JIMMA UNIVERSITY

COLLEGE OF PUBLIC HEALTH AND MEDICAL SCIENCES, DEPARTMENT OF
ENVIRONMENTAL HEALTH SECIENCE & TECHNOLOGY

POLLUTION LEVEL OF TOXIC HEAVY METALS (As, Hg, Pb, Cd AND Cu) IN WELL AND
STREAM WATER IN RELATION WITH TRADITIONAL GOLD MINING ACTIVITIES IN BERO
WEREDA, BENCH MAJI ZONE, SOUTHWEST ETHIOPIA

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A THESIS SUBMITTED TO DEPARTMENT OF ENVIRONMENTAL HEALTH SCIENCE &
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Pollution level of toxic heavy metals (As, Hg, Pb, Cd and Cu) in well water and stream water in relation with traditional gold mining activities in Bero Woreda, Bench Maji Zone, Southwest Ethiopia

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Declaration

This research paper is my original work and has not been presented for a degree in this or any other University and that all sources of materials used have been fully acknowledged.

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Abstract

The study was undertaken basically to assess the status of drinking water quality in relation with traditional gold mining activities at the gold mining areas of Bero Woreda, Bench Maji Zone, South West Ethiopia. Prior to sampling deliberate observation was made & site specific data were taken from each site. A total of 6 water samples (4 well water samples & 2 stream water samples (for reference)) were collected in February, 2011 from 3 gold mining kebeles (Sholla, Gabissa & Seyali).

Field measurements of water quality indicator parameters: Temperature (24–28 ^{0}C), pH (7.02–8.1), Electrical conductivity (927–1726 μS/cm) & Turbidity (28–230 NTU) were measured & TDS (593–1105 mg/l) was calculated from the measured EC value of the samples.

All the samples were analyzed for the toxic heavy metals: As, Hg, Cd, Pb & Cu following the recommended standard procedures. The heavy metals (As & Hg) were analyzed using hydride AAS method & the heavy metals (Cd, Pb & Cu) & major cation (Ca^{2+} & Mg^{2+}) were analyzed using Flame AAS method. From the analyses the following analytical results in (mg/l): As (0.00091–0.0031), Hg (0.00011– 0.00199), Cu (0.159) only at one well sample site, Pb & Cd below the detection limit (0.0001 mg/l) of the instrument, calcium (114.4 – 292.2) & magnesium (99.2–191.5) were obtained.

The major ions in mg/l: sulphate (1.02–80), chloride (7.4–88.3) & bicarbonate (314.5–594.5) were obtained. As, Hg, SO_4^{2-}, Cl^-, pH & turbidity were found higher in stream water samples & also As, Hg, SO_4^{-2}, Cl^- , pH , HCO_3^-, EC & turbidity were found higher in downstream than upstream water samples. The physicochemical parameters mercury, temperature, turbidity, electrical conductivity (EC), bicarbonate & TDS were found in 66.7%, 100%, 100%, 100%, 50% & 100% of the water samples in the study area respectively. These parameters were also found in 50%, 100%, 100%, 100%, 75% & 100% of the well water samples respectively higher than the WHO (1993), EU (1998) & ES (2001) recommended maximum desirable limits set for drinking water.

Key words: Traditional gold mining, Heavy metals, Shete, Underground excavation, pit-hole, Gold washing, Letto, Well water, Stream water, Bero

Abbreviations and acronyms

AAEPA	Addis Ababa Environmental Protection Authority
AAS	Atomic Absorption Spectrophotometer
ADM	Acid Mine Drainage
BWRADS	Bero Woreda Rural Agricultural Development Sector
BMZWMES	Bench Maji Zone Water, Mine and Energy Sector
EC	Electrical Conductivity
ES	Ethiopian Standard
EPA	Environmental Protection Agency
IARC	International Agency of Research on Cancer
IPCS	International Programme on Chemical Safety
JU	Jimma University
MDL	Maximum Desirable Limit
WHO	World Health Organization

Table of contents   **page**

LISTS OF TABLE

List of Figures

CHAPTER ONE: INTRODUCTION

1.1. Background

The great majority of evident in water-related health problems are the result of microbial contamination. Nevertheless, an appreciable number of serious health concerns may occur as a result of the chemical contamination of drinking-water. There are many chemicals that may occur in drinking-water; however, only a few are of immediate health concern in any given circumstance and a few chemical contaminants have been shown to cause adverse health effects in humans as a consequence of prolonged exposure through drinking-water (WHO, 2011).

Metals are ubiquitous, persistent and toxic at certain concentrations. Some metals are essential for health whereas others have no known biological function and have toxic effects. The adverse effects of some metals on the human health are well documented. Trace elements are contributed to groundwater from a variety of natural and anthropogenic sources. Once liberated to groundwater, element distributions continually modified by complex geochemical and biological processes (Newcomb & Rimstidt, 2002).

The introduction of harmful substances into the environment has been shown to have many adverse effects on human health, agricultural productivity and natural ecosystems (Garbarino, 1995). From chemical contaminants heavy metals which have been referred to as common pollutants are widely distributed in the environment with sources mainly from anthropogenic activities and from the weathering of minerals and soils (Awofolu et al. 2005). Heavy metals like Fe, Mn, Cu, Zn, Co & Ni are micronutrient for living system, their deficiency or excess can lead to a number of disorderness in human body (Jinwal, Dixit &Malik, 2009). But like As, Cd, Hg and Pb have no known bio-importance in human biochemistry and physiology and consumption even at very low concentrations can be toxic to most form of life and known to be persistent environment contamination (Nolan, 2003).

1.2. Statement of the problem

Of the anthropogenic activities mining is one of the most hazardous activities. During these activities several toxic wastes are produced and released into the surrounding environment causing pollution of air, drinking water, rivers and soils, changes in topography, hydrogeology and chemistry of terrestrial and aquatic ecosystems (Gavin, 2003).

The impacts of mining on the environment depend on the chemical composition of the ore, the depth of the deposit, local hydrologic conditions, climate, rock types, sizes of operation, the nature of the process

used to extract the mineral or element from the ore, and topography (Zenebe, 2006).The most serious environmental impacts include: mercury contamination; mass deforestation from intensive prospecting and mining; small-scale acid mine drainage (AMD) and accompanying heavy metals leaching; mass soil erosion; small scale habitat destruction and "pot holed" landscapes resulting from incomplete mine closure (Gavin, 2003).

Acid drainage is also one of the most serious environmental impacts associated with mining. It occurs when sulfide-bearing minerals, such as pyrite are exposed to oxygen or water, producing sulfuric acid. Acidic water may subsequently leach other metals in the rock, resulting in the contamination of surface and groundwater (Schmiermund & Drozd, 1997).

It is estimated that 37 to 100 million people are at risk of drinking heavy metal (arsenic, lead, mercury, cadmium & copper) contaminated drinking water and long-term exposure to heavy metals in groundwater, at concentrations over 500 μg/l causes death 1 in 10 adults (including lung, bladder and skin cancers) (WHO, 2001).

The gold mining areas of Bero Woreda which are semi-arid consists of four kebeles (Sholla, Gabissa, Seyali & Gessena) have water source from intermittent stream and well water (the only water source throughout the year) which is supposed to be polluted by toxic heavy metals due to the activities of gold mining. Thus, some of the major toxic heavy metals (As, Hg, Cd, Pb & Cu) were chosen for this study to assess their concentration level in relation with traditional mining activities based on their effects on human health.

1.3. Significance of the Study

Traditional mining like mining of gold, stone and sand are severely affecting the soil and aquatic environment. Traditional gold mining is being done irrespective of rules and regulations of mineral mining, environmental policy and resource conservation. The land is deeply excavated for extraction of gold and as a result heavy metals and other pollutants released to the ground water. These problems are also developmental obstacles which lag countries from achieving sustainable development. Ethiopia as country and Bero Woreda as a research site may also be victims of major public health and environmental problems caused by those anthropogenic activities.

Hence the study aims to assess the concentration level of the toxic heavy metals and to evaluate the contribution of gold mining activities for drinking water pollution. The study also gives especial emphasis

to communities of the mining area who use well water for drinking to be aware of about its quality status and it also helpful for health planners, environmentalist, soil and natural resource, health, water and mine sectors, etc to insight these problems and to take preventive measures. This study also provides base line information for further research activities in such area.

CHAPTER TWO: LITERATURE REVIEW

2.1. Description of Toxic Heavy Metals

2.1.1. Arsenic (As)

2.1.1.1. Occurrence of As

The most abundant As ore mineral is arsenopyrite (FeAsS). Arsenic compounds occur in three forms: (1) pentavalent (As^{+5}) organic or arsenate compounds (e.g., alkyl arsenates); (2) trivalent (As^{+3}), inorganic or arsenate compounds (e.g., sodium arsenate, arsenic trioxide); and (3) arsine gas (AsH_3), a colorless gas formed by the action of acids on arsenic (Wiley & Sons, 2004).

Natural arsenic is generally associated with sedimentary rocks of marine origin, weathered volcanic rocks, fossil fuels and geothermal areas. Mankind's activities have caused higher concentrations of arsenic to result in some places. Arsenic is associated with mining wastes, agricultural uses, wood preservation and irrigation practices. It is usually present in natural waters at concentrations of less than 1-2 μg/l. However, in waters, particularly groundwater, where there are sulfide mineral deposits and sedimentary deposits deriving from volcanic rocks, the concentrations can be significantly elevated (WHO, 2011).

2.1.1.2. Sources of Arsenic

Elevated arsenic concentrations are found in groundwater due to anthropogenic activities and natural processes. Anthropogenic activities include mining, use of arsenical pesticides, herbicides and crop desiccants, release of industrial effluents, and disposal of chemical waste. The release of arsenic from natural processes can be caused by the reduction of iron hydroxides and the oxidation of pyrite minerals including orpiment (As_2S_3) and realgar (As_2S_2). Naturally occurring arsenic in drinking water supplies may affect more than 100 million people worldwide (Bang et al., 2005).

2.1.1.3. As in aquatic environment

The concentration of arsenic in most ground waters is lower than10 μg/l and often below the detection limit of routine analytical methods. High concentrations of naturally occurring arsenic are also found in oxidising conditions where groundwater pH values are high (>8) (Smedley & Kinniburgh, 2002). In such environments, inorganic As (V) predominates and arsenic concentrations are positively correlated with those of other anion-forming species such as HCO_3^-, F^-, $H_3BO_3^-$ & $H_2VO_4^-$. The high-arsenic groundwater provinces are usually in arid or semi-arid regions where groundwater salinity is high. Evaporation has been suggested to be an important additional cause of arsenic accumulation in some arid

areas (Welch and Lico, 1998). Baseline concentrations of As in river waters are also low (in the region of 0.1– 0.8 mg /l but can range up to 2 mg/l) (Nordstrom et al., 2000).

2.1.1.4. Human health effects of As

Drinking of arsenic-contaminated water for a long time causes illnesses such as hyperkeratosis on the palms or feet, fatigue and cancer of the bladder, skin or other organs. It is believed that 1 in every 10 people ingesting high levels of arsenic (100 mg/l) could die of cancer triggered by arsenic poisoning (Sad and Abul, 2009). Higher levels of exposure result in a more serious condition; gangrene of the lower extremities or "black foot disease." Cancer of the skin also occurs. Arsenic may also replace phosphorus in bone tissue and be stored for years.

After acute poisoning, severe gastrointestinal symptoms occur within 30 minutes to 2 hours. These include vomiting, watery and bloody diarrhea, severe abdominal pain and burning esophageal pain. Vasodilatation, myocardial depression, cerebral edema and distal peripheral neuropathy may also follow. Death usually results from circulatory failure within 24 hours to 4 days. Chronic exposure results in nonspecific symptoms such as diarrhea, abdominal pain, hyper pigmentation and hyperkeratosis. A symmetrical sensory neuropathy often follows. Late changes include gangrene of the extremities, anemia, and cancer of the skin, lung and nasal tissue (Wiley & Sons, 2004).

Increased risks of lung and bladder cancer and of arsenic-associated skin lesions have been reported to be associated with ingestion of drinking-water at concentrations below 50 μg of arsenic per liter (WHO, 2011).

2.1.2. Mercury (Hg)

2.1.2. 1.Occurrence of Mercury

Mercury exists in the environment in three main chemical forms: elemental mercury $(Hg0)$, inorganic mercurous (Hg^+) and mercuric (Hg^{2+}) salts and organic methylmercury (CH_3Hg) and dimethylmercury (CH_3HgCH_3) compounds (Wiley & Sons, 2004).

2.1.2. 2.Sources of mercury

Both naturally occurring and anthropogenic processes can release mercury into air, water and soil. Emission into the atmosphere is usually the primary pathway for mercury entering the environment (Cheng & Hu, 2010). It is estimated that the total annual global input to the atmosphere from all sources (i.e., from natural and anthropogenic emissions) is around 5000–6000 t (Gray & Hines, 2006).

There are a number of natural processes that can emit Hg into the atmosphere. These processes may include geologic activities, volatilization of Hg in marine environments and emission of Hg from terrestrial environments (Gustin et al., 2008).

On the global scale, fossil fuel combustion for power and heating is the primary source of mercury emission, but in South America, gold mining contributes over 60% of total anthropogenic mercury emission in water, sediment and soil environment (Fitzgerald et al., 2007).

2.1.2.3. Toxicity and health risks of mercury exposure

Mercury is toxic to human health, posing a particular threat to the development of the child inutero and early in life. Elemental mercury, in the form of mercury vapor, is almost completely absorbed by the respiratory system, whereas ingested elemental mercury is not readily absorbed and is relatively harmless. Several large episodes of mercury poisoning have resulted from consuming seed grain treated with mercury fungicides or from eating fish contaminated with methylmercury (Willey & Sons, 2004).

Even though the mothers appeared healthy, many infants born to mothers who had eaten contaminated fish developed cerebral palsy-like symptoms and mental deficiency. Organic mercury primarily affects the nervous system, with the fetal brain being more sensitive to the toxic effects of mercury than adults. Inorganic mercury salts, however, are primarily nephrotoxicants, with the site of action being the proximal tubular cells (Willey & Sons, 2004).

2.1.3. Cadmium
2.1.3.1. Occurrence of Cd

Cadmium usually exists in minor constituent of surface and groundwater. It may exist in water as the hydrated ion as inorganic complexes such as carbonates, hydroxides, chlorides or Sulphates or as organic complexes with humic acids (Tolla, 2006). Occurrence Levels in drinking-water usually less than 1 μg/l (WHO, 2011).

Cadmium occurs in nature primarily in association with lead and zinc ores and is released near mines and smelters processing these ores. Environmental exposure to cadmium is mainly from contamination of groundwater from smelting and industrial uses as well as the use of sewage sludge as a food-crop fertilizer. Grains, cereal products, and leafy vegetables usually constitute the main source of cadmium in food (Wiley & Sons, 2012).

2.1.3.2. Human toxic effect of Cadmium

Cd is toxic by whatever route it is administered and some of the changes produced may result from its metabolic antagonism to Cu, Zn, and Fe: these include anaemia, hypertension and skin changes.

There is evidence that cadmium is carcinogenic by the inhalation route, and IARC has classified cadmium and cadmium compounds in Group 2A. The kidney is the main target organ for cadmium toxicity. After accumulation it is mainly retained in liver and kidney, causing pathological changes in hepatocytes and kidney tubules. The major effects in the persons occupationally exposed to Cd are lung diseases and renal functions (WHO, 2011).

Besides it, the exposure to Cd leads to its higher concentration in the blood and increased frequency of chromosomal deformities (WHO, 1976). Nervous symptoms of Cd toxicity include dizziness, headache, cramps, and loss of consciousness (Dipalma, 1965).

2.1.4. Lead (Pb)

2.1.4. 1.Occurrence of Pb

The most significant lead mineral is galena PbS (lead sulfide). $PbCO_3$ and $PbSO_4$ are two other lead-based minerals. Lead had been recognized as an industrial hazard before it was appreciated that house dust is a profile source of the elements from paint, the street, old batteries, solder from cans and toothpaste tube (Tolla, 2006).

Lead is rarely present in tap water as a result of its dissolution from natural sources; rather, its presence is primarily from corrosive water effects on household plumbing systems containing lead in pipes, solder, fittings or the service connections to homes. Concentrations in drinking-water are generally below 5μg/l, although much higher concentrations (above 100μg/l) have been measured where lead fittings are present. The primary source of lead is from service connections and plumbing in buildings; therefore, lead should be measured at the tap. Lead concentrations can also vary according to the period in which the water has been in contact with the lead-containing materials (WHO, 2011).

2.1.4.2. Human toxic effect of lead

Lead has no known nutritional and physiological function and it is usually toxic for organisms. Pb impends the synthesis of heme and accumulates within the red cells as well as the bones to give rise to anemia, headache, dizziness and damage to the digestive and nervous systems, so its use in some applications has been discontinued (Tolla, 2006).

Children exposed to lead pollution are under high risk of mental retardation, impaired learning ability, disturbances of peripheral nervous system and renal atrophy. The highest permissible limit of Pb concentration in drinking water is 0.01 mg/l (WHO, 1984a & 2011b).

The main targets of lead toxicity are the hematopoietic system and the nervous system. Several of the enzymes involved in the synthesis of heme are sensitive to inhibition by lead. The nervous system is another important target tissue for lead toxicity, especially in infants and young children in whom the nervous system is still developing. Even at low levels of exposure, children may show hyperactivity, decreased attention span, mental deficiencies and impaired vision. At higher levels, encephalopathy may occur in both children and adults (Willey & Sons, 2012)

2.1.5. Copper (Cu)

2.1.5.1. Occurrence of Cu

Copper occurs naturally in rock, soil, water, sediment, Air, plants and animals. Food and water are the primary sources of copper. Copper concentrations in drinking-water vary widely, with the primary source most often being the corrosion of interior copper plumbing. Levels in running or fully flushed water tend to be low, whereas those in standing or partially flushed water samples are more variable and can be substantially higher (frequently above 1 mg/l). Copper concentrations in treated water often increase during distribution, especially in systems with an acid pH or high-carbonate waters with an alkaline pH. Concentrations in drinking-water range from ≤ 0.005 to > 30 mg/l (WHO, 2011).

2.1.5.2. Health Impacts of Cu

The deficiency of Cu in human body could indirectly increase the risk of skin cancer (Vohra, 1990). Symptoms of Cu deficiency may appear, even if the amount of the metal in diet is adequate, but there is excess in sulfates, which reduce the solubility of copper- containing substances in water and so, its bioavailability for the living organism (Selinus & Frank, 2000).

Copper in the body is capable of binding bacteriotoxins and increase the activity of antibiotics (Karlson, 1987). Reduced blood concentration of the trace element has been reported in pregnancy and pathological conditions, e.g., anemia, renal disorders, leukemia, and certain type of tumors; invasive diseases caused by worms are also connected with the deficiency of Cu and Fe in the body (Passmore et al., 1974).

2.2. Physicochemical parameters

2.2.1. Temperature

The temperature affects the solubility of many chemical compounds. Increased temperatures elevate the metabolic oxygen demand, which in conjunction with reduced oxygen solubility, impacts many species. Increasing temperatures tend to elevate the solubility and toxicity of dissolved metals, while dissolved oxygen levels generally decrease with increasing temperature (Clesceri et al., 1998).

2.2.2. pH

Measurement of pH is one of the most important and frequently used tests in water chemistry. A decrease in pH increases the solubility of metals. The weathering of minerals, such as limestone or dolomite, by water becomes more rapid with a decrease in pH. High pH values tend to precipitate the heavy metals as hydroxides. Low pH levels tend to increase carbon dioxide and carbonic acid concentrations (Bartram & Balance, 1996; Reeve, 2002).

2.2.3. Electrical conductivity

The ability of the water to conduct an electric current is known as conductivity or specific conductance and depends on the concentration of ions in solution. Ions are dissolved metals and other dissolved materials (Clesceri et al., 1998).

Conductivity is measured in milliSiemens per meter ($1mS/m = 10\mu S/cm$). The measurement should be made in situ, or in the field immediately after the water sample has been obtained, because conductivity changes with storage time and is also temperature-dependent. The conductivity of natural waters is found to vary between 50 and 1500 $\mu S/cm$ (Bartram & Balance, 1996; Reeve, 2002).

It is often possible to establish a correlation between conductivity and dissolved solids for a specific body of water (dissolved solids = conductivity x 0.55 to 0.9 (the factor most often used is 0.7)) Clesceri et al., 1998). The variation of the empirical factor, from 0.55 to 0.9, depends on the ionic components in solution and on the temperature of measurement (Walker, 2001).

2.2.4. Turbidity

Turbidity in water is caused by suspended particles or colloidal matter that obstructs light transmission through the water. It may be caused by inorganic or organic matter or a combination of the two. Turbidity in some groundwater sources is a consequence of inert clay or chalk particles or the precipitation of non soluble reduced iron and other oxides when water is pumped from anaerobic waters, whereas turbidity in

surface waters may be the result of particulate matter of many types and is more likely to include attached microorganisms that are a threat to health (WHO, 2011).

Turbidity can also have a negative impact on consumer acceptability of water as a result of visible cloudiness. Turbidity from groundwater minerals or from post-precipitation of calcium carbonate from lime treatment is not necessarily a threat to health, it is an important indicator of the possible presence of contaminants that would be of concern for health, especially from inadequately treated or unfiltered surface water. Data are emerging that show an increasing risk of gastrointestinal infections that correlates with high turbidity and turbidity events in distribution (WHO, 2011).

2.2.5. Total Dissolved Solid (TDS)

The palatability of water with a total dissolved solids (TDS) level of less than about 600 mg/l is generally considered to be good; drinking-water becomes significantly and increasingly unpalatable at TDS levels greater than about 1000 mg/l. The presence of high levels of TDS may also be objectionable to consumers, owing to excessive scaling in water pipes, heaters, boilers and household appliances (WHO, 2011).

It is a measure of the amount of dissolved material in the water column. It is reported in mg/L with values in fresh water naturally ranging from 0-1000 mg/l. Dissolved salts such as sodium, chloride, magnesium and sulphate contribute to elevated filterable residue values. High concentrations of TDS limit the suitability of water as a drinking source and irrigation supply. High TDS waters may interfere with the clarity, color and taste of manufactured products (Bartram & Balance, 1996; Walker, 2001).

2.3 Major cations and major anions
2.3.1 Major cations (Ca^{2+} & Mg^{2+})

The presence of calcium and magnesium in the water indicates hardness. Other metallic ions may also contribute to hardness. Magnesium is a relatively a common constituent of natural water (Bartram & Balance, 1996).

Hardness is reported in terms of calcium carbonate and in units of milligrams per liter (mg/l). Waters with values exceeding 120 mg/l are considered hard, while values below 60 mg/l are considered soft. Harder water has the effect of reducing the toxicity of some metals (i.e., copper, lead, zinc, etc.). Soft water may have corrosive effect on metal plumbing, while hard water may result in scale deposits in the pipes. If the water has a hardness of greater than 500 mg/l, then it is normally unacceptable for most domestic purposes

and must be treated. In drinking water 80 to 100 mg/l is the optimal range (>200 mg/l is considered poor but can be tolerated) and for food processing 10-250 mg/l is optimal (Bartram & Balance, 1996).

The average abundance of calcium in streams is about 15 mg/l. The most common forms of calcium are calcium carbonate (calcite) and calcium-magnesium carbonate (dolomite). Calcium carbonate solubility is controlled by pH and dissolved carbon dioxide (Clesceri et al., 1998).

2.3.2 Major anions (HCO$_3^-$ & SO$_4^{2-}$, Cl$^-$)

2.3.2.1 Bi-carbonate (HCO$_3^-$)

The alkalinity of water is its capacity to neutralize acid (Clesceri et al., 1998). The amount of a strong acid needed to neutralize the alkalinity is called the total alkalinity and is reported in mg/l as CaCO$_3$. The alkalinity of some waters is due only to the bicarbonate of calcium and magnesium. The pH of such water does not exceed 8.3 and its total alkalinity is practically identical with its bicarbonate alkalinity. Water having a pH above 8.3 contains carbonates and possibly hydroxides in addition to bicarbonates (Bartram & Balance, 1996).

Alkalinity is significant in many uses and treatments of natural waters and wastewaters. Natural waters rarely have levels that exceed 500 mg/l. Waters that have high alkalinity values are considered undesirable because of excessive hardness and high concentrations of sodium salts. Water with low alkalinity has little capacity to buffer acidic inputs and is susceptible to acidification (low pH) (Clesceri et al., 1998).

2.3.2.2. Sulphate (SO$_4^{2-}$)

Sulfates occur naturally in numerous minerals and are used commercially, principally in the chemical industry. They are discharged into water in industrial wastes and through atmospheric deposition; however, the highest levels usually occur in groundwater and are from natural sources. (WHO, 2011).

Although sulphate is one of the major components of natural waters, its determination is of particular interest with respect to the problems of water pollution and acid rain, and for geochemical and environmental studies. Sulphate also results from the breakdown of sulphur containing organic compounds (Bartram & Balance, 1996).

The presence of sulfate in drinking-water can cause noticeable taste and very high levels might cause a laxative effect in unaccustomed consumers. Taste impairment varies with the nature of the associated cation; taste thresholds have been found to range from 250 mg/l for sodium sulfate to 1000 mg/l for calcium sulfate (WHO, 2011).

2.3.2.3. Chloride (Cl^-)

Chloride is one of the major inorganic anions in water and wastewater. The salty taste produced by chloride concentrations is variable and dependent on the chemical composition of water. Some waters containing 250 mg/l may have a detectable salty taste if the cation is sodium. On the other hand, the typical salty taste may be absent in waters containing as much as 1000 mg/l when the predominant cations are calcium and magnesium. A high concentration occurs in waters that have been in contact with chloride-containing geological formations. Otherwise, high chloride content may indicate pollution by sewage or industrial wastes (Bartram & Balance, 1996).

Higher chloride concentrations can reduce the toxicity of nitrite to aquatic life. Taste thresholds for the chloride anion depend on the associated cation and are in the range of 200–300 mg/l for sodium, potassium and calcium chloride (WHO, 2011)

CHAPTER THREE: OBJECTIVES

3.1. General objective

- To assess the pollution level of well water and stream water by toxic heavy metals in relation with traditional gold mining activities in the mining area.

3.2. Specific objectives

- To analyse for some contaminant heavy metals (As, Hg, Cd, Pb & Cu) and some major ions (Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^- & HCO_3^-) in well water and stream water in the mining area.
- To assess the correlation of the heavy metals (As, Hg, Cd, Pb & Cu) and major ions (Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^- & HCO_3^-) with respect to traditional gold mining activities.
- To evaluate the extent of pollution of stream water by the toxic heavy metals and major ions in comparison with well water pollution.
- To evaluate quality status of the drinking water through the analyzed heavy metals, major ions & measurements of water quality indicator parameters with respect to the recommended standards.

3.3. Hypothesis

Traditional gold mining activities increase the concentration level of some toxic heavy metals (As, Hg, Cd, Pb & Cu) & major ions (Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^- & HCO_3^-) in well water and stream water in the mining area.

CHAPTER FOUR: MATERIALS AND METHODS

4.1. Descriptions of the Study area

Bero Woreda is one of the Woreda of Bench Maji Zone where traditional gold mining activities are carried on. Bero is 145 km from Mizan Teferi (Administrative city of Bench Maji), 700 km from Addis Ababa and 490 km from Jimma. Administrative city of the Woreda (Jebba) is found at elevation of 1729 m. The elevation of the mining area range from 700 m up to 800 m.

According to Bero Woreda rural agricultural development sector (BWRADS) 75% of the Woreda (8 kebeles) are mid land (weynadega) and 25% (4 kebeles) of the mining area low land (kola) or semi-desert. The months of the year are classified according to the seasons of the area depending on the annual rain fall. These are May up to August –rainy season, September up to December-dry season and January up to April semi-dry season. The average maximum temperature of the area is 38^{0}C. The estimated annual precipitation of the area in the rainy season is up to 1000 ml, in early rainy season up to 500 ml and in dry season up to 200-300 ml.

4.2. Study Design

The study design was cross sectional based on laboratory analyses and observation

4.3. Study variables

4.3.1. Dependent variable

- Concentration

4.3.2. Independent variables

- Heavy metals (As, Hg, Cd, Pb & Cu)
- Major cations (Ca^{2+} & Mg^{2+})
- Major anions (HCO_3^-, NO_3^-, SO_4^{2-} & Cl^-)
- Water quality-indicator parameters (pH, T, EC, TDS & Turbidity)

4.4. Data Collection

Samples from well and stream water and observational data were collected during the fieldwork conducted in February 2012. The data collection, sampling method, analytical procedures and data treatment are described as follows.

4.4.1. Preliminary observational data

Observations were made concerning distribution and processes of mining activities, water sources and environmental situations and photographs of these and related activities were taken. The sampling sites of well and stream waters were selected based on the distribution of expected potential pollutant sources and site specific conditions. Sampling sites were thoroughly described according to their geographic location, vegetation, altitude, land use and types of physical land degradation activities around.

4.4.2. Site specific data

The specific geographic location (latitudes/longitudes) of the sampling sites and their corresponding elevation were obtained from handheld GPS (Garmin 72) reading. Letter S with number 1-6 were pre-fixed for well and stream water sampling sites. In-situ measurements of well water (well depth, depth to water, water depth) and stream water (Flow rate, depth and width) were taken using steel tap meter and water volume were calculated (Table 1) for each sampling sites according to the standard (AS3778) method, (Currey & Dunker, 2004).

4.4.2.1. Water sample site information
4.4.2.1.1. Sampling sites information at the shete

In the traditional gold mining area the only option for water supply is well water and intermittent stream water. Each inhabitant dug their own well at the shete for domestic use and gold washing. At each shete in the study area more than one hundred community wells are found. The well water sites (S-01 & S-02) and the stream water sites (S-05 & S-06) selected for the purpose of this study is at the shete. The land at the side of the stream is stippy and covered by rock.

4.4.2.1.2 Sampling sites information far from shete

The well water site Seyali Tongoch (1) (S-03) is somewhat far (around 1/2 km) from the shete and have no any vegetation and indigenous trees around. The well (depth=14 m) was dug on the dry land. The well water site Seyali Tongoch (3) (S-04) is around 200 m far from the shete and have dispersed trees. The well (depth=10 m) was dug in the same way as (S-03). The land around these sites (S-03 & S-04) was highly excavated than other sites in the kebele.

Table 1. Sample site- specific information

Site Name	Sample code	Elevation (m)	Location		Water facility	Well water information			
						Well Depth	Depth to Water	Water depth	Water vol.
Sholla Moga(2)	S-01	712	36N0741832	UTM0702332	Well dug At shete	5 m	4.5 m	0.5 m	0.2512 m3 Or 251lit.
Gabbisa Tombolla	S-02	715	36N074976	UTM0705697	Well dug at shete	7 m	6 m	1 m	0.385 m3 or 385lit.
Seyali Ton ngoch(1)	S-03	791	36N0735872	UTM0701209	Well dug at dry land	14 m	12.5 m	1.5 m	0.577m3 Or 577lit.
Seyali Ton ngoch(3)	S-04	770	36N0735872	UTM0701109	Well dug at shete	10 m	8 m	2 m	0.883m3 Or 883lit.
			Stream water site information						
Shola Che lema shete	S-05	769	36N0735593	UTM0701105	Up stream	Flow rate	Depth	width	1.6875 m3 or 1688lit.
						1.5 m/s	0.45 m	2.5 m	
Sollamoga Shete	S-06	749	36N0740732	UTM0701221	Down Stream	2 m/s	0.6 m	4 m	4.8 m3 or 4800lit.

4.5. Water quality parameter measurements

In-situ measurements (three readings per sample and average value) of some water quality parameters such as Temperature by Thermometer THL-210-090H, pH by pH meter 306311, EC by EC meter 54X002619, Turbidity by HANAN Turbidity meter HI-93703 and TDS were calculated from the measured EC values (TDS=EC x 0.64) were obtained (Table 7) based on standard operating procedures for Water Quality Sampling recommended in (Australian/New Zealand Standards (AS/NZS 5667.1:1998 and APHA, 1998) (AS/NZS, 2009). Then samples were collected from community well and stream water for heavy metals (As, Hg, Cd, Pb & Cu) and for major cations and anions analysis.

4.6. Sampling Procedures of well and stream water

Prior to sampling, at JU environmental laboratory the sampling plastic bottles were thoroughly washed by tap water, distilled water and finally by 0.1N HCl to remove metal contaminants. At each sample site sample and compositing containers were prerinsed with distilled water first and then three times with native water (water going to be sampled) prior to sample collection (Currey & Dunker, 2004).

4.6.1. Well water sampling

Four community well water sampling sites with depth range 5-14 m and with volume of water ranges 251-883 liters were selected for well water sampling (Table.1). Two bottles of well water samples (one for heavy metal analysis and one for major cations and anions analysis) were collected from each of the four sample sites (S-01 to S-04).

The water samples collected for heavy metal analysis were first filtered at field by putting 0.45 μm membrane pore-size filter paper on the funnel according to (APHA, 1998) to leave out any suspended solids that can possibly dissolve and change concentrations of the dissolved metals. Preservation after filtration was carried out using 2 ml concentrated nitric acid (conc. HNO_3- with 68-72% w/w) per one-liter sample collected for heavy metals analysis (APHA, 1998). Acidification of the samples was performed to keep metal ions from precipitating and to minimize adsorption of dissolved species on to sample container walls.

After preservation, the bottles were tightly covered with caps and labeled. A total of eight (four preserved for heavy metal analyses and four unpreserved for major cations and anions analysis) well water samples collected were stored in refrigerator at Gabissa Health Center until transported. Samples were collected, handled and preserved according to standard procedures of AS/NZ 5667.1; 1998 & APHA, 1998 (AS/NZS, 2009).

4.6.2. Stream water sampling

The stream water was divided into equal verticals and Grab samples were taken from each vertical and added to composite. Two composite-Grab samples from each upstream and downstream (S-05 & S-06) sites were collected according to standard stream water collecting procedures described in (ASNZ & APHA, 1998 & Oklahoma water resources, 2004).

Then the collected samples were filtered, acidified, labeled and stored in the same procedures as 4.6.1 above.

4.7. Sample Analyses procedure for heavy metal and major ions

The chemical analyses of water samples were carried out in the certified (ISO17025) laboratory of Addis Ababa Environmental protection Authority (AAEPA) for heavy metals (As, Hg, Cd, Pb & Cu) and for major cations (Ca^{2+} & Mg^{2+}) and for anions (HCO_3^-, Cl^- & SO_4^{2-}) in well and stream water samples. Atomic Absorption Spectrophotometer (AAS, type Nov AA400 analytical Jena) which has analytical detection limit of 0.0001 mg/l was used to analyse both heavy metals & major cations.

The instrument was calibrated with standard solutions and the R-values range from 0.992 (for Mg) to 0.999 (for Pb) (Table 2). Titration method (for HCO_3^- & Cl^-) and Spectrophotometer for SO_4^{2-} were used to determine their concentrations. In the laboratory duplicate analyses were carried out for the heavy metals and five major ions.

Table 2. Standard solution for calibration

Analyte	Standard solution	Wave length (nm)	R-value
As (ppb)	0, 0.92, 1.84, 3.68	193.7	0.996
Hg (ppb)	0, 2.24, 4.48, 8.96	253.7	0.995
Cd (ppm)	0, 0.5, 1.0, 2.0	228.8	0.998
Pb (ppm)	0, 3, 6, 10	283.3	0.999
Cu (ppm)	0, 2, 4, 8	324.8	0.999
Mg (ppm)	0, 0.15, 0.2, 0.25	285.2	0.992
Ca (ppm)	0, 1.0, 1.5, 2	422.7	0.997

4.7.1.1. Analysis for Arsenic (As)

Sample preparation (digestion) for Arsenic analyses was carried on according to the standard (APHA, 1998). prior to analysis to dissolve and remove organic materials that interfere the determination of arsenic. The samples were boiled with H_2SO_4 & H_2S_2 and the condensate was collected and then As (V) was transferred to As (III) by heating the digested sample with potassium iodide/ascorbic acid solution in the presence of HCl. Then As (III) was reduced to AsH_3 by reacting with sodium tetra borate in HCl medium. Finally the digested samples of arsenic were analyzed by the gas hydride AAS method (used for very low concentrations <100 mg/l) specified in APHA, 1998 (Currey & Dunker, 2004).

4.7.1.2. Analysis for Mercury (Hg)

 Samples for mercury analyses were digested by using sodium tetrahydroborate to decompose the mercury compounds. Then the digested samples were analyzed for mercury by the gas hydride method as specified in APHA, 1998 (Currey & Dunker, 2004).

4.7.1.3. Analyses for Cadmium (Cd), Lead (Pb) & Copper (Cu)

Samples were analyzed for Cd, Pb & Cu by using Flame AAS method following the standard procedure specified in APHA, 1998 (Currey & Dunker, 2004).

4.7.2. Major cations and anions analyses
4.7.2.1. Major cations analysis

The concentrations of Ca & Mg were determined using Flame AAS method. Then their respective conversion factors (2.497 for Ca & 4.118 for Mg) were used to obtain the concentration of their cations (Currey & Dunker, 2004).

4.7.2.2. Major anions analysis

The concentration of the Cl^- & HCO_3^- ions were determined by titration using 0.02N $AgNO_3$ & 0.05N H_2SO_4 & the concentration of SO_4^{2-} was determined by Spectrophotometer DR/2010 using standard procedure recommended in APHA, 1998 (Currey & Dunker, 2004).

4.8. Data Processing

Computer programs (Microsoft Excel & SPSS version 16) were used for data processing. Pearson's correlation was used for statistical analysis.

Correlation coefficient is used to measure the strength of the association between two continuous variables. This tells if the relation between the variables is positive or negative, that is, if one increase with the increase of the other or one decreases with increase of the other. The data were statistically computed using correlation coefficient in order to indicate the sufficiency of one variable to predict the other. Pearson's Correlation Coefficient is usually signified by *r* (rho), and can take on the values from –1.0 to 1.0. Where -1.0 is a perfect negative (inverse) correlation, 0.0 is no correlation, and 1.0 is a perfect positive correlation. The variables having coefficient value (r) > 0.5 or < –0.5 are considered significant (Taqveem, 2011).

The analytical results in well water samples were compared with stream water samples. Different national and international organizations' (WHO, EU) and national (Ethiopian) drinking water quality standards for chemicals of their significance to health were consulted for comparison of the results of this research.

Table 3. Maximum permissible values set by different national and international organizations for health and aesthetic values of drinking water

Organization	Water quality parameters in					Heavy metals in (mg/l)				
	$T(0_C)$	pH	EC (µS/cm)	Turbidity (NTU)	TDS (mg/l)	As	Hg	Cd	Pb	Cu
WHO (2011)	NGLV	NGLV		GLV (<5)		GLV 0.01	GLV 0.006**	GLV 0.003	GLV 0.01	GLV 2
WHO (1993)	15	D(6.5-8.5	250	D (<5)	NGV	0.01	0.001*	0.003	0.01	2
EU (1998)	NM	NM	250	NM	NM	0.01	0.001*	0.005	0.01	2
ES (2001)	NM	6.5-8.5 MPL		5 MPL	1000 MPL	0.01 MPL	0.001* MPL	0.003 MPL	0.01 MPL	2 MPL

NGLV=No guideline value, **NM**=Not mentioned, **GLV**=Guideline value, **D**=desirable
   **= Inorganic mercury, *=Total mercury, MPL=Maximum permissible level

4.9. Quality control and quality assurance

Analyses were done following standard procedures. To assess the precision and accuracy of results, replicate analysis was done and standard solution and blank solution was used for calibration and R-value > 0.995. The relative standard deviations were determined to find the precision of the analysis and it was obtained < 5%.

4.10. Ethical consideration

Ethical clearance was obtained from College of Public Health & Medical Science & formal letter was written to concerned bodies from Department of Environmental Health Science & Technology. Site entrance was made with the knowledge & collaboration of Woreda and kebele officials & site owners.

4.11. Dissemination of the study

The final result of the study finding will be presented to Jimma University Scientific Community & will be disseminated to College of Public Health & Medical Science, Jimma University Research Publication Office, Department of Environmental Health Science and Technology, Bench Maji Zone Chief Administrative Office, Water, Mine & Energy Office & the community of the mining area will be informed. Efforts will be made to be published in national and international Journals.

CHAPTER FIVE

5. Results and discussion

5.1. Heavy metal analyses in well and stream water samples

The analyses results and summary statistics of well and stream water samples for five heavy metals (As, Hg, Cd, Pb & Cu) are presented in (Table.4).

5.1.1. Arsenic (As)

The concentration of arsenic in most groundwaters is lower than10 µg/l and often below the detection limit of routine analytical methods (Smedley & Kinniburgh, 2002). In the study area in all well water samples the concentration of arsenic was above the detection limit the method and range from 0.00071-0.0028 mg/l but lower than 10 µg/l (0.01 mg/l) which is in line with this literature value.

The development of strongly reducing conditions at near-neutral pH values, leading to the desorption of As from mineral oxides leading to As release (Smedley & Kinniburgh, 2002).This could be the reasons for well water samples highest arsenic concentration obtained at sample site S-03 (0.0028 mg/l which is highest in temperature (28^0C), EC value and lower pH=7.02.

As the findings on gold mining activities in Latin American reported by Smedley & Kinniburgh, (2002), mining activities have been found to contribute to arsenic contamination of groundwater and it may cause the oxidation of sulphide minerals resulting in the release of arsenic into groundwater. So the traditional mining activities could not be exception of this reality to release arsenic into well water by exposing the sulphide minerals for oxidation.

Comparatively arsenic concentration in (S-04) Seyali Tongoch (3) which is located around the shete and have scattered indigenous trees around is lower than S-03 by 0.0008 mg/l or (40%).

According to Plant et al, (2004), this could be due to addition of organic matter contributed from bush burn, animal waste, decomposed plants and phytoremidation processes of plants that reduce the solubility and mobility of heavy metals, some sulphate-reducing micro organisms can respire As (V) leading to the formation of an As_2S_3 precipitate and immobilization of arsenic may also occur if iron sulphides are formed.

In the study area the highest Arsenic concentration (0.0031 mg/l) was obtained in downstream water sample (S-06) where gold soil washed but this concentration is lower compared with the arsenic

contaminated groundwater due to mining activities in Ghana 50–5000 µg/l (WHO, 2001) and the baseline concentrations in river waters 0.1– 0.8 mg /l (Nordstrom et al., 2000).

As the downstream arsenic concentration compared with the upstream, it exceeds by (0.0006 mg/l) or 10.8%. This result suggests the downstream water pollution by 10.8% arsenic could be due to gold washing. But 89.2% of arsenic concentration might come from natural weathering of arsenic containing minerals and other sources.

5.1.2. Mercury (Hg)

Mercury is present in the inorganic form in surface water and groundwater at concentrations usually below 0.5 µg/l and local mineral deposits may produce higher levels in groundwater (WHO, 2011) but in the study area in 66.7% of the samples the concentration of mercury was above the concentration of 0.5 µg/l reported by WHO.

Mercury concentration in the study area range from 0.00011 - 0.00189 mg/l with mean value of 0.0011 mg/l & SD of 0.00072 mg/l. In all samples mercury concentration were obtained above the detection limit (0.0001 mg/l) of the instrument.

Gold mining in South America contributes over 60% of total anthropogenic mercury emission in water, sediment, and soil environment (Ulrich et al., 2001; Fitzgerald et al., 2007). The highest mercury concentration was obtained in well water sample (S-04 = 0.00189 mg/l) and the concentration of this site exceed the downstream by 0.0007 mg/l = 37.04%).

The next higher concentration also obtained in the same kebele of well water sample (S-03 = 0.00168 mg/l) that also exceed the downstream by 0.0049 mg/l = 29.17%. Mercury once released into the atmosphere, it undergoes a series of chemical reactions that cause Hg (II) species to be deposited in the soil over the short or medium term; they are transformed by the environmental conditions in the soil (pH, temperature, humic acid content, microorganisms), favoring the formation of organic and inorganic compounds, which display different mobility in the soil (WHO, 2011). These environmental conditions and sever land deterioration observed in this kebele more than others might be reason for the higher mercury concentration in the study area.

In two well water samples (S-01 & S-02) mercury concentration was below the standard (0.001 mg/l). The concentration in two well water samples (S-03 & S-04) and in two stream water samples (S-05 & S-06) were greater by 68%, 69%, 11% & 19% respectively above (WHO, 1993), (ES, 2001) and (EU, 1998)

standards but the concentrations in all samples were below the standard set for inorganic mercury (0.006 mg/l) by (WHO, 2011) health based drinking water quality standard.

5.1.3. Cadmium (Cd)

The concentration of cadmium in all samples of the study area was obtained below the detection limit (0.0001 mg/l) of the instrument. This might be cadmium found in minor constituent in surface and groundwater and sediment may be a significant sink for cadmium emitted to the aquatic environment (Tolla, 2006).

5.1.4. Lead (Pb)

The concentrations lead in well and stream water samples of the study area were below the detection limit (0.0001 mg/l) of the instrument. According to (Reimann Carital,1998), lead has low environmental mobility in acid and neutral to alkaline conditions. Lead binds strongly to organic matter in soils and doesn't readily migrate to groundwater. In the study area the pH values (neutral to alkaline condition) are in agreement with this literature. This could be reason for lead not to be detected in the study area.

5.1.5. Copper (Cu)

Copper was obtained only at one water sample (S-03 = 0.159 mg/l). Absence of any vegetations and being bare land might favor for the release of copper in this sample. In the contrary copper was obtained below the detection limit (0.0001 mg/l) of the instrument in the other sample sites (S-01, S-02, S-04, S-05 & S-06) which have vegetation around.

Cu-ions form strong coordination complexes with organic matter (Stevenson, 1976a & 1991b). So the addition of organic matter from those plants and bush and 'sembelet' burns in the area might contribute in the formation of coordination complexes with copper ions. As a result copper could be adsorbed in the soil.

Table 4. Analyses results of the heavy metals concentration in mg/l

Sample sites	As		Hg		Cd	Pb	Cu
	X ± SD	Range	X ± SD	Range	X ± SD & Range		
S-01	0.00091±0.00004	0.00089–0.0009	0.00011±0.000004	0.00011-0.00012	BDL	BDL	BDL
S-02	0.00071±0.00003	0.00069–0.0007	0.00029±0.00004	0.00027-0.00032	BDL	BDL	BDL
S-03	0.0028±0.00002	0.0028–	0.00168±0.00007	0.0016-	BDL	BDL	0.159

		0.00284		0.0017			
S-04	0.00195±0.00007	0.0019–0.00199	0.0019±0.00003	0.0019-0.0019	BDL	BDL	BDL
S-05	0.0025±0.00009	0.0025–0.0026	0.00111±0.00006	0.0011-0.0012	BDL	BDL	BDL
S-06	0.0031±0.0001	0.00304–0.0031	0.00119±0.00001	0.0012-0.0012	BDL	BDL	BDL
Min.	0.00071	-	0.00011	-	-	-	-
Max.	0.0031	-	0.00189	-	-	-	-
Mean	0.00195	-	0.0011	-	-	-	-
SD	0.00099	-	0.00072	-	-	-	-

BDL= Below detection limit of the method, **X**=Mean concentration, **SD**=Standard deviation

5.2. Analyses results of major cations and anions

The samples collected were analyzed for major cations and anions (Table 5). The distribution and their associations with each other and with heavy metals (As & Hg) were presented as follow.

5.2.1. Major cations (Ca^{2+} & Mg^{2+}) analyses

Hardness of water depends mainly upon the amounts of calcium and magnesium salts or both. Waters with values exceeding 120 mg/l are considered hard, while values below 60 mg/l are considered soft. Harder water has the effect of reducing the toxicity of some metals (i.e., copper, lead, zinc, etc.). If the water has a hardness of greater than 500 mg/l, then it is normally unacceptable for most domestic purposes and must be treated. In drinking water 80 to 100 mg/l is the optimal range (>200 mg/l is considered poor but can be tolerated) and for food processing 10–250 mg/l is optimal (Bartram & Balance, 1996).

The major cations (Calcium & Magnesium) in the well and stream water rang from (114.4–292.2 mg/l) & (99.2–191.5 mg/l) with a mean value of (198.8–147.2 mg/l) respectively. From cations highest concentrations of calcium and magnesium were obtained at (S-02 =292.2 & 191.5 mg/l) respectively. These might come from dissolution of dolomite (magnesium calcite). water in all samples of the study area are acceptable for most domestic purposes because their hardness values are less than 500 mg/l but not in the optimal range for drinking (80 to 100 mg/l) (Bartram & Balance, 1996).

In the well water samples (S-02 & S-03) are considered poor (>200 mg/l) but can be tolerated and water at S-02 is not suitable for even for food processing. Generally the waters in all sites of the study area were in the desirable range (150–500 mg/l) of WHO, (1993) drinking water quality standard.

5.2.2. Major anion (HCO_3^-, SO_4^{2-} & Cl^-) analyses

A) Bicarbonate (HCO_3^-)

The alkalinity of water is its capacity to neutralize acid (Clesceri et al., 1998). The alkalinity of some waters is due only to the bicarbonate of calcium and magnesium. The pH of such water does not exceed 8.3 and its total alkalinity is practically identical with its bicarbonate alkalinity. Water having a pH above 8.3 contains carbonates and possibly hydroxides in addition to bicarbonates (Bartram & Balance, 1996).

The concentration of bicarbonate in the study area range from 314.5 to 594.5 mg/l. The highest value was obtained at S-03 (594.5 mg/l) and the least was at the S-05 (314.5 mg/l). The bicarbonate concentration in the well waters was higher than in stream waters. This indicates the well waters might have higher alkalinity which could have come from calcites of calcium and magnesium by dissolution. Silicate weathering also increases the concentration of HCO_3^- in groundwater (Lakshmana et al., 2003).

Waters that have high alkalinity values are considered undesirable because of excessive hardness. The well waters (S-02 to S-04) except S-01 are above the maximum desirable limit (500 mg/l) of WHO, (1993). Because of this excessive hardness the well waters in the study area were considered undesirable.

B) Sulphate (SO_4^{2-})

Sulphate is widely distributed in nature and may be present in natural waters in concentrations ranging from a few to several thousand mg/l (Clesceri et al., 1998). Sulphate also results from the breakdown of sulphur containing organic compounds (Bartram & Balance, 1996). The concentrations of sulfate was very low throughout the study area except at downstream (S-06 = 80 mg/l) which might have come from dissolution of gypsum due to gold washing activities in the downstream. Sulpate concentration is below WHO, (1993) & EU, (1998) drinking water quality standards 500 mg/ l & 250 mg/l respectively.

C) Chloride (Cl^-)

Chloride concentration in well water sample in (S-02 = 88.3 mg/l) is higher than other water samples of the study area. Highest calcium ion concentration also obtained in this sample. The next higher chloride was obtained in the downstream (S-06 = 80 mg/l). The higher chloride ion concentration might be come from calcium chloride salt. The chloride ion concentrations in the study area is below the standard (250 mg/l) set by WHO (1993) & EU, (1998) for drinking water.

Table **5**. Concentration of the analyzed major cations and anions in well and stream water samples in the mining area.

Sample Site	Ca^{2+}		Mg^{2+}		SO_4^{2-}		Cl^-		HCO_3^-	
	Range	X ± SD	Range	X ± SD	Range	X ± SD	Range	X ± SD	Range	X ± SD
S-01	198.2-201.01	199.61±1.99	138-140	139±1.4	35.1-35.4	35.25±0.2	16.2-16.4	16.3±0.14	396.8-397.2	397±0.28
S-02	289.4-294.9	292.15±3.9	189.4-193.7	191.6±3.04	5.01-5.07	5.04±0.04	88.2-88.4	88.3±0.14	561.4-562.4	561.9±0.71
S-03	247.2-251.7	249.45±3.2	187.5-190.3	188.9±1.98	10.2-10.8	10.5±0.4	10-10.2	10.1±0.14	594.2-594.8	594.5±0.4
S-04	174.4-175.4	174.9±0.71	147.6-152	149.8±3.1	1.01-1.03	1.02±0.01	7.2-7.6	7.4±0.28	559.3-599.4	579.4±28.4
S-05	162.2-162.9	162.6±0.5	113.5-115.7	114.6±1.6	1.02-1.07	1.05±0.04	12.2-12.4	12.3±0.14	314.2-314.8	314.5±0.4
S-06	113.7-115.1	114.4±0.99	98.9-99.5	99.2±0.4	80.01-80.06	80.04±0.04	80-80.4	80.2±0.28	323.2-324.6	323.9±0.99
Min.	-	114.4	-	99.2	-	1.02	-	7.4	-	314.5
Max.	-	292.2	-	191.5	-	80.04	-	88.3	-	594.5
Mean	-	198.8	-	147.2	-	22.2	-	35.8	-	461.9
SD	-	63.7	-	37.8	-	31.1	-	37.8	-	131.4

X=Mean, **SD**=Standard deviation

5.2.3. The association of major cations and anions in well and stream water

The correlation of each ions in the well and stream water were attempted to calculate using Pearson's correlation. As the statistical analyses result indicates all cations and anions each other have correlation but the degree of their correlation differ one with the other. Calcium has a positive correlation with magnesium (r = 0.9481), with bicarbonate (r = 0.721) and negative correlation with sulphate (r = -0.5844) at $p < 0.05$. Magnesium has positive correlation, with calcium and bicarbonate (r = 0.8947) and negative correlation with sulphate (r = -0.5945). Sulphate has a negative correlation with calcium, magnesium and bicarbonate (r = -0.5608) at $p < 0.05$. The result had shown positive correlation between calcium, magnesium and bicarbonate at $p < 0.05$. These implicate that they might have common mineral source (might be calcite and dolomite or magnesium calcite) from which released by dissolution.

The statistical analyses result also indicates the correlation of those ions with the heavy metals (As & Hg) in the water samples. The heavy metals generally negatively correlated with ions but not significant except arsenic (r = -0.5874) with calcium. Arsenic and mercury have positive correlation at $p < 0.05$.

Table 6. Correlation of major ions with ions and with the heavy metals (As & Hg) in the study area

	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Cl^-	HCO_3^-	As	Hg
Ca^{2+}	1						
Mg^{2+}	0.9481	1					
SO_4^{2-}	-0.5844	-0.5945	1				
Cl^-	0.1137	-0.0032	0.4784	1			
HCO_3^-	0.721	0.8947	-0.561	-0.1166	1		
As	-0.5874	-0.4324	0.100	-0.1703	-0.2683	1	
Hg	-0.3224	-0.0459	-0.1573	0.4184	0.2942	0.747	1

5.3. In-situ measurements of physicochemical parameters

Some physicochemical parameters (Temperature, pH, EC & turbidity) of the waters of the study area were measured at the time of sampling (Table 7). The results of these parametric measurements were presented as follows.

5.3.1. Temperature

Temperature affects parameters of water (pH, EC, rate of chemical reactions etc) & solubility of gases in various ways. The temperature values obtained from in- situ measurement of well & stream water samples vary from 24 - 28 ^oC. The average temperature values for well & stream water samples were 26^oC & 26 ^oC respectively. The sample where highest temperature measured was the second higher in arsenic, mercury, calcium & magnesium cations, sulphate & highest bicarbonate concentrations obtained. This indicates the effect of temperature in elevating the solubility of dissolved metals (Clesceri et al, 1998).The lowest temperature was measured at well water sample. The temperature measured in all water samples was above the maximum permissible limit (15 ^oC) issued by the (WHO, 1993).

5.3.2. pH

Groundwater was in general expected to be neutral to slightly alkaline in nature. A decrease in pH increases the solubility of metals. The weathering of minerals, such as limestone or dolomite, by water becomes more rapid with a decrease in pH. High pH values tend to precipitate the heavy metals as hydroxides. Low pH levels tend to increase carbon dioxide and carbonic acid concentrations (Bartram and Balance, 1996; Reeve, 2002). The pH of the well & stream water samples range from neutral (7.02) to slightly alkaline (8.1). The highest pH value was obtained at downstream & the lowest pH was recorded from well water sample. The average well & stream water pH values were 7.14 & 7.8 respectively. The slight alkalinity could possibly come from calcium carbonate bedrock weathering or

reflects the dissolution of limestone & dolomites into the well water (where calcium, magnesium & bicarbonate ions measured higher than stream water sites). This indicates high dissolution of these minerals in the soil & their cations & anions released to the aquifer.

The analysis results of major cation & anion also approve that calcium and magnesium decreased in stream as the pH value slightly increase from neutral to alkalinity. For consumption point of view, all the samples may be considered fit, the desirable limit (6.5–8.5) of WHO, (1993) as they are neither acidic nor strongly alkaline.

5.3.3. EC (Electrical Conductivity)

The conductivity of natural waters is found to vary between 50 & 1500 µS /cm coastal streams have specific conductivity values of 100 µS/cm, while interior streams range up to 500 µS/cm ((Bartram & Balance, 1996; Reeve, 2002). Increasing temperatures tend to elevate the solubility and toxicity of dissolved metals, while dissolved oxygen levels generally decrease with increasing temperature (Clesceri et al., 1998).

Electrical conductivity is a valuable indicator of the amount of material dissolved in water & its value in well & stream water samples of the study area range from 927- 1726 mg/l .The highest value of EC was measured at well water site & the lowest value was obtained at upstream water sample . The average well & stream water EC values were 1375 & 978 µS/cm respectively & maximum mean EC value was recorded in well water samples. This could be due to dissolution of minerals from the excavated soil & high temperature of the mining area. The measured EC values for all samples were above WHO (1993) & EU (1998) standard (250 µS/cm) recommended for drinking water.

5. 3. 4. Turbidity

The turbidity of the water samples were range from 28 – 230 NTU. Maximum turbidity value was measured in downstream sample site where gold washing activities were carried on & minimum value was recorded in well water sample. The mean value of turbidity in well water samples was 64 & in the stream water samples turbidity value of 159.5 was obtained which is above 2.5 times the mean value of the well water. In all water samples turbidity was 5- 46 times higher than the desirable limit of WHO (1993) & ES (2001) MPL set for drinking water.

Table 7. In-situ water quality parameter measurements of well & stream water sample of the mining area

| Sample site	Temperature (0C)		Conductivity, (µS/cm)		pH		Turbidity, (NTU)		TDS (mg/L)	
	Range	X±SD	Range	X±SD	Range	X±SD	Range	X±SD	Range	X±SD
S-01	24.01-24.03	24.02±0.01	1051-1053	1051.5±2.12	7.21-7.25	7.23±0.02	54.1-54.3	54.2±0.14	672.6-673.9	673.2±0.9
S-02	26.6-26.8	26.7± 0.14	1726-1727	1726.5±0.7	7.2-7.23	7.22±0.02	90.1-90.2	90.1±0.06	1104.6-1105.3	1105±0.6
S-03	28-28.02	28.1±0.14	1126-1126.01	1126±0.007	7.01-7.05	7.03±0.03	82.5-82.52	82.4±0.18	720.6-720.7	720.7±0.07
S-04	26.4-26.5	26.5± 0.07	1594-1596	1595±1.4	7.08-7.09	7.1±0.007	28.1-28.2	28.2±0.07	1020.2-1021.4	1020.8±0.85
S-05	24.7-24.8	24.8± 0.07	927-928	927.5±0.7	7.05-7.06	7.1±0.007	89.01-89.03	89.02±0.01	593.3-592.6	593±0.5
S-06	24.6-24.5	24.6± 0.07	1028-1028.03	1028±0.02	8.0-8.2	8.1±0.14	230-230.01	230±0.007	657.9-657.94	657.9±0.03

X=Mean, **SD**=Standard deviation

5.4. Assessment of the pollution source(s) of waters (well and stream) in the mining area

So as to identify the pollution sources for drinking water in the study area the well water & stream (reference) water analyses results were compared. Also to examine other pollution sources the analyses results of upstream were compared with downstream water samples.

5.4.1 Comparison of well water samples with stream water (reference) samples

To evaluate the contribution of the traditional gold mining activities the analyzed physicochemical parameters in well & stream water samples were compared. As it was shown in (Table 8) the concentrations (or values) of As, Hg, SO_4^{2-}, Cl-, pH & turbidity were higher in the stream water by 27.2%, 7.4%, 32.3%, 20.6%, 4.4% & 42.8% respectively than in the well waters samples. But the concentrations (or values) of calcium, magnesium, bicarbonates, temperature, EC & TDS lowered by 24.6%, 22%, 25.2%, 3%, 16.8% & 16.8% in the samples of the reference (stream water).

Well waterVs Stream water
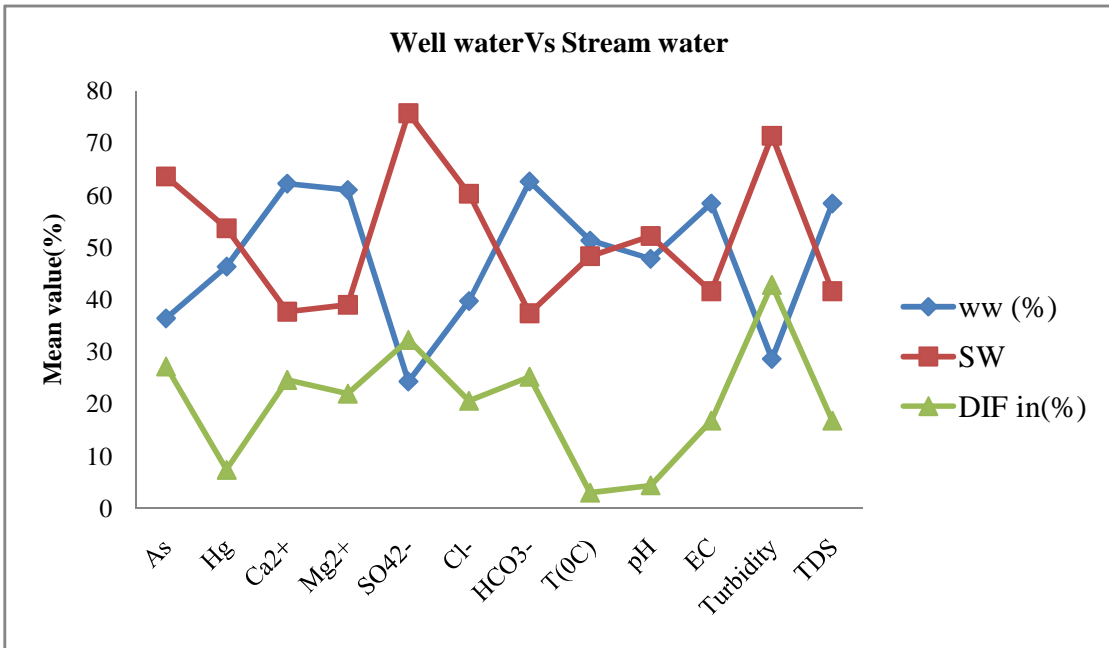
WW=Well water, **SW**=Stream water, **DIF**=Difference in percent

Figure 1 Comparison of well water and stream water samples

5.4.2. Comparison of upstream and down stream

As it was shown from the comparative results (Table 8) As, Hg, SO_4^{2-}, Cl-, HCO_3^{-}, pH, EC, Turbidity & TDS were higher in their mean values in the downstream water samples by 10.8%, 4.4%, 97.4%, 73.4%, 1.4%, 3.8%, 5.2%, 44.2% & 5.4% respectively than in the upstream water samples. The temperature of the water samples in the upstream & downstream remain the same. Ca^{2+} & Mg^{2+} were decreased in the downstream water samples by 17.4 & 7.2% respectively
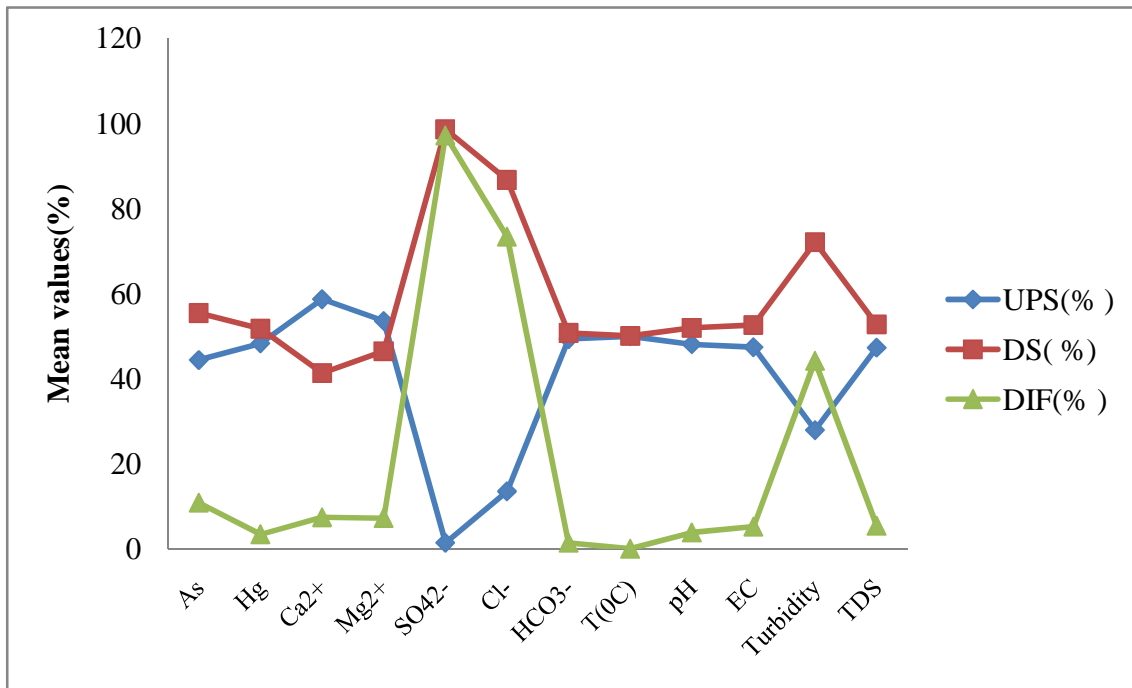
UPS=Upstream, **DS**=Downstream, **DIF**=Difference in percent
Figure 2. Comparison of upstream water sample and downstream water sample

Table 2. Comparison of the analysed well water samples with stream water (reference site) samples

Parameters		Heavy metals (mg/l)		Major cations and anions(mg/l)					Water quality parameters				
		As	Hg	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Cl-	HCO_3^-	$T(0_C)$	pH	EC (μS/cm)	Turbidity (NTU)	TDS (mg/l)
Well Water	Mean value	0.0016	0.00099	299	167.3	13	30.5	533.2	26.3	7.13	1375	63.3	880
	%	36.4	46.3	62.2	61	24.3	39.7	62.6	51.3	47.8	58.4	28.6	58.4
Stream Water	Mean value	0.0028	0.0012	138.5	106.9	40.6	46.3	319.2	25	7.8	977.5	159.5	626.5
	%	63.6	53.7	37.7	39	75.7	60.3	37.4	48.3	52.2	41.6	71.4	41.6
Difference in percent		27.2↑	7.4↑	24.6↓	22↓	32.3↑	20.6↑	25.2↓	3↓	4.4↑	16.8↓	42.8↑	16.8↓
Up stream	Mean value	0.0025	0.0011	162.6	114.6	1.1	12.3	314.5	25	7.5	927	89	593
	%	44.4	47.8	58.7	53.6	1.4	13.3	49.3	50	48.1	47.7	27.9	47.3
Down stream	Mean value	0.0031	0.0012	114.4	99.2	80	80.2	323.9	25	8.1	1028	230	660
	%	55.4	52.2	41.3	46.4	98.6	86.7	50.7	50	51.9	52.6	72.1	52.7
Difference in percent		** 10.8	** 4.4	* 17.4	* 7.2	** 97.2	** 73.4	** 1.4	*** 0	** 3.8	** 5.2	** 44.2	** 5.4

↑= Increase in the stream water (in up and down), ↓=Decrease in the stream (or increase in well water),
*=Increase in upstream (or decrease in downstream), **=Increase in downstream, ***=No variation

32

CHAPTER SIX: CONCLUSION AND RECOMMENDATION

6.1. Conclusion

Among the water quality parameters: temperature 60–80%, turbidity 5–46 times, EC in all samples were 3-6 times higher than the desirable limit. pH was in the range of the desirable limit & TDS for 33.3% of the well water samples were above the MDL.

Major ions, calcium & magnesium (as total hardness), sulphate chloride ions analyzed in all water samples were below the standard. All the samples analyzed for arsenic (As) were below the recommended value. Mercury (Hg) in four samples was above maximum recommended value (0.001 mg/l).

The natural associations among the heavy metals & heavy metals with ions the statistical analyses shown significant at ($p < 0.05$) positive correlation between As ($r = 0.8797$) & Hg ($r = 0.747$) in well water & in the study area respectively. Among heavy metals & ions, arsenic with calcium & sulphate with calcium, magnesium & bicarbonate have significant negative correlation & significant positive correlations were shown between magnesium, calcium & bicarbonate ions in the samples at ($p < 0.05$).

From the comparison of well water samples analyses results with stream water samples analyses results shown that As, Hg, SO_4^{2-}, Cl^-, pH & Turbidity were found by 27.2%, 7.4%, 32.3%, 20.6%, 4.4% & 42.8% respectively higher in stream water samples than in well water samples.

The comparison analyses results of upstream samples with downstream samples shown that As, Hg, SO_4^{2-} ,Cl^-, HCO_3^-, pH, EC, Turbidity & TDS were found by 10.8%, 4.4%, 97.2%, 73.4%, 1.4%, 3.8%, 5.2%, 44.2% & 5.4% respectively higher in downstream water samples than in the upstream water samples.

Generally from the analyzed physico-chemical parameters mercury, temperature, turbidity, electrical conductivity (EC), bicarbonate & TDS were found in 66.7%, 100%, 100%, 100%, 50% & 100% of the water samples in the study area respectively & these parameters were also found in 50%, 100%, 100%, 100%, 75% & 100% of the well water samples respectively higher than the WHO (1993), EU (1998) & ES (2001) recommended maximum desirable limits set for drinking water.

These results of the present study clearly implicate that the downstream water pollution is contributed by the gold washing activities.

6.2. Recommendations

1. Mercury and some of the parameters were found in well and stream waters above the standards set for drinking water.

This study, therefore, highly recommends the government and other responsible bodies (organizations) to put forward immediate solutions and to take appropriate corrective measures.

2. Considering important environmental variables detailed study need to be conducted to evaluate the overall impacts of traditional gold mining.

3. Absence of drinking water facilities and rehabilitation of the land are critical problems of the mining area that need to be given due attention.

4. Organizing association of gold miners and training are important prerequisites that should be done.

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ANNEX

1. Data recording format

Well water and Stream water field physicochemical parameters measurement and site specific information form

Date ——/——/——   Facility Name ————————

 Site Name————————————   Code of Sample Container _____

Volume = cross sectional area (width x depth) x flow rate (velocity)

Table 3.Well water and Stream water field physicochemical parameters measurement and site specific information

No	elevation		Depth(m)	Width (m)	Flow rate (m/s)	Volume (L)	Water quality indicator parameters				
							pH	T(C^o)	EC	TDS (mg/l)	Turbidity (NTU)

Comment_____   -
_____

Sampler name _____ Sig _____ Date _____