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Determination of the Level of Selected Heavy Metals and some physicochemical parameter in Spring, River and well Waters of Hawisa Bulo Kebele, Jimma Zone, Ethiopia

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Determination of the Level of Selected Heavy Metals and some physicochemical parameters in Spring, River and well Waters of Hawisa Bulo Kebele, Jimma Zone, Ethiopia

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POSTGRADUATE PROGRAM DIRECTORATE

I hereby certify that I have read and evaluated this Thesis entitled determination of Levels of Selected Heavy Metals and physicochemical parameters in spring, well and river prepared under my guidance by Wakshum Chala Saketa. I recommend that it be submitted as fulfilling the Thesis requirement.

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As a member of the Board of Examiners of the MSc, Thesis Open Defense Examination, I certify that I have read and evaluated the Thesis prepared by Wakshum Chala and examined the candidate. I recommend that the Thesis can be accepted as fulfilling the Thesis requirement for the degree Master of Science in Chemistry (Analytical).

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Internal Examiner	Signature	Date
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External Examiner	Signature	Date

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ABBREVEITION

APHA	American Public Health Association
WHO	World Health Organization
GFAAS	Graphite Furnace Atomic Absorption Spectro Photometer
ANOVA	Analysis of Variance
IDL	Instrumental Detection Limit
RSD	Relative Standard Deviation
SD	Standard Deviation
USA	United State of America
USEPA	United State Environmental Protection Agency
USFDA	United State Food and Drug Administration
MDL	Method Detection Limit
TSS	Total Suspended Solid
EC	Electrical Conductivity

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ABSTRACT

This study was conducted the physicochemical parameters and concentrations of six heavy metals were determined in water samples and three different water samples obtained in sites, Hawisa Bulo Kebele using Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS). The aim of the study was to determine heavy metals levels (i.e Zn, Cu, Pb, Co, Cd and Cr) in different water samples of spring, River and well water Hawisa Bulo Jimma zone. Samples were collected from different sampling position so as to represent spring, River and well water. Micro wave digestion system with early optimized procedure utilizing 3:1 mL ratio of HNO_3-HCl were utilized for water samples digestion. Concentrations of six metals (Zn, Cu, Pb, Co, Cd and Cr) was determined by Graphite Furnace Atomic Absorption Spectrophotometer and selected physicochemical property of water were determined utilizing pH meter, turbid meter measuring instruments. The results result revealed that the selected heavy metal concentrations (in range) in water samples were; Zn 1.98±0.046 - 2.003±0.142 mg/l, Cu 1.576±0.008 - 1.580±0.005 mg/l, Pb; 0.003±0.0007 - 0.034±0.002 mg/L, Co; 0.016±0.001 - 0.028±0.002 mg/l in the all water samples. The highest concentration of Zinc and copper was observed at spring water lead at well water and cobalt at river water. Except Eelectrical Conductivity and turbidity in the Jawi River looks above permitted level, the physicochemical properties of water samples were observed standard limit of WHO guide line. There was no significant difference between the three sites water were result data analyzed metals. Data were subjected to SPSS (Version 23) Software so as to signify the difference among all variables. Finally, due to some physical parameters like conductivity and turbidly and heavy metal like cupper become above the allowed permissible limit set by WHO for drinking water purpose further investigation is mandatory to look in depth the level of contaminants. The findings indicate that, there is a need to protect the quality of the river system.

Keywords: *Heavy Metals, physicochemical parameters, spring, well Waters and River water*

1. INTRODUCTION

1.1. Background of study

Water is one of the vital natural resource and without water life cannot flourish. It contains trace heavy metals like Fe, Mn, Co, and Cu which are micronutrient for living system. But, their deficiency or excess can lead to a number of disorderness in human health [1]. Although it is vital for life, water also serves as the commonest route of transmission of a number of infectious diseases [2]. According to World Health Organization (WHO2008) about, 80% of all sickness and disease in the world is caused by inadequate sanitation or unavailability of pure water. Hence it is necessary to purify and disinfect water before it is available for drinking. Drinking water quality guidelines and standards are designed to enable the provision of clean and safe water for human consumption, thereby protecting human health. These are usually based on scientifically assessed acceptable levels of toxicity to either humans or aquatic organisms [2].The availability of good quality water is an indispensable feature for preventing diseases and improving quality of life [3].

The physicochemical properties of water could be influenced by the flowing of mining effluents, agricultural effluents, industrial wastes, urban wastes along with forest run off to the river water. The increased use of metal-based fertilizer in agricultural revolution could result in continued rise in concentration of metal pollutions in fresh water reservoir due to the water run-off. Metals in water occur as complex and mixture of soluble and insoluble form, such as ionic species, inorganic and organic complexes associated with colloids and suspended particulate matter. Metals are probably the most harmful pollutants, if their concentration is higher than the permissible limits. These metals have accumulative effect at low level in drinking water. Food chain transfer also increases toxicological risk in humans [4].

The healthy aquatic ecosystem is depended on the physicochemical and biological characteristics. The quality of water in any ecosystem provides significant information about the available resources for supporting life in that ecosystem. As freshwater becomes increasingly scarce, it is necessary to pay attention to alternative sources of water and particularly among the rural and urban areas where people use well water, river and mineral (spring) waters for drinking and other domestic use monitoring of those parameters are essential to identify magnitude and source of any pollution load [5].

Therefore; there is no literature information on the level of heavy metals in Hawisa Bulo village of Gumay district, Jimma zone where peoples of the area mostly used spring water for disease therapy and rivers as well as well water for drinking purpose and that why it is aimed to determine the level of selected heavy metals in spring, river and well of the target area.

1.2. Statement of the Problem

Water quality has a direct impact on public health. The water supply system in Hawisa Bulo Kebele, Gumay District is insufficient as per the demand of consumers. The people of the area show an increasing trend of using river water, mostly driven by the unreliable and quality compromised spring water supply and in part due to the perception and expectation of pure and safe drinking water. With the increasing demand and insufficient supply, it seems that in the near future, the urban dwellers and villages would not have an option other than using spring water and rivers water. Thus evaluation of their quality is very important. Analysis of water quality in water sources is vital to assess the current status of the water sources providing that the surrounding community to use for different purpose. The present study is formulated to determine the potability of the spring water, river water and well water by assessing the level of some physical parameters (pH, EC, turbidity etc) which justifies the quality of a drinking water. Therefore, in this study, the determination of the Level of Selected Heavy Metals in Spring water, river and well water of Goda Aba Dhiba village will be investigated to answer the following basic research inquiries.

- How far the spring, river and well waters of Hawisa Bulo Kebele are exposed towards accumulation of heavy metals concentration?
- Does the Level of Selected Heavy Metals in spring, river and well waters vary?
- Is the spring water is unique in metal accumulation of metals than the well and river water?

1.3 Objectives

1.3.1. General Objective

- To investigate the some physicochemical parameters and determination of the level of selected heavy metals in spring, river and well waters using GFAAS.

1.3.2 Specific Objectives

- To determine some physicochemical parameter such as pH, Turbidity, Electrical Conductivity in spring water, river and well water
- To determine Level of Selected heavy Metals such as Zn, Pb, Cr, Co, Cu, and Cd in spring waters, River and well water.
- To compare the level of heavy metals concentration in River, Spring and well water with national and international guidelines of water quality

1.4. Significance of the study

The findings of this study will provide baseline information for further investigation indicating whether the water resources of the study area (Gumay Distruct in Hawisa Kebele at Goda Aba Dhiba) are safe or not for daily consumption indicating how the water resource is loaded by target heavy metals.

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

2. LITERATURE REVIEW

2.1. Water Pollution

Water pollution is a major global problem which requires on going evaluation and revision of water resource policy at all levels. It has been suggested that it is the leading worldwide cause of deaths and diseases and that it accounts for the deaths of more than 14,000 people daily [6]. It has been estimated that 580 people in India die of water pollution related illness every day. In addition to the acute problems of water pollution in developing countries, developed countries continue to struggle with pollution problems as well. A report from China's national development agency in 2007 said that, 1/4th the length of China's seven main rivers were so poisoned the water harmed the skin [6]

The main sources of pollution that enter surface water bodies are industries, municipal solid waste and oily wastes from garages and fuel stations. Most of the water resources are gradually becoming contaminated due to the addition of foreign materials from the surroundings. These include organic matter of plant and animal origin, land surface washing and industrial and sewage effluents. Rapid urbanization and industrialization with improper environmental planning often lead to discharge of industrial and sewage effluents into rivers [7]. A number of studies on rivers and streams indicate that poor farming practices and poor provision of sanitation facilities to the riparian communities [8], as well as leachate from open solid waste dumps which are usually located on edges of rivers inflict serious water quality deterioration [8].

2.2. Characteristics of Heavy metals and related health risks

A heavy metal is metallic element that has a relatively high density and is toxic or poisonous even at low concentrations [9]. Heavy metals exist as natural constituents of the earth crust and are persistent environmental contaminants, because they cannot be degraded or destroyed [10]. Human exposure to harmful heavy metals can occur in many ways, ranging from the consumption of contaminated food, exposure to air-borne particles, and contact or consumption of contaminated water and accumulate over a period of time [1]. Water related diseases can often be attributed to exposure to elevated heavy metal concentrations of both organic and inorganic contaminants. Many of these compounds exist naturally, but their concentration has increased as a result of anthropogenic activities [11]. Heavy metal contamination is associated with deficiencies of some essential nutrients in the human body [2]. Thus, ultimately, can result in decreased immunological defenses, disabilities associated with malnutrition, intrauterine growth retardation, impaired psychosocial faculties, and high prevalence of upper gastrointestinal cancer rates. High concentrations of lead and other heavy metals can affect the nervous system and kidneys, and may cause reproductive disorders, skin lesions, endocrinal damage, and vascular diseases [5].

Heavy metals are elements having atomic weights between 6.5 and 200.6 and a specific gravity more than 5.0. Some heavy metals are toxic or carcinogenic, and are not biodegradable and tend to accumulate in living organisms. When natural water bodies are contaminated with wastewater containing higher concentration of heavy metals, it affects aquatic life and is destructive to the environment. Once introduced in small doses for a long time in the body can cause acute or chronic poisoning. A number of heavy metals are a constant and necessary component of a living body (iron, zinc, copper, manganese, cobalt). Others such as mercury, lead, cadmium, thallium, are harmful to the body [1].

2.2.1. Copper

Copper is an essential element for the living body, because plays an important role in the synthesis of hemoglobin. Due to the volatility of the valence of copper ions they have a catalytic effect on various processes Oxo-reduction enzymes. A small amount of copper is in the liver, spleen, kidney, lung and blood. Fatal poisoning is extremely rare, and the rapid occurrence of violent vomiting removes most of the poison entered. Transitional poisoning can occur after ingestion of improperly fruit sprayed with insecticide copper or preserved foods containing added excessive amounts of copper sulphate [4]. Copper is one of the world’s most widely used metals. According to [12] the most common copper-bearing ores are sulphides, arsenates, chlorides and carbonates. It reaches aquatic systems through anthropogenic sources such as industry, mining, plating operations, usage of copper salts to control aquatic vegetation or influxes of copper containing fertilizers [13]. Copper is an essential trace element to plants, animals and even humans, and although the concentration of copper is usually low in nature, it happens in adequate quantities for growth in all aquatic environment. It is required for bone formation, maintenance of myelin within the nervous system, synthesis of hemoglobin, component of key metalloenzymes, plus it forms an important part of cytochrome oxidase, and assorted other enzymes involved in the redox reactions in the cells of animals.

It is also essential for cellular metabolism, where its concentration is well regulated, but becomes toxic at elevated levels [5]. Although copper is important, it is toxic when concentrations exceed that of natural concentrations (< 0.05 ml/L) [5]. The toxicity of copper in aquatic organisms is largely attributable to Cu^{2+} that forms complexes with other ions. A reduction in water dissolved oxygen, hardness, temperature, pH and chelating agents can increase the toxicity of copper [14]. Organic and inorganic substance can easily complex the cupric form of copper, which is the most common speciation of this metal and it is then absorbed on to particulate matter. Therefore, the free ion is rarely found except in pure acidic soft water. The chemical speciation of copper strongly depends on the pH of water [15]. Copper, in water, particulate at high pH (alkaline) and is thus not toxic, while at low pH (acidic) it is mobile, soluble and toxic [16].

2.2.2. Cobalt

Is an essential element for life system as a factor against the anemic forming part of a molecule of vitamin B12 "cobalamin". It irritates causing bone marrow hyperplasia, and consequently a significant increase in the number of red blood cells. In the tissues and organs of cobalt collects in small amounts. Causes allergic reactions and acute poisoning with paralysis of the nervous system and seizures. Chronic poisoning observed growth retardation and weight and enlarged thyroid deficiency associated with this gland [15].

2.2.3. Lead

Is a typical gray colored metal; is a soft, malleable. Density 11.34 g / cm^3, melting point 327, 4°C. All lead compounds are poisonous. The chemical compounds found to lead +2 and the oxidation state +4. In the open covered with oxide film. Lead is a component bearing alloys and soldering alloys. With lead are also carried out: the battery plates, apparatus for the production of sulphuric acid, drain water pipes, electric cable, shot, and missile components. Sheets of lead placed in the construction of large buildings to protect against vibration and noise. Lead compounds are used for the manufacture of anticorrosive paints and varnishes, pigments and mortar - currently in decline due to the harmful properties of these compounds. Lead oxides are a component of glass ware. Polysulfide rubber (as a curing agent). Tetraethyl lead $Pb(C_2H_5)_4$ and tetra methyl $Pb(CH_3)_4$ are used as anti-knock in petrol. All lead compounds are poisonous. The most common disease is lead [4]. It is a chronic lead poisoning and its salts in employees' printers, battery factories and factories of lead paint. Acute poisoning are rare. Chronic poisoning are mainly gastrointestinal and nervous systems. The main symptoms are fatigue, tiredness, muscle paralysis, gray border around the teeth, colic lead. At the same time there is proteinuria, hematuria and brain disorders. Treatment is primarily hospital, comprising administering antidotes and high levels of vitamin B1 and B12.However, the most important is the appropriate occupational health and nutrition [16]. The major sources of lead in the environment are automobile exhaust, industrial wastewater, wastewater sludge and pesticides. The global mean lead concentration in rivers is estimated to be between 1.0 to 10.0 µg/L [4]. Lead enters the aquatic environment through erosion and leaching from soil, leads dust fallout, combustion of gasoline, municipal and industrial waste discharges, runoff of fallout deposit from streets and other surfaces as well as precipitation. Lead is toxic and a major hazard to human and animals. Lead has two quite distinct toxic effects on human beings, physiological and neurological.

The necrosis and desquamation of gill epithelium as well as lamellar curling and aneurisms were the direct deleterious effects reported in chronic lead exposed Clarias gariepinus. The characteristic symptoms of chronic lead toxicity include changes in the blood parameters with severe damage to erythrocytes and leucocytes and damage in the nervous system [17]. Lead deplete major antioxidants in the cell, especially thiol containing antioxidants and enzymes that can cause significant increases in an reactive oxygen species (ROS) production, followed by a situation known as oxidative stress leading to various dysfunctions in lipids, proteins and DNA [18].

The main targets of lead toxicity are the hematopoietic and nervous systems. Several of the enzymes involved in the synthesis of home are sensitive to inhibition by lead. Besides this, the nervous system is another important target for lead toxicity, especially in infants and young children where the nervous system is still developing.

Even at low levels of exposure, children may show hyperactivity, decreased attention span, mental deficiencies and impaired vision. Lead damages the arterioles and capillaries resulting in cerebral edema and neuronal degradation. Another system affected by lead is the reproductive system. Low levels of Pb pollution could cause some adverse effects on fish health and reproduction [19] and also, to cause pathological changes in tissue and organs [19].

2.2.4 Cadmium

Cadmium is obtained as a byproduct of zinc smelters, the roasted ore reduction and separation by fractional distillation. It silvery metal, like zinc and some lead, a density of 8.65 g / cm^3 and a melting point of 321 °C. The chemical compounds found in the second oxidation state is a non-noble metal, air cover with a layer of oxide is readily with acids. Metallic cadmium is used in the manufacture of alloys, for the preparation of protective coatings (cadmium) and for the production of batteries. Cadmium Sulphide CdS and CdSe Cadmium selenide is used as a pigment for artistic purposes (cadmium yellow, cadmium orange). Cadmium has no medical use. However, poisoning him, his vapour or smoke are mainly found in the industry. Absorption of cadmium oxide fumes occurs by inhalation. They have no characteristic odour or irritation, and therefore can easily be absorbed quantities dangerous to humans. The main symptoms of poisoning is a dry throat, headache, shortness of breath, heart failure and elevated body temperature. From the digestive tract absorbs it very quickly and accumulates mainly in the liver and kidney [11]. Symptoms of poisoning occur after 4-5 hours and have ślinotokiem, persistent vomiting, severe diarrhea, and abdominal pain. Chronic poisoning develops slowly, and for the first year is asymptomatic. Only after 5 years appear articular muscle pain, shortness of breath, kidney damage, lung lesions and skeletal system [12].

Cadmium is a naturally occurring nonessential trace element and its' tendency to bio accumulate in living organisms often in hazardous levels, raises environmental concern [13]. Cadmium production, consumption and emissions to the environment have increased dramatically during the 20th century, due to its industrial use (batteries, electroplating, plastic stabilizers, pigment), and consequently lead to contamination of aquatic habitats. The use of cadmium containing fertilizer, agricultural chemicals, pesticides and sewage sludge in farm land, might also contribute to the contamination of water [14]. As a no degradable cumulative pollutant, Cd is considered capable of altering aquatic trophic levels for centuries. This heavy metal has been shown to accumulate mainly (about 65 %) in kidney, liver and gills of freshwater fish [20], but it can also be deposited in the hearts and other tissues and cause pathological changes of varying severity in above mentioned organs[21], morphological and histological alterations in liver of fishes exposed to cadmium have been documented.

Cadmium is widely known to be a highly toxic non-essential heavy metal and it does not have a role in biological process in living organisms. It is a natural element in the earth crust and usually found as a mineral with other elements. All soils and rocks, including coal and mineral fertilizer, have some cadmium in them. The use of cadmium containing fertilizer, agricultural chemicals, pesticides and sewage sludge in farm land, might also contribute to the contamination of water [21]. As a no degradable cumulative pollutant, Cd is considered capable of altering aquatic trophic levels for centuries. This heavy metal has been shown to accumulate mainly (about 75 %) in kidney, liver and gills of freshwater fish, but it can also be deposited in the hearts and other tissues and cause pathological changes of varying severity in above mentioned organs [13]. Cadmium could originate from water, sediments and food and may accumulate in the human body as may induce kidney dysfunction, skeletal damage, reproductive deficiency, carcinogenic, teratogenic, genotoxic, damage to the central nervous system and produce psychological disorder [14].

2.2.5. Zinc

Zinc is the second most abundant trace element after Fe and is an essential trace element and micronutrient in living organisms, found almost in every cell and being involved in nucleic acid synthesis and occurs in many enzymes [16]. Additionally, Zn is involved in more complicated functions, such as the immune system, neurotransmission and cell signaling [17]. It may occur in water as a free cation as soluble zinc complexes, or can be adsorbed on suspended matter. Zinc and its compounds are extensively used in commerce and in medicine. The common sources of it are galvanized ironwork, zinc chloride used in plumbing and paints containing zinc.

Zinc wastes can have a direct toxicity to fish at increased waterborne levels [18] and fisheries can be affected by either zinc alone or more often together with copper and other metals. The main target of waterborne Zn toxicity are the gills, where the Ca2+ uptake is disrupted, leading to hypocalcemia and eventual death [14]. The other endpoints of toxicity vary amongst freshwater and marine fish with the most common being survival, growth, reproduction and hatching. Also, fish kidney is considered as a target organ for Zn accumulation [13].

Zinc is a very common environmental contaminate and usually outranks all other metals and it is commonly found in association with lead and cadmium. Major sources of zinc to aquatic environment include the discharge of domestic wastewater, manufacturing processes involving metals and fallout atmosphere. Zinc is an essential element for human, animal and certain types of plant. It is also necessary for a healthy immune system, cell division and synthesis of protein and collagen which is great for wound healing and healthy skin. However, a higher amount of it can cause anemia, pancreas damage and lower levels of high density of lipoprotein cholesterol [22]. Chronically toxic are generally extensive deterioration of liver, kidneys, heart, and muscle. Chronic sub-lethal zinc concentration can also delay or inhibit the growth sexual maturity and reproduction of the fish and can also induce pathological and morphological abnormality in adult fish [22]. Zinc toxicity is modified by water chemical factors including dissolved oxygen concentration, hardness, pH and temperature of the water [23] and can also be changed through other heavy metals compounds and alkaline earths metals. High temperature tend to increase zinc toxicity, while increase in water hardness, alkalinity and organic chelators can reduce its acute lethality and low dissolved oxygen content in water increases the toxicity of zinc[24].

2.2.6. Chromium

Chromium is an essential nutrient metal, necessary for metabolism of carbohydrates [25]. Chromium enter the aquatic ecosystem through effluents discharged from leather tanneries, textiles, electroplating, metal finishing, mining, dyeing and printing industries, ceramic, photographic and pharmaceutical industries etc. [23]. Poor treatment of these effluents can lead to the presence of Cr (VI) in the surrounding water bodies, where it is commonly found at potentially harmful levels [24]. In surface waters, depending on physicochemical characteristics, the most stable forms of chromium are the oxidation states trivalent Cr (III) or (Cr^{3+}) and the hexavalent Cr (VI) or (Cr^{6+}). Hexavalent chromium (Cr^{6+}) is considered to be toxic (i.e. carcinogenic) because of its powerful oxidative potential and ability to cross cell membranes. Fish assimilate Cr by ingestion or by the gill uptake tract and accumulation in fish tissues, mainly liver, occurs at higher concentrations than those found in the environment [25,26]. The overall toxic impact on organs like gill, kidney and liver may seriously affect the metabolic, physiologic activities and could impair the growth and behavior of fish.

Toxic effects of Cr in fish include: morphological alterations, reduction of growth, production of reactive oxygen species (ROS) and impaired immune function. Acute poisoning by chromium compounds causes excess mucous secretion, damage in the gill respiratory epithelium and the fish may die with symptoms of suffocation [24]. On chronic exposures, hexavalent chromium severely affected the renal tubules causing hypertrophy of epithelial cells, reduction of tubular lumen, contraction of glomeruli and epithelial and glomerular necrosis [26].

According to [27] chromium compounds also cause renal failure leading to the loss of osmoregulatory ability and respiration in fish. Sublethal effects of chromium in fish were directly related to the inhibition of various metabolic processes. Like, the hexavalent chromium induced depletion in the profiles of liver glycogen, total protein and total lipid has been reported.

2.3. Physical parameters of water

2.3.1. Dissolved Oxygen

Dissolved oxygen (DO) is essential to all forms of aquatic life including the organisms that break down man-made pollutants. Oxygen is soluble in water and the oxygen that is dissolved in water will equilibrate with the oxygen in atmosphere. Oxygen tends to be less soluble as temperature increases. DO is an important for many chemical and biological processes taking place in water. Dissolved oxygen in water can decrease due to microbial activity, respiratory and organic decay. Dissolved oxygen value is an indicative of pollution in water and depicts an inverse relationship with water temperature [27]. In natural waters, man-made contaminant or natural organic material was consumed by microorganisms. As a result microbial activity increases, oxygen was consumed out of the water by the organisms to facilitate their digestion process then oxygen get consumed and the water become anaerobic [28].

2.3.2. Turbidity

Turbidity or Total Suspend Solids (TSS) is the material in water that affects the transparency or light scattering of the water. The measurement unit used to describe turbidity is Nephelometric Turbidity Unit (NTU). The range for natural water is 1 to 2000 NTU. Total suspended solid was typically composed of fine clay or silt particles, plankton, organic compounds, inorganic compounds or other microorganisms. These suspended particles range in size from 10 nm to 0.1 mm although in standardized laboratory tests, TSS is defined as the material that cannot pass through a 45 μm diameter filter. TSS as well as TDS can be influenced by changes in pH. Changes in the pH will cause some of the solutes to precipitate or will affect the solubility of the suspended mater. The man made sources of TSS include erosion, storm water runoff, industrial discharges, microorganisms, and eutrophication. Many fish species are sensitive to prolonged exposure to TSS and monitoring of TSS is an important criteria for assessing the quality of water. [28]

2.3.3 Temperature

Many aquatic organisms are sensitive to changes in water temperature. Temperature is an important water quality parameter and is relatively easy to measure. Water bodies will naturally show changes in temperature seasonally and daily; however, man made changes to stream water temperature will affect fish's ability to reproduce. Many lake and rivers will exhibit vertical temperature gradients as the sun will warm the upper water while deeper water will remain cooler. Some streams will increase in temperature as the stream water moves down stream through urban, industrial and agricultural areas. Environmental policies require the monitoring of stream water temperature. In most urban and industrial locations, environmental permits are required to help minimize the temperature loading to streams. [29,30]

2.3.4. Electrical Conductivity

Electrical conductivity (EC) in natural waters is the normalized measure of the water's ability to conduct electric current. This is mostly influenced by dissolved salts such as sodium chloride and potassium chloride. The common unit for electrical conductivity is Siemens per meter (S/m). Most freshwater sources will range between 0.001 to 0.1 S/m. The source of EC may be an abundance of dissolved salts due to poor irrigation management, minerals from rain water runoff, or other discharges. EC is also the measure of the water quality parameter "Total Dissolved Solids" (TDS) or salinity. At about 0.3 S/m is the point at which the health of some crops and fresh water aquatic organisms will to be affected by the salinity. Field measurements of EC reflect the amount of total dissolved solids (TDS) in natural waters. The relationship between TDS and EC can be described by the equation; TDS (mg/L) $\approx$ EC (mS/cm) X 640

When salts such as sodium chloride are in their solid form, they exist as crystals. Within the salt crystal, the sodium and the chlorine atoms are joined together in what is called an ionic chemical bond. An ionic chemical bond holds the atoms tightly together because the sodium atom will give up an electron to the chlorine thus ionizing the atoms. The sodium chloride crystal lattice has a zero net charge. Water will dissolve the sodium chloride crystal lattice and physically separate the two ions. Once in solution, the sodium ion and the chloride ion will float around in the solution separately and randomly. This is generally true for all inorganic salts. Once in a solution, the ions will float apart and become two separate species dissolved in the water. Typical, charged ions exist separately in a solution. If the water dries up, the cations and the anions will find each other and fuse back into a crystal lattice with a zero net charge [28].

2.3.5. PH

pH is the measure of the acid/base activity in solution. In natural waters, the pH scale at room temperature runs from 0 to 14. The pH of natural water can provide important information about many chemical and biological processes and provides indirect correlations to a number of different impairments. Most metals will become more soluble in water as the pH decreases. The amount of dissolved metals in solution negatively affects the health of the aquatic organisms [27] For optimal growth and survival, they need the pH of their water body to be within a certain range. Although each organism has an ideal pH, most aquatic organisms prefer pH in the range 6.5–8.0. Outside of this range, organisms become physiologically stressed. Reproduction can be impacted by out of pH range, and organisms may even die if the pH gets too far from their optimal range. Changes in pH also influence the availability of plant nutrients, such as phosphate, ammonia, iron and trace metals in the water [28].

The pH is a measure of the hydrogen ion concentration in water. Drinking water with a pH between 6.5 to 8.5 is generally considered satisfactory. Acid water tend to be corrosive to plumbing and faucets, particularly, if the pH is below 6. Alkaline waters are less corrosive; water with a pH above 8.5 may tend to have a biter or soda-like taste

3. MATERIALS AND METHODS

3.1. Chemicals and Reagents

All the reagents and chemicals used in the present study were analytical grade. Stock solution (1000) ppm standards of heavy metals (Cr, Zn, Cd, Pb, Cu and Co), Nitric acid, HNO_3 (Spectrosol, England) (65%), hydrochloric acid HCl, (37%), Deionized water was used for all preparation and dilution purposes

3.2. Instruments and Apparatus

The instrument used was fully automated PC-controlled Graphite Furnace Atomic Absorption Spectrophotometer Model NOVAA 400P equipped with hollow cathode lamps namely Cadmium, Zinc, Chromium, Copper, Cobalt and lead were used throughout the experiment. PH-meter EC- meter-; Dissolved Oxygen, Turbidity meter and thermometer was used for the determination of water pH, EC, DO, Turbidity and Temperature, Erlenmeyer flasks, volumetric flasks, Microwave Digester, polyethylene bottle

3.3 Description of the Study Area

Spring water, river and well water locate in Toba town far 5 km from spring water the depth difference between the two water is 60 meters, spring water from river. Spring water and Jawi river were located at Hawisa Bulo, Jimma Zone, Oromia Region which is geographically located at $08^{0,}$ 85.3’29’’N, 0220, 34.942′E and about 75 km away from Jimma in southwestern of Ethiopia.

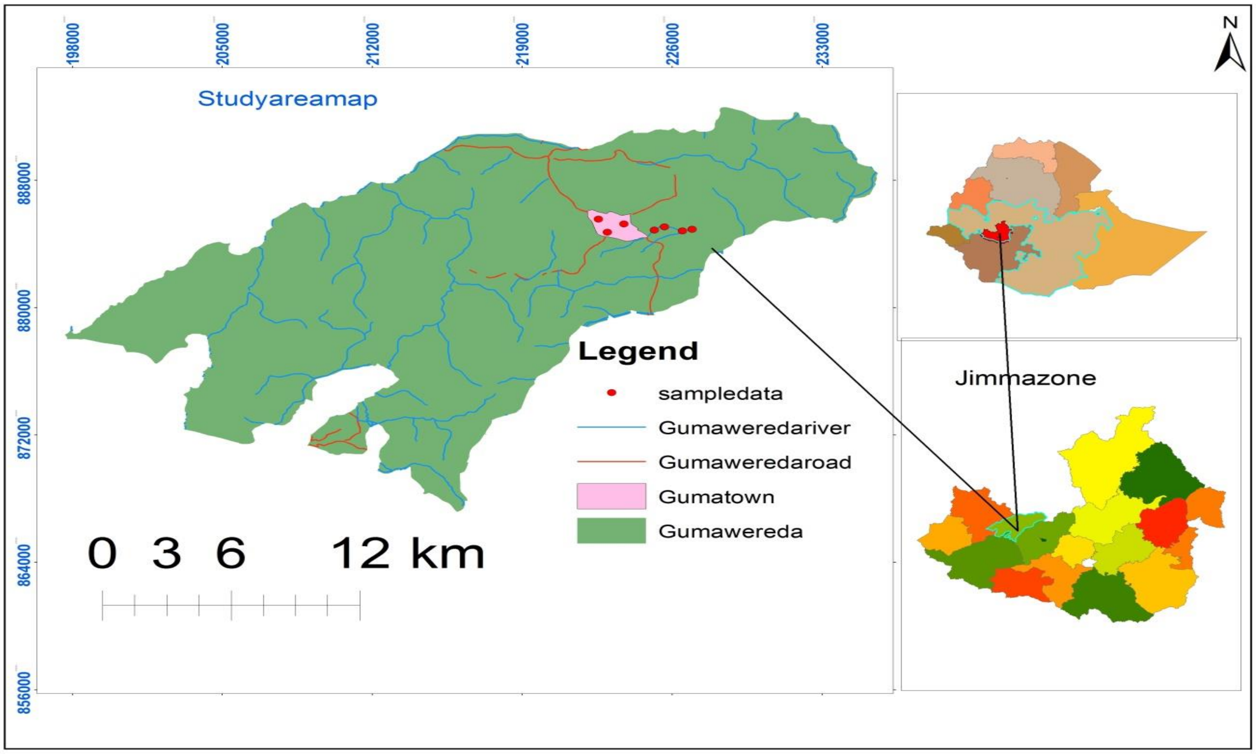

Figure: 1 Map of Gumay showing samples location Hawisa Bulo Kebele

3.4. Sampling and Sample Preparation techniques

Spring, well, and river water samples were collected from three different Stations in the Morning Hours between 6:00 to 8:00 am, on may 2018 in one litters capacity polythene bottles separately, without any air bubbles and prior to the collection, bottles were thoroughly washed and rinsed with sample to avoid any possible contamination in bottling and every precautionary measure was taken. Physicochemical Parameters like conductivity, dissolved oxygen and pH was recorded at the time of sample collection. Before sample collection polyethylene bottles were cleaned by tap water, followed by HNO_3 (10%), and finally by deionized water. Then the water samples was transported to Jimma University Analytical Chemistry Research laboratory (in ice-box) and kept in a refrigerator below 4^oC until analysis was carried out**.**

3.5. Digestion of water samples for the analyses of (Cu, Co, Cr, Pb, Zn and Cd)

Digestion of water sample took place in triplicate according to the Methods developed by the United State Environmental Protection Agency (USEPA) [33]. 50 mL water samples were digested at 150- 180 ^oC by a Micro wave Digestion instrument by adding of concentrated Nitric acid (65%) HNO_3 and concentrated Hydrochloric acid (37%) HCl in 3:1 ratio as per the procedure until the digestion was completed for 30 minutes. Then the Teflon tube was removed and cooled at 50 ^oC Each of the digested water samples was filtered with filter paper in to a 100 mL volumetric flask and filled up to the mark with deionized water by addition of 2 mL of nitric acid to get a clear solution[31,32].

Figure 2: Method of samples preparation and digestion by microwave digester

3.6. Method Validation for Metal Analysis

3.6.1. Iinstrument calibration

Calibration curves were constructed to determine the concentration of the heavy metals in the sample solutions. Intermediate standard solution of each metal was prepared from stock standard solutions containing 1000 mg/L of Cd, Cr, Pb, Cu, Zn and Co. According to the instrument operation manual to attain its better sensitivity, the working standards were then aspirated one after the other into the Graphite Furnace Atomic Absorption Spectrometer and its absorbance was recorded. Calibration curves were plotted with different points for each metal standard solution using absorbance against concentrations (mg/L). Immediately after calibration using the standard solutions, the sample solutions were aspirated into the GFAAS instrument and the instrument response become recorded [33]

3.6.2. Limit of Detection

Limit of detection (LOD) is the minimum concentration of analyte that can be detected but not necessarily quantified with an acceptable uncertainty. LOD for each metal was determined from analysis of five replicates of method blanks which was digested in the same digestion procedure as the actual samples [34,35]. LOD is calculated as

$$LOD = 3 \times s_{bl}$$

Where s_{bl} is the standard deviation of the method blank.

3.6.3. Limit of quantification

The limit of quantification (LOQ) is the lowest concentration of an analyte in a sample which can be quantitatively determined with acceptable uncertainty. LOQ was obtained from triplicate analysis of five method blanks which were digested in the same digestion procedure as the actual samples [36]. The LOQ was calculated as

$$LOQ = 10 \times s_{bl}$$

where sbl is the standard deviation of the method blank.

3.7.3. Precision And Accuracy

Precision and accuracy of the results was assessed by determining recovery and repeatability by spiking known concentration of analyte and repeated measurements. For doing so, each sample was spiked in replicates of five at near mid-range calibration concentration. The spiked sample was digested and analyzed following the same analytical procedure as the water samples. Precision is expressed as relative standard deviation (RSD) of replicate results. The relative standard deviations of the sample were obtained as:

$$\%RSD = \frac{standard\ deviation}{mean\ value} x100$$

The percentage recoveries of the analyte are calculated to evaluate the accuracy of the analytical procedure. Recovery was then calculated as [31]

$$\%\boldsymbol{R} = \frac{\textit{Conc.in spiked sample} - \textit{conc.unspiked sample}}{\textit{actual spike conc.}} \ \textbf{x100}$$

3.7.4 Statistical Analysis

Significance of variation in metal concentration with in the three Sample River, spring and well water was analyzed utilizing the statistical tool (ANOVA) at $P \leq 0.05$. The correlation analysis was also carried out to determine the relationship between the concentrations of metal ions in water.

4. RESULTS AND DISCUSSION

4.l. Analytical performance study

Calibration curves for Cr, Cd, Zn, Pb, Co and Cu were obtained by using suitable standard solutions prepared from stock solutions. These curves were obtained by plotting absorbance readings against corresponding concentrations of the metals investigated with optimized instrument conditions.

Table 4.1. Concentrations of working standard solutions for GFAAS instrument calibration and its response towards correlation coefficients and detection limit.

Metal	Concentration of working standard (mg/L) solution	Correlation coefficient (R^2)	IDL (mg/l)	MDL (mg/l)	QOL (mg/l)
Cr	0.05,0.5, 0.1,1.5,2.5	0.999	0.0001	0.011	0.04
Cu	0.05,0.5, 0.1,1.5,2.5	0.999	0.0001	0.003	0.010
Zn	0.05,0.5, 0.1,1.5,2.5	0.999	0.00005	0.001	0.003
Cd	0.05,0.5.0.1, 1, 1.5, 2.5	0.999	0.0001	0.002	0.007
Pb	0.05,0.5.0.1, 1, 1.5, 2.5	0.999	0.0007	0.003	0.010
Co	0.05,0.5, 0.1,1.5,2.5	0.999	0.0003	0.002	0.003

The validation parameters indicated in the table above indicate that he determination coefficient (R^2) values that are closer to 1 good agreement between instrument and method detection limit.

4.2. Recovery Test

The accuracy of method used for this study were validated by spiking known standards for recovery determination which is usually helpful in the absence of certified reference material (CRM) to evaluate the accuracy of the method applied for the analyte determination. The percent recoveries were calculated after small and known amounts of the heavy metals from the stock solutions were spiked in to the water to be digested.

Table 4.2. Recovery and precise test results of metals for spring, well water and river water matrix spiked samples.

Metal	Conc. In sample (mg/l)	Amount added (mg/l)	Conc. In spiked (mg/l)	Recovery (%)
Pb	0.01887	2	2.05472	101.6
Zn	0.227596	1.5	1.44353	81.1
Cu	0.047604	1.5	1.340132	86.2

As shown in table, the percentage recovery for the water samples lie in the range of 81.1 – 101.6 %, which are within the acceptable range for each metal indicating good accuracy for the analysis procedure [37].

4.3. Level of heavy metals in water samples

The concentration of heavy metals (Cr, Zn, Cu, Cr, Cd and Pb) in water samples using Graphite furnace atomic absorption spectrometry (GFAAS) are presented as an average of the determination of triplicate analysis [38].

Table.4.3. Average Concentration Target Heavy Metals (Mean ± SD) (mg/L) For n = 3.

Site	Zn	Cu	Pb	Cd	Co	Cr
Well water	1.98±0.046	1.57±0.0009	0.0034±0.002	BDL	BDL	BDL
Spring water	2.045±0.067	1.58±0.005	0.0135±0.015	BDL	0.016±0.007	BDL
River	1.985±0.029	1.577±0.002	0.003±0.0007	BDL	0.028±0.009	BDL
Mean	2.003±0.142	1.576±0.008	0.02±0.005	-	0.022±0.003	-
RSD %	7.08	0.51	2.5		15	
WHO 2008	5	2	0.05	0.003	0.5	0.05

BDL is Below of Detection Limit

Zn was detected appreciably in all the water samples. Zn level ranged from 1.98 to 2.045 mg/L. Zn was relatively highest in spring water than other water samples. Well water had the lower Zn level among the three water samples with the concentration level of 1.98 mg/L, But the amount Zn found in spring water sample is less than that in recommended 3.0 mgL^{-1} for drinking water by WHO and EPA[39,40]. In mineralized spring water the level of recommended by WHO does not pose a hazard to health [41]. Therefore, the spring water samples as well as the well water and Jawi river could not be a treat on humans upon drinking these waters as far as Zn is concerned. This indicates that water from the sampled water contain the right proportion of Zn which is an essential plant and human nutrient element [42].

Lead (Pb): is a toxic and non-essential metal having no nutritional value to living organisms and its level ranges (0.003-0.04 mg L^{-1}. Pb level was higher in the spring water than the river and well waters but the level range in all samples were below the level recommended for good health, since the levels of Pb in all the water samples were lower than the accepted value of WHO guideline, 0.05 mg/L for drinking water[43,44].

Copper is an essential substance to human life, but in high doses it can cause anemia, liver and kidney damage, and stomach and intestinal irritation [45]. Copper occurs in drinking water from copper pipes, as well as from additives designed to control algal growth. In these study the concentration of Cu in Well water, spring water and River water samples were below permissible limit of WHO maximum allowable concentration 2 mg/l in drinking water standard [46, 47]. For human health risk concerns, the concentrations of Cu in these samples were far below the maximum permissible limit therefore, regular consumption of water with such low amounts of Cu could not lead to any serious health risk as far as Cu is concerned. Thus copper is an essential plant and human nutrient element.

The Cr and Cd concentration content level below detection of limit and hence, it is possible to say all the studied water samples are safe interims Cd and Cr metal. Generally, the distribution pattern of heavy metals concentration in mineral water samples looks greater except Co in River water [48].

4.4. Stastical Analysis

Data were analyzed using SPSS (Version 23) Soft water and Micro excel soft 2007 ware data was generated and presented for all variables as Mean ±SD.

One-way analysis of variance (ANOVA) was made at 95% confidence level. The results showed that there is a significant differences ($p < 0.05$) in the concentrations of the heavy metals Zn, Cu, and Pb among the analyzed water samples while significant variation was observed at ($p < 0.05$) for concentration of Cobalt in all the three water samples[47].

4.5. Correlation Analysis

Pearson's correlation coefficient was used to examine the relationship between the various heavy metals in the water samples from all the sample sites. The correlation matrix of the relationship between heavy metals concentration of water samples reported that high correlation coefficient (near +1 or −1) means a good relation between two variables at a significant level of 0.05%. It can be strongly correlated, if $r > 0.7$, whereas r values between 0.5 and 0.7 shows moderate correlation between two different parameters [49].

Table 4.5. Correlation coefficient (r) matrix for heavy metals concentration in water samples

Metal	Zn	Cu	Pb	Cd
Zn	1			
Cu	0.680*	1		
Pb	0.215	0.002	1	
Cd	0.748*	0.958**	0.228	1

As can be seen from the Table the results of the correlation coefficients showed strong positive correlation between*Cd with Cu ($r=0.958^{**}$), Cr with Co($r=0.862^{**}$), Zn with Cd ($r = 0.748^{*}$). This strong positive correlation shows that the elements are closely associated, thus suggesting their common origin. There were also moderate positive correlations Zn with Cu ($r = 0.680^{*}$) [49].

4.6. Comparison of Heavy Metal Concentration from the Current Study with those Reported on the Literature

The comparison of heavy metal concentration of the current study with literature reports from different countries on the levels of selected heavy metals in water samples.

Table 4.6. Comparison of heavy metals in Jawi river, Mineral and well water (mg/L) with reported literatures.[48,58]

Heavy Metals	Concentration (mg/L)	Location	References
Zn	1.98±0.046- 2.045±0.067	Hawisa Bulo	Present study
	0.069-0.18	Egypt	Authman and Abbas, 2007
	0.01-5.62	Tanzania	Kisamo, 2003
Cu	1.57±0.0009 - 1.58±0.005	Hawisa Bulo	Present study
	0.03-0.21	Arbanch	Belay and Eshete, 2014
Pb	0.003±0.0007 - 0.0135±0.015	Hawisa Bulo	Present study
	6.5-7.59	Sirlanka	Senarathne and Pathirate
Co	0.016±0.007 - 0.028±0.009	Hawisa Bulo	Present study
	0.072 - 0.097	Ambo	Mulugeta, 2014

The selected heavy metals obtained results for this specific work get compared with similar works and it looks not as such frustrating but the signal is indicating as continuous monitoring is mandatory [52,53].

4.7. Analysis for Some Physicochemical Parameters

Table 4.7. pH, Turbidity and Electrical conductivity values for the three water samples (n=3).

Types physical properties	Water Samples (Mean ±SD)		
	Well water	Spring water	Jawi river
PH	7.94±1.51	6.97±0.32	7.9±0.29
Turbidity (NTU)	5.97±0.06	2.160±0.02	24.73±0.06
Electrical conductivity(EC) (µS/cm)	269±0.00	93.867±0.058	1245.33±537.33

4.7.1. pH

In this study, the concentration of hydrogen ion (pH) ranges between 6.97 to 7.94 and the minimum value recording at site spring water and the maximum value recorded at site River water and the variations are significant at $P<0.05$. All the water samples analyzed have concentration within the safe limit of 6.5 to 8.5 standard set by the WHO [51].

Therefore according to the USEPA guidelines all the spring water as well as the well water samples are suitable for drinking. The pH is a measure of the hydrogen ion concentration and indicates whether the water is acidic or alkaline [50, 51].

4.7.2. Electrical conductivity (EC)

Electrical conductivity (EC) is a measure of the ability of aqueous solution to carry an electric current that depends on the presence and total levels of ions, their mobility and valence. The EC is a valuable measure of the amount of metal ions dissolved in wastewater.

In present study, the values of EC in all sampling points were ranged from 93.87 to 1245.33. The minimum value EC is recorded at site spring water and the maximum value recorded at site river water. The values obtained in all sampling sites were within the standard value of WHO drinking water quality which is 500µS/cm. So well water and spring water are good for use [59]. But Jawi river water is above maximum WHO guide line it may waste water an estimate of the presence of certain ions in water such as carbonate, bicarbonates, chloride, sulphate, nitrate, sodium, potassium, calcium, magnesium, all of which carry an electrical charge. The presence of these chemical constituents gives water the ability to conduct electricity. Compared to these standards, spring water and well water site and of River had electrical conductivity values above the maximum permissible limit. This is a clear indication of the river water contains high quantity of dissolved ionic salts that might not be safe both to humans and other domestic animals [56].

4.7.3. Turbidity

Turbidity is a measure of cloudiness of water. It has no health effects. However, turbidity can interfere with disinfection and provide a medium for microbial growth. High turbidity may indicate the presence of disease causing organisms. These organisms include bacteria, viruses, and parasites that can cause symptoms such as nausea, cramps, diarrhea, and associated headaches [57,58]. The average turbidity value of the Jawi River and well water were above the limits of allowed drinking water quality, according to the WHO standard, which is 5 NTU .The mean values of turbidity varied from 2.16 NTU to 24.73 NTU. While the average turbidity value of the three sample sites of the water 2.16 NTU. The maximum turbidity value has been observed at the river sample site one and was 24.73 NTU. This might be due to the soil erosion and discharging of waste plant materials, it is a place where by-products of wild life and other animal wastes enter in to the river, which may increase turbidity [60,61].

5. CONCLUSIONS AND RECOMMENDATION

5.1. Conclusion

The obtained result reviled high concentration Zinc and Copper were observed in spring water that indicates there can be natural sources from the nearby rocks and except Cr and Cd found below the detection of limit other metals were detected in all the samples implying requirement of further analysis. Except pH in all water samples among the selected physical parameters which is in a safe range for all water samples, Electrical conductivity and turbidity of Jawi River is above the standard for drinking water set by the World Health Organization (WHO).

5.2. Recommendation

The researcher recommends the following

- ✓ Seasonal variation based investigation of heavy metals in all the three water sample is necessary due to some implication of heavy metals in all water samples utilizing more sensitive instruments.
- ✓ It is also important to investigate the level other potential water contaminants such as chemicals, microbial and more heavy metals for a longer period of time for the reason some obtained physical parameters above permissible limit may cause bacterial growth.

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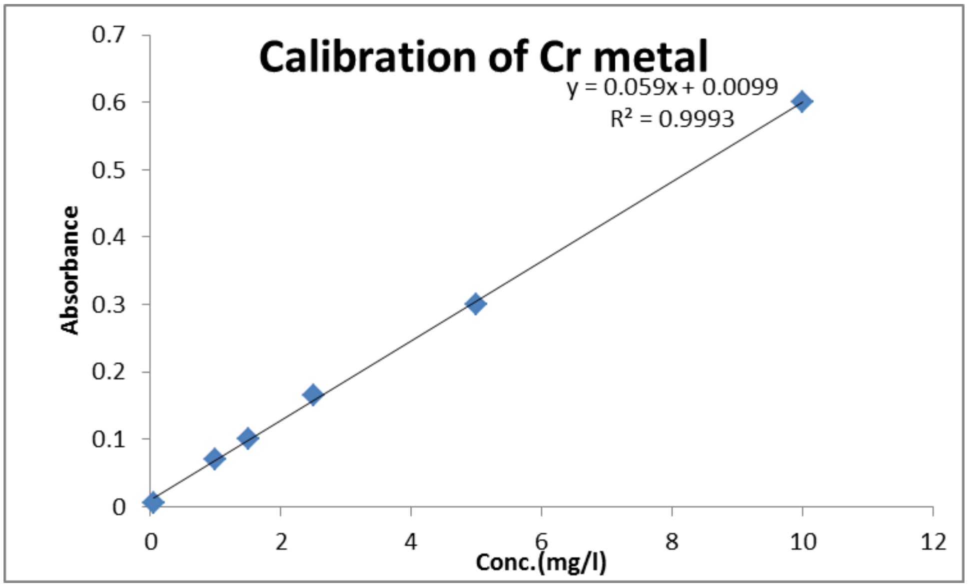
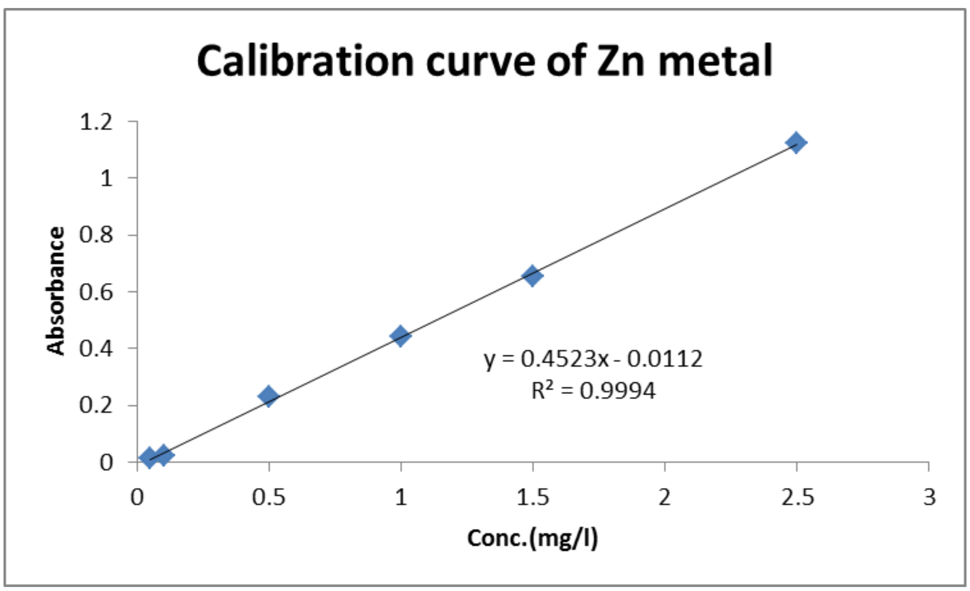
Appendices

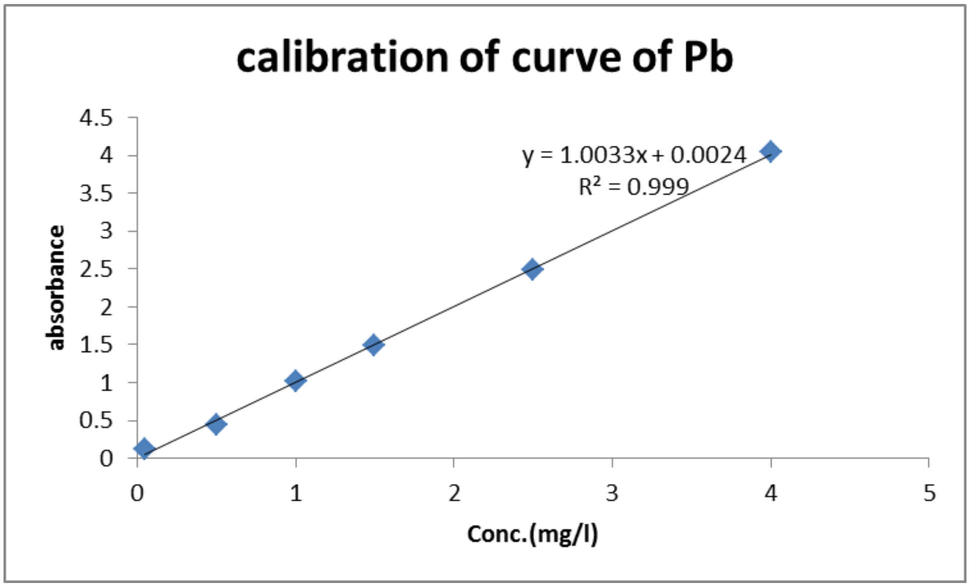
Appendix 1: Calibration Curves of heavy metals for River, spring and well water samples

A.



B.




calibration of curve of Pb
y = 1.0033x + 0.0024
R² = 0.999
absorbance
Conc.(mg/l)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
0
1
2
3
4
5

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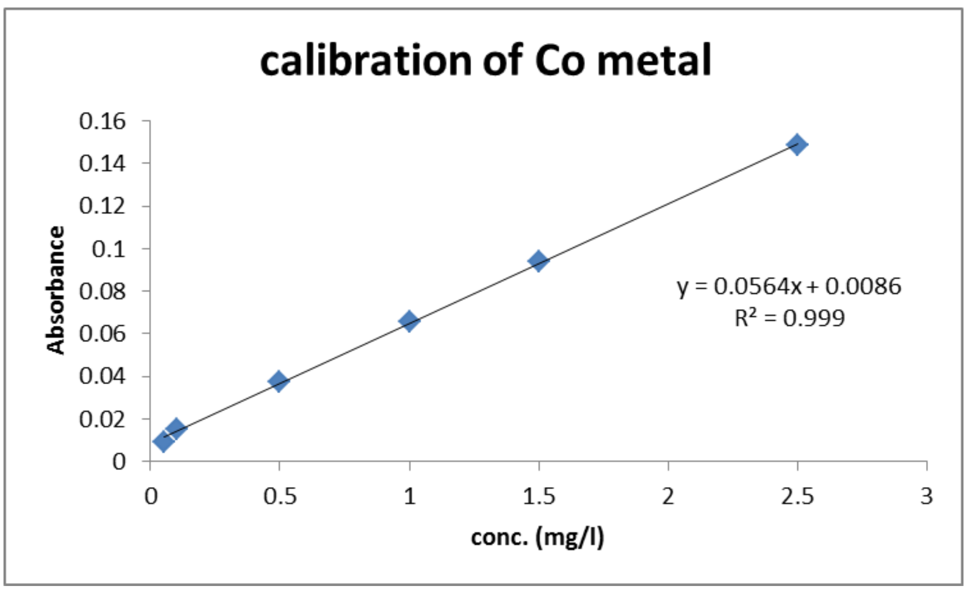
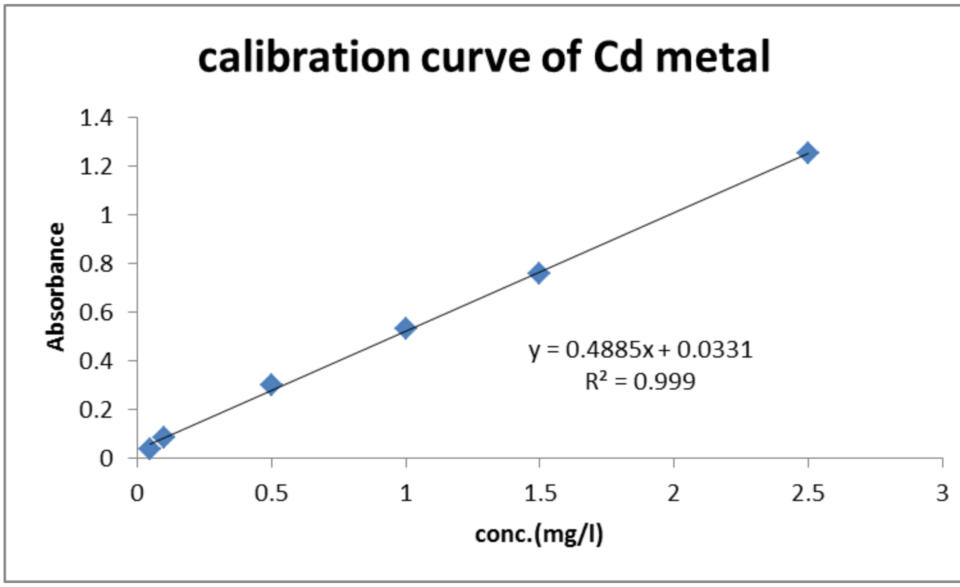
D.

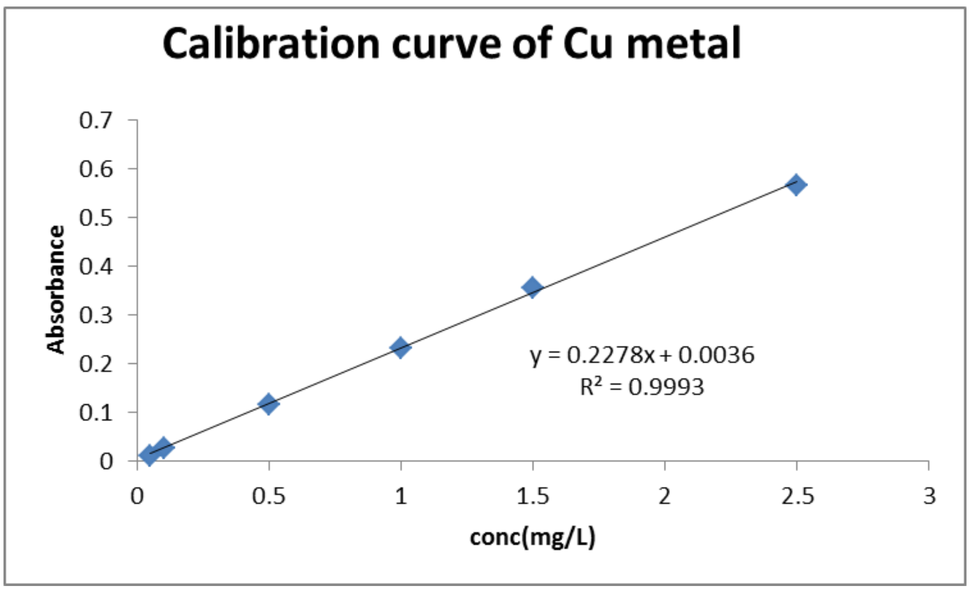

calibration of Co metal
y = 0.0564x + 0.0086
R² = 0.999
Absorbance
conc. (mg/l)
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0
0.5
1
1.5
2
2.5
3



calibration curve of Cd metal
Absorbance
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
0.5
1
1.5
2
2.5
3
conc.(mg/l)
y = 0.4885x + 0.0331
R² = 0.999

E.

F.



Calibration curve of Cu metal
Absorbance
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.5
1
1.5
2
2.5
3
conc(mg/L)
y = 0.2278x + 0.0036
R² = 0.9993

ANOVA between and within selected heavy metals in dirking water from different source of samples at 95% confidence level

Heavy Metals	Sources of varation	Degree of reedom	F calc.	P values.
Zn	Between samples	2	1.468	0.303
	Within samples	6		
	Total	8		
Cu	Between samples	2	3.811	0.085
	Within samples	6		
	Total	8		
Pb	Between samples	2	1.419	0.313
	Within samples	6		
	Total	8		
Cd	Between samples	2	8.867	0.016
	Within samples	6		
	Total	8		
Co	Between samples	2	15.464	0.004
	Within samples	6		
	Total	8		
Cr	Between samples	2	17.688	0.003
	Within samples	6		
	Total	8		

ANOVA between and within physical in dirking water from different source of samples at 95% confidence level

Physical parameter	Source of variation	Degree of freedom	F calculate	P value
PH	Between samples	2	1731.267	0.000
	Within samples	6		
	Total	8		
Turbidity	Between samples	2	26199.684	0.000
	Within samples	6		
	Total	8		
EC	Between samples	2	798922.580	0.000
	Within samples	6		
	Total	8		