ASSESSEMENT OF PHYSICO-CHEMICAL PARAMETERS AND SOME SELECTED HEAVY METALS OF DRINKING QALLE RIVER WATER, EAST WOLLEGA ZONE, ETHIOPIA.

BY

BELACHEW OLANI DURESSA

A THESIS SUBMITTED TO

DEPARTMENT OF APPLIED CHEMISTRY

SCHOOL OF APPLIED NATURAL SCIENCE

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF MASTER'S IN CHEMISTRY

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DECLARATION

I hereby declare that this MSC thesis is my original work and has not been presented for a degree in any other university, and all sources of material used for this thesis have been duly acknowledged.

Name:-Belachew Olani Duressa

Signature:-_____

This MSC thesis has been submitted for examination with my approval as thesis advisor.

Name: Eshetu Bekele (phD)

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Date of submission_____

ADVISOR'S APPROVAL SHEET

To: Applied Chemistry department

Subject: Thesis Submission

This is to certify that the thesis entitled "**Assessement of Physico-chemical parameters and some selected heavy metals of drinking Qalle River water, East Wollega Zone, Ethiopia.**" submitted in partial fulfillment of the requirements for the degree of Master's in Chemistry the graduate program of the department of -Chemistry and has been carried out by Belachew Olani Duressa with Id. No GSS/0209/05, under my/our supervision. Therefore, I recommend that the student has fulfilled the requirements and hence hereby he can submit the thesis to the department.

Eshetu Bekele (PhD)	_____	_____
Name of major Advisor	Signature	Date

APPROVAL OF BOARD OF EXAMINERS

We, the undersigned, members of the Board of Examiners of the final open defense by Belachew Olani Duressa have read and evaluated his thesis entitled "Assessement of Physico-chemical parameters and some selected heavy metals of drinking Qalle River water, East Wollega Zone, Ethiopia." This is, therefore, to certify that the thesis has been accepted in partial fulfillment of the requirement of the Degree of Masters of Science in chemistry complies with respect to the originality and quality signed by examining committee.

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ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectrometry.
ANOVA	Analysis of Variance.
DO	Dissolved Oxygen.
EBT	Erichrome Black-T.
EC	Electrical Conductivity.
EDTA	Ethylene Diamine Tetra Acetic acid.
EEPA	Ethiopian Environmental Protection Authority.
FAAS	Flame atomic Absorption Spectrometry.
IDL	Instrumental Detection Limit.
SD	Standard Deviation.
MDL	Method Detection Limit.
LRB	Laboratory Reagent Blank
UV-Vis	Ultraviolet-Visible.
APHA	American Public Health Association.
TSAWQG	Tentative South Africa Water Quality guidelines.
USEPA	United States Environmental Protection Agency.
WHO	World Health Organization.

ABSTRACT

The purpose of the present study was to assess the quality of Qalle River water at Kiramu District nearby Kiramu town, East Wollega Zone, Oromia Regional State, Ethiopia. Three sample sites were chosen along the Qalle main stream point sources namely Up Stream, Middle Stream and Down Stream. In the present study 14 physicochemical parameters of drinking water quality were analyzed in order to understand the characteristic and quality status of the three streams of Qalle River water. These parameters were analyzed in standard water laboratory procedures by employing in situ measurements (temperature, pH and EC), classical methods (TA, TDS, TH, Cl^- SO_4^{-2}, Ca, Mg) and instrumental methods (NO_3^-, PO_4^{-3} ,Na^+, K^+, Pb, Cu, Cd and Mn). The water samples of the streams were collected in April, 2017. The measured mean value of temperature, pH, EC, TDS and DO was ranged from 24.2 to 24.25 ^{0}c, 6 to 6.05, 81.7 to 83.7 µs/cm, 54 to 59 mg/L and 8.55 to 9.03 mg/L, respectively. The measured mean concentration of Na^+, K^+, Mg^{+2} and Ca^{+2} was ranged from 4.7 to 7.5 mg/L, 5 to 5.2 mg/L, 2.75 to 3.49 mg/L and 6.66 to7.07 mg/L, respectively and the measured mean value for total alkalinity, total hardness, chlorides, sulfates, nitrates and phosphates was range from 20 to 22 mg/L, 29.12 to 32.24 mg/L, 1.07 to 2.14 mg/L, 15.53 to 19.63 mg/L, 0.42 to 0.51 mg/L and 0.25 to 0.335 mg/L, respectively. Also the mean concentration of four heavy metals was measured, and among these four heavy metals the mean concentration of two of them (Pb and Cd) were not detected (ND) at ppm level in three sites of Qalle River water. However, the mean value of Cu and Mn in mg/L was ranged from 0.54 to 0.68 mg/L and 0.287 to 0.469 mg/L respectively. The analyzed parameters in water samples were below and agreed with the currently recommended guidelines for drinking water quality except for that of pH, DO, Cu and Mn. The level of pollution is more pronounced at middle-stream and down-stream for the heavy metals sampling sites this is because of the dumping of domestic wastes or waste from both livestock and humans may leached to sites of Qalle River. Finally the results of one way ANOVA showed that the difference between sites statistically significant ($P<0.05$) for all parameters.

*Key Phrases: Qalle River, Physic**o**-chemical parameters, Heavy metals, Pollution*

1. INTRODUCTION

1.1 Background of the Study

Water is one of the most important and abundant resource in nature. It is also an essential constituent of all animals and vegetables and forms about 70% of the matter of earth crust (APHA, 1980). It is mostly used for industrial and municipal purposes (Gasim *et al*., 2007). It is difficult to imagine clean and sanitary environment without water. Water pollution occurs when pollutants are discharged directly or indirectly to water bodies without adequate treatment to remove harmful compounds. Water pollution affects human, plants and organisms living in these bodies of water. In almost all cases the effect is damaging not only to individual and populations but also the natural biological communities. It has been suggested that water pollution is the leading worldwide cause of deaths and disease (Larry, 2006). Source of surface water pollution are generally grouped into two categories based on their origin. Point and non-point source, point source occurs when harmful chemicals or effluents are discharged directly into a river or other source of water. The non-point source occurs when the harmful pollutants are discharged indirectly through the water runoffs caused by heavy rainfall. For example when the fertilizers added to crops is discharged into a stream or lake by a water runoff. Each source of contamination has its own damaging effects to plants, animals and ultimately to human health, while point sources can be monitored and controlled it is difficult to monitor and regulate a nonpoint source. Most streams and lakes today get contaminate through nonpoint sources of pollution (Ghosh and Bright Hub, 2012). Drinking water may be contaminated by different contaminants such as bacteria, viruses, heavy metals, nitrates and salts which have found their way in to water supplies due to inadequate treatment and disposal of waste and over use of limited water resource (Singh and Mosley, 2003). Even in the absence of anthropogenic sources of contaminates, natural sources are also a potential contributor of higher levels of metals and other chemicals that can harm human health. This is highlighted recently in Bangladesh where natural levels of arsenic in ground water found to be causing harmful effects on the population (Anawara *et al*., 2002). The quality of water used for drinking, domestic purpose, food production or recreational purposes has an important impact on health (WHO, 2013).Water is a dynamic system containing living as well as non-living, organic, inorganic, soluble as well as insoluble substances. Good-quality drinking water may be consumed in any desired amount without adverse effect on health. Such water is

called ‘potable’. It is free from harmful levels of impurities such as bacteria, viruses, minerals, and organic substances. It is also aesthetically acceptable and is free of unpleasant impurities, such as objectionable taste, color, turbidity, and odor. In the ecosystem water is considered to be the most important component for the life but day by day quality of water become degraded (Manjar et al., 2010). Hence, physical, chemical and biological properties of the river water do not continue for a long period of time without interruption. It has been suggested that it is the leading cause of deaths and diseases worldwide (Rasheed *et al*., 2013).This urges frequent monitoring of surface water to get information on the status of the quality 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. Cobalt, copper, iron, manganese, molybdenum, selenium, and zinc are needed at low levels as catalysts for enzyme activities. 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 (Jennings *et al*., 1996). Ensuring quality of surface water used for human consumption with respect to these trace elements is also a basic factor in guaranteeing public health (WHO, 2013). In general, before water can be described as potable, it has to comply with certain physical, chemical and microbiological standards (Ezel, 2012). Hence, it is very important to continuously assess the quality of water source used for household consumption and compare the results with National and International standards. In this research, physico-chemical parameters of environmental indicators, the level of common cations and anions, some heavy metals of river water are determined by standard methods.

1.2 Statement of the Problem

Water is the basic needs for living organisms in the world. Good drinking water quality is essential for the wellbeing of all people. People consume water daily to drink, bath, and prepare food and others. Drinking water comes from ground sources such as groundwater and aquifers. It can also be obtained from surface water such as rivers, streams and glaciers. But in nature, all water contains some impurities. In rural and urban areas of Kiramu District, surface water is the major source for drinking and domestic purposes. These resources may be adulterate by wild-life, domestic wastewater discharges, pathogens, agricultural activities. As water flows in streams, accumulates in lakes and filters through the layers of soil and rock in the ground, it dissolves and absorbs the substance that come in contact with it. Especially,

irregular supply of water through piped water system has forced the population to use whatever quality of water available in the nearby water sources. However, at certain level, minerals may consider contaminants that can make water unpalatable or even unsafe. This leads to water born diseases and other health impacts. Drinking water must be free from all diseases and hazards affecting human health. A regular monitoring of water quality for improvement not only prevents disease and hazards but also checks the water resources from getting further polluted (Trivedy and Goel, 1996). Thus, the great problem which initiates the researcher is that the Babo Kiramu rural area communities are using water of untested quality for drinking and other purposes. According to Kiramu District public health center, symptoms such as hypertension, vomiting, headache, Strokes and typhoid are some of health problems that have been faced on 45-60% of patients per day. These health problems may be caused by contamination of drinking water sources in the District. As information obtained from Districts' Water and Irrigation Bureau, river water is the main source of drinking water in rural areas. Thus, the quality of drinking water should be tasted and appropriate monitoring programs must be established to maintain water safety for public use. Thus, the present paper is to cheeck the levels or concentration of some of Physico-chemical parameters, selected heavy metals (Cd, Pb, Cu, Mn) of Qalle River water from three different sites of Qalle River water of Kiramu District, East Wollega Zone, Western Ethiopia by using AAS, UV-Vis, flame photometry, titration method, argentometric method and turbdimetric method to compare the values with the national and international guidelines recommended for drinking water standards.

1.3 Objectives of the Study

1.3.1 General Objective

The overall objective of this research is to determine the level of physico-chemical parameters and concentration of some selected heavy metal in Qalle River water located in Kiramu District Western Ethiopia, Oromia region.

1.3.2 Specific Objectives of the Study

- To determine the selected physico-chemical (temperature, electrical conductivity, pH, TDS, DO, TA, TH, Ca, Mg, Na, K, Cl-, NO_3^- ,PO_4^{-3} ,SO_4^{-2})properties of Kiramu Qalle River.

- To determine the concentration of some selected heavy metals (Pb, Cu, Cd and Mn) in Kiramu Qalle River.
- To compare the level of physico-chemical parameters and heavy metal concentration of Qalle river water of these sites with international standards of water quality.
- To compare the level of physic-chemical parameters among the sites of Qalle River water.

1.4 Significance of the Study

The study has the following significances:

- Help to know those chemicals which affect quality of Qalle River water.
- Create awareness among the local people about their water quality standards that they use in different activities.
- It is used to compare the quality of drinking water remains within accepted standards.
- It is used as base line information for further investigation on the quality of Qalle river water of these sites.
- Help Government organization and Non-Government organization to take appropriate measures if necessary.

2. LITERATURE REVIEW

2.1 The Need for Water Quality Supply

Water quality refers to the chemical and physical characteristics of water. It involves the process of evaluation of the physical and chemical nature in relation to natural quality, human effects and intended uses, particularly uses which may affect human health and aquatic system. The water quality of rivers, streams and lakes changes with seasons and this has profound influence on the population density of aquatic plants and animals (Lawson, 2011). The most common standards used to assess water quality relate to health of ecosystems, safety of human contact and drinking water. Water quality depends on the local geology and ecosystem, as well as human uses such as use of water bodies as sink (Johnson *et al.*, 1997). Anthropogenic activities, natural process such as erosion, weathering geochemical and geological characteristics of the environment as well as every in increasing population the world have kept changes in natural water bodies constant (WHO, 2008).

Monitoring of water quality will ensure protection of water health (WHO, 2011). The parameters for water quality are determined by the intended use. Water quality tends to be focused on water that is treated for human consumption, water for domestic use, or in the environment. In rural areas and villages of Ethiopia, water for human consumption, drinking, washing (bathing), for preparation of food etc, is obtained from rivers, streams, shallow, wells, springs, lakes, ponds and rainfall. Water quality Standards have been established to regulate substances that potentially affect human health, environment and aesthetic qualities of water. The WHO guideline for Drinking Water Standards, United States Specification for Drinking Water and European Union Specification for Drinking Water are among the recognized water quality standards.

Dissolved minerals may affect suitability of water for a range of industrial and domestic purposes. The most familiar of these is the presence of ions of calcium and magnesium which interfere with the cleaning action of soap, and can form hard sulfate and soft carbonate deposits in water heaters or boilers. Hard water may be softened by removing these ions. Environmental water quality, also called ambient water quality, relates to water bodies such as lakes, rivers, and oceans. Water quality standards for surface waters vary significantly due to different environmental conditions, ecosystems, and intended human uses. Toxic substances can present a health hazard for non-drinking purposes such as irrigation, swimming, and

rafting uses. These conditions may also affect wildlife, which use the water for drinking or as a habitat. Generally river water is the major source of drinking water in rural areas. This drinking water may be contaminated by different contaminants which have an impact on the health and economic status of the consumers. The contamination may be physical (temperature, turbidity, color, suspended), chemical (organic and inorganic, dissolved oxygen (DO), pH, alkalinity, pesticides, etc. Thus, the majority of rural communities use water from contaminated or doubtful sources, which expose the people to various water-borne diseases (MWR, FDER, 2004). The present study was focused on assessing the physico-chemical characteristics of drinking water sources of stream water of Kiramu district in the study area of Babo Qalle river water. Thus, the drinking water must be free from hazardous compounds and the quality of river water of these areas should be tasted by using Atomic absorption spectrometer and other techniques.

Atomic absorption spectrometer is an important technique for the quantitative determination of element concentration, and is also very suitable method for monitoring the levels of heavy metals in natural waters .This methods measures the concentration of elements by passing light in specific wave length emitted by a radiation source of a particular element through cloud of atoms from a sample. It is based on the phenomenon that the atom in the ground state absorbs the light of wavelengths that are characteristic to each element when light is passed through the atoms in the vapor state. Because this absorption of light depends on the concentration of atoms in the vapor, the concentration of the target element in the water sample is determined from the measured absorbance (perkin-Elmer, 1996).

River water is defined as natural flowing water course usually fresh water, flowing towards an ocean, Sea, lake or another river. They are used as water supplies and can be a reliable and relatively inexpensive source of drinking water if they are developed and maintained properly. Water quality is also important to consider before using river as a water supply. When considering using a river as source of drinking water, it is important to ensure that the rate of flow that fluctuates greatly through the year is an indication that the source is unreliable or many have the potential for contamination.

2.2 Physico-Chemical Parameters

Drinking water, or potable water, is defined as having acceptable quality in terms of its physical and chemical parameters so that it can be safely used for drinking and cooking (WHO). WHO defines drinking water to be safe if and only if no any significant health risks during its life span of the scheme and when it is consumed. This thesis also encompasses on investigating drinking river water quality characterization status. Water must be tested with in different physic-chemical parameters, selection of parameter of testing of water of solely depend on for what purpose we are going to use that water and at what extent we need, it's purity and quality. Some physical test should be performed for testing for its physical appearance such as temperature, pH, TDS, EC, and etc. While chemical tests should be performed for its performed dissolved oxygen(DO), Alkalinity, Hardness and metal ions : Na^{+}, K^{+}, Ca^{+2}, Mg^{+2} ; some an ions Cl^{-},NO_3^{-}, PO_4^{-3}, SO_4^{-2} and some selected heavy metals :Pb, Cu, Cd and Mn were determined. Water for human consumers must be free from organism and chemical substance and such large concentration may affect health (Uba S.T, 2013). The pollution of water increased due to human pollution, industrialization, the use of fertilizers in agriculture activities. Parameters such as temperature, nutrient hardness, alkalinity, dissolved oxygen and etc. are some of the important factors that determining the growth of living organism in hence water body (Kose. E 2014).

2.2.1 Temperature

The most common physical assessment of water quality is the measurement of temperature. Temperature impacts both the chemical and biological characteristics of surface water. Temperature is an important biologically significant factor, which plays an important role in the metabolic activities of the organism (Gopalkrushna *et.al*, 2011). The temperature of water can affect it in many different ways. 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 corrosion when the temperature goes up, water will hold more dissolved solids (like salt or sugar) but less dissolved oxygen. The opposite is true for colder water that contains more oxygen, which is better for animal life like fish and insect larvae.

2.2.2 pH

pH is a term used universally to express the intensity of the acid or alkaline condition of a solution. It is a measurement of the activity of the hydrogen atom, because the hydrogen activity is a good representation of the alkalinity or acidity of water. For drinking water, the WHO guideline set the pH in the range of 6.5 to 8.5 (WHO, 2008 and Chapman, 1996). Human activities like industrial operations and toxic waste disposal have effect on the pH of water sources. A change in the pH of water can have a consequence on aquatic life which is extremely sensitive to changes in water temperature and composition. For aquatic life, pH should be between 6.5 to 9.0 and in irrigation waters the pH should not fall outside a range of 4.5 to 9.0 to protect plants (Weiner, 2007).

2.2.3 Electrical Conductivity (E/C)

Conductivity is a measure of the ability of water or solution to carry an electrical current. Conductivity in water is affected by the presence of inorganic dissolved solids. Organic compounds do not conduct electrical current very well and therefore have a low conductivity when in water. Conductivity is also affected by temperature, the warmer the water, the higher the conductivity. For this reason, conductivity is reported as conductivity at 25 degrees Celsius. Low values of conductance are the characteristic of high-quality, low-nutrient waters. High values of conductance can be indicative of salinity problems but also are observed in eutrophic water ways where plant nutrients (fertilizer) are in greater abundance. A sudden change in electrical conductivity can indicate a direct discharge or other source of pollution into the water. Conductivity in streams and rivers is affected primarily by the geology of the area through which the water flows. Discharges to streams can change the conductivity depending on their make-up. Conductivity is measured in micro Siemens per centimeter (μs/cm).

2.2.4 Total Dissolved Solids

TDS represents the total concentration of dissolved substances in water. Solids refer to matter dissolved in water or waste water. Solids may affect water or effluent quality adversely in a number of ways. Total dissolved solid is the portion of solids that passes through the filter of 2.0μm (smaller) nominal pore size under specified conditions. The TDS in waters constitute mainly CO_3^{-2}, HCO_3^{-}, Cl^{-}, SO_4^{-2}, Ca^{+2}, Mg^{+2}, K^{+}, dissolved metals, dissolved organics and

other substances accounts for a small portion of the dissolved residues in water. TDS in drinking water originate from natural sources, sewage, urban run-off and chemicals used in the water treatment process, and the nature of piping or hardware used to convey the water (Maiti, 2004). Taste problems in water often arise from the presence of high TDS levels with certain metals present particularly copper and manganese (Pradhan and Pirasteh, 2011; WHO, 2011; Weiner, 2008). Dissolved solids and residues in drinking water tend to change the waters physical and chemical nature of drinking water (WHO, 2004).Water with high dissolved solids is not preferred by consumers in drinking, the presence of harmful dissolved compounds arsenic, mercury can be dangerous in water even where the total solid concentration is relatively low with their health effects (AWWA, 2000). The WHO recommends limit of total dissolved solid concentration of drinking water should be 1000mg/L (Hutton, 1996). Waters with high dissolved solids generally are of inferior palatability and may induce an unfavorable physiological reaction in the transient consumer.

2.2.5 Dissolved Oxygen

The oxygen comes into water through two processes. The first is photosynthesis. Plants and algae in the water produce oxygen during day time. Those same plants consume oxygen during the night. If there are many plants in the water, oxygen levels may increase as the day goes on and plants are photosynthesizing more. And oxygen also enters directly from the atmosphere. Tumbling water mixes and dissolves atmospheric oxygen. The presence of dissolved oxygen is essential to maintain the higher forms of biological life and to keep proper balance of various pollutants thus making the water body health. Therefore, dissolved Oxygen (DO) is an important parameter in water quality assessment and reflects the physical and biological processes prevailing in the water. 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. Generally, the DO levels in natural and waste water depend on the physical, chemical and biological activities in the water body. Its solubility is related to pressure and temperature. In fresh water , DO reaches 14.6mg/L at 0^0c and approximately 9.1, 8.3 and 7mg/L at 20^0c, 25^0c and 35^0c and 1 atmospheric pressure respectively (S. K maiti, 2004). The oxygen depleting substances reduces the available DO. During the summer months, the rate of biological oxidation is highly increased, while

unfortunately, the DO concentration is at its minimum due to higher temperature (APHA, 1999).

2.2.6 Alkalinity

Alkalinity is a normal characteristic of natural waters that provides buffering capacities and maintains the pH of water within the range from 6.5 to 8.5. Alkalinity in natural water is due to primarily to the carbonations. Alkalinity of water varies in concentration with geographical location, depending particularly up on the character of rocks and the soils in the area. Alkalinity of water is its capacity to neutralize a strong acid and it is normally due to the presence of bicarbonate, carbonate and hydroxide compound of calcium, sodium and potassium. The total alkalinity values for samples to be investigated are prescribed by (WHO, 2011).The results of alkalinity are usually reported as mg $CaCO_3$ per liter of water and calculated as follows:

Phenolphthalein alkalinity, (mg CaCO3)/L = $\frac{C \times N \times 50 \times 1000}{Volume\ of\ sample}$

Total alkalinity, (mg CaCO3)/L = $\frac{(C+D) \times N \times 50 \times 1000}{Volume\ of\ sample}$, where C is the volume in mL of HCl solution used to reach pH = 8.3, D is the volume in mL of HCl solution used to reach pH = 4.4, N is the concentration of standard HCl solution in normality, and V is the volume of sample in mL (Zhang, 2007 and Weiner, 2008).

2.2.7 Total Hardness

Hardness is the property of water which prevents the lather formation with soaps by formation of complex with calcium and magnesium present in water (B. Venkates wara Rao, 2011). Water hardness is determined by the concentration of multivalent cat ions in the water. Common cat ions found in hard water include Calcium cat ions and magnesium cat ions. Hardness in natural water is due to primarily to calcium and magnesium ions. Hardness is most commonly expressed as mg/L of $CaCO_3$. Calcium carbonate scales formed in water heating systems are called lime scale (Weingartner, 2006 and Nitsch *et al*., 2005). The non-carbonate hardness was called permanent hardness, because it cannot be removed by boiling. Non-carbonate hardness cations are associated with sulfates, chloride and nitrate ions of Ca and Mg. The surface waters are softer than the ground waters. The hardness of water reflects the nature of geological formation with which it has been in contact (Maiti, 2004).

2.3 Major Chemical Parameters

2.3.1 Calcium

The greatest concentration of Calcium comes from lime stone, gypsum and dolomite. Calcium is one of the most common elements on the earth (Williams, R.J.P, 1998).It dissolves out of almost all rocks and is, consequently, detected in many waters. An excess in calcium can alter the water taste or cause scaling problems in pipes and household appliances. In the reduction of the content of calcium and magnesium ions dissolved in water it is recommended that the calcium content never goes under 60 mg/L. The World Health Organization has recommended a minimum calcium daily intake of about 700 mg. Water with low concentration of calcium, may be associated with higher risk of fracture in children, certain neurodegenerative diseases, pre-term birth and low weight at birth and some types of cancer.

2.3.2 Magnesium

Magnesium is, with sodium and calcium, among the cat ions most commonly found in drinking water. Mg is an essential nutrient for plants and animals, essential for bone and cell development. The daily recommended in take is 150-500 mg/day, of which drinking water can supply from 12 to 250 mg/day, depending on the Mg concentration and assuming ingestion of 2 L/day. In general, the presence of Mg in water is beneficial and no limits on Mg have been established for protection of human or aquatic health (Weiner, 2008). There are no primary or secondary drinking water standards for Mg. Mg in drinking water may provide nutritional benefits for persons with Mg deficient diets (USEPA, 2006). Low magnesium content of drinking water seems to be associated with a higher risk of motor neuronal diseases, pregnancy diseases and some types of cancer (UNEP/WHO, 1996).

2.3.3 Chloride (Cl^-)

Chlorides concentrations are found in practically all natural waters; this is due to common inorganic anion present in the water. Man and animals excrete high quantities of chloride; therefore, it indicates sewage contamination (Soni H.B et al, 2013). Chloride in drinking water originates from natural sources (NaCl, KCl and $CaCl_2$), sewage and industrial effluents, urban runoff containing de-icing salt and saline intrusion. Excessive chloride concentrations increase rates of corrosion of metals in the distribution system, depending on the alkalinity of the water. No health-based guideline value is proposed for chloride in drinking-water. However,

chloride concentrations in excess of about 250 mg/l can give rise to detectable taste in water (WHO, 2011).

2.3.4 Sulfates (SO_4^{-2})

Sulfate occurs naturally in drinking water. They have detoxifying effect on the liver and stimulate the function of the gall bladder and the aid the digestive function as well. Sulfate in drinking water has a secondary maximum contaminant level of 250mg/L, based on aesthetic effects (that means taste and odor). SO_4^{2-} ions are discharged into surface water through industrial wastes and atmospheric deposition of SO_2 (USEPA, 2008).The presence of sulfate in drinking water may also cause noticeable taste and may contribute to the corrosion of distribution n system (WHO, 2008 and USEPA, 2012).

2.3.5 Nitrate (NO_3^-)

Nitrate is used mainly in inorganic fertilizers. Nitrates (NO_3^-) are essential source of nitrogen (N) for plants. The greatest use of nitrates is as a fertilizer; nitrates taken into the body are converted to nitrites. Nitrate levels in drinking water can also be an indicator of overall water quality. High concentrations of nitrate in surface or groundwater generally indicate agricultural contamination from fertilizers and manure seepage (California Department of Public Health, 2012; WHO, 2011). Surface water contains nitrate due to leaching of nitrate with the percolating water. Elevated nitrate levels may suggest the possible presence of other contaminants such as disease-causing organisms from sewage, pesticides, or other inorganic and organic compounds that could cause health problems. And also excess intake of nitrate causes methaemoglobinaemia in infants and suspect of certain form of cancer risk. The US Environmental Protection Agency has set the Maximum Contaminant Level of nitrate as nitrogen (NO_3-N) at 10 mg/L for the safety of drinking water. Nitrate levels at or above this level have been known to cause a potentially fatal blood disorder in infants under six months of age called methemoglobinemia or "blue-baby" syndrome (USEPA, 2012).

2.3.6 Phosphate (PO_4^{3-})

Phosphates are the naturally occurring form of the element phosphorous, found in many phosphate minerals. The highest values of phosphate concentration in the river water is due to the discharge of disposal of phosphate from the disposal of domestic sewage and surface run-off from phosphate containing fertilizers deposits and links with the surface running water (K.

Esengul *et al.*, 2014). Phosphate may occur in river water as result of domestic sewage, detergents, and agricultural effluents with fertilizers.

2.3.7 Sodium (Na)

Sodium is an element very diffused on earth and in the biosphere; even if in nature it is almost never in its pure form, but mainly in form of salt (NaCl). However, the taste does not always indicate safeness. Sodium compounds are used in many applications, including caustic soda, salt, fertilizers and water treatment chemicals (APHA, 1999). Sodium is an important constituent for determining the quality of irrigation water. Most Na salts are readily soluble in water, but take no active part in chemical reactions. The taste threshold concentration of Na in water depends on the associated anion and the temperature of the solution. At room temperature, the average taste threshold for Na is about200 mg/L. No health-based guideline value has been derived for Na in drinking water, as the contribution from drinking-water to daily intake is small (WHO, 2011).

2.3.8 Potassium (K)

Potassium is an essential element in humans and other living organisms (Csuros M and Csuros. C, 2002). The average abundance of K in the earth's crust is 1.84%; in soils it has a range of 0.1 to 2.6%; in streams it is 2.3mg/L, and in ground waters it has a range of 0.5 to 10mg/L. Generally, K occurs widely in the environment, including all natural waters. Potassium is deficient in rare but many led to depression, muscle weakness; heart rhythm disorder etc, according to WHO (2004) standard concentration of potassium in drinking water is 12 mg/L.

2.4 Heavy Metals

The term heavy metal refers to metallic chemical elements that have relatively high density, toxic or poisonous at low concentration values. Heavy metal contamination is a major environmental concern due to the toxicity, carcinogenicity and mutagen city even at low concentration. They can cause damage to practically all organs of the body. The main sources of the heavy metal ions directly are food and water and indirectly, industrial activities. Drinking water is also an important source for heavy metals for humans (Afzali *et al.*, 2005 and Shishehbore *et al.*, 2005). Some of these metals exhibit extreme toxicity even at low levels under certain conditions (B.A Osuntogun and M.U Nzenna et al., 2004). In this regard, WHO

set an international reference point as standard for safe drinking water (WHO, 2004 and FDRE MoH, 2011).

2.4.1 Health Concerns of Some Heavy Metals (Mn, Cu, Pb, Cd)

Manganese (Mn) is an essential element for humans and animals. No health-based guideline value for Mn in drinking-water is proposed since it is not of health concern at levels found in drinking-water and is one of the most abundant metals in Earth's crust, usually occurring with iron (WHO, 2011). It does not occur in nature as the elemental metal (free in nature), but is found in various salts and minerals, frequently along with iron compounds. Soils, sediments, and metamorphic and sedimentary rocks are significant natural sources of Mn (Weiner, 2008). Mn is a ubiquitous element that is essential for normal physiologic functioning in all animal species. Manganese concentration higher than 0.1mg/L is considered as unsafe for industrial and domestic use (WHO, 1996). Health problems in humans may arise from both deficient and excess intakes of Mn. It is present in high concentration in mitochondrial fraction of human kidney, liver, and pancreases. Very large doses of infested Mn can cause some diseases and liver damages (Underwood, 2000). In natural waters, a substantial fraction of Mn is present in suspended form. In surface waters, divalent manganese (Mn^{2+}) is rapidly oxidized to insoluble manganese dioxide (MnO_2), which then precipitates as a black solid often observed as black stains on rocks. In drinking water distribution systems, precipitation of MnO_2 may cause unsightly black staining of fixtures and laundry (WHO, 2011 and Weiner, 2008). Thus any quantitative risk assessment for Mn must consider that, although Mn is an essential nutrient, excessive intake causes toxic symptoms (Weiner, 2008).¨

Copper (Cu) is considered as an essential trace element for plants and animals. Cu in a drinking water supply usually arises from the corrosive action of water leaching Cu from Cu pipes in buildings. High concentrations can interfere with the intended domestic uses of the water. Staining of sanitary ware and laundry may occur at Cu concentrations above 1 mg/L. Contamination of drinking water with high level of copper may lead to chronic anemia (Acharya et al., 2008). Copper compounds are used in fungicides, algicides, insecticides and wood preservatives. Copper compounds can be added to fertilizers and animal feeds as a nutrient to support plant and animal growth (Landner and Lindestrom, 1999; ATSDR, 2002). Copper sulfate pentahydrate is sometimes added to surface water for the control of algae (NSF, 2000). Copper(II) ion is the major species in water up to pH 6; at pH 6–9.3, aqueous

CuCO3 is prevalent; and at pH 9.3–10.7, the aqueous $[Cu(CO_3)_2]^{2-}$ ion predominates (Stumm and Morgan, 1996).The effects are much higher in children under one year old than adults. However, long term exposure which is more than 14 days to copper in the drinking water can cause serious problems like kidney and liver damages in infants (Solylak *et al.*, 1998).

Lead (Pb), has an atomic number 82, atomic weight 207.19, and a specific gravity of 11.34. Lead accounts for most cases of pediatric heavy metal poisoning (Roberts, 1999). The main sources of lead entering an ecosystem are atmospheric lead (primarily from automobile emissions), paint chips, used ammunition, fertilizers and pesticides and lead-acid batteries or other industrial products. Lead is non-essential for plants and animals (APHA, 1999). It is one of the metals that have the most damaging effects on human health. It can enter the human body through uptake of food, water and air. High concentration of lead in the body can cause death or permanent damage to the central nervous system, brain, and kidneys (Hanaa *et al.*, 2000).

Cadmium (Cd), is non essential for plants and animals. There is no evidence indicating its essentiality to humans (Hogan, 2010). Cadmium is introduced into the environment from paint and pigments, and plastic stabilizers, mining and smelting operations and industrial operations, including electroplating, reprocessing cadmium scrap, and incineration of cadmium containing plastics. It is used in nickel-cadmium batteries, PVC plastics, and paint pigments. Cadmium can be found in soils because insecticides, fungicides, sludge, and commercial fertilizers that contain cadmium are used in agriculture. Cadmium emissions are also from fossil fuel use and cigarettes. It may enter drinking water as a result of corrosion of galvanized pipe. Cadmium dispersed in the environment can persist in soils and sediments for decades. At higher concentrations, it is known to have a toxic potential. Cadmium is highly toxic and responsible for several cases of poisoning through food. Small quantities of cadmium cause adverse changes in the arteries of human kidney. It replaces zinc biochemically and causes high blood pressures, kidney damage etc (Rajappa *et al.*, 2010). A drinking water guideline value of 0.005 mg/l has been set for cadmium (WHO, 2011)

2.4.2 Analytical Methods for Heavy Metal Analysis.

The analysis of heavy metals was carried out by atomic absorption spectrometry (FAAS) as recommended United States Environmental Protection Agency (USEPA). Atomic absorption

Spectrometry (AAS) is an analytical method for quantification of different elements in solution samples. The atomic absorption uses essentially monochromatic radiation to excite vaporized atoms in their ground state. The instrument consists of a light source, a cell (consisting of the aspirated sample), a monochromator and a detection system. The light source usually a hallow cathode tube emits essentially line radiation of the same wave length as that being absorbed by the element under study. This is accomplished by making the source out of sample element. Thus if Cu is to be determined a lamp having a copper cathode is used (Maiti, 2004). Therefore; samples was analyzed for heavy metals by FAAS from the time of sample collection. The samples filtered in order to remove coarse particles to preserve the analytical instrumentation and then, the filtrate was acidified with concentrated nitric acid (69-72% HNO3) by adding 10mL of the acid into 100 mL of the sample solution. The acidified samples were preserved in refrigerator for analysis.

3. MATERIAL AND METHODS

3.1 Description of the Study Area

The study was carried out in Oromia National Regional State of Kiramu District. Kiramu is one of the District found in East Wollega Zone of Oromia Regional State, Ethiopia, at total distance of 328 km from capital city of Ethiopia, Addis Ababa and 140 km from capital of Zone, Nekemte, Western part of Ethiopia. According to the recent statistical data the Kiramu District has 19 kebeles with a total population greater than 83,000 (Kiramu District Bureau). From this kebeles Kiramu, Bagin, Babo, Lalistu Sombo, Tokuma-Kokofe, Marga-Jiregna and Gudina-Jirenga are the most populated areas (information from Kiramu District Bureau). The agro-ecological and climate conditions involves of the study area are three highland area, middle highland and lowland area. There are several rivers in surrounding areas, for example Burqa-Walda, Qalle-river, Halaltu-river, Dubuq-river and Libano-river are the dominant rivers found in surrounding area (information from Water and Irrigation Bureau). Since majority of the societies are depend on agricultural activities and this drinking river water may be contaminated by agricultural activities through soil erosion .To estimate these different factors affect the quality of river water consumed in Babo Kiramu the samples was collected from three sites of Qalle River water (the up-stream, the middle-stream and the down-stream).

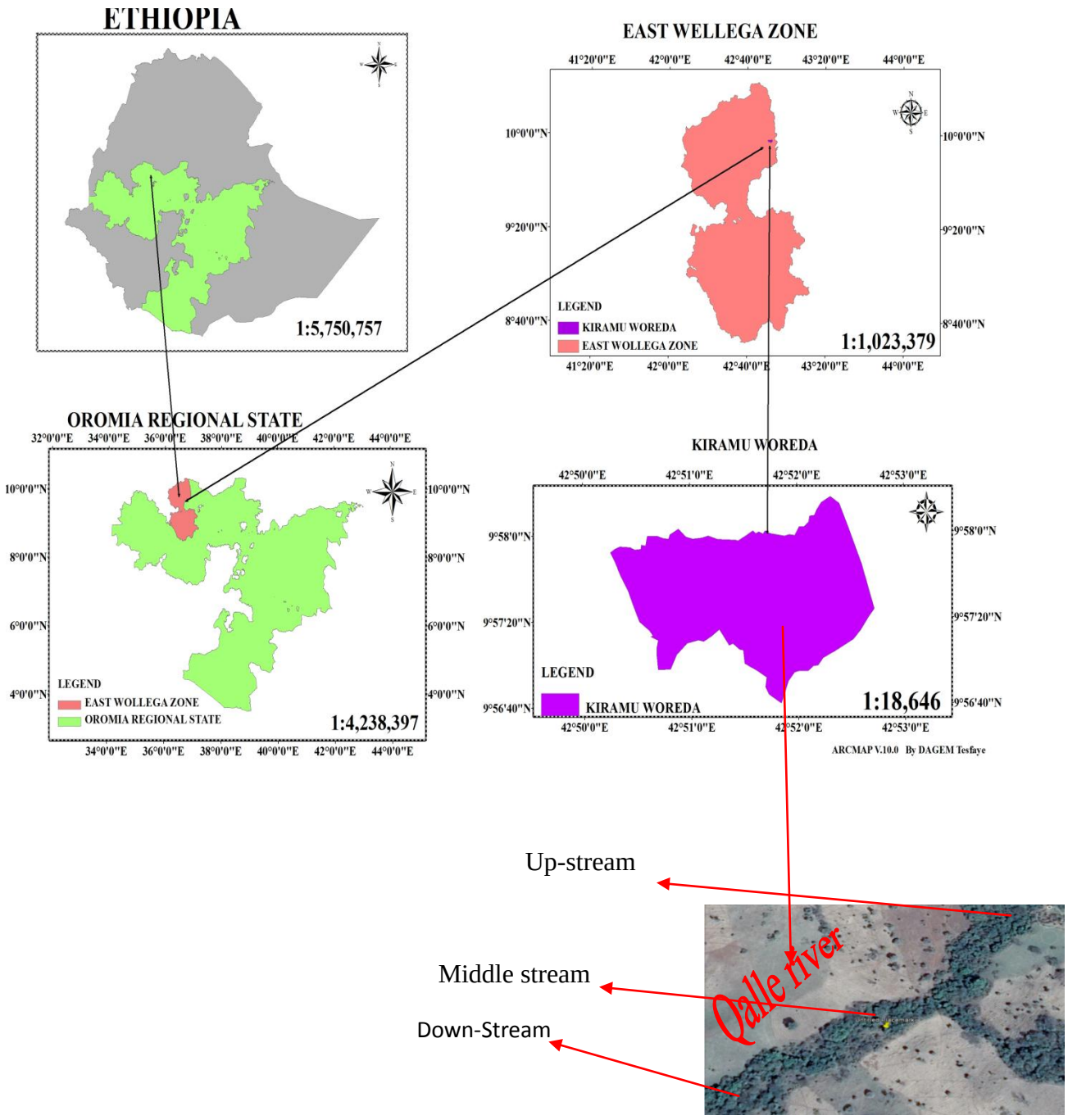

Fig. 1 Map of the study area.

Source: A.R.T MAP V 10.1.

3.2 Cleaning procedures of sampling equipment

The water samples for analysis of physico-chemical parameters were collected in contaminant-free plastic bottles. All sampling polyethylene bottles were thoroughly washed with tap water and detergent, rinsed with distilled water and then soaked with 10% (v/v) HNO_3 for 24 hrs. And the containers were rinsed with de-ionzed water before being used for sampling. Containers were finally rinsed with sample water prior to actual sample collection before being used for sampling. Polyethylene bottles used for water sampling of PO_4^{-3} analysis was thoroughly washed with tap water and well rinsed with chromic acid followed by distilled water. For heavy metals analysis samples were preserved by acidifying with 1.5mL con. HNO_3 to pH< 2, immediately after sampling then stored in refrigerator at 4^0C. Sample containers were labeled on the field using appropriate code as S_U, S_M, S_D for identification.

3.3 Water Sample Collection and Preservation

After preliminary surveys of sampling sites for one day the three sampling sites were identified based on the assess and objective of the study. After identification of sampling sites, a total of 15 water samples were collected in pre cleaned polyethylene bottles from three sampling sites of Qalle River during the dry season. Representative Qalle River water samples from selected sites, with a distance of 500 m from each were collected for analysis. The point of sample collections were selected based on the agricultural activities around the area and suspected pollutants that leached to the Qalle River water. That means, the first site (upstream) was selected because the site is used only by domestic animals; the second site (middle stream) was selected because the area is used for residential area and water is used for bathing, laundry and used by domestic animals. The third point of sample site (downstream) is selected because the site is surrounded by agriculture, used for laundry and also used by domestic animals. All samples were collected in same day in containers. Representative water samples from sampling sites were collected into polyethylene bottles by grab sampling technique. In each grab sampling techniques minimum of 100 mL to 250 mL sample was collected. For each sampling sites grab method of sampling is used for day break, noon and evening time. A total of 12 liters were collected from all site and 4 liters were collected from each sites. Composite sample is the mixture of grab samples collected at the same sampling point at different times and these samples were used for analysis, because the composite sample can

provide more meaningful data than grab samples (S. K. Maiti, 2004). The samples were collected in the month of April, 2009 from three points per a day at daybreak, noon and evening time. The composite sample containing bottles were preserved at a temperature of 4^0C. The bottles that contain composite samples were preserved using ice-box and transported to Addis Ababa University for analysis and reached before 48 hrs after total sample collection. The collected water samples were kept in refrigerator at 4^0c in the Addis Ababa University with that of plastic polyethylene bottles at the same temperature until the time of analysis.

Table 1 Detailed Sample location**.**

Location code	Location name	Specific area water to be sampled	Type of water sample
Up-Stream	Babo	Qalle River	River water
Middle-Stream	Babo	Qalle River	River water
Down-Stream	Babo	Qalle River	River water

3.4 Glass Wares and Instruments

Polyethylene bottles, Ice-box, a mercury thermometer (0-100^{0}C), Portable pH-meter, portable conductivity meter (model LF 90), beakers, stirrers, desiccators, drying oven, DR/2000 spectrophotometer for SO_4^{-2} determination, FAAS (model ZEEnit 700p, Germany), volumetric flasks (50, 100, 250, 500 and 1000 mL), volumetric pipettes (1, 5 and 10 mL), burette (50 mL), measuring cylinder (10, 25 and 50 mL), beakers (250 mL), a hot plate, glove, spatula, filter paper (Whatman®, No. 41, England), electronic analytical balance with ±0.00001 g precision (AA-200DS, Denver Instrument Company), ELICO-SL 164 UV-Vis Spectrophotometer for PO_4^{-3}, NO_3^- determination , SpectrAA.20 Plus Flame Photometer for determination of Na and K.

3.5 Chemicals and reagents

All chemicals and reagents were of analytical grade. Con. HNO_3 (69-72%, UNI-CHEM® Chemical reagents, India), was used for the sample digestions. For heavy metal analysis commercially available certified reference material (CRM) 1000mg/L (Geological Survey of

Japan. Geochemical Certified Reference Materials) stock standard solution of each metal (Pb, Cu, Cd and Mn) solutions were used. 2.542g of NaCl (99.80%, UNI-CHEM® Chemical reagents, India) and 1.907g KCl for preparation of stock solution of Na and K respectively. 1.627g KNO_3 (99%, General Purpose Reagent, BDH Chemicals Ltd Poole England) for preparing stock solution of NO_3^- and anhydrous extra pure 1.433g K_2HPO_4 (98-99%, KIRAN LIGHT LABORATORIES™) were used for the preparation of PO_4^{3-} stock solution. Disodium salt of EDTA (99%, UNI-CHEM® Chemical reagents, India), EBT (99.5%, UNICHEM® Chemical reagents, India), Na_2CO_3 anhydrous (99%, Scientific Limited Northampton, United Kingdom) and $CaCO_3$ (96%, FINKEM, Analytical grade crystals) were used for determination of total hardness. H_2SO_4 (96.0-98.0%, UNI-CHEM® Chemical reagents, India) was used for determination of total alkalinity. $AgNO_3$ (99%, LOBA CHEMIE PVT.LTD.INDIA) was used for argentometric titration for the determination of chloride. $BaCl_2$ (UNI-CHEM® Chemical reagents, India) was used for determination of SO_4^{2-}. Distilled water was used for all preparations and dilutions of solutions.

3.6 In situ Analysis

3.6.1 Temperature

Temperature was measured with a mercury thermometer ($0\text{-}100^0$c) for each grab of samples and average value was used. Readings were made with the thermometer immersed in water long enough to permit complete equilibration (APHA, 1999).

3.6.2 pH

pH of Qalle Water was measured with a portable pH-meter (Model HI 9023). The pH-meter was calibrated with buffer solutions of pH 4, 7.0 and 9.2 according to the procedures given on the manufacturer's instruction manual.

Procedure: Calibrating the pH meter with buffer solutions of pH of 4.0, 7.0 and 9.2.

- Buffer of different pH was prepared by dissolving commercially available standard buffer tablets in 100mL distilled water.
- The pH meter was calibrated before and after measurements prior to each site.
- After calibration, rinse the probe with distilled water and place in sample solution.
- Establish equilibrium between electrodes and sample by stirring sample to ensure homogeneity.

- Finally, observe and record the pH value.

3.6.3 Electrical Conductivity (EC)

The electrical conductivity (EC) was measured with the help of portable conductivity meter (Model LF 90). Standard KCl (0.01M) was prepared by dissolving 0.7456g anhydrous KCl in distilled water and make up to 1000mL at 25^0C.This is standard reference solution , which at 25^0C has a specific conductance of 1412 μs/cm used to calibrate conductivity meter.

Procedure:

- ✓ Rinse the conductivity cell with at least three portion of the sample.
- ✓ Adjust the instrument to 1412 by increasing or decreasing temperature that is found on the instrument.
- ✓ Immerse the conductivity cell in to the solution.
- ✓ Observe and record the conductivity in μs/cm.

3.7 Laboratory Sample Analysis

3.7.1 Dissolved Oxygen (DO)

The measurement of dissolved oxygen in water samples were done by Azide modification method as described below:

Procedure:

- Add the sample in bottle (300 mL).
- Add 1mL of manganese sulfate followed by 1 mL of alkali-iodide-azide solution.
- Place the stopper carefully to exclude air bubbles and mix by inverting the bottle repeatedly for at least 15 minutes. Allow the precipitate to settle leaving about 150 mL of clear supernatant.
- Carefully remove the stopper and immediately add 1 mL of conc. H_2SO_4, close the bottle and mix with the gentle inversion until the precipitate completely dissolves.
- Titrate 100 mL contents of the bottle with 0.25N sodium thiosulphate solution using starch as an indicator.
- At the end point the blue color turns to colorless.

Calculation: When only a part of the sample of the content is titrated, that means 100 mL

DO in mg/L=$\frac{mL\ of\ titrant \times Normality \times 8 \times 1000}{Volume\ of\ Sample}$

3.7.2 Total Dissolved Solid (TDS)

Procedure:

- ✓ Take evaporating dish of suitable size (a 500mL capacity beaker), make it clean, dry at 105^0C, cool in a desicator and note initial weight (W_1).
- ✓ Filter about 100mL of sample through filter paper (Whatman No 41) and take the filtrate in the evaporating dish.
- ✓ Evaporate the sample in hot air oven at 180^0C, after the whole water is evaporated, cool the evaporating dish in a desicator and take the final weight (W_2).

Calculation: TDS (mg/L) = $\frac{W2-W1}{V} \times 1000 \times 1000$ Where; W_1= Initial weight of evaporating dish, W_2= Final weight of evaporating dish, V= volume of sample taken (mL) (S.K. Maiti, 2004).

3.7.3 Classical Methods of Analysis

All parameters including total hardness (EDTA Titrimetric Method 'Section 2340 C'), calcium (EDTA Titrimetric Method 'Section 3500-Ca B'), magnesium (Calculation Method 'Section 3500-Mg B'), and chloride (Argentometric Method 'Section 4500-Cl– B') were analyzed following the procedures given by a standard method (APHA, 1999). Total alkalinity was determined by titrimetric method following the procedure given by handbook of methods in environmental studies (S. K. Maiti, 2004).

3.8 Instrumental Methods of Analysis

3.8.1 Atomic Absorption Spectrophotometric Analysis (AAS) of Heavy Metals

Heavy metals such as Pb, Cu, Cd and Mn were analyzed by FAAS with the model of ZEEnit 700p at Addis Ababa University. AAS equipped with deuterium ark background correctors, cathode lamp for each respective element, and air-acetylene flame was used.

3.8.1.1 Digestion of sample with nitric acid for metal analysis

Digestion is used to increase the concentration of the metals (analytes) that is found in the water sample by evaporating the water solution and to convert metals associated with particulates to a form usually the free metal that can be determined by atomic absorption spectrometry.

Procedure:Mixing (homogenizing) precisely the sample in its container.

- ✓ Taking 100mL of sample into conical flask using measuring cylinder.
- ✓ Addition of 10mL con. HNO_3.
- ✓ Bring to a slow boil and evaporate in digester to about 20mL.
- ✓ Continue heating until digestion is complete as digestion shown by clear solution.
- ✓ Wash down the walls of the beaker with distilled water and then filter.
- ✓ Transfer the filtrate to a 50mL volumetric flask, cool and make up the volume.
- ✓ Use portion of this solution for required metal analysis.

3.8.1.2 Analytical procedures for metal analysis and standard preparation.

In this study, the concentrations of Pb, Cu, Cd and Mn in Qalle River water available in Kiramu Babo the up-stream; Middle-stream and Down-stream water samples were quantitatively determined using FAAS. Stock solution was used to prepare intermediate standard solution and then from intermediate standard solution working standard solutions were prepared for each analyte from their stock solutions. For Pb, Cu, Cd and Mn commercially available stock standard solution of 1000 mg/L were used; For Na 1000 mg/L of stock standard solution was prepared by dissolving 2.542 g NaCl in distilled water and make up to 1000 mL. For K 1000 mg/L stock standard solution was prepared by dissolving 1.907 g of KCl in distilled water and diluting to 1000 mL. For nitrate 1000 mg/L of stock standard solution was prepared by dissolving 1.627 g of KNO_3 in distilled water and diluting to 1000 mL. For phosphate 1000 mg/L of stock standard solution was prepared by dissolving 1.433 g of anhydrous KH_2PO_4 in distilled water then dilute to 1000 mL.

3.8.1.3 Preparation of Working Standard Solutions

1000 mg/L stock solutions of each analyte were used to prepare 100 mg/L intermediate standard solutions. The 100 mg/L of each analyte was used to prepare the 10mg/L working standard solutions. Finally working standards were taken from this solution and added to 10 mL sample holder and dilute with distilled water till 10 mL. For Na, K, NO_3^- and PO_4^{-3} intermediate standard solutions were prepared from each of their 1000 mg/L stock solutions separately. From 1000 mg/L stock solution 100 mg/L intermediate standard solution 10 mg/L was prepared in separate 50 mL volumetric flask and diluting it with dionized water.

Four points of calibration curves were established by running the prepared standard solutions in flame atomic absorption spectrometer to check the instrument performance. Immediately

after calibration, the sample solutions were aspirated into the FAAS instrument and readings of the metal concentrations were recorded. Three replicate determinations were carried out on each sample for accuracy. The same analytical procedures were employed for the determination of elements in six blank samples. Therefore, in the use of FAAS for trace metal analysis optimization of the operating conditions is very critical. Wave length, energy, lamp current and burner alignment and slit width were optimized for Lead, Copper, Cadmium and Manganese analysis (Table 3).

3.8.1.4 Calibration Curves

The calibration curve was used to check the instrument performance and as soon as the concentration of heavy metals in water samples were measured by the instrument. The calibration curves for each metal were preparing four concentration of known solution versus its corresponding absorbance measured by FAAS as shown in Table 2.

Table 2 Concentration of standard solutions for FAAS instrument calibration, correlation coefficient and regression equation of calibration curves.

Heavy metal	Concentration (mg/L)	Absorbance	Correlation coefficient (R^2)	Regression equation.
Pb	1	0.028	0.999	Y=0.030x-0.002
	2	0.059		
	3	0.088		
	4	0.119		
Cu	0.25	0.057	0.999	Y=0.223x+0.002
	0.5	0.116		
	1	0.225		
	2	0.45		
Cd	0.25	0.112	0.999	Y=0.417x+0.008
	0.5	0.223		
	1	0.419		
	2	0.845		
Mn	0.25	0.042	0.999	Y=0.100x+0.017
	1	0.118		
	1.5	0.169		
	2	0.218		

3.8.1.5 Determination of the heavy metals concentration in water sample by FAAS.

The concentration of Pb, Cu, Cd and Mn were determined by FAAS using air/acetylene flame. The heavy metals were analyzed by further diluting the acidified samples. Dilution was required to bring the concentration of the metals within the linear range of the calibration curve. All the analysis were carried out using FAAS at the specific wave length for each heavy metal, as shown in Table 3.

Table 3 The instrument operating conditions for determination of heavy metals in the water samples by FAAS.

Element	Wavelength (nm)	Current (mA)	Energy	Slit Width(nm)	Instrumental detection limit (mg/L)	Oxidant/Fuel
Lead	283.3	2	71.5	1.2	0.06	Air-C_2H_2
Copper	324.8	2	73.5	1.2	0.007	Air-C_2H_2
Cadmium	228.8	2	82.2	1.2	0.0024	Air-C_2H_2
Manganese	279.5	2	90	0.2	0.006	Air-C_2H_2

3.8.1.5.1 Recovery test result for Pb, Cu, Cd and Mn

Table 4 Mean percent recovery obtained from analysis of heavy metals by FAAS.

Sample sites	Parameters	Concentration (mg/L)				
		Un-Spiked sample	Spiked sample	Amount Added	Amount found	Percent of recovery
Up-stream	Pb	BDL				
	Cu	0.545	1.029	0.5	0.484	96.86
	Cd	BDL				
	Mn	0.273	0.831	0.5	0.558	89.6
Middle Stream	Pb	BDL				
	Cu	0.599	1.089	0.5	0.490	98.07
	Cd	BDL				
	Mn	0.368	0.906	0.5	0.538	89.6
Down Stream	Pb	BDL				
	Cu	0.676	1.154	0.5	0.478	95.65
	Cd	BDL				
	Mn	0.443	0.8935	0.5	0.4505	89.8

Amount found = Amount spiked sample value - Amount un spiked sample value.

Percent recovery = $\frac{Amount\ found}{Known\ amount\ of\ standard\ added} \times 100$

Or Percent recovery = $\frac{Spiked\ sample\ value - Un\ spiked\ sample\ value}{Known\ amount\ of\ standard\ added} \times 100$

The percentage recoveries laid in between 89.6 to 98.07 for FAAS as described in Table 4. These imply that, the measured results are within acceptance range which is all within the recommended range for the matrix spike recovery 80% - 120% (APHA, 1999). Implies that good recoveries were obtained in all samples validating that the obtained digestion procedure has good accuracy.

3.8.2 Analysis of Na and K using Flame photometry

Flame photometric method was used for the analysis of Na and K based on the principles of emission of electromagnetic radiation in the visible and ultraviolet regions of the spectrum by atoms after electronic excitation in flames (Fifield and Kealey, 2000; Jeffery *et al*., 1989).

Table 5 Flame photometric Working conditions.

Parameter	Wave length(nm)	Flame gases
Na	589	Air-Acetylene
K	769	Air-Acetylene

Na and K were determined based on emission spectroscopy, which deals with the excitation of electrons from ground state to higher energy state and coming back to its original state with the emission of light. The solution is sprayed as a fine mist into a non-luminous flame, which becomes colored according to the characteristic emission of the metal. Emission light intensity is measured by a photo-detector at a wave length of 589 nm for Na and at 769 nm for K. The intensity of light emitted is approximately proportional to concentration of the element of interest in solution (APHA, 1999).

Procedure was done by preparing of calibration standards in the range of 1 to 9 mg/L because the calibration standard concentrations were within the working linear range of the instrument used for analysis. By following manufacturer's recommendation for selecting proper wave length, adjusting slit width and sensitivity appropriate fuel and oxidant gas pressures determine emission intensity at 589 nm for Na and at 769 nm for K.

For Sodium and Potassium Calibration Data four points of calibration standards were used to check instrument performance.

Table 6 the Mean percent recovery obtained from spiking Analysis of Na and K.

Sampling Sites	Parameters	Un-spiked sample(mg/L)	Spiked sample(mg/L)	Amount Added(mg/L)	Amount Found(mg/L)	Percent Recovery
Up-Stream	Na	7.50	8.53	1	1.03	103
	K	5.17	6.09	1	0.92	92
Middle Stream	Na	7.20	8.11	1	0.91	91
	K	5.03	6.90	1	0.87	87
Down Stream	Na	4.67	5.65	1	0.98	98
	K	5.17	6.05	1	0.88	88

Laboratory fortified matrix (LFM) is an additional portion of a sample to which known amounts of the analytes of interest are added before sample preparation and processed through all of the sample preparation and analysis steps. The LFM is used to evaluate analyte recovery in a sample matrix. The analysis of LFM was done by spiking the sample with concentration at near mid range calibration for each analytes. The percent recovery obtained from the matrix spike results was used to estimate the accuracy of the method in the presence of interference effect and it was calculated as follow (APHA).

%Recovery on spike = $\frac{Spiked\ sample\ value - unspiked\ sample\ value}{Standard\ added}$ x 100

3.8.3 Analysis of PO_4^{-3} and NO_3^- Using UV-Vis Spectrophotometric Method.

Table 7 UV-Vis spectrophotometric Working conditions

Parameter	Wave length(nm)	Band pass (nm)	Cell type (cm)	Cell length
Phosphate(PO_4^{-3})	690	2.6	Quartz	1.0
Nitrate (NO_3^-)	220 and 275	1.8	Quartz	1.0

UV-Vis Spectrophotometric method was used for the analysis of NO_3^- and PO_4^{3-} based on the Principles of absorption of electromagnetic radiation in the visible and ultraviolet regions of the Spectrum resulting changes in the electronic structure of ions and molecules (Fifield and Kealey, 2000; Jeffery *et al*., 1989).

3.8.3.1 Phosphate (PO_4^{-3})

The phosphate concentration in water samples were determined by the procedure recommended by APHA (1995).

3.8.3.1.1 Calibration and Linearity of Instrumental Response of Phosphate (PO_4^{-3})

Calibration curves showing absorbance versus concentration were prepared by direct analysis of four calibration standard solutions.

Table 8 Calibration graph of phosphate.

Parameter	Concentration (mg/L)	Absorbance	Correlation Coefficient(R^2)	Regression equation
Phosphate	0.25	0.181		
	0.5	0.334		
	0.75	0.50	0.998	Y=0.671x+0.005
	1	0.685		

As observed from calibration curve the correlation coefficient value of phosphate is 0.998 (Table 8). The value is greater than the minimum correlation coefficient of 0.995 which is given by (APHA, 1999). Therefore, it indicates the good relationship between the instrument response and verified concentration.

3.8.3.2 Nitrate (NO_3^-)

The nitrate in water samples was determined by ultraviolet spectrophtometric screening method recommended by S.K Maiti (2004).

3.8.3.2.1 Calibration and Linearity of Instrumental Response of Nitrate (NO_3^-)

Calibration curves of nitrate showing absorbance versus concentration were prepared by direct analysis of four calibration standard solution at specific wave length.

Table 9 calibration graph of nitrate.

Parameter	Concentration(mg/L)	Absorbance	Correlation coefficient(R^2)	Regression Equation.
Nitrate	0.25	0.015	0.998	Y=0.037x+0.005
	1	0.045		
	1.5	0.061		
	2	0.082		

Table 10 Recovery test result for the mean concentration of PO_4^{-3} and NO_3^- by UV-Vis Spectrophotometer.

Sample Sites	Parameters	Concentration (mg/L)				
		Un-Spiked sample	Spiked sample	Known amount of standard Added	Amount Found	%Recovery
Up steam	PO_4^{-3}	0.25	0.54	0.3	0.29	96.7
	NO_3^-	0.470	0.86	0.4	0.39	97.5
Middle Stream	PO_4^{-3}	0.307	0.604	0.3	0.297	99
	NO_3^-	0.420	0.84	0.4	0.42	105
Down Stream	PO_4^{-3}	0.333	0.64	0.3	0.307	102.3
	NO_3^-	0.513	0.93	0.4	0.417	104

Tables 10 shows that the mean recoveries were found within acceptable range which are all within the recommended range for the matrix spike recovery 80% - 120% (APHA, 1999). Thus good recoveries were obtained in all samples validating that the obtained procedure has good accuracy and precision.

3.8.4 Turbidimetric Method For Analysis SO_4^{-2}

The stock standard solution of sulfate was prepared by dissolving 0.147g of anhydrous Na_2SO_4 in distilled water and diluted to 1000 mL. Then from 1000 mL stock solution the intermediate standard solution was prepared. 10 mL was taken from 1000 mL of the stock solution into 100 mL to prepare 100 mg/L and then make up the volume. From 100 mg/L of intermediate standard solution 50 mL was taken in to 100 mL to prepare 50 mg/L and make up the volume. Then the working standards were taken from 50 mg/L of the solution. The concentration of sulfate in water samples was determined by turbidimetric method following the procedure given by handbook of methods in environmental studies (S. K. Maiti, 2004).

3.8.5 Quality Control /Quality Assurance Procedure

3.8.5.1 Preparation of Calibration Standard Solutions

The effectiveness of any monitoring effort depends on its QC program (Weiner, 2007). Because quality control is the set of principles and practices, which, if strictly followed in a sampling and analysis program, it can produces data of known and defensible quality. The calibration standard solutions were used to calibrate the instrument response with respect to the analyte concentration. Standard solutions of five points including calibration blank were prepared for each analyte from their respective intermediate standard solutions from 10 mg/L for metals and also 10 mg/L for NO_3^- and PO_4^{-3}. The calibration standard concentrations were within the working linear range of the instrument used for analysis.

3.8.5.2 Determination of Method Detection Limit

The method detection limit 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. The general accepted definition of method detection limit is the concentration that gives a signal three times the standard deviation of the blank or background signal (Peter, E. J, Kirk, C, 2002). In this study method detection limit for the analysis of heavy metals using FAAS in water samples were determined from reagent blank, that means 10 mL of concentrated nitric acid (69-72% HNO_3), which was used for acidifying the sample solutions, were added to 100 mL of distilled water that was used for washing apparatus and for the dilution of standard solutions. For nitrate and phosphate analysis 100 mL distilled water plus 1N of 1mL HCl and 100 mL distilled water plus 4 mL molybdate reagent plus 0.5 mL

stannous chiloride reagent-I were used as laboratory reagent blank (LRB), respectively (APHA, 1999). Then from these measurements, the standard deviation (S) was calculated. And then the method detection limit of each element was determined as three times the standard deviation of the blank solution (3σBlank, n=6). In this study the method detection limit was done by taking six blank samples. For heavy metals (Pb, Cu, Cd and Mn) by applying the same procedure as the sample and then each of the analyts were (Pb, Cu, Cd and Mn) determined from the sample by FAAS.

Table 11 Instrument method detection limits for the analysis of water samples by FAAS, Flame photometry and UV-Vissible spectrophotometer.

Detection Limits				
Element	Technique	IDL(mg/L)	Standard deviation of the blank (mg/L)	MDL(mg/L)
Pb	FAAS	0.06	0.043	0.129
Cu	FAAS	0.007	0.028	0.084
Cd	FAAS	0.0024	0.055	0.165
Mn	FAAS	0.006	0.07	0.21
Na	Flame Photometer	0.03	0.047	0.141
K	Flame Photometer	0.11	0.44	0.132
PO_4^{-3}	UV-Vis spectrophotometer	0.057	0.231	0.693
NO_3-	UV-Vis spectrophotometer	0.063	0.307	0.921

As observed from the Table 11 above the value of instrumental detection limit (IDL) given for each analyte was below the method detection limit(MDL) indicating good sensitivity of the measuring instrument for the analysis and MDL were greater than the IDL, hence the result of the analysis could be reliable. The instrumental detection limit was gained from the instrument

for each analyte. The standard deviation was calculated from blank sample and the method detection limit was calculated from three times the standard deviation of the blank sample solution.

3.8.6 Recovery Test

Method validation is a way of testing a particular analytical method to see if it is suitable for its intended purpose. The validation process begins in method development in that the documentation, reporting the validation data must include a record of the method development process, giving details of the conditions explored and the rational of the progression of the process .The accuracy of the analytical procedure was investigated by spiking a suitable known amount of the analyte into the sample having a known concentration of the analyte and analyzing the spiked sample along with the original sample. In order to evaluate the validity of the analytical procedure, the recovery test was done for heavy metals by taking samples into one flask as; first 1000 mg/L stock solution of certified reference material was bought commercially. That is from 1000 mg/L heavy metals standard stock solution which was used for preparation of 100mg/L intermediate standard solution and then from intermediate standard solution 10mg/L working standards were prepared. Then from working standards of each stock metal solution 1 ppm of lead, 0.5 ppm of Copper, 0.5 ppm of Cadmium and 0.5 ppm of Mn, standard solution were spiked in to the sample . That is 1 mL of Pb, 0.5mL Cu, 0.5 mL of Cd and 0.5 mL of Mn were taken from the working standards. Then the same digestion procedure was followed for non-spiked and spiked sample. The same analytical procedure was followed for non-spiked and spiked water samples side by side. Each sample was analyzed for their respective spiked metals by AAS. The recovery test for sample was performed in triplicate .Triplicate of the spiked samples was taken and evaluated with non-spiked samples and finally the recovery tests were calculated by the formulas given bellow :

$$\% \text{ Recovery} = \frac{(Mean\ of\ the\ spiked\ sample - mean\ of\ non\ spiked\ sample)\left(\frac{mg}{L}\right)}{Amount\ standard\ Added\ \left(\frac{mg}{L}\right)}$$

3.8.7 One-Way Analysis of Variance (ANOVA)

The obtained data were also treated with one-way ANOVA to assess the variations of the parameters among the sites of Qalle River water samples analyzed by using Excel 2007 software. In other words, analysis of variance was performed using a One-way ANOVA and the Least Significance Difference (LSD) to test if significance difference existed between mean concentrations of heavy metals and other parameters of the different sites of Qalle River water. Significant difference was tested at 95% confidence level ($P<0.05$).

4. RESULTS AND DISCUSSION

4.1 Accuracy and Precision

Accuracy and precision are probably the most often quoted terms to express the extent of errors in a given analytical result. Analytical results must be evaluated to decide on the best values to report and attempt to establish the probable limits of errors of the values (Clesceri and L. C, 1998). The analyst thus concerned with the question of precision (repeatability of results), that is the agreement between the set of results. It can be determined by standard deviation, variance, relative standard deviation and range of series of measurements. In this study the precision of the results were evaluated by the pooled standard deviation and relative standard deviation of the results of the three sample sites with replicate measurements of each sample were used for the analysis of analytes in each water samples.

4.2 Recovery Test Results

The percentage recovery lied in between (89.6 to 98.86) for FAAS as shown in Table 15. Thus the mean percent recovery of LFM in all sampling sites are with in the recommended range for matrix spike recovery of 80 -120%. Thus good recoveries were obtained in all samples validating that the proposed procedure has good accuracy and precision.

Table 12 Recovery test result for the mean concentration of heavy metals analyzed by FAAS

Sample sites	Parameters	Concentration (mg/L)				
		Un-Spiked sample	Spiked sample	Amount Added	Amount found	Percent of recovery
Up-stream	Pb	ND				
	Cu	0.545	1.029	0.5	0.484	96.860
	Cd	ND				
	Mn	0.273	0.830	0.5	0.557	89.6
Middle Stream	Pb	ND				
	Cu	0.599	1.089	0.5	0.490	98.07
	Cd	ND				
	Mn	0.368	0.906	0.5	0.538	89.6
Down Stream	Pb	ND				
	Cu	0.676	1.15	0.5	0.478	95.65
	Cd	ND				
	Mn	0.443	0.893	0.5	0.45	89.8

Note: ND: not detectd.

: Amount added= known amount of standard added.

: Amount found=Amount of spiked sample –Amount of un-spiked sample value.

: Percentage recovery $= \frac{spiked\ sample\ value - unspiked\ sample\ value}{known\ amount\ of\ standard\ added} \times 100$

: Or Percentage recovery $= \frac{Mean\ of\ spike\ sample\ value - Mean\ of\ unspiked\ sampe\ value}{Known\ amount\ of\ standard\ added} \times 100$

: Or Percent Recovery$= \frac{Amount\ found}{Known\ amount\ of\ standard\ added} \times 100$

Table 13 The average concentration of some common ions in mg/L and physico-chemical parameters in Qalle River water samples.

Parameters	Concentration /Values in the samples (mean± SD)		
	Qalle River Water		
	Upstream	Middle Stream	Down Stream
Temperature (^{0}c)	24.2±0.42	24.3±0.35	24±0.99
Ph	6±0.28	6.04±0.08	6.05±0.07
EC (µs/cm)	83.7±0.42	81.7±0.42	82.4±0.92
DO (mg/L)	8.9±0.14	8.55±0.13	9.03±0.32
TDS (mg/L)	59±1.41	54	58
TA (mg/L)	20	20	22
Mg (mg/L)	3.49	2.75±0.35	3.25±0.34
Ca (mg/L)	7.08±0.59	7.08±0.59	6.66
TH (mg/L)	32.24±1.47	29.12	30.16±1.47
Cl^- (mg/L)	2.14	1.07	2.14
SO_4^{-2} (mg/L)	16.24±0.18	15.53±0.45	19.63±0.32

Table 14 The average Concentration of Pb, Cu, Cd, Mn, Na, K, PO_4^{-3} and NO_3^- in Qalle River water samples by FAAS, Flame photometry and UV-Vis.

Parameters	Concentration /Values in the samples (mean± SD)		
	River Water		
	Upstream	Middle Stream	Down Stream
Pb (mg/L)	ND	ND	ND
Cu (mg/L)	0.54	0.6	0.68
Cd (mg/L)	ND	ND	ND
Mn	0.29±0.01	0.39	0.47±0.01
Na (mg/L)	7.5	7.2	4.7
K (mg/L)	5.2	5	5.15±0.07
PO_4^{-3} (mg/L)	0.25	0.31±0.01	0.34±0.01
NO_3^- (mg/L)	0.47±0.01	0.42±0.01	0.51

4.3 Analysis of Physico-Chemical Parameters of Qalle River water samples.

As described in Table 13 and Table 14 the mean results of some common physico-chemical parameters of Qalle River water samples collected from three sampling sites are presented. The mean values were obtained from replicate measurements.

4.3.1 Temperature

Temperature was measured at different times in each grab samples and the average value was taken. In present study temperature range was range from 24^0C (downstream) to 24.25^0C (middle stream). The minimum temperature is recorded as 24^0C at location of downstream of river water sampling and maximum of 24.25^0C is found at middle stream. The LSD value is greater than the difference between the mean values all sites of Qalle River water and one-way ANOVA test ($p = 0.05$) showed that the temperatures varied insignificantly between the sites at different times of the Qalle river water sample. This indicates that temperature and amount of shade around the sites of Qalle River water is not varied.

4.3.2 pH

pH has no direct adverse effect on human health, however, according to USEPA guidelines, the maximum desirable limit of pH is from 6.5-8.5 (Rakesh, K.M, Walia, T.P.S, Lark, B.S, Sumanjit, 2006). The pH of water ranges between 6 (Upstream) to 6.05 (Downstream), which lie below the WHO minimum allowable drinking water quality ranges. The obtained results indicated that all the three sites of Qalle River are nearly acidic because the pH value is less than 7. At normal drinking water pH level and bicarbonate are the main contributors to alkalinity. As the pH value decreases the alkalinity decreases and the vice versa is true. The result indicates that containing low bicarbonates reacts with H^+ ions from water thereby decreasing the pH of water. Since the value of LSD is greater than that of the difference between mean values of the sites, the one-way ANOVA ($p = 0.05$) showed that the pH are not significantly differ between the studied water sites, this is due to the no variation of acidity among the sites of Qalle river water sample.

4.3.3 Electrical Conductivity

In this study, the average electrical conductivity value ranges between 81.7 μs/cm in middle stream to 83.7 μs/cm in upstream in Qalle River water. The current study gave the results below the guidelines for drinking water quality (Appendix I). Therefore, no issues concerned

with electrical conductivity if the waters to be used for drinking. Because of the difference between mean values of the result is greater than the calculated LSD values, the analysis of one-way ANOVA between the sites of Qalle River water ($p = 0.05$) showed that electrical conductivity between the sites of Qalle River water varied significantly. This could be due to the variation of TDS between the sites of Qalle river water; variation of ionic strength of the water between the sites and also waste from livestock and humans wastes at different sites.

4.3.4 Dissolved Oxygen (DO)

The oxygen come into water through two processes. The first is photosynthesis and oxygen also enters directly from the atmosphere. The average value of DO analyzed for Qalle River water sample ranges between 8.55±0.134 (middle stream) to 9.03±0.32 mg/L (downstream). The actual amount of DO in water varies depending on the temperature. Solubility of oxygen decreases as water temperature increases. As water heats up, gases are driven out of the water. The maximum DO value was found at the downstream because the downstream is characterized by lowest temperature than the other sites and the minimum DO value was found at middle stream of the river water. As levels of DO in water drops below 5 mg/L, the aquatic life is put under stress. The current study gave the results above the guidelines for drinking water quality (Appendix I). Therefore, there may be adverse effect concerned with DO if the Qalle River water is used for drinking purpose. Because the DO value is above the guidelines for drinking water quality in Qalle River water and in natural water it depends on physical, chemical and biological activities in the water. Since the LSD value is greater than the difference the mean values of sites of Qalle River water, the analysis of one-way ANOVA ($p = 0.05$) indicated that the DO between the sites of Qalle river water is not varied significantly. This implies that no variation production of oxygen by plants and algae in the water and the no variation of air temperature around the sites of the river.

4.3.5 Total Dissolved Solids (TDS)

The laboratory measured TDS values were distributed between the minimum mean value of 54 mg/L (Middle stream) and maximum mean value of 59 mg/L (Upstream). The TDS values from each sites of Qalle River water were below the WHO for drinking water quality standard (Appendix I). This indicates that no palatability problem concerned with TDS of the studied Qalle River water. Because of the difference between the mean values of the sites of Qalle River water is greater than that of the calculated LSD value, the analysis of one-way ANOVA

(p=0.05) showed that the TDS between the studied river water sites varied significantly. This could be from the variation of dissolved substances; waste from livestock and humans among the sites of Qalle river water.

4.3.6 Total Hardness (TH)

The result obtained from laboratory water quality analysis for Qalle River water at three sampling sites on total hardness has average value of 29.12 mg/L $CaCO_3$ (middle stream) to 32.24 mg/L $CaCO_3$ (upstream). Thus all the analyzed samples meet WHO drinking water guidelines standards of 500 mg/L $CaCO_3$. This indicates that no hardness related problems and soap consuming property of waters. That means the result recorded at all sampling site were lower than WHO standard for drinking water quality. Since the difference between the mean values are greater than the calculated LSD value, the one-way ANOVA (p = 0.05) showed that the total hardness values between the sites of Qalle river water is not varied significantly. This indicates that no variation of hardness causing cations (Ca^{+2}, Mg^{+2}) and anions (HCO_3^-, SO_4^{-2}, Cl^-, NO_3^-).

4.3.7 Calcium and Magnesium

The Ca and Mg of the investigated sites of Qalle River water could be due to the contact between the water body and the rock layers. Because the Qalle River water is naturally occurred river that come out on the earth's surface by crossing rock layers which leach these minerals and others to the water body. The Ca mean values in each site of Qalle river water were ranged from the minimum value 6.66 mg/L (Downstream) to the maximum of 7.705 mg/L (Upstream) and Mg mean values were ranged from the minimum value 2.75 mg/L (Middle stream) to 3.49 mg/L (Upstream). The study results for Ca and Mg are below the current recommended maximum value for drinking water quality standard (Appendix I). One-way ANOVA test (p = 0.05) found that both Ca and Mg between the studied sites of Qalle River water not varied significantly. Because the calculated LSD value is greater than the difference between the mean values. This might be due to the no variation in mineral composition of the rocks from which these metals are leached.

4.3.8 Chloride (Cl^-)

The Cl^- ions in the studied Qalle River water was possibly due to the natural sources since there are no available industrial sources from the study area. The Cl^- concentration in the

investigated sites of the Qalle River water was ranged from the minimum value 1.07 mg/L in Middle stream to 2.14 mg/L in Down-stream. Chloride may affect acceptability of drinking water by offering a salty taste to water. Since the determined values for all sites of Qalle River water were below the guideline values for drinking water quality, no taste effects associated with the studied sites of the Qalle River water. Since the difference between the mean values are greater than that of the calculated LSD value, the one-way ANOVA test ($p = 0.05$) showed that the Cl^- concentrations between the studied sites of Qalle River water is varied significantly. This could be due to the difference in solubility of NaCl, KCl and $CaCl_2$ salts.

4.3.9 Sulfate (SO_4^{2-})

The SO_4^{2-} ions in all sites of Qalle River water were ranged from the mean values of 15.53 mg/L (Middle stream) to 19.63 mg/L (Downstream). As it is mentioned in the review part, the presence of SO_4^{2-} in drinking water can cause noticeable taste. The investigated water sites of Qalle River water have SO_4^{2-} less than the taste threshold value (<250 mg/L) recommended by WHO (2011). Also on comparison with other guideline values for drinking water quality, no problem associated with SO_4^{2-} of the studied water if it is applicable for drinking purpose. One-way ANOVA test ($p = 0.05$) showed that the SO_4^{2-} concentrations among the studied sites of Qalle River water were significantly different. Because the calculated LSD value is less than that of the difference between the mean values of the sites of Qalle River water. This could be due to as mentioned in the review part, the variation of natural sources and the extent of atmospheric deposition of SO_4^{2-} around the Qalle River.

4.3.10 Total Alkalinity (TA)

The laboratory study result of alkalinity was found between the minimum mean of 20 mg/L (Upstream) and the maximum mean of 22 mg/L (Downstream). The results indicate that upstream site contains low bicarbonates, which implies as alkalinity decreases the pH of water decreases. The determined alkalinity mean values for each sites of the river are below the maximum permissible value for drinking water quality (Appendix I). This indicates that no unpleasant taste associated with the alkalinity of the studied waters. Because of the calculated LSD value is less than that of the difference between the mean values of the sites of Qalle River water, the ANOVA test ($p = 0.05$) showed that the alkalinity between the water sites varied significantly. This could be due to the variation of the concentration of bicarbonate sources at different sites of Qalle River water.

4.3.11 Phosphate

Water may contain PO_4^{3-} derived from natural contact with minerals or through pollution from application of fertilizer and sewage. Phosphorus is also a constituent of animal wastes (Chandra *et al*. 2012 and Weiner, 2008). The PO_4^{3-} in the studied sites of Qalle River water was possibly from fertilizers that farmers applied in agriculture and the natural contact with minerals when the water bodies come across the layers of various minerals. The obtained results were varied between the minimum mean 0.25 mg/L in up stream and the maximum mean 0.34 mg/L in Downstream. Currently no guideline value proposed by WHO and other national organizations for PO_4^{3-} in drinking water quality (Appendix I). The results of one-way ANOVA ($p = 0.05$) found that the PO_4^{3-} concentrations between the tested sites of Qalle River water varied significantly. Because the difference between mean values of the sites of Qalle River water is greater than the calculated LSD value. This could be due to variation of dumping of waste in to the river (waste from livestock and humans), agriculture around the sites of the river, Laundry and bathes.

4.3.12 Nitrates

The nitrate ion is the common form of combined nitrogen found in natural waters. NO_3^- is found naturally in the environment and is an important plant nutrient. NO_3^- can reach surface 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 (WHO, 2011). The result obtained from analysis of three sites of Qalle River water sample showed, the level of nitrate in the river water is well below the WHO recommended limit of 50 mg/L, and therefore, the concentration of nitrate in the Qalle River water does not pose health concern and ranges between 0.42 mg/L to 0.51 mg/L which Indicates that the obtained results are below the currently recommended guideline values for drinking water (Appendix I). Because of the LSD value is greater than that of the difference between mean values of the sites of Qalle River water, the analysis of one-way ANOVA test ($p = 0.05$) showed that the NO_3^- concentrations among the sites of Qalle River water were not varied significantly. This might be because of the current study was conducted during drying season which may not contribute to leaching of chemical fertilizers and animal manure that leads to variation significantly.

4.3.13 Sodium (Na)

In this study the average concentration of Na is compared in each sites of Qalle River water sample. The maximum amount is determined upstream (7.5 mg/L) and the lowest is at downstream water sample which is 4.7 mg/L. According to WHO guidelines for maximum concentration level of sodium in drinking water recommendation less than 200 mg/L. Sodium may affect the test of drinking water at level above 200 mg/L (Mahmoud A, 2001). Therefore, according to this study all the samples below WHO guidelines. These values are below the drinking water quality guideline value currently recommended by WHO and different national organizations, indicating no taste problems concerned with Na in the water sites. One-way ANOVA test ($p = 0.05$) found that the Na concentrations between the studied sites of Qalle River water varied significantly. Because the LSD value is less than the difference between the mean values of the sites of Qalle water. This could be from the variation of NaCl salt deposits and disposal of domestic waste (waste of both livestock and human) among the sites of the Qalle River water.

4.3.14 Potassium (K)

From the current study, calculated average values of K concentrations for each Site of the Qalle River water was within the range of the mean value 5 mg/L in Middle stream to the maximum value 5.2 mg/L in Upstream. All values are below the maximum value recommended for drinking water quality (Appendix I) indicating no health risks concerned with K at levels found in these sites of Qalle River water. Since the LSD value is greater than that of the difference between sites of Qalle River water, the one-way ANOVA test ($p = 0.05$) found that concentrations of K between the sites of Qalle River water not varied significantly.

4.3.15 Copper (Cu)

Cu concentrations in the investigated sites of the Qalle River water were found between the minimum mean of 0.54 mg/L (up-stream) and maximum mean 0.68 mg/L (down-stream). According to WHO (2011), at levels above 5 mg/L, Cu imparts a color and an undesirable bitter taste to water. The detected values were below the WHO and different national guidelines for drinking water quality standard (Appendix I). Therefore, no health and aesthetic problems associated with Cu for drinking the Qalle River water. One-way ANOVA result ($p = 0.05$) found that the Cu concentrations between the studied waters varied significantly.

Because the LSD value is less than that of the difference between the mean values of Qalle River water. This could be due to the dumping of domestic wastes at sites, staining of sanitary ware and laundry occur at the different sites, cu compounds used in fungicides, insecticides and added to fertilizers and animal feeds as nutrient support and animal growth.

4.3.16 Lead

Lead is the most significant of all heavy metals because it is toxic, very common (Gregoraadou *et al.,* 2001) and harmful even in small amounts. Lead enters the human body in many ways .It can be inhaled in dust from lead paints, or waste gases from leaded gasoline. It is found in trace amounts in various foods, notably in fish, which are heavily subjected to industrial pollution. In the studied sites of the Qalle River water fertilizers and pesticides are considered as the main source of lead but lead is not detected, because there are no industries around the studied area. However, the lead concentration was found to be below instrumental detection limit in water samples, hence this undetected value shows that the level of lead in drinking Qalle River water is not exceeded the current guideline value of international (WHO) was 0.01mg/L. Therefore the drinking water samples currently analyzed have no any health effect on humans upon drinking this water in case of lead concentration level.

4.3.17 Manganese

In this study the maximum level of Manganese (0.469 mg/L) was found in down-stream and the minimum level was found at up-stream (0.289mg/L). All values are above the WHO and different national guideline values for drinking water quality standard (Appendix I). Therefore, there may be an adverse effect concerned with Mn if the Qalle River water is used for drinking purpose. Since the difference between the mean values of the sites are greater than that of the calculated LSD value, the one-way ANOVA ($p = 0.05$) showed that the Mn concentrations between sites of Qalle River water was varied significantly. This variation may be due to variation of precipitation of MnO_2 may cause unsightly black staining of fixtures and laundary at sights of the river.

4.3.18 Cadmium

As mentioned in the literature review the suspected source of Cd in the studied area is soil (insecticides, fungicides, fertilizers that gained commercially and sludge). Because acute exposure of Cd can cause nausea, vomiting, diarrhea, muscle cramps, salivation, sensory

disturbances, liver injury, convulsions, shock, and renal failure. However, Cd was found to be BDL in all the water samples, which is within the WHO guideline for drinking water 0.001 mg/L. The USEPA Primary Drinking Water Standard (2012) for Cd is less than 0.005 mg/L. Hence, Cd does not pose any health problem if Qalle River is used for drinking. Acute cadmium poisoning symptoms are similar to those of food poisoning. It is associated with cause of kidney disease and linked to hypertension. The cadmium concentration in unpolluted waters is usually below 0.001 mg/L (Dabeka, R. W; Lawrence, J. F, Wagner, H. P, 2002). Furthermore, in this study, the Cd concentration was found to be below (ND) in Qalle river water samples, hence this undetected value shows the level of cadmium in drinking water is not exceeded the current guideline value of international (WHO) standard (0.001 mg/L).

4.4 Statistical Analysis

4.4.1 Analysis of Variance

In this study, the water samples were collected from three sites of Qalle River water and the metal level of each sample was analyzed by spectrophotometer, FAAS and Flame photometer. During the process of sample preparation and analysis a number of random errors may be introduced in each aliquot and in each replicate measurement. The variation in sample mean of the analyte was tested by using ANOVA followed by list significance difference (LSD) between sample mean values whether the source for variation was from experimental procedure or heterogeneity among the samples. To know whether the compositions of the samples of the Qalle River water samples were significantly different or not it is important to use the application of analysis of variance (ANOVA). Analysis of variance was performed using one-way ANOVA and LSD to test if significance difference between mean concentrations of heavy metals and other parameters of different sites of Qalle River water. The calculation of one way ANOVA for practical purpose was done on computer using Excel software (James, N.M, 2000). In this study Excel software was used to calculate the ANOVA for testing the significant differences in the composition of sites of Qalle River water samples. To know the significance different between the means of the determinations the least significance difference (LSD) must be calculated and considered. If the calculated (LSD) value is greater than that of the difference between the mean value then there is no significance difference among mean value is observed; and if calculated (LSD) value is less than that of the difference between among the mean value of the sites of Qalle River water

then there is a significance difference among the mean value of sites of Qalle River water sample. Any difference larger than the LSD is considered a significant result. Therefore in the comparison of the composition of sites of the river water samples, there were significant differences observed between the means of the determination of EC, TDS, Na, TA, Cl^-, SO_4^{-2}, PO_4^{-3}, Cu and Mn.

4.5 Comparison of Current Results with Some National and International Guidelines

Drinking water may be contaminated by a range of chemical, microbial and physical hazards that could pose risk to health if they are present at high levels. Examples of chemical hazards include Pb, As, F-, Cr, Cd, etc. and microbial hazards ,include bacteria, viruses and parasites, such as Vibrio cholera, hepatitis A virus, and Cryptosporidium parvum, respectively. Physical hazards include glass chips and metal fragments. Because of the large number of possible hazards in drinking water, the development of standards for drinking water requires significant resources and expertise, which many countries are unable to afford. Fortunately, guidance is available at the international level. The WHO publishes guidelines for drinking water quality which many countries use as the basis to establish their own standards. The guidelines represent a scientific assessment of the risk to health from biological and chemical constituents of drinking water and of the effectiveness of associated control measures. WHO recommends that social, economic and environmental factors be taken into account through a risk-benefit approach when adapting the guideline values to national standards. In this experiment national and international guidelines in which the nations have developed their own standards depending up on the guidance of WHO guideline were considered for comparing the results are within the limit of guidelines of drinking water or not. The results summarized in Appendix II and III. The current study results were compared with WHO and different national guidelines for drinking water quality, and except for some analyzed parameters (pH, DO, Cu and Mn), all analyzed parameters were below and agreed with the established guideline values for drinking water quality. Therefore, because of some parameters of (pH, DO, Cu and Mn) the analyzed Qalle River water may not be suitable for drinking purpose.

5. CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Safe water is a precondition for health and development. Therefore, it necessitates knowing the quality of water for drinking purpose. In this study, three sites of drinking Qalle River water (Up-stream, Middle-stream and Down-stream) of Babo Kiramu rural area, East Wollega was analyzed for some selected physico-chemical parameters and some selected heavy metals (temperature, pH, EC, TDS, DO, TA, TH, PO_4^{3-}, NO_3^-, SO_4^{2-} , Cl^-, Ca, Mg, Na, K, Pb, Mn, Cd, Cu,). During the study temperature, pH and EC were measured at site of sample collection. The TA, TH, TDS, Cl^-, Ca and Mg were determined by classical methods of analysis in laboratory. PO_4^{3-}, NO_3^-, Na, SO_4^{2-}, K, Pb, Cu, Mn and Cd were determined by instrumental methods of analysis in laboratory. All analysis were carried out according to the procedures given in the standard methods (APHA, 1999). The obtained results of all the parameters were compared between the sites of Qalle River water. One-way ANOVA test ($p = 0.05$) showed that some physico-chemical parameters of (EC, TDS, TA, Na, Cu, Mn, Cl^-, PO_4^{-3} and SO_4^{-2}) varied significantly between the studied sites of Qalle River water. Among the four heavy metals Pb and Cd in water samples were not detected (ND). From one-way ANOVA test ($p = 0.05$), reported heavy metals (Cu and Mn) and some physico-chemical parameters varied significantly between the sites of the Qalle River water. The variation of the determined parameters between the studied sites of Qalle River water are most probably from natural sources. The current study results were compared with WHO and different national guidelines for drinking water quality, and except for some analyzed parameters (pH, DO, Cu and Mn), all analyzed parameters were below and agreed with the established guideline values for drinking. Therefore, because of some parameters (pH, DO, Cu and Mn) the analyzed Qalle River water may not be suitable for drinking purpose. Generally, the importance of the quality of water for human consumption (regarding both health and aesthetic based quality) makes it necessary to investigate and keep up to norms, including limits for all the parameters that directly affect human health.

5.2 Recommendation

Based on the results and conclusions of this study, it is possible to give the following recommendation:

1. Since the Qalle River water crosses different areas in the Kiramu District and serves for drinking, domestic and irrigation purpose; there should be increased environmental sanitation education by district assemblies in communities to prevent contamination of this water resource and subsequent transmission of water-related disease.
2. Further studies need to be done on other heavy metals and the biological quality of the waters in order to improve the acceptability of the waters for drinking and irrigation.
3. The present study was conducted during the dry season so that it is recommended to do the research in the remaining seasons of the year, mainly during the summer season. Because drying season may not contribute to leaching of chemical fertilizers and animal manure to Qalle River water.

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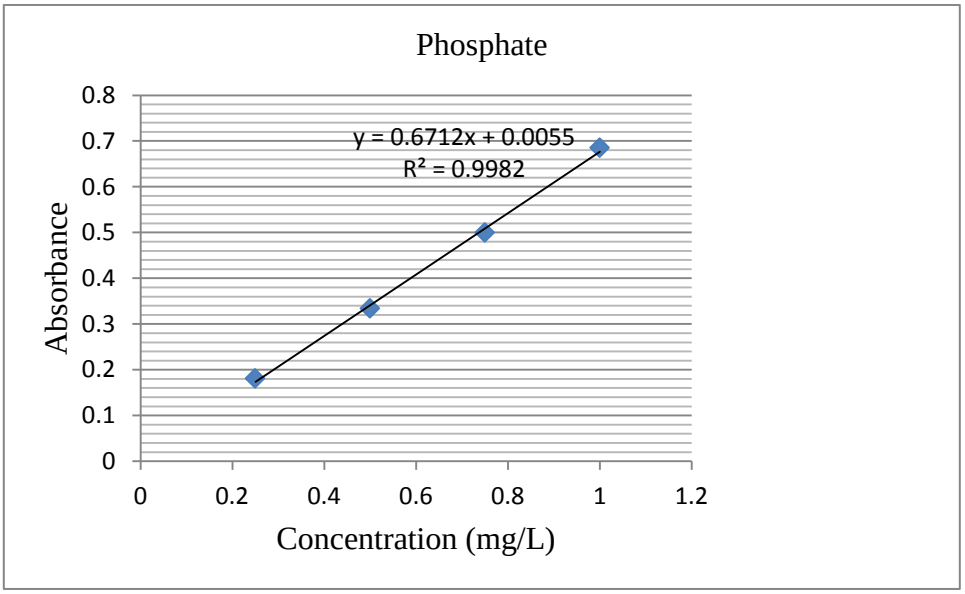
APPENDICES

Appendix I: Guidelines for Drinking Water Quality (for *health risk and aesthetic value*) set by different national and international organizations.

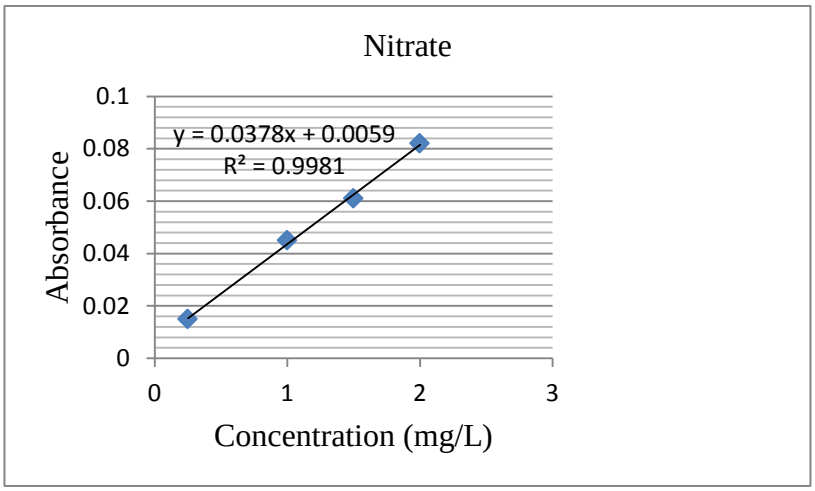
Parameter	Ethiopia, 2011	USEPA, 2012	Pakistan, 2008	WHO, 2011	EEPA, 2003	This Study
Temperature (^{0}c)	NM	NM	NM	-	-	24.2-24.9
pH	6.5 – 8.5	6.5 -8.5	6.5 -8.5	6.5 – 8.5	6 – 9	6-6.05
EC (µs/cm)	NM	NM	NM	-	1000	81.7-83.7
TDS (mg/L)	1000	500	1000	1000	NM	54-59
DO (mg/L)	-	-	-	5-7	-	8.55-9.03
TA(mg/L)	200	NM	NM	NM	NM	20-22
TH (mg/L)	300	NM	<500	200	NM	29.1- 32.2
NO_3-1(mg/L)	50	10	≤50	50	50	0.42-0.51
PO_4-3(mg/L)	NM	NM	NM	NM	NM	0.25-0.335
SO_4-2(mg/L)	250	250	200	250	200	15.53-19.63
Cl^- (mg/L)	250	250	<250	250	200	1.07-2.14
Ca (mg/L)	75	-	75	NM	NM	6.66-7.07
Mg (mg/L)	50	250	50	NM	NM	2.75-2.49
Na (mg/L)	200	20	NM	200	NM	4.7-7.5
K (mg/L)	1.5	NM	NM	NM	NM	5-5.2
Cu (mg/L)	2	1.3	2	2.1	0.112	0.54-0.68
Cd (mg/L)	0.003	0.005	0.01	0.001	0.005	-
Pb (mg/L)	-	0.015	-	0.01	-	-
Mn (mg/L)	0.5	0.05	≤0.5	0.4	0.3	0.28-0.46

NM = Not Mentioned.

Appendix II: Calibration and Linearity of instrumental response of PO_4^{-3} and NO_3-

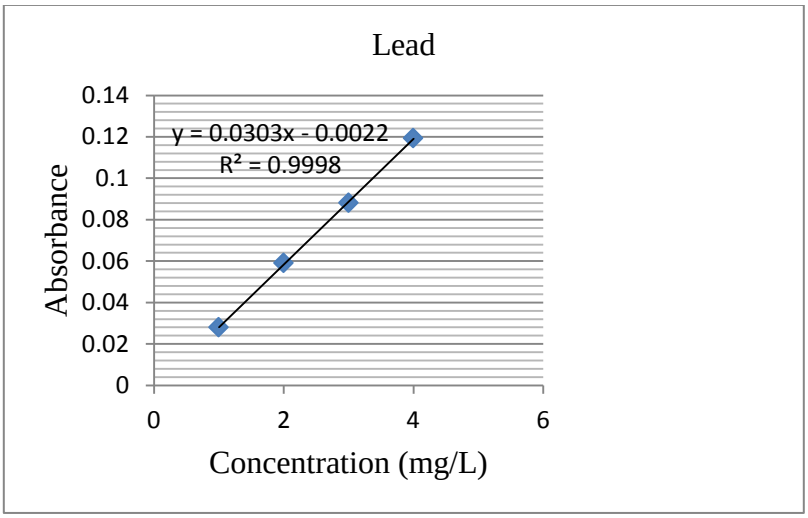


(a) Calibration curve of phosphate.

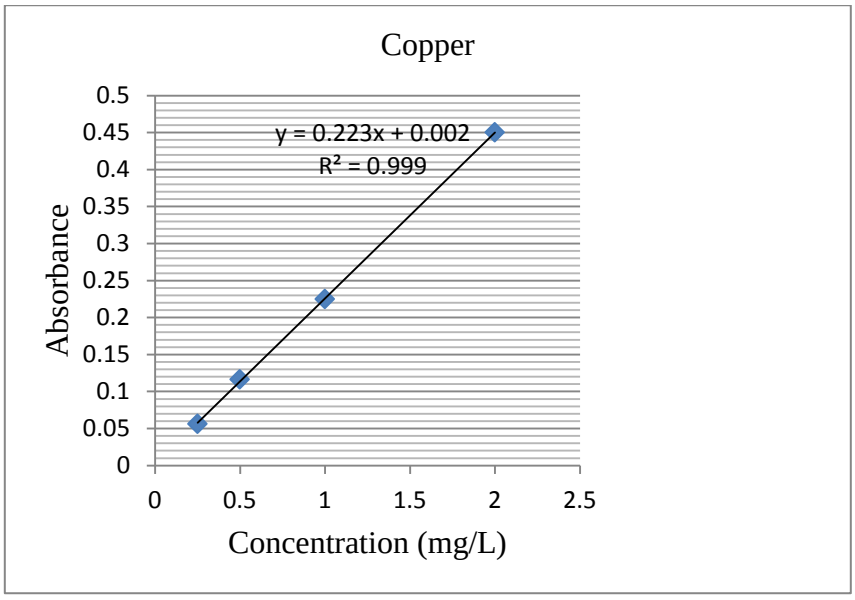


(b) Calibration curve of nitrate.

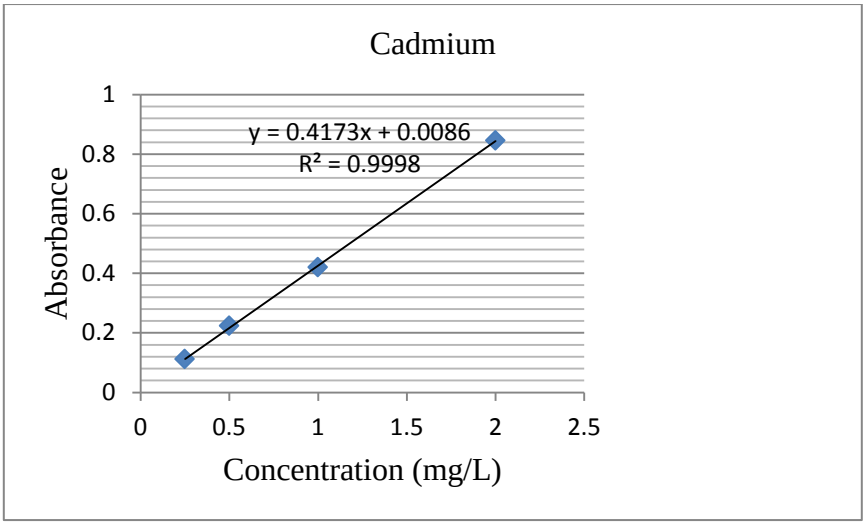
Appendix III: AAS Spectrophotometric calibration curve for the determined heavy metals.



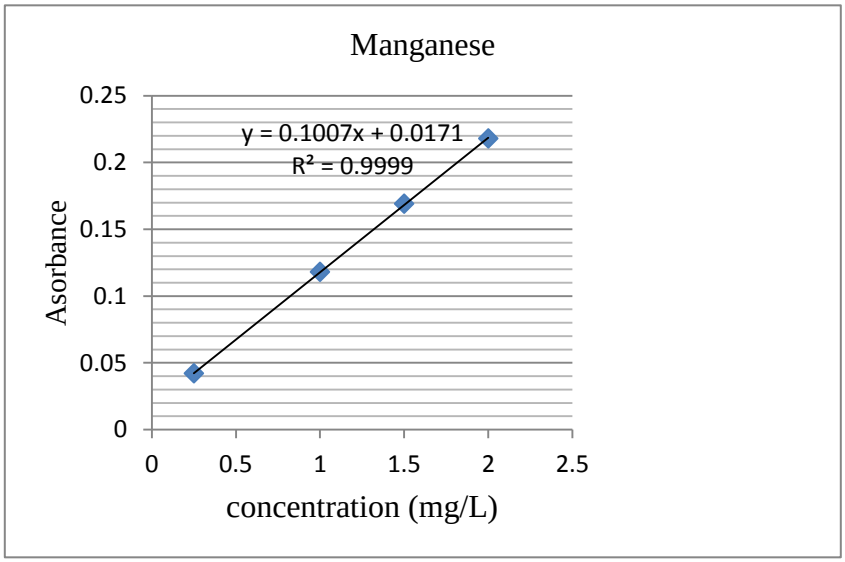
(a) calibration curve of Lead.



(b) Calibration curve of Copper.



(c) Calibration curve of Cadmium



(d) calibration curve of Mn