JIMMA UNIVERSITY

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DEPARTMENT OF CHEMISTRY

M.Sc THESIS ON

LEVEL OF SELECTED HEAVY METALS IN DRINKING WATER OF ASSOSA DISTRICT, ASSOSA ZONE, BENISHANGUL GUMUZ REGIONAL STATE, SOUTH WEST ETHIOPIA.

BY Maereg Wondye

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JIMMA UNIVERSITY

ETHIOPIA

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This is to certify that a thesis submitted by Maereg wondye**:** Level of selected heavy metals in drinking water in Assosa district, Assosa Zone, Benishangul Gumuz regional state, south west Ethiopia in partial fulfillment of M. Sc degree in Chemistry (Analytical stream) complies with the regulations of the university and meets the accepted standards with respect to originality and quality.

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Abbreviations

APHA - American public health association

EPA - Environmental protection agency

ICP-OES - Inductively coupled plasma-optical emission spectrometry

PPm - Parts per million

UNEP - United Nations Environmental Program

USEPA- United states environmental protection agency

UNESCO - United nation educational science and cultural organization

UNICEF - United nations international children’s fund

WHO - World health organization

Abstract

Heavy metals are identified as one among a wide ranges of drinking water contaminants. They enter to human body mainly through drinking water and food. Therefore, knowing the status of heavy metals in drinking water is important to monitor the quality of water.This research dealt with determination of the levels of five heavy metals namely: Fe, Cu, Zn, Cd and Pb in the groundwater of 11 different Kebeles of Assosa district,Benishangul Gumuz regional state, Ethiopia. Samples from each Kebele were collected for four consecutive days from May 22-26/2017 and transported to Jimma university chemistry department research laboratory. EPA 3005A method was used for digestion of the water samples.Accordingly 50 mL of triplicate samples were digested by mixing with 1 mL concentrated (69%) HNO_3*, 2.5 mL concentrated (37%) HCl and 4 drops of (30%)* H_2O_2 *until the volume was reached 15 mL.. Calibration curve for each metal was prepared by plotting the emission intensity as a function of metal standard concentration. The correlation coefficients of the calibration curves were 0.999 for Fe, Zn, Cd, and Pb whereas 0.996 for Cu. The recoveries for almost all metals analyzed were in the range of 70% - 130% except Pb which had 66% in Alubo. Thus, all the results are in the acceptable range. The levels of these metals were determined by analyzing the digested samples using Inductivly coupled plasma- optical emmision spectrometry (ICP-OES). All samples analyzed contained one or more of the five metals under determination each in varying concentration. Fe concentration varied from* 0.367 ± 0.19 *to* 1.36 ± 0.39 *mg/L,Cu varied from* 0.072 ± 0.09 *to* 0.096 ± 0.17 *mg/L, Zn varied from* 0.142 ± 0.48 *to* 0.519 ± 0.77 *mg/L.The observed results showed that the concentrations of Fe, Cu and Zn were not detected in some samples similarly, Cd was also not detected in two samples and its concentration was below LOQ in all other samples whereas Pb was not detected in all cases. Statistical data analyses showed that concentration of Fe, Cu, Cd and Zn were significantly diffrent at 95% confidence level in the water samples..The overall mean concentration of metals in the analyzed water sources followed the order of Fe > Zn >Cu . In general, the result obtained in this study indicated that Cu, Zn, Cd and Pb metals are in their safe level in all water samples. But the concentration of iron is above the WHO limit. Accordingly, it is recommended to follow up the content of heavy metals in the well waters of the study area.*

Key words: Drinking water, ICP-OES, heavy metals.

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1. Introduction

Water is basic for living organisms in the world. Water is among the most essential requisites that nature provides to sustain life for plants and animals. Water having secured first priority amongst man's needs, it is also the life-blood of industry namely: manufacturing, generation of electric power, transportation and recreation [1].

Human consumed water daily to drink, clean, prepare food and other purposes. Water could be obtained in air as water vapor and in the ground from springs, wells, boreholes water and in the surface in the form of ocean, river, lakes, streams and ponds, which covers about three-fourth of the earth crust. Excluding fats, water comprises approximately 70% of human body by mass [2]. Having safe drinking water and basic sanitation is a need and right for human being.Yet 884 million people around the world live without safe drinking water and 2.5 billion people still lack access to improved sanitation [3]. More than 70% of earth crust is covered with water, but many people have short of water for themselves, their animals and their crops. There are many sources of water to human but many people depend on surface water and ground water. Ground water is one of the major importance to the civilization, because it is the larger reserved of drinkable water in region were human can live [4]. Water treatment involves physical, chemical, and biological changes to transfer contaminated water into potable water. Determination of water quality is one of the most important aspects in groundwater studies. Groundwater is highly valued because of certain properties not possessed by surface water [5, 6]. People around the world have used groundwater as a source of drinking water, and even today more than half of the world's population depends on groundwater for survival. In recent times, increasing focus is being given to studies on groundwater contamination. Because, groundwater is directly in contact with soil, rock, and plant, the constituents of these sources might contaminate the groundwater [7,8].

Trace elements constitute a natural component of the earth crust and they are not biodegradable, hence persist in the environment. Trace elements may come from natural sources, leached from rocks and soils according to their geochemical mobility or come from anthropogenic sources, as the result of human land occupation and industrial pollution [9].

Depending on their solubility, these metals may eventually become associated with suspended particulate matter and accumulate in the bottom sediments. The increase of industrial activities has intensified environmental pollution problems and the deterioration of several aquatic ecosystems with the accumulation of metals in biota and flora [10]. Although trace metals at low concentrations are essential to life, at high concentrations, may become hazardous.

Heavy metals pollution represents a serious problem as these metals leach into ground water or soil, which is detrimental to human health. Ground water pollution is a consequence of several activities like chemical manufacturing, painting and coating and mining.

These days, there has been an increasing health related concern associated with the quality of drinking water in developing countries. According to a recent report by UNICEF/ WHO, about 780 million people in the developing world lack access to potable water due to largely microbiological and chemical contaminations [11]. Drinking water sources in developing countries are under increasing threat from contaminations by chemical, physical and microbial pollutants. Known sources (both naturally occurring and anthropogenic) of chemical contamination of water supplies include organic and inorganic substances from industrial effluents, municipal wastes, petroleum derived hydrocarbons, detergents, mining, agricultural pesticides and fertilizers [12,13]. However, it has been reported that groundwater also contains enhanced concentrations of arsenic, iron, fluoride, radioactive elements and nitrates as well as some other heavy metals attributed to natural processes as well as human mediated activities [14].

Trace metals, among a wide range of contaminants, are consistently of health concern due to their toxicity potentials at very low concentrations, and tendency to bioaccumlate in tissues of living organisms over time [15]. They gain entrance into human systems via contaminated drinking water, food and air. Once in the body, the bioavailable form of these metals can compete with, and displace essential minerals such as zinc, copper, magnesium and calcium; and interfere with organ system function [16]. Even if no sources of anthropogenic contamination exist, natural sources are also equally potential to contribute higher levels of some metals and other chemicals that can harm human health. This is highlighted recently in Bangladesh where natural levels of arsenic in groundwater were found to be causing harmful effects on the population [17].

Toxic metals such as mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Ti) and lead (Pb) have no beneficial effects in humans, long-term exposure to these metals may cause more severe disruptions in the normal functioning of the organ systems where the metals are accumulated [18]. However, as micronutrients, some trace metals such as Zn, Cu, Fe and Mn are required by the body in small amounts for metabolic activities. But, at higher concentrations they can also cause adverse health effects [19].

In Ethiopia, the dominant source of drinking water used to supply major urban and rural communities is from wells, rivers, lakes and springs [20]. Even though, there are no systematic and comprehensive water quality assessment programs in the country, there are increasing indications of water contamination problems in some parts of the country. The major causes of this contamination could be soil erosion, domestic waste from urban and rural areas and industrial wastes [21].

This research work was aimed to assess the concentrations of Fe, Pb, Cu, Zn and Cd in drinking water of Assosa district which is located in Assosa Zone, Benishangul Gumuz regional state, south west Ethiopia. It also attempted to compare the concentrations of these metals with the water quality permissible limits specified by WHO.

1.1 Statement of the problem

Heavy metals such as Pb, Cu, Zn, Cd, and Fe may be present in an environment through natural and anthropogenic causes and the presence of Fe, Zn and Cu in trace concentrations is important for human health and development but, Pb and Cd have no known benefit. On the contrary, if the concentration of these heavy metals surpasses the maximum admissible levels as stipulated by various organizations such as world health organization and American public health association they may cause acute toxicity. For example, lead accumulation in the body adversely affects many enzymatic systems causing lead poisoning of the heme system. High levels of iron in the body can cause a condition known as hemochromatosis, affecting the liver, pancreas and heart [22].

In the current situation ground water contamination has become one of the main environmental problems. There are various categories of the contaminant but heavy metals are of particular concern due to their toxicity even at low concentration. Therefore, regular monitoring of the concentrations of heavy metals in drinking water is important and it is necessary to investigate the concentration of heavy metals of the drinking water, which is groundwater, in Assosa district.

1.2 Objectives:-

1.2.1 General objective:-

To determine the level of some selected heavy metals in drinking water of Assosa district, Assosa zone, Benishangul Gumuz Regional State.

1.2.2 Specific Objectives:-

i. To determine the level of some selected heavy metals in well drinking water.
ii. To evaluate the status of selected heavy metals pollution in drinking water.
iii. To compare the concentration of Fe, Cu, Zn, Cd and Pb metals with the recommended WHO Permissible limits.
iv. To compare with other studies.

1.3 Significance of the study

There are no reports so far in the litrature on the study of heavy metals content in the study area. Hence, the proposed study may provide a base line data on the level of heavy metals in Assosadistrict.

It is also essential to determine the concentration of heavy metals present in drinking water which helps to provide information that will improve or enhance good quality of drinking water in the region.

1.4 Scope and Limitations of the study:

The research only focuses with the purpose of determining the presence and concentration of some heavy metals (Fe, Cu, Zn, Cd and Pb) in drinking water of Assosa district. Because some of these metals (Cd, Pb) are among the ‘‘top 20 hazardous substances’’ listed by the Agency for toxic substances and disease registry (ATSDR) which are of great concern to human health and the environment [23]. Most of these metals were identified as they had adverse health effect particularily in children when improperly managed [24].

The water samples that were collected are limited in number and place due to the resource incapability that would be encountered to cover the full cost of the study and also difficulty of transporting water samples from the study area to Jimma university chemistry department research laboratory.

2. Literature review

Water is abundant on the planet which we live as a whole, but fresh potable water is not always available at the right time or the right place for human or ecosystem use. It is undoubtedly the most precious natural resource, vital to life and a fundamental political issue Drinking water of good quality is essential for human health and development. The importance of clean water, clean air and safe working conditions spawned the public health era in the mid of 1850s [25].

2.1 Quality ofdrinking water

Good quality drinking water may be consumed in any desired amount without adverse effects on health. Such water is called 'potable'. It is free from harmful materials such as bacteria, viruses, minerals, undesired content of heavy metals and organic substances. It is also aesthetically acceptable and is free of unpleasant impurities, such as objectionable taste, color, turbidity, and odor. As fresh water supplies are further stretched to meet the demands of industry, agriculture and an ever-expanding population, the shortage of safe and accessible drinking water will become a major challenge in many parts of the world. In the wake of several major outbreaks involving food and water, there is a growing concern for the safety and quality of drinking water. The most common problems in household water supplies may be attributed to hardness, iron, sulfides, sodium chloride, acidity, and disease producing pathogens, such as bacteria and viruses [26]. The purity of drinking water also depends on the sources and water type. The water used may be from any source, including spring water; well water purified water, municipal water, or even contaminated water [23].
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 World Health Organization (WHO) publishes guidelines for drinking-water quality which many countries use as the basis to establish their own national standards. The guidelines represent a scientific assessment of the risks 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 have been taken into account through a risk-benefit approach when adapting the guideline values to national standards. As the WHO Guidelines for drinking-water

quality are meant to be the scientific point of departure for standards development, including bottled water; actual standards will sometimes vary from the guidelines [27].

2.Sources of water pollution

Water is essential for the existence of all life forms. In addition to household uses, water is vital for agriculture, industry, fishery and tourism etc. Water Pollution is a global problem. It occurred when humans began to farm the land and settle in villages and towns many thousands of years ago [28]. There are numerous sources of pollutants that could deteriorate the quality of water resources. In developing countries sources of pollution from domestic, agricultural, industrial activities are unregulated [29].

Increasing population, urbanization and industrialization has led to the decreased availability of water. The quality of water used is also being deteriorated as it is getting more and more polluted. A large amount of water is discharged back after domestic and industrial usage. This is contaminated with domestic waste reaches beyond certain allowed concentrations, Water pollution may be defined as the contamination of streams, lakes, seas, underground water or oceans by substances, which are harmful for living beings. If the concentration of substances naturally present in water increases then also the water is said to be polluted.

Naturally occurring contaminants are generally the result of leaching from geologic formations and are found primarily in groundwater [23]. Man -made pollution of water is either due to point source which is caused by discharge of pollutants from specific location for example discharge from factories sewage treatment plants and oil tankers into rivers, or non-point source which occurs from rainfall or melting of snow and the run-off washes away pollutants into lakes, rivers and coastal waters [30].

Water may be called polluted when the following parameters reach beyond a specified concentration in water.

i). ***Physical parameters***. Colour, odour, turbidity, taste and temperature constitutes the physical parameters and is good indicators of contamination.

For instance, colour and turbidity are visible evidences of polluted water while an offensive odour or a bitter and difference than normal taste also makes water unfit for drinking.

ii).***Chemical parameters***: These include the amount of carbonates, sulphates, chlorides, fluorides, nitrates, and metal ions. These chemicals form the total dissolved solids, present in water.

iii). ***Biological parameters***: The biological parameters include matter like algae, fungi, viruses, protozoa and bacteria. The life forms present in water are affected to a good extent by the presence of pollutants. The pollutants in water may cause a reduction in the population of both lower and higher plant and animal lives. Thus, the biological parameters give an indirect indication of the amount of pollution in water.

Water pollutants refer to the substances which are capable of making any physical, chemical or biological change in the water body. These have undesirable effect on living organisms. The water used for domestic, agricultural and industrial purposes is discharged with some undesirable impurities in it. This contamination leads to the pollution of water, which is generally called the fresh water pollution. Fresh water pollution may be classified into two types: surface water pollution and ground water pollution.

2.3.Groundwater pollution

Ground water in its natural state tends to be relatively free from contaminants in most areas. Because it is a widely used source of drinking water, pollution of ground water can be very serious problem. The groundwater quality of Ethiopia is both anthropogenically and naturally affected [31].The main quality controls are: geomorphological and geographical conditions, climate, geology (geological structures, rock composition, weathering and geothermal activities), physico-chemical factors (temperature, pressure, chemical properties of elements, solubility of chemical compounds, pH, etc.),biological factors (effects of micro-organisms, plants and animals) and anthropogenic influences [32].

When the polluted water seeps into the ground and enters an aquifer it results into groundwater pollution. Most of our villages and many townships, ground water is the only source of drinking water. Therefore, pollution of groundwater is a matter of serious concern.

Groundwater gets polluted in a number of ways. The dumping of raw sewage on soil, seepage pits and septic tanks cause pollution of groundwater. The soluble pollutants are able to mix with the groundwater. In addition to these, the excessive use of nitrogenous fertilizers and unchecked release of toxic wastes and even carcinogenic substances by industrial units many result in slow trickling down through the earth’s surface and mixing with the groundwater [33]. This problem is very serious especially in areas where water table is high (i.e., where water is available near surface of earth).

The ground water can move over large distances by virtue of the large empty space available below the earth's surface. This way if some impurities seep into the ground water at one point, they may be observed at a different point far removed from the point of source. In such a case it is difficult to estimate the source of water pollution. However, suspended impurities and bacterial contaminants are removed in the process of seepage by the soil acting as an absorbent and filter, and water acting as a solvent [34].

Since the movement of groundwater through the porous rock is very slow, pollutants which get mixed with the groundwater are not readily diluted [35]. Furthermore, groundwater does not have access to air (in contrast to surface water) therefore, oxidation of pollutants into harmless products in groundwater does not occur.

2.4.Heavy metals and their toxicity

Metals occur naturally in the earth's crust and their contents in the environment can vary between different regions resulting in spatial variation of background concentrations. The distribution of metals in the environment is governed by the properties of metals and influence of the environmental factors. The term "heavy metals" refer to elements having atomic weights between 6 .5 and 200.6 and a specific gravity more than 5.0 [36].Heavy metal can enter surface or ground water through natural sources, industrial sewage, and leakage from urban or agricultural areas, water pipes walls or even from domestic sources. Some heavy metals are toxic or carcinogenic, and are not biodegradable and tend to accumulate in living organisms [37]. When natural water bodies are contaminated with wastewater containing higher concentration of heavy metals, it affects aquatic life and is destructive to the environment. Bioaccumulations of heavy metals in the body through food chain lead to a variety of incurable diseases when people drink the water or eat the food contaminated by heavy metals [38]. Some heavy metals namely, cobalt, copper, iron, manganese, molybdenum, vanadium, strontium, and zinc are required in trace amount by living organisms. However, they can be detrimental to the organism when they are in excessive level. Non-essential heavy metals of particular concern to surface water systems are cadmium, chromium, mercury, lead, arsenic, and antimony [36]. Many toxic heavy metals are present in water supplies, usually at high levels. Treatment and potabilisation plants work are very well reducing these toxic heavy metals to safe levels.

2.5. Human health effects and sources of some heavy metals

Heavy metals are quite essential to maintain various biochemical and physiological functions in living organisms when in very low concentrations; however they become noxious when they exceed certain threshold concentrations.

Heavy metals are individual metals and metal compounds that have many adverse health effects and last for a long period of time, heavy metal exposure continues and is increasing in many parts of the world. Heavy metals are significant environmental pollutants and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons [39, 40]. Health risks of heavy metals include reduced growth and development, cancer, organ damage, nervous system damage and in extreme cases death. The most commonly found heavy metals in waste water include arsenic, cadmium, chromium, copper, lead, nickel, and zinc, all of which cause risks for human health and the environment [41]. Heavy metals enter the surroundings by natural means and through human activities. Various sources of heavy metals include soil erosion, natural weathering of the earth's crust, mining, industrial effluents, urban runoff, sewage discharge, insect or disease control agents applied to crops, and many others [42].

Heavy metal toxicity can lower energy levels and damage the functioning of the brain, lungs, kidney, liver, blood composition and other important organs. Long-term exposure can lead to gradually progressing physical, muscular, and neurological degenerative processes that imitate diseases such as multiple sclerosis, Parkinson's disease, Alzheimer's disease and muscular dystrophy. Repeated long-term exposure of some metals and their compounds may even cause cancer [43]. The toxicity level of a few heavy metals can be just above the background concentrations that are being present naturally in the environment. Hence thorough knowledge of heavy metals is rather important for providing proper defensive measures against their excessive contact [44].

Although these metals have crucial biological functions in plants and animals, sometimes their chemical coordination and oxidation-reduction properties have given them an additional benefit so that they can escape control mechanisms such as homeostasis, transport, compartmentalization and binding to required cell constituents. These metals bind with protein sites which are not made for them by displacing original metals from their natural binding sites causing malfunctioning of cells and ultimately toxicity. Previous research has found that oxidative deterioration of biological macromolecules is primarily due to binding of heavy metals to the DNA and nuclear proteins [45]. Generally, humans are exposed to these metals by ingestion (drinking or eating) or inhalation (breathing).Working in or living near an industrial site which utilizes these metals and their compounds increases ones risk of exposure, as does living near a site where these metals have been improperly disposed. The toxicity of metal ions to mammalians systems is due to chemical reactivity of the ions with cellular structural proteins, enzymes and membrane system. The target organs of specific metal toxicities are usually those organs that accumulate the highest concentrations of the metal in vivo. This is often dependent on the route of exposure and the chemical compound of the metal i.e. its valiancy state, volatility, lipid solubility etc. Certain metals such as chromium and nickel have been linked with cancers in exposed human populations. Metals have been shown to causes acute as well as chronic poisoning in man and other experimental animals. Harmful effects of individual metals are presented briefly below.

i. Cadmium

Soils and rocks, including coal and mineral fertilizers, contain some amount of cadmium. Cadmium is the seventh most toxic heavy metal. It is a byproduct of zinc production which humans or animals may get exposed to it at work or in the environment. Once this metal gets absorbed by humans, it will accumulate inside the body throughout life. This metal was first used in World War I as a substitute for tin and in paint industries as a pigment.

In today's scenario, it is also being used in rechargeable batteries, for special alloys production and also present in tobacco smoke. About three-fourths of cadmium is used in alkaline batteries as an electrode component, the remaining part is used in coatings, pigments and plating and as a plastic stabilizer. Humans may get exposed to this metal primarily by inhalation and ingestion and can suffer from acute and chronic intoxications. In the US, more than 500,000 workers get exposed to toxic cadmium each year as per. The agency for toxic substances and disease registry [46, 47]. Researchers have shown that in China the total area polluted by cadmium is more than 11,000 hectares and its annual amount of industrial waste of cadmium discharged into the environment is assessed to be more than 680 tons. In Japan and China, environmental cadmium exposure is comparatively higher than in any other country [48]. Cadmium is a highly toxic nonessential heavy metal that is well recognized for its adverse influence on the enzymatic systems of cells and oxidative stress. Cadmium has many uses including batteries, pigments, plastics and metal coatings and is widely used in electroplating [49]. Cadmium and its compounds are classified as Group 1 carcinogens for humans by the

International Agency for Research on Cancer [50]. Cadmium is released into the environment through natural activities such as volcanic eruptions, weathering, river transport and some human activities such as mining, smelting, tobacco smoking, incineration of municipal waste, and manufacture of fertilizers. Although cadmium emissions have been noticeably reduced in most industrialized countries, it is a remaining source of fear for workers and people living in the polluted areas. Cadmium can cause both acute and chronic intoxications [51]. Cadmium is highly toxic to the kidney and it accumulates in the proximal tubular cells in higher concentrations.

Cadmium can cause bone mineralization either through bone damage or by renal dysfunction. Studies on humans and animals have revealed that osteoporosis (skeletal damage) is a critical effect of cadmium exposure along with disturbances in calcium metabolism, formation of renal stones and hyper calciuria. Inhaling higher levels of cadmium can cause severe damage to the lungs. If cadmium is ingested in higher amounts, it can lead to stomach irritation and result in vomiting and diarrhea. On very long exposure time at lower concentrations, it can become deposited in the kidney and finally lead to kidney disease, fragile bones and lung damage [46].

Cadmium and its compounds are highly water soluble compared to other metals. Their bioavailability is very high and hence it tends to bio accumulate. Long-term exposure to cadmium can result in morph pathological changes in the kidneys. Smokers are more susceptible for cadmium intoxication than non-smokers. Tobacco is the main source of cadmium uptake in smokers as tobacco plants, like other plants, can accumulate cadmium from the soil. Non-smokers are exposed to cadmium via food and some other pathways. Yet cadmium uptake through other pathways is much lower [52]. Cadmium interacts with essential nutrients through which it causes its toxicity effects. Experimental analysis in animals has shown that 50% of cadmium gets absorbed in the lungs and less in the gastrointestinal tract. Premature birth and reduced birth weights are the issues that arise if cadmium exposure is high during human pregnancy [50].

ii. **Iron**

Iron is the most abundant transition metal in the earth's crust. Biologically it is the most important nutrient for most living creatures as it is the cofactor for many vital proteins and enzymes. Iron mediated reactions support most of the aerobic organisms in their respiration process. It is one of the vital components of organisms like algae and of enzymes such as cytochromes and catalase, as well as of oxygen transporting proteins, such as hemoglobin and myoglobin [53]. Iron is an attractive transition metal for various biological redox processes due to its inter-conversion between ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions [54]. The source of iron in surface water is anthropogenic and is related to mining activities.

The concentration of dissolved iron in the deep ocean is normally 0.6 nM. In freshwater the concentration is very low with a detection level of 5 µg/L, where as in groundwater the concentration of dissolved iron is very high with 20 mg/L (EPA). In countries like Lithuania, many people have been exposed to elevated levels of iron through drinking water, as the collected groundwater exceeded the permissible limit set by the European Union Directive 98/83/EC on the quality of drinking water [55].

If it is not shielded properly, it can catalyze the reactions involving the formation of radicals which can damage biomolecules, cells, tissues and the whole organism. Iron poisoning has always been a topic of interest mainly to pediatricians. Children are highly susceptible to iron toxicity as they are exposed to a maximum of iron containing products [56].

Excess iron uptake is a serious problem in developed and meat eating countries and it increases the risk of cancer. Workers who are highly exposed to asbestos that contains almost 30% of iron are at high risk of asbestosis, which is the second most important cause for lung cancer [57]. It is said that asbestos associated cancer is linked to free radicals. Loose intracellular iron can also promote DNA damage. Iron can initiate cancer mainly by the process of oxidation of DNA molecules [58]. Iron salts such as iron sulfate, iron sulfate monohydrate and iron sulfate heptahydrate are of low acute toxicity when exposure is through oral, dermal and inhalation routes and hence they have been placed in toxicity category 3. Furthermore, iron salts are considered to be safe by the Food and Drug Administration and their toxic effects are very much negligible. Formation of free radicals is the outcome of iron toxicity [59]. During normal and pathological cell processing, byproducts such as superoxide and hydrogen peroxide are formed, which are considered to be free radicals [60].

These free radicals are actually neutralized by enzymes such as superoxide dismutase, catalase and glutathione peroxidase but the superoxide molecule has the ability to release iron from ferritin and that free iron reacts with more and more of superoxide and hydrogen peroxide forming highly toxic free radicals such as hydroxyl radical [61]. Hydroxyl radicals are dangerous as they can inactivate certain enzymes, initiate lipid peroxidation, depolymerize polysaccharides and can cause DNA strand breaks. This can sometimes result in cell death [62]. The shortage of iron causes disease called “anemia’’ and prolonged consumption of drinking water with high concentration of iron may lead to liver disease called as haermosiderosis [63, 64].

iii. Lead

Lead is a highly toxic metal whose widespread use has caused extensive environmental contamination and health problems in many parts of the world. Lead is a bright silvery metal, slightly bluish in a dry atmosphere. It begins to tarnish on contact with air, thereby forming a complex mixture of compounds, depending on the given conditions.

The sources of lead exposure include mainly industrial processes, food and smoking, drinking water and domestic sources. The sources of lead were gasoline and house paint, which has been extended to lead bullets, plumbing pipes, pewter pitchers, storage batteries, toys and faucets [65]. In the US, more than 100 to 200,000 tons of lead per year is being released from vehicle exhausts. Some is taken up by plants, fixation to soil and flow into water bodies, hence human exposure of lead in the general population is either due to food or drinking water [66]. The ionic mechanism of lead toxicity occurs mainly due to the ability of lead metal ions to replace other bivalent cations like Ca^{2+}, Mg^{2+}, Fe^{2+} and monovalent cations like Na^{+}, which ultimately disturbs the biological metabolism of the cell. The ionic mechanism of lead toxicity causes significant changes in various biological processes such as cell adhesion, intra- and inter-cellular signaling, protein folding, maturation, apoptosis, ionic transportation, enzyme regulation, and release of neurotransmitters. Lead can substitute calcium even in picomolar concentration affecting protein kinase C, which regulates neural excitation and memory storage [67].

Human activities such as mining, manufacturing and fossil fuel burning has resulted in the accumulation of lead and its compounds in the environment, including air, water and soil. Lead is used for the production of batteries, cosmetics, metal products such as ammunitions, solder and pipes, *etc.* [49]. Lead is highly toxic and hence its use in various products, such as paints, gasoline, *etc.*, has been considerably reduced nowadays.

The main sources of lead exposure are lead based paints, gasoline, cosmetics, toys, household dust, contaminated soil, industrial emissions [68].

Lead poisoning was considered to be a classic disease and the signs that were seen in children and adults were mainly pertaining to the central nervous system and the gastrointestinal tract [69]. Lead poisoning can also occur from drinking water. The pipes that carry the water may be made of lead and its compounds which can contaminate the water [70]. According to the Environmental Protection Agency (EPA), lead is considered a carcinogen. Lead has major effects on different parts of the body. Lead distribution in the body initially depends on the blood flow into various tissues and almost 95% of lead is deposited in the form of insoluble phosphate in skeletal bones [71]. Toxicity of lead, also called lead poisoning, can be either acute or chronic.

Acute exposure can cause loss of appetite, headache, hypertension, abdominal pain, renal dysfunction, fatigue, sleeplessness, arthritis, hallucinations and vertigo. Acute exposure mainly occurs in the place of work and in some manufacturing industries which make use of lead.

Chronic exposure of lead can result in mental retardation, birth defects, psychosis, autism, allergies, dyslexia, weight loss, hyperactivity, paralysis, muscular weakness, brain damage, kidney damage and may even cause death [50]. The increase in blood lead concentration affecting a person's IQ [72]. Although lead poisoning is preventable it still remains a dangerous disease which can affect most of the organs. The plasma membrane moves into the interstitial spaces of the brain when the blood brain barrier is exposed to elevated levels of lead concentration, resulting in a condition called edema [73]. It disrupts the intracellular second messenger systems and alters the functioning of the central nervous system, whose protection is highly important. Environmental and domestic sources of lead ions are the main cause of the disease but with proper precautionary measures it is possible to reduce the risk associated with lead toxicity [70].

iv. ***Copper***

Copper is a reddish metallic element that is one of the most widely used of metals.

It is an essential element in all plants and animals. It is mostly carried in the bloodstream on a Plasma protein called ceruloplasmin. When copper is first absorbed in the gut, it is transported to the liver bound to albumin. Copper is also found in a variety of enzymes. A normal healthy adult should take an average of 0.9 mg/day of copper however, research on the subject recommends 3.0 mg/day copper intake. Because of its role in facilitating iron uptake, copper deficiency can often cause anemia related symptoms [74].

Copper is toxic in uncontrolled quantities. The suggested safe level of copper in drinking water for humans varies depending on the source, but pegged at 1.5 to 2 mg/L. In toxicity, copper can inhibit the enzyme dihydrophilhydrase, an enzyme involved in haemopoiesis. A significant portion of the toxicity of copper comes from its ability to accept and donate single electron as it changes oxidation state. This catalyses reaction is used in the production of very reactive radical ions such as hydroxyl radicals. The enzymes use this catalytic activity of copper and that it is associated with and is thus only toxic when unsequestered and unmediated. An inherited condition called Wilson's disease causes the body to retain copper since the liver into the bile does not excrete it. This disease if not treated can lead to brain and liver damage. Mental illness isschizophreniais because of heightened levels of copper. Copper toxicity is generally related to health concerns including stomach cramps, nausea, vomiting diarrhea, cancer, liver damage and kidney disease [75]. High levels of copper in water have also been found to damage marine life. Contamination of drinking water with high level of copper may lead to chronic anemia [76].

v. Zinc

Zinc is one of the important trace elements that play a vital role in the physiological and metabolic process of many organisms. It is required by the human body in small amounts. Nevertheless, higher concentrations of zinc can be toxic to the organism [77]. Zinc toxicity leads to diarrhea. It plays an important role in protein synthesis and is a metal which shows fairly low concentration in surface water due to its restricted mobility from the place of rock weathering or from the natural sources [63].

Zinc pollution is often associated with mining and smelting. Usually cadmium is often found as a guest element in ZnS and other ores. Zinc readily undergoes oxidation to Zn^{2+}. ZnS (sphalerite) ore often occurs together with PbS (galena), the main ore of Pb. Zn pollution is often associated with lead and copper [74]. Soils and water from areas of historical or active lead- zinc mining tend to have higher concentrations of these heavy metals than other areas where mining has not occurred. These trace element concentrations decrease with increasing distance down-stream from the mining activity [78].

3. Materials and methods

3.1. Description of the study area

This study was conducted in Assosa district which is located in Assosa Zone Benishangul Gumuz Regional state. It is 669.83 km far away from Addis Ababa and located in south west part of Ethiopia. Geographically it lies between 8°30’ and 40° 27’ N latitude and 34 21’ and 39 1’ E longitude and 1464 meters altitude above sea level.

3.2.Sampling and preservation

A total of 33 well water samples were collected from the selected sampling areas. The samples were collected three times per day that is in the morning, mid- day and at the evening from each sample site. The samples were collected in prewashed (with detergent, dil. HNO_3, distilled water respectively) 2 L plastic bottles from May 22 - 26/2017 for four consecutive days. Only 0.5 L of water sample was taken from each 2 L water samples. Sample preservation methods were intended to retain the collected sample as closely as possible to its original state in the underground environment. The preservation was done by adding 5 mL of nitric acid to every 0.5 L of the water sample. The samples were stored properly and then transported to Jimma University, chemistry department research laboratory. For convenience of sample preparation the morning, mid-day and evening time samples were mixed for each sample sites. Finally the water samples were stored properly until analysis.

3.3. Instrumentation and apparatuses

3.3.1.Instrument

Inductively coupled plasma- optical emission spectrometry (ICP-OES) 8000 perkinElmer Optima (U.S) equipped with a meinhard nebulizer, a glass cyclonic spray chamber connected with nitrogen and argon tubes. A software was used for spectral data analysis . The samples were analyzed using ICP-OES for the determination of Fe, Cu, Zn, Cd and Pb metals at their corresponding wave length 238.204, 327.393, 206.203, 228.802 and 220.353 nm respectively. The computer software provided by Perkin Elmer processed the spectral data calculating sample concentrations in mg/L. Each element concentration was measured in triplicates.

3.3.2.Chemicals and reagents

Chemicals and reagents that were used for the laboratory works were all analytical grade: Nitric acid (HNO_3, (69%),LOBA chemie, India), Hydrochloric acid (HCl, (37%), LOBA chemie, India), Hydrogen peroxide (H_2O_2, (30%) and standard solution of Pb, Fe, Zn, Cd, and Cu metals. Double distilled water was used for dilution of intermediate metal standard solutions and samples prior to analysis and rinsing glassware and sample bottles.

3.3.3.1.Sample preparation

i. Digestion ofwater samples

EPA 3005A method was used for digestion of the water samples [79]. Typically, 50 mL of sample was mixed with 1 mL concentrated (69%) HNO_3, 2.5 mL concentrated (37%) HCl and 4 drops of (30%) H_2O_2 in a beaker and heated on a hot plate for about 15- 20 min. The beaker was removed from a hot plate and allowed to cool at room temperature. It was then filtered through Whatmann 41 filter paper. The final volume was adjusted to 50 mL with double distilled water and stored for analysis at 4^0C in a refrigrator [80]. All sample digestion processes were conducted in Jimma University chemistry department of research laboratory.

3.3.4.1. Instrument operating conditions

The optimal instrumental conditions for ICP-OES instrument are given in Table 1.

Table 1. Instrument operating conditions for the analysis of trace metals in drinking water samples

Elements	Wave length (nm)	Gas flows (L/Min)		RF source (watts)
		Plasma	Nebulizer	
Fe	238.204			
Cu	327.393			
Zn	206.203	8.00	0.70	1500
Cd	228.802			
Pb	220.353			

3.3.4.2. Calibration curve

Calibration curves were prepared to determine the concentration of the metals in water samples. The calibration were done using five series of working standards solutions. The working standard solutions of each metal were prepared from 100 mg/L intermediate standard solutions of their respective metals. Calibration curve for each metal analyzed was prepared by plotting the emission intensity as a function of metal standard concentration. The correlation coefficients of the calibration curve for each of the metals were presented in Table 2.The calbration curves were persented in appendix 1.

Table 2. The correlation coefficients of the calibration curves for each metals

Element	Concentration of working standard solution (mg/L)	Correlation coefficient(R^2)
Fe	0.05, 0.75, 1.45, 2.15, 2.85	0.999
Cu	0.1, 0.8, 1.5, 2.2, 2.9	0.996
Zn	0.1, 0.8, 1.5, 2.2, 2.9	0.999
Cd	0.04, 0.74, 1.44, 2.14, 2.84	0.999
Pb	0.1, 0.8, 1.5, 2.2, 2.9	0.999

3.3.4.3. Method detection limit

Method detection limit is the minimum concentration of analyte that can be measured and reported with 95% confidence level that the analyte concentration is greater than zero [81]. In other words, it is the lowest analyte concentration that can be detected with 95% confidence level in blank samples. Detection limit of certain method may vary greatly often with matrix and experimental procedures [82]. The method detection limit estimation indicated that if the concentration of the respective element is at least equal to the detection limit, it can be detected but not necessarily quantified at the given confidence level.

Five blank solutions were digested following the same procedure as the samples and each of the blank sample was analyzed for the selected metals (Cd, Cu, Pb, Fe and Zn) and their concentrations were determined by ICP-OES. The mean concentration and standard deviation for each metal were calculated from the five blank measurements to determine LOD of the instrument. In this research work LOD was determined using the following formula.

LOD = Mean blank + $3.3S_{blank}$, where S = standard deviation, LOD= limit of detection, n = 5

3.3.4.4. Limit of quantitation (LOQ)

The lowest concentration level at which a measurement is quantitatively meaningful is called the limit of quantitation (LOQ).The LOQ is most often defined as 10 times the standard deviation of the blank [83].In this study, LOQ was obtained from the mean and standard deviation of five reagent blanks Which were digested in the same digestion procedure for water samples. Therefore, LOQ was determined using the following formula.

$$LOQ = \text{Mean blank} + 10xS_{blank},$$

Table 3.Instrument detection limit, method detection limit and limit of quantitation for the metals analyzed

Elements	LOD (mg/L)	LOQ(mg/L)	IDL(mg/L)
Fe	0.40	0.44	0.0046
Cu	0.07	0.07	0.0097
Zn	0.12	0.13	0.0059
Cd	0.005	0.008	0.0027
Pb	0.06	0.06	0.042

3.3.4.5. Recovery test

Direct determination of the validity of the digestion procedure for analysis of the water samples with respect to each of the selected metals (Pb, Cu, Fe, Zn and Cd) might not be possible because of the absence of certified reference materials for these metals. Instead, spiking method of the digestion procedure was used for this purpose. The efficiency of the digestion procedure used for digesting the water samples was estimated by adding 1 mg/L of each metal standard solution in to 50mL of water samples. The spiked samples were then digested in the same manner as original sample. The percentage recoveries were calculated by using the formula given below [84].

$$\text{Percentage recovery} \quad = \frac{Cs - Co}{Ca} X100\%$$

Where: Cs - Concentration of the spiked sample, Co- Concentration of non-spiked sample and Ca - Concentration of metal added.

3.4.Data analysis

In this study different statistical methods were used to evaluate whether there was a difference in results of analysis or not. And if there is a difference, statistical analysis would indicate whether the difference is significant or not. However, for this research a one way ANOVA was used for statistical data analysis [81].

All data analyses were performed using descriptive statistical analysis. The data obtained were tabulated and presented with uncertainty (RSD). The various results were also compared by using one way ANOVA [81].

4.Result and discussions

4.1. Precision of results

In this study the precision of the results were determined as relative standard deviation (%RSD) of the results of triplicate measurements of samples. The values of RSD are less than 10% for all the studied metals except for Cd which had higher %RSD values in three sites. Therefore, the precision of the results obtained by ICP-OES were almost appropriate.

4.2 Recovery study

The efficiency and accuracy of the method was evaluated by using both the digests of spiked and non-spiked samples. The recoveries of most metals in the samples analyzed were in the range of 70% - 130% except Pb which had 66% in Alubo [85] . In general, 98% of the elements analyzed had recoveries within the acceptable range. The results confirmed thatgood recoveries were observed for almost all metals analysed in the water samples that could validate the procedure had good accuracy. The results were given in table 4 below.

Table 4.percentage recoveries for metals

Sample sites	Percentage recoveries (%)				
	Fe	Cu	Zn	Cd	Pb
Abrahamo	99	112	81	89	86
Alubo	125	122	84	96	66
Amba-11	131	129	118	72	104
Amba-12	115	118	77	92	82
Amba-3	89	82	128	86	88
Tsetse Adurnunu	124	126	120	118	85
Megele-38	118	114	83	91	87
Selga-22	107	119	91	95	77
Baro	126	104	97	120	72
Komeshiga-27	113	107	110	118	91
Amba-13	132	114	110	125	91

4.3. Determination of metal concentrations by ICP-OES.

The concentration of each metal was determined as the mean of the triplicate measurements in mg/L and presented as Mean ± RSD.The values are given in table 5.

Table 5. concentration of some heavy metals in mg/L in drinking water samples in some kebeles of Assosa district (Mean ± RSD, n= 3).

Sample sites	Fe	Cu	Zn	Cd	Pb
	Mean ± RSD	Mean ± RSD	Mean ± RSD	Mean ± RSD	Mean ± RSD
Abrahamo	ND	ND	ND	ND	ND
Alubo	ND	ND	ND	ND	ND
Amba-11	0.559 ± 0.69	ND	0.142 ± 0.48	BQ	ND
Amba-12	0.659 ± 0.48	ND	0.159 ± 0.31	BQ	ND
Amba-3	1.223 ± 0.48	ND	0.519 ± 0.77	BQ	ND
Tsetse-Adurnunu	0.751 ± 0.85	0.096 ± 0.17	0.178 ± 0.45	BQ	ND
Megele-38	BQ	0.081 ± 0.05	ND	BQ	ND
Selga-22	0.848 ± 0.37	0.072 ± 0.11	0.671 ± 0.36	BQ	ND
Baro	ND	0.073 ± 0.09	0.168 ± 0.28	BQ	ND
Komeshiga-27	1.360 ± 0.39	0.073 ± 0.18	ND	BQ	ND
Amba-13	0.874 ± 1.00	ND	ND	BQ	ND

Note: ND—Not Detection, BQ— Below quantitation limit

4.4. Discussion

The five elements studied in this research work : Fe, Cu, Zn, Cd and Pb have maximum acceptable concentration of 0.3 mg/L, 2 mg/L, 5 mg/L, 0.005 mg/L, and 0.05 mg/L, respectively in drinking water as recommended by WHO (86, 89). The findings of this study was compared with standard limits of these metals specified by the WHO.

Iron (Fe): The obtained iron content varied from 0.559 ± 0.69 - 1.360 ± 0.394 mg/L (except Abrahamo,Alubo and Baro sites which were ND whereas Megele-38 was BQ). The minimum concentration of Fewas obtained from sample in Amba-11 and the maximum was obtained from sample in Komeshiga-27. As it was indicated in table 5, 63.6% of the water samples contained Fe. All studied water samples except Abrahamo, Alubo, Megele-38 and Baro contain Fe above the limit of WHO i.e 0.3 mg/L for drinking water standards [86]. The high level of Fe may be due to corrosion of iron discharge from steel pipes, mineral composition of rocks, soil composition and characteristics [87, 88].

Copper (Cu): The concentration ofCu metal was determined in five sample sites, but in the remaining six samples the level detected was below the LOQ as it was shown in table 5. Among the five sites the minimum 0.072 ± 0.112 mg/L and the maximum of

0.096 ± 0.0.17 mg/L of Cu concentrations were obtained in Selga-22 and Tsetse Adurnunu respectively. From a total of 11 samples analyzed for Cu, 45.45% of samples contained Cu metal above the LOQ. In general, the concentrations of Cu in all analyzed water samples were within the permissible limit of WHO drinking water guideline which is 2 mg/L [89]. The result of this study indicated that Cu metal concentrations in all sample sites are in agreement with the standard value of copper recommended by WHO and it has no health problems for humans. Therefore, the drinking waters in the study areas have safe level ofCu metal.

Zinc (Zn): In this study, Zn metal concentration was observed in six sample sites and it was detected but not quantified in theremaining five samplesas it was shown in table 5. Among the six sites the minimum of 0.142 ± 0.485 mg/L and the maximum of
0.671 ± 0.364 mg/L were obtained in Amba-11 and Selga-22 respectively. Among all the samples analyzed 54.55% of them contained Zn metal above LOQ.However, the concentrations of Zn in all analyzed samples were below the permissible limit of WHO drinking water standard. The WHO acceptable limit for Zn in drinking water is 5 mg/L [86]. Therefore,the obtained Zn metal level in the studied water samplesis safe for consumption.

Cadmium (Cd): the result obtained for the analysis of Cd, showed that it was not detected in Alubo and Abrahamo sites. Although its level is below the LOQ, the remaining 9 samples contained Cd. Thus, the obtained result indicated that the studied water is safe for drinking.

Lead (Pb): In all studied samples Pb was not detected. Thus, the obtained result indicated that the studied water is safe for drinking.

4.5.Comparison of this study with other studies.

As it was shown in table 6, the concentration of Fe and Cu are higher in drinking waters of Assosa than Fe and Cu in drinking waters of Gedio whereas the concentration of Zn is lower in Assosa than in Gedio. But Cd and Pb metals were not determined in both study areas except Cd in two sites in Assosa. These studies showed that Cu and Zn metals have concentrations below the WHO permissible limit but, Fe metal has concentrations above the WHO permissible limit in the two studies. Therefore, the drinking waters in these study areas have safe level of Cu, Zn, Cd and Pb metals. The variation in the concentration of these metals in the two studies might be due to geographical location, the instrumenst used for analysis and the mineral contents that contain these metals.

Table 6 Comparison of the concentrations of some heavy metals b/n water samples of Assosa and Gedio.

Element	Present study		Other study [88]	
	Concentration (mg/L)	Study area	Concentration (mg/L)	Study area
Fe	0.559 -1.36	Assosa district, Assosa zone, B/G	ND - 0.60	Gedio zone, SNNRS
Cu	0.072 -0.096		0.050 - 0.054	
Zn	0.142 -0.671		0.53 – 0.98	
Cd	BQ		ND	
Pb	ND		ND	

ND = *Not detected*

4.6. Statistical data analysis

In this research work the significance difference in concentration of metals in water samples was determined based on the one way ANOVA for Fe, Cu and Zn. The results of the one way ANOVA (for Fe, Zn and Cu metals) at 95% confidence level (P = 0.05) showed that the sources of variation (between groups and within groups), P, F calculated and F critical values. These are important components to decide whether there is statistically significance difference in the mean concentrations or not. In general for this particular study $P < 0.05$ and $F_{cal} > F_{crit}$ for Fe, Cu and Zn which is evidentially considered to say the results of this study clearly confirmed that there were significance differences in concentrations of the three metals in the analized sample.

The sources of variation between sample concentrations might be the difference in mineral composition of rocks and soils, the presence of naturally dissolved and undissolved metal compounds in ground water as well as errors that might be introduced during sample preparation processes [88, 90].

Table 7. Result of one way ANOVA between and within groups in water samples.

Metals	Sources of variation	Degree of Freedom	$F_{calculated}$	P- value	$F_{critical}$
Fe	Between groups	6	8392.749	0.00	2.847726
	Within groups	14			
Cu	Between groups	4	23905.04	0.00	3.47805
	Within groups	10			
Zn	Between groups	5	39889.5	0.00	3.105875
	Within groups	12			

5. Conclusions and Recommendations

5.1 Conclusions

The primary objective of this study was to determine some selected heavy metals (Fe, Cu, Zn, Cd, Pb) in drinking water of 11 Kebeles' of Assosa district, Assosa zone, Benishangul Gumuz Regional state, Ethiopia. Determination of heavy metals in drinking water is very important because, they affect human health if exceeded the permissible limit recommended by WHO.

The study revealed that a sample preparation using an open beaker digestion method was a reliable method for quantitative determination of the metals in drinking water samples of the district.

The result of recovery test was found in the range of 70- 130% for almost all metals analyzed which is in the acceptable range the exception is Pb which has 66% in Alubo.

The concentrations of Fe, Cu, Zn, Cd and Pb metals in drinking water sources were determined by ICP-OES. According to the WHO guidelines the result obtained in this study indicated that Cu, Zn, Cd and Pb metals are in their safe level in all water samples. Therefore, the water sources were safe for drinking and other domestic uses, but concentration of Fe metal exceeded WHO standard limit. This could be due to the mineral and soil composition of Fe content as well as Fe discharge from steel pipes.

The statistical analysis indicated that there were significant differences in the concentration of Fe, Cu and Zn metals within the analyzed water samples at 95% confidence level ($P = 0.05$).The variation in concentration of these metals in the analyzed water samples could be mainly come from the mineral composition of rocks and soils as well as errors that might be introduced during sample preparation processes.

However, no concentration of metal elements or any metal has been reported as being safe, because long term exposure to low concentration is equally harmful. Indeed some are essential in life processes, in the cases of Fe, Zn and Cu at moderate concentrations, quantities extremely low can still pose danger especially when exposed for extended period of time [91].

5.2 Recommendations

In this study the concentrations of Fe, Cu, Zn, Cd and Pb metals were determined only in 11 kebeles of Assosa district but, there are other parameters and heavy metals that affect the quality of drinking water. Therefore, it is advisable to other researchers to conduct additional studies including some other heavy metals and parameters in all Kebeles of the district and other districts to ensure the quality of water.

It is recommended to follow up the content of heavy metals in the well waters of the study area.

It was advisable to replace the steel pipes by PVC pipes for those wells constructed from steel pipes unless the concentration of iron metal may increases above permissible level from time to time.

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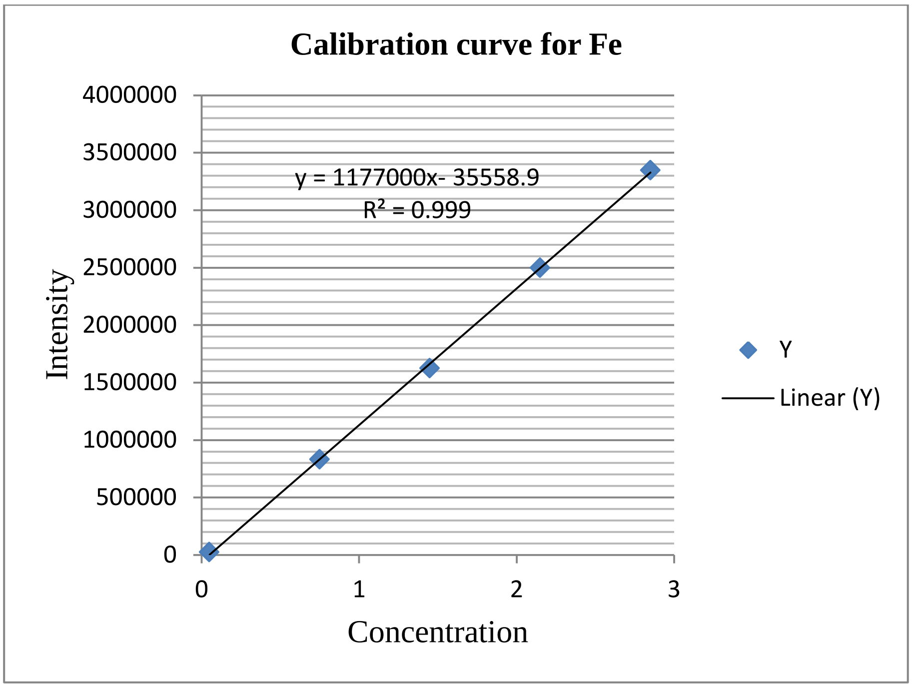
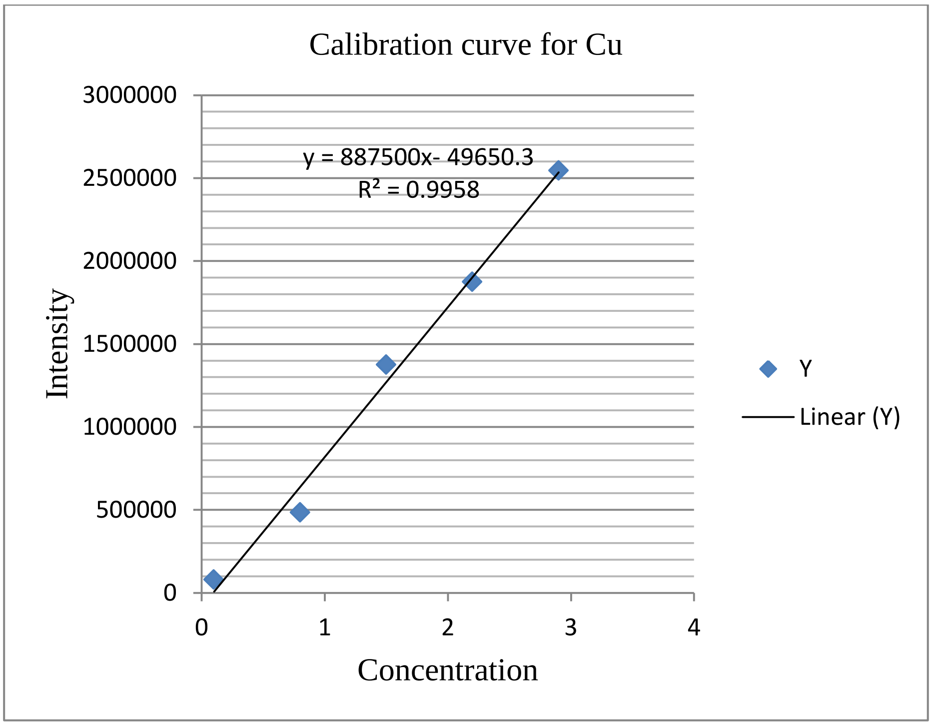
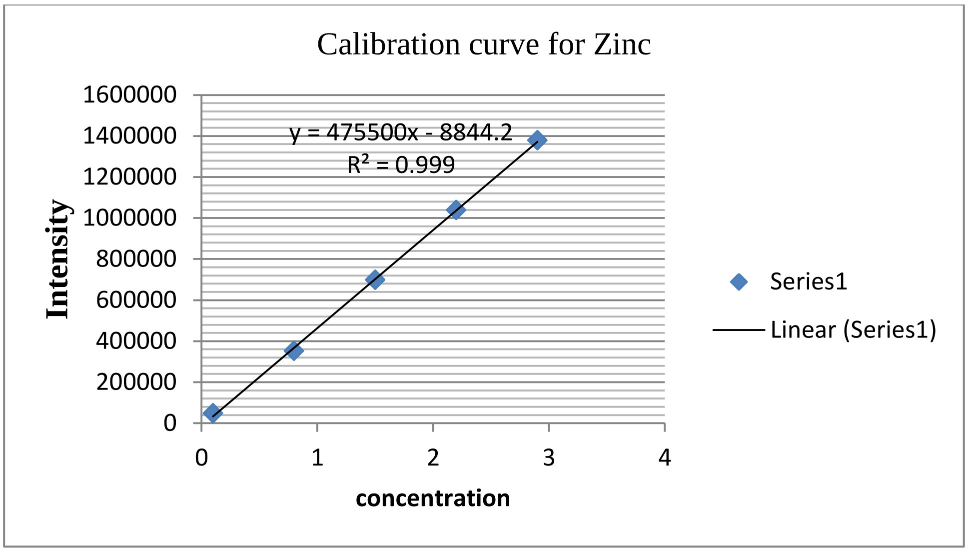
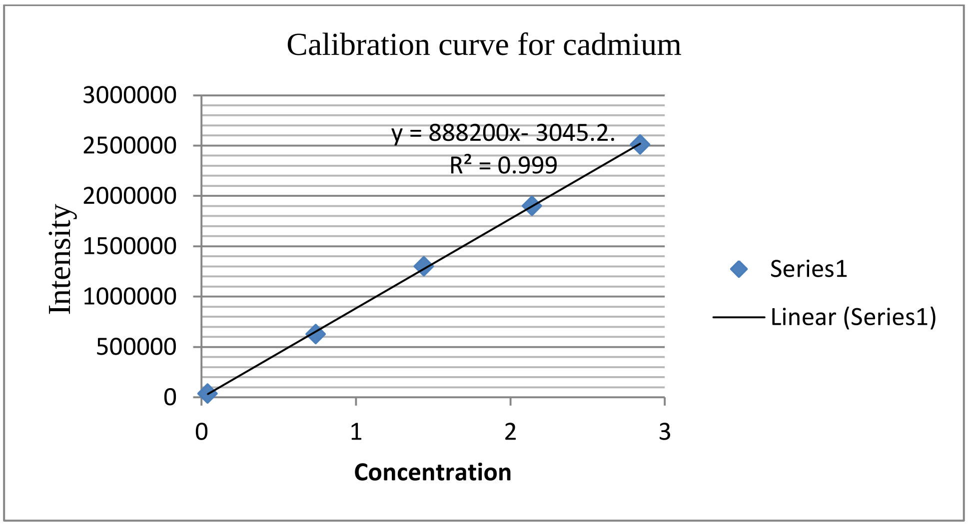
Appendix

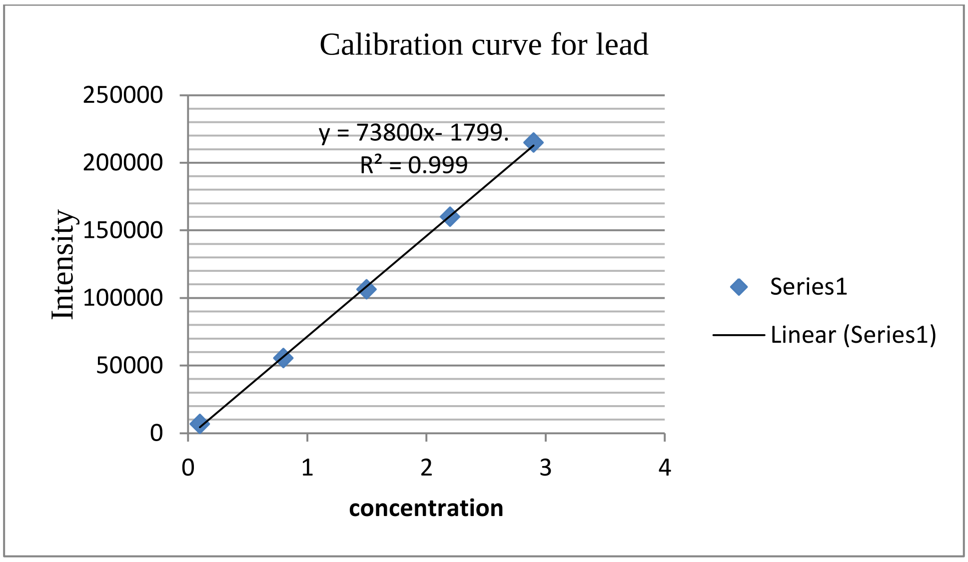
I. Calibration curves for metals during calibration of the instrument.






Calibration curve for Zinc
Intensity
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
y = 475500x - 8844.2
R² = 0.999
0
1
2
3
4
concentration
Series1
Linear (Series1)


Calibration curve for cadmium
Intensity
3000000
2500000
2000000
1500000
1000000
500000
0
y = 888200x- 3045.2.
R² = 0.999
0
1
2
3
Concentration
Series1
Linear (Series1)


Calibration curve for lead
Intensity
250000
200000
150000
100000
50000
0
y = 73800x- 1799.
R² = 0.999
0
1
2
3
4
concentration
Series1
Linear (Series1)