10 ± 5.50	178.60 ± 2.50	0.00
pH	7.30 ± 0.04	6.96 ± 0.10	6.97 ± 0.05	7.21 ± 0.05	6.98 ± 0.05	8.18 ± 0.08	8.30 ± 0.04	7.60 ± 0.06	7.64 ± 0.03	0.00
Turbidity (NTU)	1.27 ± 0.01	1.17 ± 0.02	2.71 ± 0.11	2.42 ± 0.06	2.60 ± 0.05	8.26 ± 0.02	11.77 ± 0.18	1.47 ± 0.13	2.19 ± 0.13	0.00
DO (mg/L)	4.6 ± 0.20	3.5 ± 0.70	2.9 ± 0.20	3.20 ± 0.10	3.40 ± 0.30	6.00 ± 0.10	5.90 ± 0.30	3.40 ± 0.30	3.30 ± 0.20	0.00
NO_2^-(mg/L)	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.01± 0.00	0.12 ± 0.00	0.12 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.00
NO_3^-(mg/L)	31.70 ± 0.10	31.47 ± 0.16	32.6 ± 0.06	33.60 ± 0.12	32.90 ± 0.50	10.20 ± 0.15	10.30 ± 0.35	4.00 ± 0.12	4.30 ± 0.18	0.00
SO_4^{2-} (mg/L)	23.30 ± 0.60	23.0 ± 1.00	28.7 ± 0.58	29.30 ± 0.58	27.70 ± 0.58	34.70 ± 0.58	37.30 ± 0.58	23.30 ± 0.58	25.70 ± 0.58	0.00
PO_4^{3-} (mg/L)	0.37 ± 0.01	0.37 ± 0.02	0.31 ± 0.01	0.31 ± 0.01	0.29 ± 0.01	0.57 ± 0.02	0.57 ± 0.01	0.11 ± 0.01	0.21 ± 0.01	0.00

TW (T): Tap water from tanker water; TW (H): Tap water from resident homes; GDJWW: Goda Jimata well water; DMWW: Doro manaka well water; KWW: Katila well water; KRW: Koce river water; WRW: Watira river water; KHDSWW: Koce hand-dug sand well water; and WHDSWW: Watira hand-dug sand well water.

Comparisons of studied physicochemical parameters with international and national maximum permissible limits (MPL) for drinking water were shown in Table 3.

Table3: Comparison of physicochemical parameters of the studied water samples with international and national standards for drinking water**.**

Parameters	**Drinking water Standards**			
	WHO [2, 19]	**US EPA [42]**	**ES - 261 [19, 52]**	**Present study**
Temp ($^{\circ}C$)	30	-	-	19.90 - 23.50
EC (µS/cm)	500	500	-	186.00 – 910.00
TDS (mg/L)	1000	500	1000	90.40 – 466.00
pH	6.5- 8.5	6.5 – 8.5	6.5-8.5	6.96 – 8.30
Turbidity (NTU)	5	7	5	1.17 – 11.77
DO (mg/L)	-	6.5 – 8	-	2.90 – 6.00
NO_2^-(mg/L)	3	1	3	0.01 – 0.02
NO_3^-(mg/L)	50	50	50	4.00 – 33.60
SO_4^{2-} (mg/L)	500	500	250	23.00 – 37.30
PO_4^{3-} (mg/L)	5	5	5	0.11 – 0.57

The average value, $\bar{X}$ ± SD, of the physical parameters including temperature, conductivity, TDS, pH, dissolved oxygen, turbidity, nitrite, nitrate, sulphate and phosphate of the drinking water samples were given in Table 2.

Temperature

Water temperature is one of the controlling factors for dynamics of aquatic environments, because it interferes in the organism metabolism, influencing the reproduction, accelerating the reactions and increasing the degradation rate of organic matter. 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, odour, colour and corrosion [2]. The present investigation reveals that temperature of the samples were in the range of 19.90 - 23.50°C, with minimum value from Koce hand-dug sand river water and maximum from Watira main river water (Table.2) and is found within the permissible limit of WHO (2011) (Table.3). The water temperatures during sampling period across the sampling sites were significantly different (ANOVA, $P < 0.05$) among the sites of the studied drinking water samples (Table.2). The fluctuation in water temperature usually depends on geographic location, sampling time, and temperature of effluent entering [4]. So, the maximum temperature recorded may indicate the more polluted sites.

Electrical conductivity

EC is a measure of water's ability to conduct an electric current is related to the amount of dissolved minerals in water, but it does not give an indication of which element is present but higher value of EC is a good indicator of the presence of contaminants such as sodium, potassium, chloride or sulphate and so on [4]. Electrical conductivity is used to indicate the total ionized constituent of water. It is directly related to sum of the cations and anions [50]. According to WHO (2008) standards, EC value of drinking water quality should not exceeded 500 µs/cm. Low values are characteristic of high quality of the waters. High values of conductance can be indicative of salinity problems but also are observed in eutrophic water ways where plant nutrients or fertilizer are in greater abundance. Very high values are good indicators of possible polluted sites [20].

Analysis of the results show that all the samples from tap and well water samples have EC value greater than the maximum permissible limit of WHO (2008) and US EPA(1999) standards, while all samples from river water samples have EC values were below maximum permissible limit. The range of EC of the samples was from 186.00 – 910.00 µs/cm with minimum from Koce main river water and maximum from Doro Manaqa well water sample. Very high values of EC were recorded for samples collected from Doro Manaqa well water and Tanker tap water respectively. Thus the water has very high electrical conductivity, implying the presence of reduced level of ionic species and very low results clearly indicate the water in the systems are characterized by low ionized and has the low level of ionic concentration activity due to low concentrations of dissolved solids. The minimum value of conductivity of water may be a sign as ions responsible for the conductivity were precipitate out or settling on the riverbed or being absorbed by aquatic plants. The mean concentration values of electrical conductivity of the drinking water samples varied significantly ($P \leq 0.05$) among the sampling sites (Table.2). Since, the conductivity of the water is a function of the number of charged ion in solution; it is another measure of dissolved materials.

Total dissolved solid

TDS comprise inorganic salts (principally calcium, magnesium, potassium, sodium, bicarbonates, chlorides and sulfates) and small amounts of organic matter that are dissolved in water. TDS in drinking-water originates from natural sources, sewage, urban runoff and industrial wastewater. According to WHO (2011), there is no health-based guideline value for TDS has been proposed. But the palatability of water with a total dissolved solids 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 [2]. All samples analyzed were contains TDS value less than 600 mg/L. It was within the limit and considered be good (Table.3).

pH:

pH is the indicator of acidic or alkaline condition of water status. It is controlled by the dissolved chemical compounds [50]. When water has a pH that is too low, it will lead to corrosion and pitting of pipes in plumbing and distribution systems. This can lead to health problems if metal particles are leached into the water supply from the corroded pipes [47].

Analysis of the results show that all the samples from river, tap and well water samples have pH value in the range of permissible limit of WHO (2011), ES-261 and US EPA(1999) standards. The ranges of pH of the samples were from 6.96 – 8.30 with minimum from Qaxila well water and maximum from Watira main river water samples. Very high values of pH were recorded for samples collected from both main river water samples, while well water samples have low values. The overall result indicates that the water sources are within the desirable and suitable range.

Basically, the pH is determined by the amount of dissolved carbon dioxide [CO_2], which forms carbonic acid in water. pH of well water can also be lowered by organic acids from decaying vegetation, or the dissolution of sulfide minerals[50]. The slight basic nature of the river water may be mainly due to the limestone basin of the all the locations and the river water is exposed to the atmosphere may can increase dissolved oxygen concentrations, causing a reduced metal ions to oxidized and precipitate as hydroxide.

Turbidity

Turbidity in water is caused by suspended particles or colloidal matter that obstructs light transmission through the water. It has no health effects. However, turbidity can provide a medium for microbial growth. High turbidity may indicate the presence of disease causing organisms. These organisms include bacteria, viruses, and parasites that can cause symptoms such as nausea, cramps, diarrhea, and associated headaches. According to the WHO (2011) and ES-261 standards for turbidity, the allowable permissible limit value must always be low, preferably lower than 1 NTU but maximum permissible limit is 5 NTU [2].

Analysis of the results shows that the samples from tanker and Resident home tap water have low turbidity value within permissible limit when it compared with the others (Table.3). Well water samples and sand soil river water samples have turbidity value greater than tanker and Resident home tap water sample but within permissible limit and the two main river water samples are above maximum permissible limit of WHO (2011) and ES-261 standards. The maximum water fluctuation 8.26 ± 0.02 and 11.77 ± 0.18 NTU were recorded in two main river water, it may be due to look of rain and presence of suspended particles. The water bodies were turbid and cloudy; this may be due to refuse dump and surface run - off.

Dissolved oxygen

According to WHO (2011), dissolved oxygen has no health-based guideline value recommendation. But Depletion of dissolved oxygen in water supplies can encourage the microbial reduction of nitrate to nitrite and sulfate to sulfide. It can also cause an increase in the concentration of ferrous iron in solution, with subsequent discoloration at the tap when the water is aerated [48]. According to US EPA (1999), healthy water should generally have dissolved oxygen concentrations above 6.5 - 8 mg/L.

Analysis of the results show that all the water samples have DO value bellow the range of permissible limit of US EPA(1999). This may be indicated that susceptible to pollution. Heavy use of fertilizers and dumping of human waste can pollute water quickly and lead to oxygen starvation. The range of DO of the samples was from 2.90 ± 0.02 to 6.00 ± 0.10 mg/L with minimum from Goda Jimata well water and maximum from Watira main river water samples. Very high values of DO were recorded for samples collected from both main river water samples, while the low value was recorded for samples collected from Goda Jimata well water and intermediate values were from resident home tap and Tanker water samples. Exposure of the sample to the atmosphere can increase dissolved oxygen concentrations.

A different water sample contains different amounts of dissolved oxygen. A fast flowing river usually contains more dissolved oxygen than a slow moving one because it mixes rapidly with air containing oxygen while moving over rocks, logs and debris in the stream. The highest concentration of oxygen is found in the water stretches where the greatest amount of mixing occurs. Slow moving rivers have less oxygen in them.

Nitrite

The mean nitrite concentration measured shows the maximum value of 0.12 ± 0.006 mg/L at site of both main rivers and a minimum value of 0.01 ± 0.006 mg/L at site of both hand-dug sand river waters. Analysis of the results show that all the samples from river, tap and well water samples have nitrite values in the range of permissible limit of WHO (2011), ES-261 and US EPA(1999) standards (Table.3). Therefore, there is no health effect regards to this parameters on the customers. However, the maximum concentration has recorded at main river is probably from agricultural chemicals and nitrogen containing chemical. The mean concentration of nitrite among the sites differed significantly ($P < 0.05$) (Table 2). Expected source of nitrite in this river can be from nitrogen containing organic matter, commercial fertilizers, and naturally from mineral rocks decomposition. Many effluents, including sewage, are rich in ammonia, which in turn can lead to increased nitrites concentration. High level of nitrite in river water may indicate pollution site.

Nitrate

Nitrate can reach both surface water and ground water as a consequence of agricultural activity (including excess application of inorganic nitrogenous fertilizers and manures), from waste water disposal and from oxidation of nitrogenous waste products in human and animal excreta, including septic tanks. Surface water nitrate concentrations can change rapidly owing to surface run off fertilizer and de nitrification by bacteria, but ground water concentrations generally show relatively slow changes. Some ground waters may also have nitrate contamination as a consequence of leaching from natural vegetation [2].

Nitrate mean concentration range from a minimum of 4 ± 0.12 to a maximum of 33.6 ± 0.12 mg/L of Koce hand-dug sand river water and Doro Manaqa well water respectively. Analysis of the results show that all the samples from river, tap and well water samples have nitrate values in the range of permissible limit of WHO (2011), ES-261 and US EPA(1999) standards (Table.3). Therefore, there is no health effect regards to this parameters on the customers.

The results of nitrate ion levels in the sampling sites were, well > tap > main river > hand-dug sand river water. Nitrate is a well-known contaminant of ground and stream water. However, the current results may not likely be a land mark for safety because while nitrate is a common nitrogenous compound due to natural processes of the nitrogen cycle, anthropogenic sources could greatly increase the nitrate concentration of nitrogen-rich fertilizers and manure [42]. Nitrates enter water supplies from the breakdown of natural vegetation or decomposing plant, the use of inorganic and organic fertilizers in modern agriculture and from the oxidation of nitrogen compounds in sewage effluents and industrial wastes [46].

Phosphate

Phosphates are extensively used in detergent formulations and washing powders. Agricultural fertilizers normally contain phosphate minerals and phosphates also arise from the breakdown of plant materials and in animal wastes. Phosphates can therefore enter water courses through a variety of routes particularly domestic and industrial effluents and run-off from agricultural land [46].

The highest phosphate levels was recorded at both main river with a concentration of 0.57 ± 0.02 mg/L, while the lowest concentration was 0.16 ± 0.01 mg/L recorded at both hand-dug sand river water samples. Analysis of the results show that all the samples from river, tap and well water samples have phosphate values in the range of permissible limit of WHO (2011) (table.3). Therefore, there is no health effect regards to this parameters on the customers. The highest concentration of phosphates at both main river water samples could be attributed to the farming activities being undertaken where there is use of phosphate fertilizers. It could also be due to cloth washing activities being performed by residents of town to this water using phosphate containing detergents. The minimum value may indicate the hand-dug sand is a good filtrate.

Sulfate

The presence of sulfate in drinking water can cause noticeable taste. It is generally considered that taste impairment is minimal at levels below 250 mg/L. No health-based guideline is proposed for sulfate. However, because of the gastrointestinal effects resulting from ingestion of drinking water containing high sulfate levels, it is recommended that health authorities be notified of sources of drinking water that contain sulfate concentrations in excess of 500 mg/l. The presence of sulfate in drinking water may also cause noticeable taste and may contribute to the corrosion of distribution systems [2]. In the present study the Watira main river water showed the maximum value of sulphate (37.3 ± 0.58 mg/L). It is within the limit. Therefore, there is no health effect regards to this parameters on the customers. The high value recorded in the river water sample might be due to the river is rich in gypsum which leach sulphate and the poor management of municipal waste discharged into the river.

4.2 Concentration of Heavy Metals in Water Samples

Before determination of the metal contents of the water samples LOD and LOQ were determined. The obtained LOD were 0.017, 0.004 , 0.076 and 0.012 mg/L as well as LOQ were 0.043 mg/L, 0.013, 0.174 and 0.029 mg/L for Cu, Pb, Cd and Cr, respectively. The precision and accuracy of the analytical method has calculated in terms of SD and %R, respectively. The obtained %R and standard deviations were in acceptable ranges, %R (80 -120%) and SD < 20% of the mean the measurements indicating the reliability of the method [19]. Recover studies were performed by spiking TW (T), KWW and WHDSWW samples with 1.5 mg/L of each heavy metal and the results are presented in Table 4.

Table4: Concentrations (mg/L) of spiked and unspiked samples with percent of recovery

Metals	TW (T)			KWW			WHDSWW		
	C_{sp}	C_{usp}	%R	C_{sp}	C_{usp}	%R	C_{sp}	C_{usp}	%R
Cu	1.45	0.1	90.00	1.36	0.1	84.00	1.43	0.11	87.00
Pb	1.38	0.00	92.00	1.44	0.00	96.00	1.21	0.00	81.00
Cd	1.27	0.00	85.00	1.21	0.00	81.00	1.21	0.00	81.00
Cr	1.21	0.00	81.00	1.23	0.00	82.00	1.25	0.00	83.00

The obtained concentrations of the studied heavy metals were presented in Table5.

Table5: The concentrations of selected metals in water samples (mean ± SD, n = 9) and statistical P-value.

Parameter	TW (T)	TW (H)	GDJ WW	DMW W	KW W	KRW	WRW	KHD SWW	WHDS WW	p-value
Pb (mg/L)	BDL	BDL	BDL	BDL	BDL	0.30 ± 0.030	0.22 ± 0.030	BDL	BDL	0.00
Cu (mg/L)	0.10 ± 0.005	0.10 ± 0.005	0.09 ± 0.010	0.08 ± 0.005	0.10± 0.005	0.14 ± 0.010	0.13 ± 0.005	0.12 ± 0.005	0.11 ± 0.005	0.00
Cd (mg/L)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	
Cr (mg/L)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	

BDL: below detection limit of the method

Comparison of levels of selected heavy metals with international and national maximum permissible limits (MPL) for drinking water were shown in Table 6.

Table6: Comparison of levels of selected heavy metals of the studied water samples with international and national standards for drinking water**.**

metals	Drinking water Standards			
	WHO [2, 19]	**US EPA [42]**	**ES - 261 [19, 52]**	**Present study**
Pb (mg/L)	0.010	0.015	0.010	0.22 – 0.3
Cu (mg/L)	2.000	1.300	2.000	0.08 – 0.14
Cd (mg/L)	0.003	0.005	0.003	BD
Cr (mg/L)	0.050	0.100	0.050	BD

Lead

Lead is both a toxic and non-essential metal having no nutritional value to living organisms. It was seen that, the level of Pb ranges from 0.004 to 0.30 ± 0.03 mg/L) in (Table.5). From this, it could be observed that Pb level found in the study area of Koce Main River (0.30 ± 0.03 mg/L) and Watira Main River (0.22 ± 0.03 mg/L) were greater than the standard value given for Pb by WHO and ES-261 which is 0.01 mg/L. This shows that high traffic density found near the study area played a significant role in the level of Pb in the both River water. This is may be due to car washing, domestic waste, deteriorating household paints, and disposal of lead batteries, which have discharged through small tributaries that passing through the center of the town has probably attributed to the increase in Pb concentration. The agricultural activities practiced around the river may also contributed to the observed high levels of lead, since this metal can occur as impurities in fertilizers and metal based pesticides, compost and generator west, since it used for irrigation. More recently, cases of lead poisoning have reported in Rebu River Woliso Ethiopia. It has concluded that, lead contamination of water bodies (streams and rivers) and environment lead to the death of several people and animals. Most of the lead we take has removed from our bodies in urine; however, as exposure to lead is cumulative over time, there still risk of buildup, particularly in children. Lead concentrations have effect on three human systems: blood forming system, nerve system and renal system [19]. Therefore, there was health related risk due to the presence of Pb in drinking water of the study areas.

Chromium

Chromium is an essential micronutrient for animals and plants, and is considered as a biological and pollution significant element. Chromium in excess amounts can be toxic especially in the hexavalent form. Sub chronic and chronic exposure to chromic acid can cause dermatitis and ulceration of the skin. Long-term exposure can cause kidney, liver, circulatory and nerve tissue damages. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high level of chromium [14].

In this study, chromium was not detected in all of the sampling areas. Since the WHO and ES-261 maximum admissible limit of chromium in drinking water was almost equal with the method detection limit; there was no health related risk due to the presence of chromium in drinking water of the study areas.

Cadmium

It is a non-essential element and is highly toxic to marine and freshwater aquatic life. It is found in low concentration in rocks, petroleum and coal. It can enter the surface and ground water when dissolve in acidic water. It can also enter in environment from metal plating, industrial discharge, water pipes, paints, mining waste, batteries and pigments, landfill leachate and plastic stabilizers. In human body biochemically it can replaces Zn and causes liver and kidney damage, high blood pressure, anemia, destroys red blood cells and testicular tissue [51].

Cadmium concentration was found to be below the detection limit in all of the sampling areas. According to WHO standards and ES-261, the permissible limit in drinking water for cadmium is $\leq$ 0.003 mg/L. The results obtained were below the recommended value of WHO and ES-261 guideline for heavy metal in drinking water. Therefore, there is no health effect regards to this parameters on the customers.

Copper

Copper is a metal that is naturally present in the environment, but the levels of contamination can be increased around agricultural land, metal pipes and metal fittings. The World Health Organization and ES-261 has established a 2.0 mg/L of Cu as maximum permissible limit guidance level in drinking water supply. The most common health effects of the excessive consumption of copper bearing water would be; nausea, vomiting, diarrhea, upset stomach, and dizziness. If extreme intake of copper occurs, kidney and liver damage is possible.

Accordingly the laboratory results of the study area were shown in Table.5 the ranges of Cu concentration of the samples were from 0.083 ± 0.005 to 0.140 ± 0.010 mg/L with minimum from Doro Manaqa well water and maximum from Watira main river water samples. Analysis of the results show that all the samples from river, tap and well water samples have Cu value bellow maximum permissible limit of WHO (2011), ES-261 and US EPA(1999) standards (Table.6). Therefore, there is no health effect regards to this parameters on the customers.

4.3 Comparisons of the concentration of Heavy Metals among the water samples

In this study, the total mean concentration of Cu was the highest and Cd/Cr was found to be the least. Generally, the overall mean concentration of heavy metals in River water in decreasing order of Pb (0.259 ± 0.03) > Cu (0.136 ± 0.008 mg/L) > Cd/Cr (BDL), the overall mean concentration of heavy metals in hand-dug sand well water in decreasing order of Cu (0.102 ± 0.005 mg/L) > Cd/Cr/Pb (BDL), the overall mean concentration of heavy metals in well water in decreasing order of Cu (0.089 ± 0.005 mg/L) > Cd/Cr/Pb (BDL) and the overall mean concentrations of the heavy metals in tap water in decreasing order was as follows; Cu (0.103 ± 0.005 mg/L) > Pb/ Cd/Cr (BDL).

5. CONCLUSION

The physicochemical characteristics of water samples in the study area suggested that there was no much harmful chemical contamination. This study concluded that the dissolved oxygen of river, well and tap water values, electrical conductivity of well and tap water values and turbidity of both main river values are not within the range of permissible limit. It is also concluded from present study the average concentrations of heavy metals in drinking water sources of the study area was in decreasing order of Pb > Cu > Cd/Cr. Maximum concentration of lead in water sample used for drinking exceeded the permissible limits. Concentration of Cu in drinking water samples was within permissible limit. Concentration of chromium and cadmium in drinking water samples was blow detection limit. Since the three heavy metals were lower than drinking water standards, it indicate that there was no instant risk due to the exposure to these heavy metals but constant ingestion of these heavy metals can damage the health of local community on the longer run. It is essential to monitor and prevent the pollution load in drinking water as it has a direct link to human health.

6. RECOMMENDATION

The value of some physicochemical water quality parameters from the laboratory analysis of electrical conductivity of well and tap water values, turbidity of both main river values were recorded as maximum value when compared with WHO, EPA and Ethiopian drinking water standards. Among heavy metals lead was recorded above the maximum limit at both main rivers and resident home tap water. Generally, the increment of all parameters may be controlled by treatment process; but there is no water treatment plant of Bantu town. The concerned body should take immediate mechanism in order to control increment of contaminants getting into water bodies and also revise their water treatment process. From all sampling sites, both hand-dug sand water samples for almost all parameters were within minimum and maximum permissible limit of WHO, USEPA and Ethiopian drinking water standards. So, when there is no tap drinking water because of absence of electrical power, customers better use hand-dug sand river water than main river water. The final recommendation to the town will be, please take into consideration this research value and check your water treatment process or mechanism.

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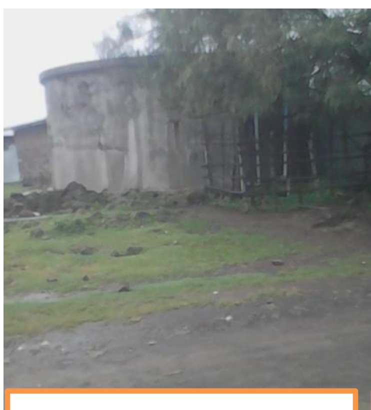
8. Appendices

Appendix1: sampling sites of drinking water of Bantu town.

Watira hand-dug sand water

Watira main river water



Tanker

Tap water source

Metal pipe used for distribution of water

Koce hand-dug sand water

Appendix2: Image showing investigation of water sample in laboratory.

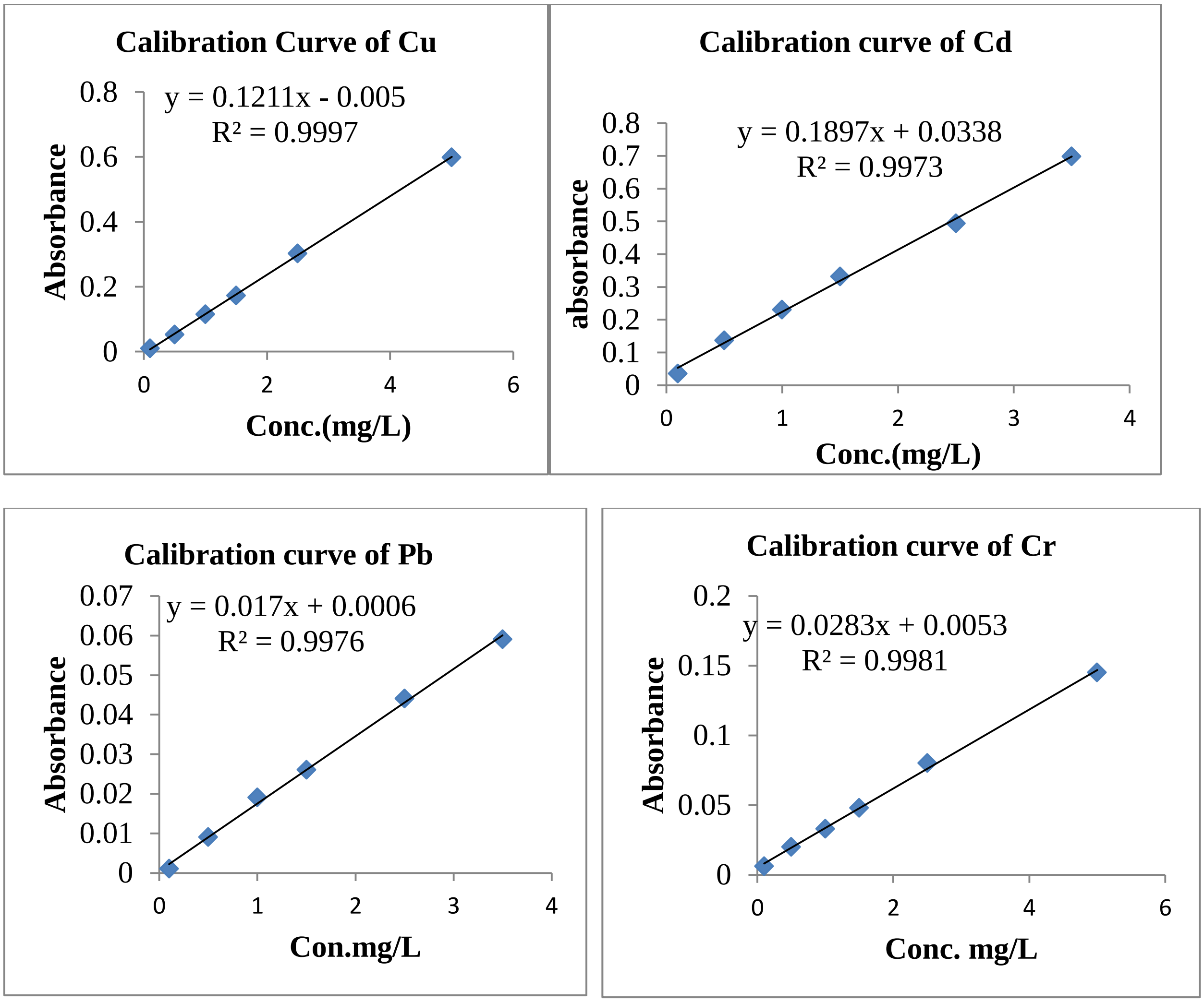
Poly ethylene bottles preparation for sampling

Distilled water preparation

Sample preparation for digestion and digestion process

Nitrate concentration determination

Appendix3: Calibration curve for standard solution of the analyzed metal.

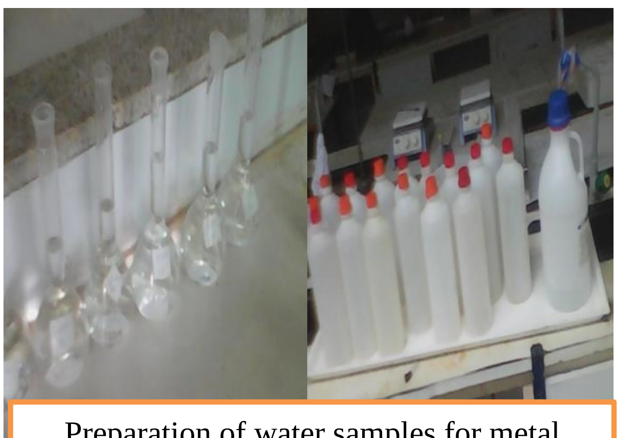


Appendix4: Regression equations, correlation coefficient, quantification and detection limit.

Heavy metal	Wave length in (nm)	Regression equation	Correlation coefficient	SD of blank	LOD	LOQ	Flame system
Cu	324.7	Y= 0.1211x - 0.005	R^2 = 0.9997	0.004	0.017	0.043	Air/acetylene
Pb	283.2	Y= 0.017 x + 0.006	R^2 = 0.9976	0.022	0.004	0.013	Air/acetylene
Cd	228.9	Y= 0.1897x + 0.0338	R^2 = 0.9973	0.003	0.076	0.174	Air/acetylene
Cr	357.9	Y= 0.0283x + 0.0053	R^2 = 0.9981	0.02	0.012	0.029	Air/acetylene

Appendix5: Images of instruments used for physicochemical and heavy metal analysis of drinking water samples.

FAAS instrument



Preparation of water samples for metal

Measuring turbidity of water sample

Photometer used for measuring nitrite, nitrate, sulfate and phosphate.