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COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCES

MASTER OF SCIENCE IN WATER MANAGEMENT

DEPARTMENT OF AQUATIC ECOSYSTEMS MANAGEMENT

Assessment of the Effect of Artisanal Gold Mining on Heavy metals Concentrations and Associated Potential Public Health Risk: The case of May Sieley River of the Shire, Tigray region, Ethiopia

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A thesis submitted to the Africa Centre of Excellence for Water Management (ACEWM) in partial fulfillment of the requirements for Master's Degree in Water Management (Aquatic Ecosystems Management) of Addis Ababa University.

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ADDIS ABABA UNIVERSITY

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Declaration

I, HABINEZA Elias, hereby declare that this research report is my own work towards the MSc degree and that, to the best of my knowledge, it contains no material previously published by another person nor material, which has been accepted for the award of any other degree of the University, except where due acknowledgement has been made in text.

HABINEZA Elias Signature: ……

Dedication

I would like to dedicate this thesis to:

Almighty God

My beloved parents

My siblings

All my friends.

Acknowledgement

I would like to express my special thanks to the Government of Ethiopia and Africa Center of Excellence for Water Management sponsored by World Bank for granting me this golden opportunity to pursue my studies for Master of Science.

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List of abbreviations

AGM: Artisanal Gold Mining

ASGM: Artisanal and Small-scale Gold Mining

HMs: Heavy Metals

AMD: Acid Mine Drainage

HHRA: Human Health Risk Assessment

ILCR: Incremental Lifetime Cancer Risk

GPS: Global Positioning Systems

DWG: Drinking Water Guideline

BDL: Below Detectable Limit

HQ: Hazard Quotient

HI: Hazard Index

ILCR: Incremental Lifetime Cancer Risk

Abstract

Artisanal gold mining (AGM), in third world countries including Ethiopia has become a livelihood diversification strategy, which makes significant contribution to poverty alleviation. Although artisanal gold mining provides enormous economic benefits, the mining activities are carried out at the expense of the environment and public health due to pollution with heavy metals (HMs). The protection of public health and aquatic resources necessitates the availability of scientific information on pollution with heavy metals. The present study was, therefore, conducted to investigate the efffect of artisanal gold mining on the levels of selected heavy metals in May Sieley River (Tigray) and evaluate the potential human health risk. Surface sediment and water samples were collected from upstream, midstream and downstream sites (USS, MSS &DSS) respectively, during the dry and post-rainy periods and were analyzed for Pb, Cd, Cu, As, Cr, Hg, Ni, and Zn by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). The concentrations of heavy metals in water samples were compared with WHO and Ethiopian standards for drinking water and assessment of human health risk was made following the guidelines provided by the US Environment Protection Agency. Temperature, pH and dissolved oxygen were measured *insitu* and were found to be within acceptable ranges and did not show large variations. The differences in HMs concentrations in water among sampling sites during both seasons were not marked except for Cu and Zinc in dry season, although Zn, Cu, Hg, Cd and Pb were higher at the MSS suggesting the association of their levels primarily with AGM. The differences in the concentrations of all HMs in water samples between seasons were marked. The concentrations of HMs in sediment samples varied markedly between the two seasons. The differences in HMs concentrations in sediments among sampling sites during dry seasons were marked for Cu, Zn, Pb and As while in post-rainy season, differences were not marked except for Ni and Pb. The concentrations of all HMs except Nickel in sediment samples of the dry season were higher at the MSS, while they were higher at USS during the post-rainy season. The present results suggest that both AGM and natural sources associated with the weathering of rocks have made contributions to the metal pollution of May Sieley River. Hg and As were above WHO and Ethiopian standards for drinking water in the dry season in all sampling sites, while Cr, Cd, Pb and As were above the same standards for drinking water in the post-rainy season in all sites, except Hg (in one sample of MSS) and Ni (in one sample of DSS). The HQ values for As, Pb, Hg and Cd for both age groups were at unacceptable non-carcinogenic potential health risk levels (HQ>1), while As and Cd for adults and As, Cd and Hg for children, are likely to have chronic effects (Q>10). The Sum of HQs (HI) of analyzed metals was far greater than 1 for both age groups, children being at greater risk. This raises concern about the non-carcinogenic adverse health effects of using the river water for drinking and other household purposes. The results of the ILCR assessment for Arsenic, Lead, Cadmium, Chromium and Nickel indicated that the carcinogenic effect associated with these metals is not acceptable. The study has revealed that the river water is not safe due to HMs pollution, AGM should be managed to reduce its contribution to the pollution of water bodies with heavy metals. The government needs to assist and empower the miners so that they can carry out their activities sustainably and in an environmentally friendly way. Further monitoring of the impact of traditional gold mining on HMs pollution by considering aquatic organisms in order to assess their biomagnification along the food chains is also recommended.

Keywords: Heavy metals, Artisanal gold mining, May Sieley River, Human health risk.

1. Introduction

1.1. Background of the study

Mineral exploitation can provide a significant income for community and boost the economic development of a particular country. Gold mining has been the most commonly practiced mineral exploitation worldwide. Artisanal and small-scale gold mining is a globally-significant industry, providing rural employment directly to at least 15 million people and indirectly to over 100 million in more than 70 countries (Tieguhong *et al*., 2009). In the leading of gold-producing countries like South Africa and Ghana, artisanal gold mining has brought economic success stories of booming national income in Africa (Awudi, 2002). It has been an integral part of the economy for many developing countries (Yaw and Gold, 2016). In Tanzania, small-scale gold mining is perceived as a 'ladder that sends people to wealth' (Fisher *et al*., 2009). However, in most African countries, the mining of Gold is being carried out mainly through artisanal or traditional ways. Artisanal gold mining has become a livelihood diversification strategy in third world countries (Intergovernmental Forum on Mining and Minerals, 2017). Miners can earn higher incomes through mining than through other traditional activities (Funoh, 2014). Therefore, it can contribute to poverty alleviation and provides many opportunities for rural people.

Gold occurrences are widespread in Ethiopia and exploitation of placer gold dates as far back as at least 3,500 years, when the Egyptians sailed along the red sea and travelled up into what later became Ethiopia to trade gold. Currently, the total population in Ethiopia involved in gold mining (legal and illegal) is estimated at 1.24 million (Yohannes Yihdego *et al*., 2018). Mining for gold is a key development sector in the country. However, small scale and traditional gold mining activities are commonly practiced throughout the country, while modern gold mining is still limited. Artisanal and small-scale gold mining has made considerable contribution to gold production in Ethiopia, with artisanal miners exploiting a number of placer gold deposits in different parts of the country. Based on some assessment studies, the amount of gold mined and marketed by artisanal miners all over the country was estimated to be more than 3 tonnes per year. Excluding the gold supplied by cooperatives and multi-national companies, Tigray regional state, Northern greenbelt, contributed 1733.42 Kg gold to the National Bank of Ethiopia in 2012 (Hailemariam *et al*., 2015).

Tigray region of Ethiopia is highly rich in minerals and mining for gold is very common. Due to its geological history and type of basement rock, which consists of hydrothermal quartz veins within the Neoproterozoic low grade basement rocks, metavolcanics and metasedimentary rocks, gold mineralization is commonly found in Tigray, Northwest of Ethiopia (Giday and Bheemalingeswara, 2017).

The traditional gold mining involving panning technique has received a boost in Tigray during the last two decades following the new government policies whereby miners are encouraged to peg claims and operate legally. Consequently, it has become a source of livelihood and employment for many landless and unemployed citizens and an important source of hard currency (Hagos *et al*., 2016). According to the Ministry of Mines and Energy (2009), the amount of foreign currency earning from the sales of exported minerals such as gold, tantalite concentrate platinum, decorative dimension stones and gemstones has been about 135 million dollars per year for the last few years, which contributes up to 7-10% of the total foreign currency earning from export of the country. Gold export, which was just 5 million USD in 2001, has attained a large increase to 602 million USD in 2012 (KEFI Minerals plc, 2015).

Although mining provides enormous social and economic benefits to nations, the long-term adverse effects on the environment and public health cannot be overlooked (Akabzaa, 2000). It has been shown that mining activities are carried out at the expense of the environment and public health. Heavy metal pollution of aquatic ecosystems is becoming a problem of global concern, Hagos *et al* (2016) concluded a rapid drying up and pollution of water sources, extreme land disturbance and soil erosion, destruction of vegetation and biodiversity loss in the Tigray region are attributable to this mining activity. Human activities such as mining threaten water sources, with water being described as “mining’s most common victim" (Aboka *et al*., 2018). Excessive inputs of trace metals, especially cadmium, chromium, mercury, lead, arsenic, copper and zinc to ground and surface waters have resulted in the deterioration of their water quality thereby affecting aquatic organisms (Olowu *et al*., 2010).

Of all contaminant metals, mercury is by far the most toxic, and the only metal capable of biomagnification in almost all food chains, with its concentrations rising in accordance with the trophic levels of the species (UNEP, 2002)). Mercury (Hg) amalgamation is the preferred gold recovery method employed by artisanal gold miners. In this practice, mercury metal is used to

extract gold from ore as a stable amalgam. The amalgam is then heated to evaporate the mercury and isolate the gold (Louisa and Justin, 2018). However, the process releases much mercury to the environment as artisanal miners release almost 2 g of mercury to environment to produce just 1 g of gold. As a result, mercury along with other heavy metals can be released into water bodies (streams or rivers) found around the mining site and then transported to downstream water bodies (lakes or reservoirs) or may accumulate in soils and sediments such that they can be loaded into water bodies trough runoff. Misuse of mercury can result in serious health hazards to miners involved in gold extraction, and local inhabitants, which may be exposed to mercury via the food chain (Hinton *et al*., 2003). Tailings are the major wastes produced from gold extraction and contain high amounts of heavy metals. These metals spread in an uncontrolled manner into surrounding environments upon exposure to water or through dispersal by wind (Fashola *et al*., 2016) eventually finding their ways into a river. Furthermore, they can contaminate groundwater aquifers. High metal waters can cause contamination of the scarce local groundwater through the solubilization of toxic metals (Abdul-wahab and Marikar, 2011). The increase in the prevalence of liver-related diseases of humans in the northwestern region of Ethiopia, restricted to the Shire area since 1980 (Ahmed, 2015) has been a new public health issue of national concern.

The protection of public health and aquatic resources necessitates the availability of scientific information on pollution with heavy metals, which are causes of many health problems including cancer. The gathering of sufficient scientific information on water quality status and pollution level and sources are important for the implementation of sustainable water-use management strategies (Duressa Tamene and Seyoum, 2015) as well as protecting the community from water-related outbreaks of ailments and chronic diseases. Data on the levels of heavy metals in the May Sieley River, which is found in the proximity of the Adnigsti mining site located at Laelay Adiyabo may serve as an alarm signaling the need to treat, or avoid using the river water and develop strategies for mitigation measures. Therefore, this study was conducted to assess the effect of artisanal gold mining activities on the concentrations of heavy metals in May Sieley River and assess the potential human health risk associated with the use of its water.

1.2. Problem statement

Gold mining is important to the economy of Ethiopia. However, artisanal gold mining mostly uses mercury to extract gold from rocks and sediments, with consequent release of large quantities of mercury, along with other heavy metals, into rivers and lakes. Heavy metal contamination may have devastating effects on the ecological balance of the recipient aquatic ecosystem and the resident diverse organisms (Farombi *et al*., 2007). Heavy metals are life-threatening pollutants owing to their toxicity. Each heavy metal is potentially dangerous because of its bioaccumulation through the food chains (Aycicek *et al*., 2008). Their continuous accumulation in water bodies is, therefore, directly or indirectly, a public health concern since they can contaminate people via drinking water, food organisms such as fish or other aquatic products and they may also impact the biodiversity of aquatic organisms. Chronic exposure to heavy metals and metalloids at relatively low levels can cause adverse health effects (Agency for Toxic Substances and Disease Registry, 2008).

Different researchers have addressed the impact of traditional and small-scale gold mining on the terrestrial environment. Mehari Girmay (2018) assessed the impacts of Artisanal Gold Mining on vegetation ecology in Shire Districts. Hailemariam Meaza *et al* (2015) conducted a research on the effects of small-scale gold mining on the miners and local communities in a semi-arid region of Ethiopia. Hagos *et al* (2016) also studied the participation of traditional gold mining and its impact on natural resources in the area of Asgede Tsimbla, Tigray. However, relatively little attention has been paid to its impact on aquatic ecosystems, which are more vulnerable owing to the use of their water as a medium for gravity separation in artisanal and small-scale gold mining. The protection of public health and aquatic resources necessitates the availability of scientific information on pollution with heavy metals, which are causes of many health problems including cancer. Thus, the relevance and significance of a study on the heavy metal pollution of May Sieley River, which is located in the vicinity of Adgnisti mining site found in one of the Shire districts of northern Tigray is unquestionable.

1.3. Research questions

- What are the concentrations of selected heavy metals in May Sieley River?
- What levels of relevant physico-chemical parameters (temperature, DO and pH) characterize the river water at the sampling sites?
- Are there potential health risks associated with the use of May Sieley River water?

1.4. Research objectives

1.4.1. General objective

To investigate the effect of artisanal gold mining activities on the concentrations of heavy metals in May Sieley River and their implications for public health.

1.4.2. Specific objectives

- To measure the concentrations of selected heavy metals in May Sieley River
- To determine the levels of some other physico-chemical parameters of water (Temperature, DO and PH), which may have a bearing on the mobility of heavy metals.
- To evaluate the health risks associated with the use of May Sieley River water

1.5. Significance of the study

The findings of this research will help to raise awareness about the effect of artisanal gold mining on aquatic ecosystems. The data that emanated from the study may help planners and decision makers to develop workable gold mining policies and strategies to enhance sustainable development. The research results may also suggest some mitigation measures to be taken in order to reduce the vulnerability of aquatic ecosystems to the impacts of artisanal gold mining. Moreover, the results of the present study will serve as baseline information on the impact of artisanal gold mining on aquatic ecosystems for further research activities.

1.6. Scope and limitation of the study

The study was conducted to examine the effect of artisanal gold mining activities on of heavy metal concentrations into May Sieley River of the Shire area and assess the potential public health risk associated with the use of its water. The frequency of sampling of the present study was only once per month due to deterring financial constraints. Moreover, sampling was carried out only in February (Dry period) and October (Post-rainy period) owing to logistic and other problems. Data that emanated from the analysis of these samples may not, therefore, be adequate to demonstrate the extent of pollution of the river with heavy metals as months of the major rainy season are not included. Furthermore, our research did not address the extent of accumulation of heavy metals in aquatic animals, which are consumed by humans. The study was conducted during the time of Covid-19 outbreak, which has hindered many activities.

2. Literature Review

2.0. Heavy metals

Heavy metals are natural elements characterized by high atomic mass and density. Although they typically occur in rather low concentrations, they can be found all through the crust of our planet. Commonly, a density of at least 5 g cm^{-3} is used to define a heavy metal and to differentiate it from other light metals. They include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), zinc (Zn), nickel (Ni), copper (Cu) and lead (Pb) (Koller and Saleh, 2012). Some metals have critically important physiological and biochemical functions in biological systems, and either their deficiency or excess can lead to disturbance of metabolism thereby causing various diseases. They play important physiological and biochemical roles in the body as they may be part of biomolecules such as enzymes, which catalyze biochemical reactions in the body (Hazrat *et al*., 2019). One third of enzymes need metal ions for their catalytic activity (David *et al*., 2012). Therefore, some metals and metalloids are essential for biological life. But, at their higher concentrations, they may cause toxicity and health hazards and can have a negative impact on aquatic ecosystems and the food chains (Arantes *et al.*, 2016). Heavy metals are classified based on their relative importance to public health (Table 1).

Table 1: Classification of heavy metals based on their relative importance to public health (Source: Goyer e*t al*., 2004)

Nutritionally essential metals	**Metals with possible beneficial effects**	**Metals with no known beneficial effects**
Cobalt Chromium III Copper Iron Manganese Molybdenum Selenium Zinc	Boron Nickel Silicon Vanadium	Aluminum Antimony Arsenic Barium Beryllium Cadmium Lead Mercury Silver Strontium Thallium

Arsenic, cadmium, lead, and mercury, and their inorganic compounds, have no known nutritional or beneficial effects on human health but are ubiquitous in nature and present in air, water, and soil, so that some level of exposure is not readily preventable and they are probably the most

potentially toxic metals in the environment (Goyer *et al*., 2004). Other metals which are nutritionally essential or have possible beneficial effects can cause health problems at higher concentrations.

In rocks, Heavy metals exist as their ores in different chemical forms, from which they are recovered as minerals. Heavy metal ores include Sulphides, such as Iron, Arsenic, Lead, lead-zinc, Cobalt, Gold, Silver and Nickel Sulphides; Oxides such as Aluminium, manganese, Gold, Selenium and Antimony. Some heavy metals including Iron, Copper and Cobalt exist and can be recovered as both Sulphide and Oxide ores (Duruibe *et al*., 2007). The source of heavy metals pollutants can be geogenic, via natural weathering process or anthropogenic, whereby different human activities lead to high loading of heavy metals to different media of ecosystems. The heavy metals concentrations in a specific environment are mainly dependent upon the geology of the area. However, the anthropogenic activities found in that area can have a significant contribution. Heavy metals such as chromium, mercury, lead, cadmium, copper, iron, zinc, nickel, etc. are major environmental pollutants, particularly in areas with higher anthropogenic activity. Prolonged exposure and higher accumulation of such heavy metals can have deleterious effects on human life, soil, air and aquatic biota (Ravindra *et al*., 2018). Heavy metals have received global attention thanks to their toxicity and bio-accumulative nature. Unlike other pollutants, they cannot be degraded into other forms that are less toxic but are rather bioaccumulated in animals and plants of food chains.

2.1. Gold mining and heavy metal pollution

River is one of the surface water bodies, which human societies have been using for economic activities up to the present time (Duressa Tamene and Seyoum, 2015). It has been used as a medium for panning in gold mining activities. One of the most important contributors to metal pollution of river basins is mining activities, while mine tailings consisting of residues of mining activities, which are released accidentally or deliberately into river systems, are the second most important contributors of pollution of rivers with heavy metals (Smolders *et al*., 2003). This can amplify the levels of heavy metals in the river. One of the wastes that have been implicated around mining sites is heavy metal (Abiya *et al*., 2019). Mining activities are highly associated with water. According to Hagos *et al* (2016), absolute dependence on the use of large amounts of water of mining operations determines the location of mining operations as close to water sources as

possible and at the water source, they further pointed out that there is a significant variation in the intensity of participation of local people in artisanal mining among seasons, with intensive participation occurring in the summer season. It was indicated in Ethiopian Extractive Industries Transparency Initiative (2016) that the unavailability of water for mining process has become the most critical factor in the process of mineral production as the rivers are dry during most of the seasons. The disruption and acceleration of the natural process of the geochemical cycle through anthropogenic activities like gold mining has led to most soils of rural and urban settings accumulating heavy metals above the recommended levels (D'Amore *et al*., 2005). These metals leach out in an uncontrolled manner into surrounding environments on exposure to water or through dispersal by wind (Fashola *et al.*, 2016).

Heavy metal pollution of watercourses can occur after air pollution. Smelting and burning of coal, oil and waste bring about heavy metal pollution of the atmosphere (Sardar *et al*., 2013). This can lead to secondary pollution whereby heavy metals from the atmosphere in aerosol form can contaminate aquatic ecosystems. Heavy metals released into the atmosphere in volcanic eruptions and in different industrial emissions also ultimately return to the land and cause contamination of waters and soils. Since heavy metals are persistent in the environment, they either accumulate in biota or leach down into ground waters (Hazrat *et al*., 2019). Emissions of mercury to the air from both anthropogenic and natural sources are in inorganic forms that can be converted biologically in soil and water to methylmercury (World Health Organization, 2007), which is a very dangerous neurotoxic contaminant that bioaccumulates through food chain.

2.2. Distribution of heavy metals in aquatic ecosystems and its relation to physicochemical factors.

The distribution of heavy metals in an aquatic ecosystem depends on the nature of heavy metals and the environmental conditions. Some species are readily soluble, while others are not, with the latter tending to precipitate to the sediments. Most heavy metals are quickly deposited into the sediment after entering rivers, and are much more concentrated in the sediment than in the water body of riverine systems (Liu *et al*., 2018). Sediment solids can hold up to a million times more metal than an equivalent volume of water. The exact proportion of a chemical held by sediment relative to water is a function of a metal's chemistry as well as the chemistry of the sediment solid and the surrounding environment (U. S. Environmental Protection Agency, 2007).Unlike organic

chemicals, the majority of metals cannot be easily metabolized into less toxic compounds, characteristic of them being lack of biodegradability (Stefania *et al*., 2017).

Heavy metals are of high ecological significance since they are not removed from water as a result of self-purification, The elevation of metal levels in a reservoir is shown mainly by an increase of their concentrations in the bottom sediment (Naggar *et al*., 2018). Through precipitation of their compounds or by ion exchange into soils and muds, heavy metal pollutants can be localized and lay dormant (Baby *et al*., 2011). In the aquatic environment, heavy metal cations can occur in many forms: ions, ions bound to different ligands, and precipitated molecules that can be adsorbed on suspended particles and colloids or themselves suspended in the water(Namieśnik and Rabajczyk, 2015). The more they form complex structures. the more toxic they become. It should be noted that in the case of some of these metals, complexes can be formed with organic materials (so-called "organometallics"), the resultant compounds being very toxic indeed, perhaps far more so than the un-complexed elements. Examples of such noxious materials are methylmercury and tributyltin (U. S. Environmental Protection Agency, 2001)

Metals from both geogenic and anthropogenic origin, once they enter an aquatic system, become a part of water-sediment equilibrium. Conventionally, sediments act as a sink but they can release trapped metals as a result of aquatic perturbations like change in pH and redox potential and availability of organic and inorganic complexing ligands. The mobility of the metals from the sediments to the overlying water and vice versa, to a large extent, will depend upon the metal species present there (Gupta *et al*., 2013)

Besides other factors like metal speciation and the presence of organic or inorganic complexes, pH, Temperature, Dissolved Oxygen, and Redox conditions are the major factors that regulate the solubility and bioavailability of heavy metals. These factors could also modulate the metal toxicity in an aquatic ecosystem (Bonnail *et al*., 2016). The heavy metals deposited into the sediments can then, under the influence of these factors, be released into water thereby resulting in high concentrations of heavy metals in water above the recommended limits. High pH values promote adsorption and precipitation, while low pH can actually weaken the strength of metal association and consquently favor the release of metals by sediments (Zhang *et al*., 2014). Temperature is an important factor in the aquatic ecosystem as it regulates almost all physical, chemical, and biological reactions, with high water temperature increasing the rate of microbial activity and

favoring other chemical reactions that promote the release of metals from sediments. Redox reactions influence the speciation and mobility of heavy metals (Rinklebe *et al*., 2016). However, the efficiency and rate of action depends on the nature of a metal or metalloid. Haiyan *et al* (2013) reported in his study that the heavy metals release rates were affected to a much greater extent under the low pH (4–7) condition than at high pH (8–10) condition and that at higher temperature (30–35◦C) the release rates of metals were increased more rapidly than at low temperature, the release of Zn, Cu, Cr, and Pb increased under the aerobic condition, while the release of Cd increased under anaerobic condition.

2.3. Acid mine drainage

Acid mine drainage (AMD) forms when sulfide minerals are exposed to oxidizing conditions in coal and metal mining, highway construction, and other large-scale excavations (Barnhisel *et al*., 2000). AMD, which is mostly found in environments around abandoned mines, it is one of the dangerous effects of artisanal mining that can interfere with or immensely damage the aquatic environment. It has been tremendously impacting aquatic ecosystems in different parts of the world and its effects are unbearable. According to Gray (2016), these effects can be loosely categorized as chemical, physical, biological and ecological, although the overall impact on the community structure is the elimination of species, simplifying the food chain and so significantly reducing ecological stability, which increase vulnerability of aquatic ecosystems.

The study conducted in Kenya by Ogola *et al* (2002) revealed that River Kuja was adversely affected by the Macalder tailings through a stream that passes at the foot of the tailings. The water in the stream was strongly acidic due to acid drainage from the tailings especially in rainy season when much sulphuric acid is produced from the Macalder tailings and this finds its way into river Kuja. The drainage of contaminated and low pH water into waterways resulted in the death of fish and other elements of aquatic ecosystems, as well as contamination of soil and groundwater. Degeneration of low pH drainage enhances the dissolution of heavy metals in water. In addition to contribution of acid to surface waters, AMD may cause metals such as arsenic, cadmium, copper, silver, and zinc to leach from mine wastes (U. S. Environmental Protection Agency, 1994).

2.4. Bioaccumulation of heavy metals in food chains

Bioaccumulation is the accumulation of contaminants by species in concentrations that are orders of magnitude higher than those in the surrounding environment (Baby *et al*., 2010). The heavy metals have bio-accumulative nature once they are introduced into a certain medium of environment and hence affect food chains. The concentrations of the metals increase from lower trophic levels to the higher. The metals accumulated in aquatic organisms can be transferred up to humans through the consumption of fish and other aquatic food products. Fishes being one of the main aquatic organisms in the food chain often accumulate large amounts of certain metals (Baby *et al*., 2010). The increasing concentration through the food chain was found to cause higher retention time of toxic substances than that of other normal food components (Mulu Berhe *et al*., 2012). The metal contaminants in aquatic systems usually remain either in soluble or suspension form and finally tend to settle down at the bottom or are taken up by the organisms.

The study conducted by Abraha Asgedom *et al* (2012) in Lake Hashenge of Tigray indicated that there was high accumulation (above the permissible limits issued by FAO/WHO, 1989) of Pb, Cr, Cd, Co and Zn in the flesh and bone of the fishes. However, they couldn't identify the point source to which that high pollution could be attributed. Metal bioavailability controls their accumulation in aquatic organisms. The metals' uptake paths are through the permeable epidermis if the metals are in dissolved forms or through food ingestion if the metals are in particulate forms. However, ingestion is considered to be the major path for metal uptake.

2.6. Toxicity of heavy metals

The World Health Organization predicts that by 2030, 12 million deaths worldwide will be due to cancer; however, 30% to 40% of these deaths are considered to be preventable (U.S. Department of Health and Human Services, 2011). Some heavy metals are known to have carcinogenic effect, with prolonged exposure to them increasing the prevalence of cancer worldwide. However, heavy metals cause other non-carcinogenic health problems. Heavy metal pollution is known to be the cause of various diseases globally, such as the Minamata disease (organic mercury poisoning), Itai-itai disease (cadmium poisoning), Arsenous acid poisoning, and air pollution-related asthma (Matsuo, 2003).

Metals constitute an important class of the toxic substances encountered in day-to-day life during occupational and environmental circumstances. Toxicity of heavy metals can lessen the energy levels and damage the functioning of brain, kidney, lungs, liver, blood composition and other significant organs. Continuing exposure to some metals may lead to progressively progressing physical, muscular and neurological degenerative processes that replicate the diseases such as multiple sclerosis, Alzheimer's disease, Parkinson's disease and muscular dystrophy (Showkat Bhat *et al*., 2019). In 2010, 463 deaths of children from lead poisoning were recorded in an ASGM community in northwestern Nigeria, Zamfara (Dooyema *et al*., 2012).

Heavy metals commonly found in waste water include, cadmium, arsenic, chromium, lead, copper, zinc and nickel. All of these are causing risks to human health and the environmental balance by entering the surroundings via natural means and through the human activities (Beyersmann and Hartwig, 2008). However, the individual metal exhibits specific signs of toxicity. The biotoxic effect of heavy metal refers to the harmful effects of heavy metals on the body when consumed above the biological recommended limits (Heanacho *et al*., 2017). In biological systems, heavy metals have been reported to affect cellular organelles and components such as cell membrane, mitochondria, lysosome, endoplasmic reticulum, nuclei, and some enzymes involved in metabolism, detoxification, and damage repair (Wang and Shi, 2002). For fetuses, infants, and children (especially young children), heavy metals are known to present serious hazards, which can include impairment of physical and mental development, damage to internal organs and the nervous system, some forms of cancer, and even mortality. Lead and mercury have the capacity to cross the placental barrier, causing potential fetal brain damage (Robert, 2007). A brief account of each heavy metal selected in this study is given below.

Arsenic

Arsenic is a ubiquitous element that is detected at low concentrations in virtually all environmental matrices. The major inorganic forms of arsenic include the trivalent Arsenite and the pentavalent arsenate. The organic forms are the methylated metabolites – Monomethylarsonic acid (MMA), Dimethylarsinic acid (DMA) and Trimethylarsine Oxide (Ravinder *et al.*, 2019). This element has long been associated with criminal activity and still is an emotionally highly charged topic, as large homicidal doses can cause cholera like symptoms (acute poisoning) and death. Ingestion of low dose via food or water is the main pathway of this metalloid into the organism, where absorption takes place in the stomach and intestines, followed by release into the bloodstream. In chronic

poisoning, arsenic is then converted by the liver to a less toxic form, from where it is eventually largely excreted in the urine (Saha *et al.*, 1999).

Exposure to arsenic can lead to either acute or chronic toxicity. Acute arsenic poisoning can lead to the destruction of blood vessels, gastrointestinal tissue and can affect the heart and brain (Godwill *et al*., 2019). It has been a life-threatening pollutant and public health concern in Bangladesh, with more than 50 million people having been chronically exposed to arsenic by drinking groundwater with arsenic concentration exceeding the World Health Organization (WHO) standard (10 µg/L) (Rathor, 2017).The WHO Drinking Water Guideline (DWG) value is 0.01mg/L or 10 µg/L.

Lead

Lead is a highly toxic metal and its routine use has caused excess environmental contamination and health related problems in many parts of the globe (Sharma and Dubey, 2005). It is a widely used metal, but it is simultaneously a versatile, subtle, and persistent poison (Nikolas *et al*., 2005). Lead is commonly found in soils especially near roadways, older houses, old orchards, mining areas, industrial sites, near power plants, incinerators, landfills, and hazardous waste sites. People living near hazardous waste sites may be exposed to lead and chemicals that contain lead by breathing air, drinking water, eating foods, or swallowing dust or dirt that contain lead (Agency for Toxic Substances and Disease Registry, 2007) According to the Environmental Protection Agency (EPA), lead is considered a potent carcinogenic factor and it affects major parts of the body because its distribution in body depends primarily on blood flow in the various tissues and nearly ninety five percent of lead is deposited in the skeletal bones in the form of insoluble phosphate (Arif *et al*., 2015). According to the standards set by WHO/FAO the permissible limit for Lead is 0.01mg/L.

Lead poses severe health effects among children. At high levels of exposure, lead attacks the brain and central nervous system to cause coma, convulsions and even death. In particular, lead affects children's brain development resulting in reduced intelligence quotient (IQ), behavioural changes such as reduced attention span and increased antisocial behaviour, and reduced educational attainment. Lead exposure also causes anaemia, hypertension, renal impairment, immunotoxicity and toxicity to the reproductive organs (Heanacho *et al*., 2017).

Mercury

Mercury is a heavy metal belonging to the transition element series of the periodic table. It is unique in that it exists or is found in nature in three forms (elemental, inorganic, and organic), with each having its own profile of toxicity. At room temperature, elemental mercury exists as a liquid, which has a high vapor pressure and is released into the environment as mercury vapor. Mercury also exists as a cation with oxidation states of +1 (mercurous) or +2 (mercuric). Methylmercury is the most frequently encountered compound of the organic form found in the environment, and is formed as a result of the methylation of inorganic (mercuric) form of mercury by microorganisms found in soil and water. It is a widespread environmental toxicant and pollutant, which induces severe alterations in the body tissues and causes a wide range of adverse health effects. Both humans and animals are exposed to various chemical forms of mercury in the environment (Ravinder *et al*., 2019)

Large amounts of mercury that remain in mine tailings, landfills and sediments, as well as stockpiles, continue to present a threat of future release. Elevated methylmercury levels have been measured in numerous freshwater and marine fish species throughout the world. The highest levels are found in large predatory fish and fish-consuming mammals (UNEP, 2002) Nervous system is sensitive to all the types of mercury as its increased exposure alters the functions of brain and leads to shyness, memory problems, tremors, irritability and changes in vision or hearing (Schumm *et al*., 2005) According to the standards set by WHO/FAO, the Hg permissible limit for drinking water is 0.001mg/L.

Cadmium

Cadmium is a heavy metal of considerable environmental and occupational concern. It is widely distributed in the earth's crust at an average concentration of about 0.1 mg/kg. The highest level of cadmium compounds in the environment is accumulated in sedimentary rocks, and marine phosphates contain about 15 mg cadmium/kg. Cadmium is frequently used in various industrial activities. The major industrial applications of cadmium include the production of alloys, pigments, and batteries. Although the use of cadmium in batteries has shown considerable growth in recent years, its commercial use has declined in developed countries in response to environmental concerns (Ravinder *et al*., 2019).

In world ranking, cadmium is the seventh most toxic heavy metal as per Agency for Toxic Substances and Disease Registry (ATSDR). Cadmium is the by-product of zinc creation. Humans or animals may get exposed to this metal during work hours or in the environmental surroundings and it can accumulate inside the human body throughout life after it is absorbed by the body (Valko *et al*., 2005)**.** Cadmium is released into the environment by weathering, river transport, volcanic eruptions and various human activities (mining, smelting, tobacco smoking, incineration of municipal waste, and manufacture of fertilizers) (Ahmad *et al*., 2019) Exposure to chromium compounds may result in the formation of ulcers, which will persist for months and heal very slowly. These chromium-caused ulcers on the nasal septum are very common in chromate workers. Exposure with the higher amounts of chromium compounds in humans can lead to inhibition of enzyme erythrocyte glutathione reductase, this inhibition lowers the capacity to reduce methemoglobin to hemoglobin (Mulware, 2013). The WHO permissible limit for DWG is 0.01 mg/L.

Chromium

It is the seventh most abundant element on the earth's crust (Ahmad *et al*., 2019) Cr has an atomic number 24 in periodic table and has a relative atomic mass of 51.996. Chromium occurs in several oxidation states, Cr^{2+} to Cr^{6+} in the environment. Cr, which is present in 0 oxidation state is biologically inert and is not naturally present in Earth's crust while Cr (III) and Cr (VI) originate from industries. The available form of chromium is as Halides, Oxides and Sulphides. It is the +2-oxidation state of chromium, which is unstable and can be easily oxidized to +3 form in the presence of air. Chromium is responsible for the toxic effects observed in humans and it can cause allergy and cancer in humans and animals. Hexavalent chromium is responsible for all carcinogenic activity of chromium in comparison to the trivalent chromium (Shekhawat *et al*., 2016). The WHO's permissible limit of Cr for drinking water is 0.05mg/L.

Nickel

Nickel, a known heavy metal, is found at very low levels in the environment. Nickel is available in all soil types and meteorites and also erupts from volcanic emissions. In the environment, nickel is principally bound with oxygen or sulfur and forms oxides or sulfides in the earth's crust. The vast industrial use of nickel, its production, recycling and disposal have led to widespread environmental pollution (Kusal *et al*., 2019). It is present in plants, microorganisms and essentially required for haemopoiitic process, but influences iron adsorption and metabolism in human body.

Increased nickel concentration leads to nausea, giddiness, vomiting and headache, etc (Zelealem and Sathishkumar, 2020). Nickel is a potentially toxic heavy metal that affects multiple organs of living systems. Moreover, the toxicities of nickel are manifested based on the manner of exposure, dose and duration(Kusal *et al*., 2019). The WHO's permissible limit of Ni for Drinking Water is 0.07 mg/L.

Zinc

It is well known for its role as a cofactor for Superoxide dismutase (SOD), and it protects biological structures from damage caused by free radicals by maintaining adequate levels of SOD and Metallothioneins, as well as preventing interaction between chemical groups with iron (Arif *et al*., 2015). Taking too much zinc into the body through food, water, or dietary supplements can also affect health. The levels of zinc that produce adverse health effects are much higher than the Recommended Dietary Allowances (RDAs) for zinc of 11 mg/day for men and 8 mg/day for women. If large doses of zinc (10–15 times higher than the RDA) are taken by mouth even for a short time, stomach cramps, nausea, and vomiting may occur. Ingesting high levels of zinc for several months may cause anemia, damage the pancreas, and decrease levels of high-density lipoprotein (HDL) cholesterol (Agency for Toxic Substances and Diseases Registry, 2002). There is no WHO standard for Zinc but the Ethiopian standard for drinking water is 5mg/L.

Copper

It is a toxic metal pollutant found in the soil and water of industrialized areas, which causes continuous issues for agriculture product contamination and human health hazards (Chiou and Hsu, 2019). However, it is an essential trace mineral that is vitally important for physical and mental health. It is not poisonous in its metallic state but some of its salts are poisonous, especially the most common salts of copper such as sulphate or the blue vitriol (Nila Tutia) and the sub-acetate or Verdigris (Zangal). Copper sulphate is a crystalline salt with blue colour and metallic taste. In a small dose of 0.5 g, it acts as an emetic, but in large doses, as an irritant poison producing gastric and intestinal irritation (Badiye *et al*., 2013). The WHO permissible limit for drinking water is 2mg/L.

3. Materials and Methods

3.1. Description of study area

The study was conducted in Tigray region, northern part of Ethiopia, specifically in Shire. Shire is found in northwestern Tigray, Ethiopia. Geographically, it is located b/n 14006’.22.65’’North latitude and 38002.18’65" East longitude and at an altitude of 1924 m a.s.l. The Tigray region is the northernmost part of Ethiopia, and occupies an area of~54,000 km^2. It is bordered by Eritrea in the north and Sudan in the west. Tigray has a population of about 6 million, and is repeatedly cited in civilization, historic, and cultural lists of humanity (such as Axum obelisks and Ark of the Covenant). Tigray is rich in mineral resources, which include gold, copper, silver, iron, zinc, lead and nickel, as well as oil shale (Yohannes *et al*., 2018). Asbestos, silica and, kaolinite, graphite, gypsum, gemstone, marble, granite, slate, limestone, and dolomite are among the non-metallic minerals that also exist in Tigray.

Small scale and artisanal gold mining is a relatively common activity in Tigray. It has been associated with water pollution in Shire since mining sites are mostly located along the banks of rivers and small streams and the miners rely on panning technique in mining gold. According to Mehari Germay (2018), panning triggers land degradation, water pollution, siltation and degradation of vegetation. In addition, release of chemicals including mercury to the terrestrial and aquatic ecosystems leads to the damage both of life and the environments. The following figure shows the area of study.

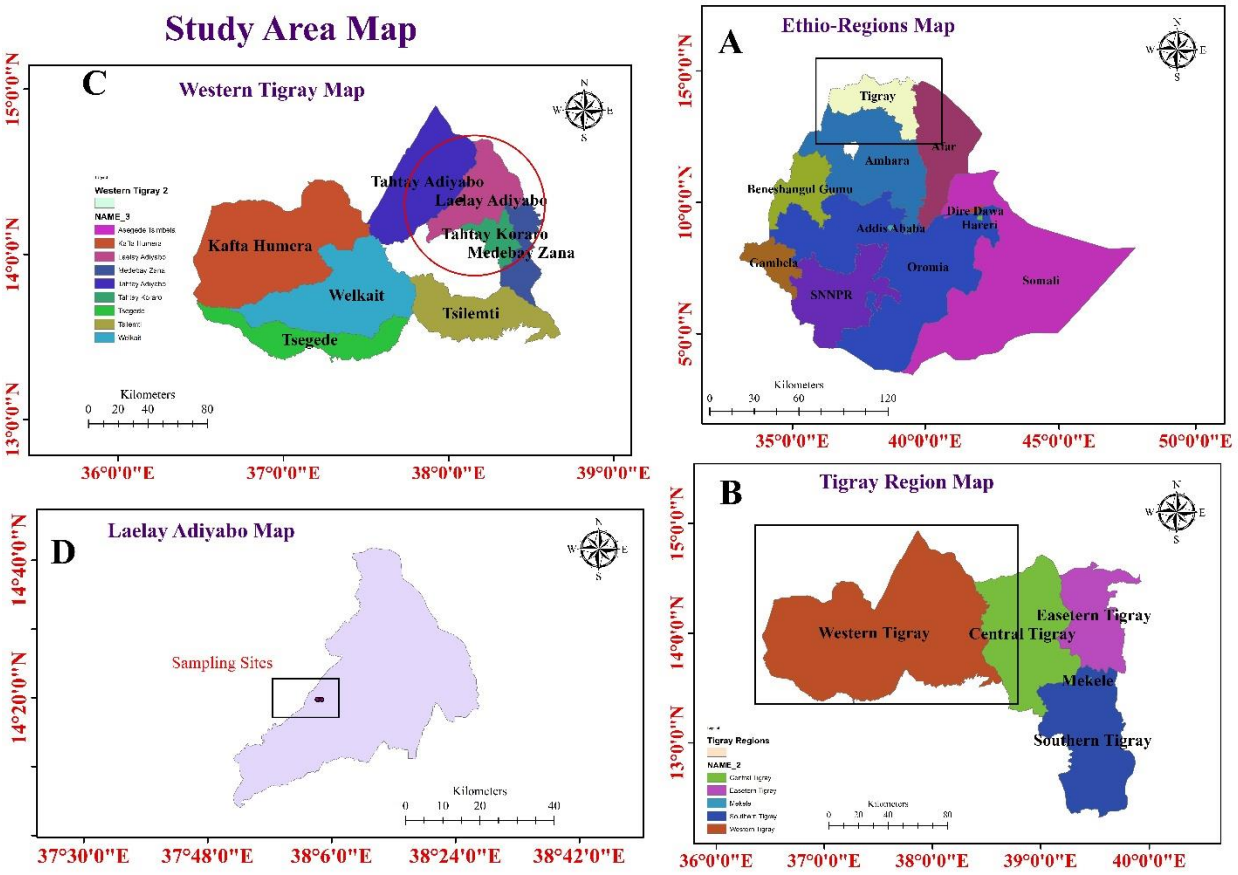

Figure 1: A map showing the study area

The present study was specifically conducted in Laelay Adyabo, Adgnisti village where May Sieley River flows in proximity with Adgnisti gold mining site. Laelay Adyabo is one of the districts where high artisanal mining are found, ranked as the second mining woreda in Tigray after Asgede Tsimbla based on the 2008 E.C annual report of Tigray Region Bureau of Water, Mineral and Energy Resources (Cheepurupalli *et al.*, 2019), The place is a very remote area, which is located very far away from the main road of Adyabo, which connects to Shire town. It is characterized by steep mountains along which the river flows. The type of mining that is being conducted in the study area is deep mining, which involves excavation of a pit up to 10 meters depth for alluvial deposits and 35 meters depth inside hard rocks till the gold bearing gravel horizon is reached (Cheepurupalli *et al.*, 2019).The figures below show a partial view of Adgnisti mining site (Fig. 2) and a small segment of the May Sieley River (Fig. 3).

Figure 2: A picture showing Adgnisti mining site: Photo taken by the author

Figure 3: A picture showing May Sieley River with gold containing ore to be washed into the river (Middle segment), Source: Photo taken by the author

3.2. Description of sampling sites

The May Sieley River is a perennial river characterized by a very changing morphology. The part of the river that served as Upstream site for our research, is very rocky and the water flows around big rocks, which create variations in flow rate. It is characterized by waterfalls and large stagnated

waters, which harbor different aquatic animal and plant species. The water is clear and there is no change of color. The figure below shows the upstream part of the river.

Figure 4: A picture showing the upstream sampling site, source: Photo taken by the author

The middle segment sampling site is characterized by colored water due to washing of gold containing ore (see Figure 3) in that segment of the river. Water flows slowly because it is relatively flat and there are no rocks. It exhibits high siltation, which adversely affects aquatic ecology. The aquatic organisms are relatively very few.

The downstream sampling site, which is mor rocky than the middle segment sampling site, is characterized by colored water due to the panning, which was carried out in the middle segment. The abundance of aquatic organisms was higher than that of the middle segment, but still lower than that of upstream sampling site. The figure below shows downstream sampling site.

Figure 5: A picture showing the downstream sampling site source: Photo taken by the author

The figure below shows the distribution of sampling sites

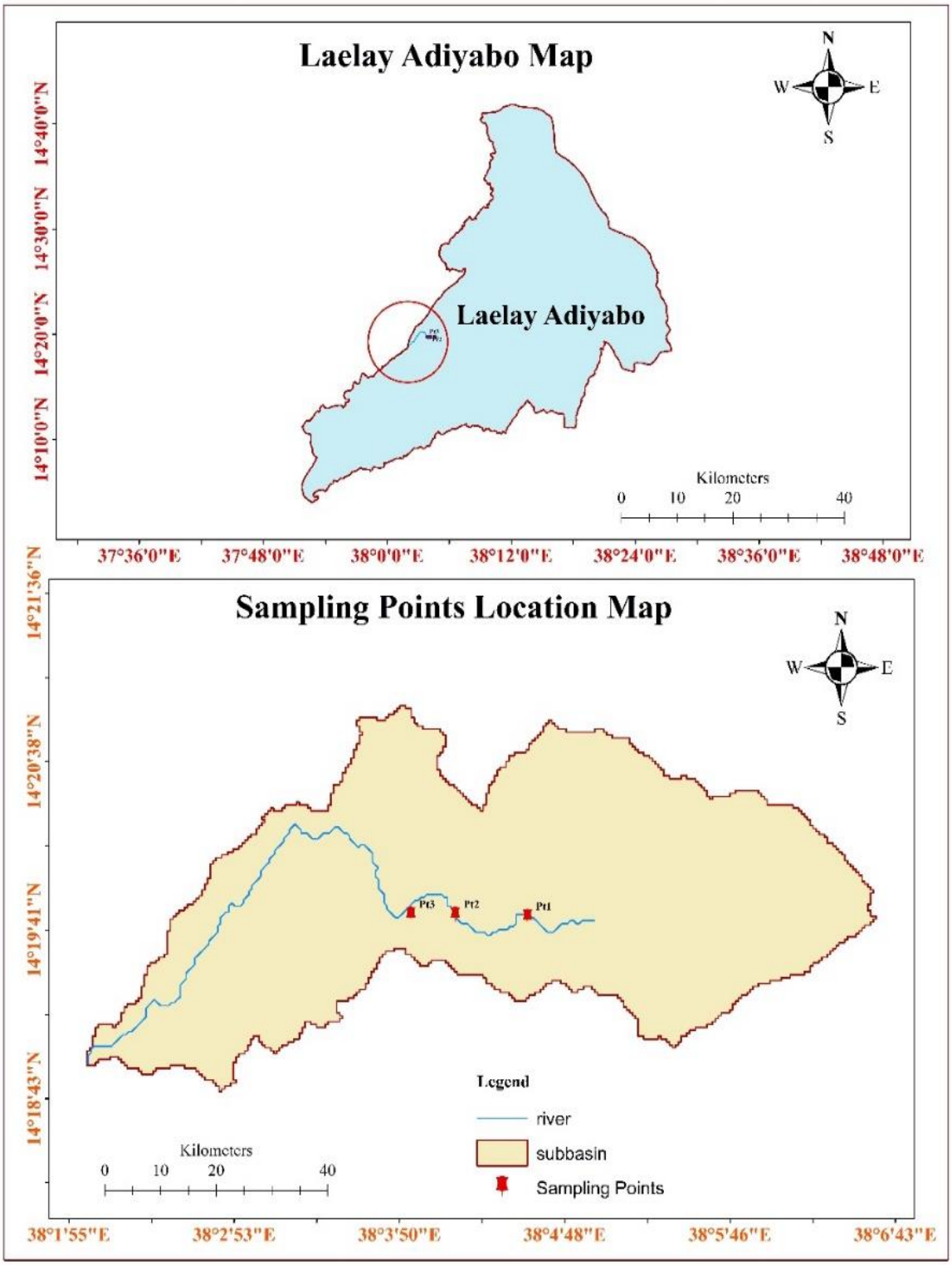

Figure 6: A map showing the sampling sites

(Pt1 = USS, Pt2 = MSS and Pt3 = DSS)

3.3. Sampling Protocol

A reconnaissance survey was conducted in January,2020 to facilitate the selection of sampling sites. A total of 3 sampling sites were selected based on accessibility, safety and proximity to the mining site. The sampling sites are representative of the upstream, downstream and middle segment of the river close to the active mining and processing area where the washing of gold containing ore is done. The distance between two sampling sites is approximately 500 meters.

The upstream sampling site was selected such that it serves as a reference site. Sampling was conducted monthly during the dry (February,2020) and post-rainy (October,2020) periods. Due to the dissuading financial constraint (which prevented us from having separate samples collected from several points within each sampling site), two composite samples of both water and sediment were taken from all sampling sites by facing upstream to avoid contamination. Each composite sample was made of a mixture of three samples collected from different points within a sampling site. A total of six composite water samples (W) and six composite sediment samples (S) were taken for each period. The table below describes the sampling sites and the physical status of samples.

Table 2: Geographical position of Sampling sites, Identification codes and the physical status of samples.

Sampling sites	**Coordinates**	**Sample coding**	**Description of samples (Physical status)**
Upstream (USS)	14º 19’ 45. 253’ N 38 º 4’ 35.14” E	USS W1, USS W2 USS S1, USS S2	Water: colorless Sediments: silty sand
Middle segment (MSS)	14º19’45.726” N 38 º4’ 9.871” E	MSS W1, MSS W2 MSS S1, MSS S2	Water: colored Sediments: muddy sand
Downstream (DSS)	14 º 19’ 45.879” N 38 º 3’ 54.496” E	DSS W1, DSS W2 DSS S1, DSS S2	Water: colored Sediments: silty sand

Source: Author’s field observation

With help of GPS, the coordinates for each sampling site were taken in order to facilitate their location. Prior to the collection of water samples**,** 1-liter high density polyethylene (HDPE) sample bottles were washed with a metal-free detergent solution, rinsed with tap water and then filled with 10% nitric acid (to remove metal contaminants from the bottle) and allowed to stand for 24 hours in a hot water bath (70 ^{o}C) and then washed and rinsed with distilled and deionized water. Sampling bottles were, then, washed 3-4 times with water from the exact site of sampling prior to collection of the samples. Water samples were collected from the near-surface region of the center of the main flow (about 2-4 cm below the surface) by directly filling the sample bottles. The storage and transportation of the water samples to the laboratory was done following standard protocols (APHA, 1999) to ensure consistency and data quality.

Sediment samples (300–400 g wet weight) were collected from the same sampling points (wadable locations) (USEPA, 2013) from which water samples were collected using a stainless steel scoop, grasp sampling technique (Ohio Environmental Protection Agency, 2001). All sediment samples were sealed in clean polyethylene bags and together with water samples were put in a cooled box on site. The cooled samples were brought to the HORTICOOP ETHIOPIA PLC where they were kept in refrigerator at 4 ^{0}C before they were further processed (APHA, 1999).

3.4. In situ measurements, preparation and analysis of samples, validation of analytical method and collection of additional data

River dimensions were recorded at all sampling sites. River dimensions were recorded using a measuring tape to measure the channel width and meter stick with measuring tape to measure the depth of the river. pH, Temperature and DO were measured *in situ* at all sampling points using portable multi-meter (HACH, HQ40d with different probes), which was calibrated prior to use.

In this study, which was both quantitative and qualitative assessment, primary data were collected through laboratory analysis of water and sediments samples for selected heavy metals.

Determination of heavy metals in water and sediment samples requires pretreatment of the samples. In the laboratory, the hand trowel was washed with a detergent, rinsed and dried before each use so as to minimize contamination. Sediment samples were air dried for one week, sieved mechanically using a 0.5 mm sieve, homogenized and ground to 0.063 mm fine powder by using mortar and pestle because metals are known to adhere to fine particles.

After which, 1.25 g of each sample was digested with 20 mL aqua regia (HCl/HNO_3 3:1 ratio) in a beaker (open-beaker digestion) on a thermostatically controlled hot plate (Model CB 302). The digests were heated to near dryness and cooled to ambient temperature. Then 5.0 mL of hydrogen peroxide was added in parts to complete the digestion and the resulting mixture heated again to near dryness in a fume cupboard. The beaker walls were washed with 10 mL of deionised water and 5 mL HCl were added, mixed and heated again. The resulting digest was allowed to cool and transferred into a 50 mL standard flask and made up to the mark with ionized water (Sekabira *et al*., 2010). Selected heavy metal elements were then analyzed by direct aspiration of the sample solution into Inductively Double Coupled Plasma Optical Emission Spectroscopy (SPECTRO ARCOS ICP-OES, Germany) following the procedure outlined in the manufacturer's manual. The Optimum Procedure for Digestion of water samples involved use of 50mL water, 4mL of HNO_3 and 1 mL of HCl at 250 ^oC for three hours on a hot plate.

Color Observation; Yellow --------- pale yellow -------Colorless

The volume of the digested sample was maintained at 25ml after filtering it into 50 ml Erlenmeyer flask.

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), which is the most powerful method with high sensitivity, precision, and accuracy (Ghosh *et al*., 2016) was used for the analysis of selected heavy metals. Therefore, the concentrations of heavy metals, namely Lead (Pb), Cadmium (Cd), Copper (Cu), Arsenic (As), Chromium (Cr), Mercury (Hg), Nickel (Ni), and Zinc (Zn) in both water and sediment samples were measured in the laboratory using the ICP-OES method. Those HMs were selected based on their effect to public health and their association to mining pollution.

All the measuring conditions were configured as follows: plasma power (1400W), average plasma flow rate (6.41 L/min.), pumping speed (30 rpm), nebulizer flow (0.8 L/ min.), nebulizer pressure (1.96 bar), Argon pressure (6.75 bar), and torch positions and measuring time are configured according to the standard. The calibration and standardization of the spectra method was performed according to the standard protocols set for the instrument. The standardization is undertaken daily: it is a quick procedure for correcting measuring intensities so that the correct concentrations of element is obtained using the original calibration curve. Calibration correlation

factor on a regular basis falls between 0.996 to 0.9996 for all metal elements. There is good correlation between concentration and emission intensities of the analyzed elements.

3.5. Potential Human Health Risk Assessment

The residents inhabiting the study area were interviewed for basic information about their usage of May Sieley River. All respondents replied that they normally use the river water for drinking and other household activities as well as for watering livestock. Therefore, a potential human health risk assessment was done to assess the health risks associated with the use of river water by the people in the study area. The human health risk assessment was done on adults and children age groups.

The measured concentration of the heavy metals in the water samples were compared with the WHO guideline values (permissible limits) for drinking water (WHO, 2011) and Ethiopian drinking water quality standards (2013) to evaluate the potential public health risk associated with the use of the river water as a source of drinking water supply. Moreover, Human Health Risk Assessment was also made based on mathematical models developed by the United States Environmental Protection Agency (USEPA 2007). Many other researchers used this method to predict the public health problem that may be associated with exposure to a certain chemical or other environmental contaminant. Non-Carcinogenic Risk Assessment was done by calculating Chronic Daily Intake (CDI) via ingestion route, non-cancer hazard quotient (HQ) and hazard index (HI). Carcinogenic Risk Assessment was done by calculating Incremental Lifetime Cancer Risk (ILCR).

The human health risk assessment methodology introduced by the Environmental Protection Agency of the United States (US EPA) was used to assess the human health risks associated with the long-term use of May Sieley River by inhabitants of the study area. Risk assessment is defined as the processes of estimating the probability of occurrence of any given probable magnitude of adverse health effects over a specified time period. The health risk assessment of each contaminant is normally based on the estimation of the risk level and is classified as non-carcinogenic health hazards or carcinogenic hazards (Wongsasuluk *et al*., 2013). The main pathways of exposure include ingestion, inhalation, and dermal contact. Ingestion was reported to be the major route of exposure to heavy metals (Rourke *et al*., 1999). In our study, ingestion was, therefore, considered as the route of exposure to heavy metals.

1. Non-Carcinogenic Risk Assessment

A) Chronic Daily Intake (CDI) via ingestion

$$CDI_{\textbf{ingestion}} = \frac{Cw * DI * EF * ED}{BW * AT * 365 days/yr} \quad \text{..... (eq.1)}$$

Where, **Cw** (in mg/L) is the concentration of heavy metals in water, **DI** (in L/day) is the daily average intake of water in the area, 2L for adults and 1Lfor children, **BW** = Body weight (kg); 60 kg for an adult, 10 kg for a child, and **EF** = Exposure frequency (days $year^{-1}$) = 350 days $year^{-1}$, **ED** = Exposure duration (years) = 30 years for an adult, 6 years for a child. **AT** = Averaging exposure time (days) = ED*365 which equals to 2190 days and 10950 days for children and adults respectively (Wongsasuluk *et al*., 2013) while **AT** = 70 years (25,550 days) for carcinogenic effects for both children and adults (United Nuclear Corporation, 2011).

The input assumptions and their values for computing the noncarcinogenic and carcinogenic risk were used according to US EPA guidelines.

Table 3: The toxicity responses (dose response) to heavy metals as the oral reference dose (RfD) and oral slope factor (SF). *(*Source: Wongsasuluk *et al*., 2013)

Heavy metals	Oral RfD (mg/kg/day)	Oral SF (mg/kg-day) $^{-1}$
As	$3*10^{-4}$	1.50
Cd	$5.0*10^{-4}$	n.d
Cr	$3*10^{-3}$	n.d
Cu	$4*10^{-2}$	n.d
Hg	$3*10^{-4}$	n.d
Pb	$3.5*10^{-3}$	n.d
Ni	$2*10^{-2}$	n.d
Zn	0.3	n.d

n.d: not determined

The CSF values for Cd, Cr, Pb and Ni are 6.1,41,8.5 and 0.84 $(mg/kg\text{-}day)^{-1}$ respectively (Mohammadi *et al.*, 2019).

B) Hazard quotient (HQ)

The HQ for each heavy metal was estimated using the ratio of computed average chronic daily intake (CDI) (mg/kg/day) of a metal ingested with contaminated water to the reference oral dose (RfD) through oral ingestion for the residents.

Hazard quotient $(HQ) = \frac{CDI}{RfD}$ ………………………………... (eq.2)

C) Non-cancer Hazard Index (HI)

The sum of all HQs gives an estimation of total potential health risks or HI. The calculation of the HI caused by water is presented below.

$HI = \sum_{n=1}^{8} HQs$……………………………..............................(eq.3)

Where HI is obtained by summation of hazard quotient of each metal, n = numbers of elements observed.

If the value of HQ exceeds or equal 1, there is an unacceptable risk of adverse non-carcinogenic effects on health, while if the HQ is less than 1, it is at an acceptable level (Mohammadi *et al.*, 2019). Then, If the HQ is >10, then it suggests high chronic risk (Asamene *et al*., 2020).

2.Carcinogenic Risk Assessment

Carcinogenic health effects were assessed by using the Incremental Lifetime Cancer Risk (ILCR), defined as the incremental probability of a person developing any type of cancer over a lifetime as a result of twenty-four hours per day exposure to a given daily amount of a carcinogenic element for seventy years. Oral slope factor, that estimates the chance of an individual developing cancer through oral means through exposure to pollutant levels over time and Chronic Daily Intake dose (CDI) calculated for every heavy metal were used to calculate ILCR. In this study, As, Ni, Cr, Cd and Pb were considered for carcinogenic risk assessment as they are regarded as probable human carcinogens, According to Asamene *et al* (2020), they are grouped as follows: (Cd (Group B1, probable human carcinogen), As and Cr(VI) (Group A, human carcinogen), Pb (Group B2,

probable human carcinogen) and Ni (Group A, human carcinogen) and (Cu, Fe, Zn, B and Mn) as noncarcinogenic.

The equation for calculating Lifetime Cancer Risk is presented below:

ILCR =CDI × SF……..…. (eq.4)

Where, SF is the cancer slope factor and is defined as the risk generated by a lifetime average amount of one mg/kg/day of carcinogen chemical and is contaminant specific (Ighariemu *et al*., 2019).

According to the U.S. EPA, the value of cancer risk in the range of 10^{-6} to 10^{-4} is an acceptable or tolerable risk, a risk of less than 10^{-6} can be ignored, and a risk exceeding 10^{-4} is considered to be unacceptable (USEPA, 2007).

3.6. Data presentation and analysis

Descriptive statistics with the help of Microsoft Excel was employed to describe our data set. Sigma plot version 11 was used for presentation of results.

4. Results and discussion

4.1. River dimensions

The morphology of May Sieley River exhibits high variability due to geographical disposition and land use. The river dimensions (Total width, water covered width and depth) were taken at each sampling site. During the dry season, the measurements recorded for total width, water covered width and depth were 16.6m, 2.1m and 10 cm for respectively, at the USS, 16.0m,5.9m and 12cm, respectively at the MSS, and 14.5m, 1.6m and 25cm, respectively at the DSS. During the post-rainy season, the measurements recorded for total width, water covered width and depth were 16.6m, 8.8m and 38cm cm, respectively at the USS. 16.0m, 6.8m and 30 cm, respectively at the MSS and 14.5m, 3.4m and 23cm, respectively at the DSS.

4.2. Physicochemical parameters measured in situ

During sample collection, some physicochemical parameters (Temperature, Dissolved Oxygen and pH) of the water were measured at the sampling sites (Table 4), using appropriate instruments.

Table 4: Physicochemical parameters measured *insitu*

	DRY SEASON			POST RAINY SEASON		
PARAMETER	**USS**	**MSS**	**DSS**	**USS**	**MSS**	**DSS**
Temperature(˚C)	26.2	26	25.9	24	22.5	23
Dissolved Oxygen (mg/L)	7.5	6.6	8.0	8.5	7.1	8.9
pH	8.4	8.4	7.75	8.4	8.2	7.6

During the study period, water temperature in the river showed slight seasonal variations ranging from 22.5 to 26.2 ^{0}C, and with higher water temperature during the dry season. The mean water temperature of the study river (24.6 ^{0}C) is lower than the mean water temperature value (25.65 ^{0}C) reported for Upper Awash River, Ethiopia by Fasil *et al* (2013) although it is still higher than the mean water temperature of Mojo River (19.98^{0}C) reported by (Duressa Tamene and Seyoum,

2015). pH is among the most important variables that influence the behavior of metals in aquatic environments. The availability and toxicity of chemical species of many heavy metals in aquatic environment has been altered by the pH of the water body (Mekonnen *et al*., 2018). In this study, pH values ranged from 7.6 to 8.4, which lies within the favorable range set by WHO/APHA (6.5 – 8.5). There was no marked variation in pH between seasons although the pH values were relatively lower at the MSS during both sampling seasons. The results indicate that at all sampling sites and during both seasons, the river water was alkaline. There seems to be no problem related to acid mine drainage in this river. Dissolved oxygen is one of the factors that affect the flux and speciation of metals. The measured DO varied between 6.6 and 8.9. The maximum was registered during the post-rainy season at the downstream site, while the minimum was recorded at the mid-segment site during the dry season. The increase in DO from the dry season to the post-rainy season may be attributed to the high flow rate of the water during the latter that increases mixing of the river water and subsequent dissolution of atmospheric oxygen**.** Similarly, (Duressa Tamene and Seyoum, 2015) reported a decline in DO values from the wet to the dry season. The DO level was low at the midstream site during both seasons, which may have been caused by the low flow rate, lack of aquatic plants, and increased turbidity. The mean DO was 7.76 mg L^{-1}, which is considerably higher than the mean DO recorded for Awash River (6.48 mg L^{-1})(Temesgen Elik and Seyoum, 2018). The levels of analyzed physico-chemical parameters are found in favorable ranges with no markable spatial variations between seasons and do not show a direct association with the levels of HMs, however, any change with those parameters along with others which were not measured in this study, may cause high concentration of HMs in water column from sediments which are heavily polluted.

4.3. Face-to-face interviews

A face-to-face interview with 50 respondents randomly selected from miners found in Adgnisti mining site was conducted in October. Of all respondents, 27 were females (54%) and 23 were males (46 %). 25 respondents (50%) were married, while 24 respondents (48%) were single and 1 respondent (2%) was widowed. 21 respondents were under 18, which represents 48% of the total, while 20 respondents were aged between 18 and 25, which represents 40% of the total. Those who were aged between 26 and 40 were 9 respondents, representing 12% of the total. 34 respondents (68%) had primary school level education, while 16 respondents (32%) had secondary school level

education. None of the respondents had post-secondary level education. 16 respondents (32%) had mining experience of less than 1 year, while 20 respondents (40%) had mining experience of 1 to 5 years. 10 respondents (20%) had 6 to 10 years of mining experience, while 4 respondents (8%) had above ten years of experience in mining operations. 30 respondents (60%) participate in mining but have other sources of income as well, Agriculture is the first (97%) among other sources of income. 20 respondents (40%) rely only on mining as source of income. 44 respondents (88%) had never received training about mining. All respondents said that they use the river water for drinking, and other household purposes and for watering livestock. Spade, hoe, plastic bags, Dolla (basin used for washing), basica, hammers, mortar and pestle are the main mining materials used in that study area.

4. 4. Heavy metal concentrations in water and sediments samples

The concentrations of selected heavy metals in water and sediment samples collected from three sampling sites of the river namely, upstream sampling site (USS), middle segment sampling site (MSS) and downstream sampling site (DSS) in dry season and post-rainy season, are shown in table 5-9 and seasonal variations are illustrated in figure 7-14.

Table 5: Concentrations of Heavy metals in water samples of the dry season in comparison with WHO and Ethiopian standards (permissible limits).

PARAMETER	USS W1(mg/L)	USS W2(mg/L)	AVERAGE	MSS W1(mg/L)	MSS W2(mg/L)	AVERAGE	DSS W1(mg/L)	DSS W2(mg/L)	AVERAGE	WHO Guideline (mg/L)	Ethiopian standard (mg/L)
Copper	0.006	0.002	0.004	0.058	0.068	0.063	0.01	0.006	0.008	2	2
Zinc	0.004	0.021	0.0125	0.006	0.09	0.048	0.005	0.001	0.003	-	5
Nickel	BDL	BDL	-	BDL	BDL	-	BDL	BDL	-	0.07	-
Chromium	0.018	0.023	0.0205	0.024	0.032	0.028	0.03	0.025	0.0275	0.05	0.05
Cadmium	BDL	BDL	-	BDL	BDL	-	BDL	BDL	-	0.03	0.003
Mercury	0.09	0.09	0.09	0.044	0.09	0.067	0.096	0.09	0.093	0.001	0.001
Lead	BDL	BDL	-	BDL	0.002	0.001	BDL	BDL	-	0.01	0.01
Arsenic	0.042	0.042	0.042	0.04	0.038	0.039	0.058	0.036	0.047	0.01	0.01

BDL: Below Detectable Limit (considered to be 0 in analysis)

W1: water sample 1; **W2**: water sample 2; **S1**: sediment sample 1; **S2**: sediment sample 2

Table 6:Heavy metals concentrations in sediment samples of the dry season

PARAMETER	USS S1(mg/kg)	USS S2(mg/kg)	AVERAGE	MSS S1(mg/kg)	MSS S2(mg/kg)	AVERAGE	DSS S1(mg/kg)	DSS S2(mg/kg)	AVERAGE
Copper	62.68	54.52	58.6	2131.6	938.8	1535.2	56.24	52.28	54.26
Zinc	56.64	52.2	54.42	183.16	33828.4	17005.78	69.44	56.24	62.84
Nickel	28	24.6	26.3	8.36	7.12	7.74	19.08	13.16	16.12
Chromium	57.08	53.52	55.3	59.32	56.64	57.98	35.68	27.6	31.64
Cadmium	2.44	2.32	2.38	4.76	1.96	3.36	2.12	1.4	1.76
Mercury	5.04	4.64	4.84	12.24	5.56	8.9	4.32	3.48	3.9
Lead	22.08	30.56	26.32	340.4	215.6	278	39.96	23.16	31.56
Arsenic	13.16	11.68	12.42	29.92	16.92	23.42	12.4	8.96	10.68

Table 7:Heavy metals concentrations in water samples of the post-rainy season in comparison with WHO and Ethiopian standards (permissible limits).

PARAMETER	USS W1(mg/L)	USS W2(mg/L)	AVERAGE	MSS W1(mg/L)	MSS W2(mg/L)	AVERAGE	DSS W1(mg/L)	DSS W2(mg/L)	AVERAGE	WHO Guideline (mg/L)	Ethiopian standards (mg/L)	
Copper	0.022	0.012	0.017	0.012	0.024	0.018	0.018	0.007	0.0125	2		2
Zinc	0.116	0.061	0.0885	0.053	0.081	0.067	0.08	0.052	0.066	-		5
Nickel	0.044	0.045	0.0445	0.01	0.021	0.0155	0.087	0.053	0.07	0.07		-
Chromium	0.51	0.415	0.4625	0.406	0.409	0.4075	0.435	0.41	0.4225	0.05		0.05
Cadmium	0.214	0.177	0.1955	0.163	0.135	0.149	0.129	0.185	0.157	0.03		0.003
Mercury	BDL	BDL	-	BDL	0.055	0.0275	BDL	BDL	BDL	0.001		0.001
Lead	0.759	0.48	0.6195	0.416	0.515	0.4655	0.516	0.69	0.603	0.01		0.01
Arsenic	1.041	0.419	0.73	0.783	0.746	0.7645	0.627	0.545	0.586	0.01		0.01

BDL: Below Detectable Limit (considered to be 0 in analysis)

W1: water sample 1; **W2**: water sample 2; **S1**: sediment sample 1; **S2**: sediment sample 2

Table 8: Heavy metals concentrations in sediment samples of the post-rainy season

PARAMETER	USS S1(mg/kg)	USS S2(mg/kg)	AVERAGE	MSS S1(mg/kg)	MSS S2(mg/kg)	AVERAGE	DSS S1 (mg/kg)	DSS S2(mg/kg)	AVERAGE
Copper	114.85	110.15	112.5	83.56	51.53	67.545	90.57	83.99	87.28
Zinc	158.75	153.17	155.96	69.37	43.93	56.65	126.88	134.64	130.76
Nickel	159.07	145.08	152.075	119.57	60.2	89.885	113.63	110	111.815
Chromium	180.27	170.41	175.34	113.39	61.77	87.58	2825	105.97	1465.485
Cadmium	225.6	227.88	226.74	109.63	63.24	86.435	160.43	156.69	158.56
Mercury	627.5	444.24	535.87	118.77	70.52	94.645	815	975	895
Lead	5631.67	6165	5898.34	6513.33	3717.33	5115.33	5850	5900	5875
Arsenic	4128.33	4415	4271.67	415.1	1920	1167.55	5155	2791.67	3973.335

Table 9: Comparison of mean concentrations (MC) of heavy metals in water and sediments samples of the dry and post-rainy season.

	DRY SEASON						RAINY SEASON					
	Mean conc. Water			Mean conc. Sediments			Mean conc. Water			Mean conc. Sediments		
PARAMETER	**USS**	**MSS**	**DSS**	**USS**	**MSS**	**DSS**	**USS**	**MSS**	**DSS**	**USS**	**MSS**	**DSS**
Copper	0.004	0.063	0.008	58.6	1535.2	54.26	0.017	0.018	0.0125	112.5	67.545	87.28
Zinc	0.013	0.048	0.003	54.42	17005.8	62.84	0.0885	0.067	0.066	155.95	56.65	130.76
Nickel	-	-	-	26.3	7.74	16.12	0.0445	0.0155	0.07	152.075	89.885	111.815
Chromium	0.021	0.028	0.0275	55.3	57.98	31.64	0.4625	0.4075	0.4225	175.34	87.58	1465.485
Cadmium	-	-	-	2.38	3.36	1.76	0.1955	0.149	0.157	226.74	86.435	158.56
Mercury	0.09	0.069	0.093	4.84	8.9	3.9	-	0.0275	-	535.85	94.645	895
Lead	-	0.001	-	26.32	278	31.56	0.6195	0.4655	0.603	5898.34	5115.33	5875
Arsenic	0.042	0.039	0.047	12.42	23.42	10.68	0.73	0.7645	0.586	4271.67	1167.55	3973.335

The concentrations of Cu in water samples of both seasons ranged from 0.002 of the USS in the dry season to 0.068 mg/L of the MSS in the dry season). These are lower than the concentrations in samples from Awash River (0.44–1.69 mg L^{-1}) reported by Temesgen Elik and Seyoum (2018) although they are mostly higher than those for Tekeze River (5.00 - 22.00 μg L^{-1}) reported by Mulu Berhe *et al.* (2012). At all the sampling sites of the river, the values recorded were below the permissible limit during both seasons. Cu concentrations in sediment samples (mg/kg) varied from 52.28 of the DSS in the dry season to 2131.6 of the MSS also in the dry season, which are mostly significantly higher that the Cu concentrations in sediment samples from Denube River, Romania (7.24 - 86.52 mg/kg; Mihaela *et al.*, 2014) and Seybouse River, Algeria (maximum= 145.15±35.2 mg/kg ; Louhi *et al.*, 2012). The spatial trend of variations in the mean concentrations of Cu in water was in the order MSS > DSS > USS in the dry season, and in the order MSS > USS > DSS in the post-rainy season. The spatial trend of variations in the mean concentrations of Cu in sediment samples was in the order MSS > USS> DSS in the dry season, and in the order USS>DSS>MSS in the post-rainy season.

A)Copper distribution in dry season **B) Copper distribution in post-rainy season**

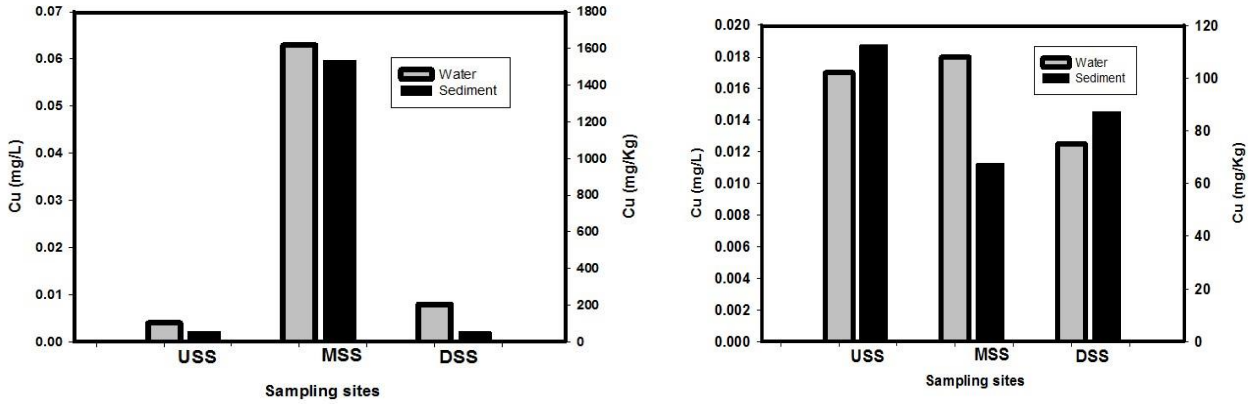

Figure 7: A) Copper distribution in dry season (A) and in post-rainy season(B)

The concentrations of Zinc in water samples (mg/L) of both seasons ranged from 0.001 of DSS in the dry season to 0.09 of the MSS in the dry season, which are significantly lower than those in Ribu River of the Oromia region (0.21±0.01-0.39±0.05 mg/L) reported by Mekonnen *et al* (2018) and Awash River (0.96–2.14 mg L^{-1}) recorded by Temesgen Elik and Seyoum(2018). At all sampling sites of the river, the values recorded were below the permissible limits during both seasons. Zn concentrations in sediment samples (mg/kg) varied from 52.2 of USS in the dry season) to 33828.4 l of MSS in the dry season. These are almost entirely higher than the Zn

concentrations in sediment samples from Awash River basin (142.44-1210.04 mg/kg) reported by Niguse Bekele *et al* (2018) and Pearl River Estuary, China (140.4-508.6 mg/kg) documented by Jiao *et al* (2018). The mean concentrations of Zn in water varied spatially in the order MSS > USS > DSS in the dry season, and in the order USS > MSS > DSS in the post-rainy season. The spatial trend of variations in the mean concentrations of Zn in sediment samples was in the order MSS > DSS > USS in the dry season, and in the order USS>DSS>MSS in the post-rainy season.

A) Zinc distribution in dry season **B) Zinc distribution in post-rainy n season**

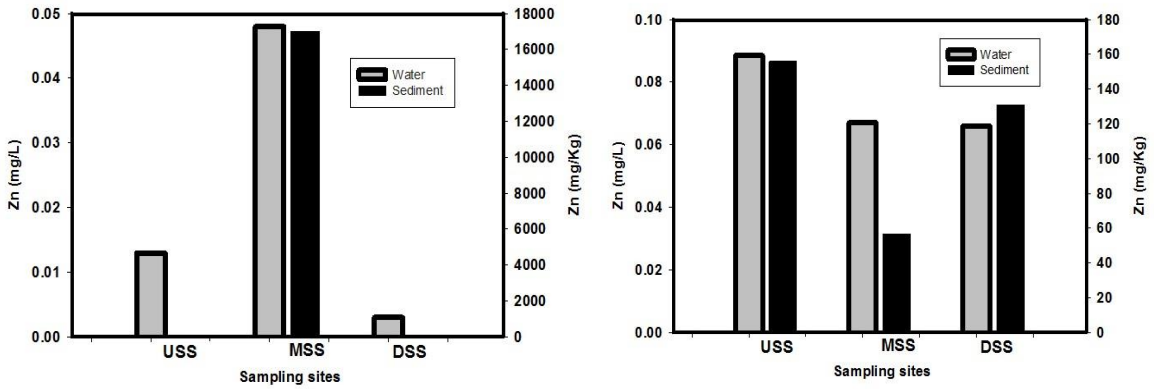

Figure 8: Zinc distribution in dry season(A) and in post-rainy season(B)

The concentrations of Ni in water samples (mg/L) of both seasons ranged from BDL of all sampling site in the dry season to 0.087of MSS in the post-rainy season. These levels are higher than the Ni concentrations in samples from Revué River of Mozambique (0.00061-0.0023mg/L) reported by Mujere and Isidro (2017). At all the sampling sites of the present study river, all values except one sample of DSS collected during the post-rainy season were below the permissible limit during both dry and post-rainy seasons. Ni concentrations in sediment samples (mg/kg) varied from 7.12 of the MSS in the dry season to 2825 of the USS in the post-rainy season. which are largely significantly higher than the Ni concentrations in sediment samples from Akaki River and Aba Samuel reservoir (14.6-36.2 mg/kg) reported by Kassegne *et al.* (2018) and those recorded for Tsaeda Agam River (12.42-26.30 mg/kg) by Mezgebe *et al* (2015). The mean concentrations of Ni in water varied spatially in a decreasing order of DSS > USS > MSS in the post-rainy season, Ni concentrations were, however, below the detectable limit of the method of analysis in samples of the dry season. The spatial trend of variations in the mean concentrations of Ni in sediments were in the order USS>DSS>MSS in both the dry and post-rainy seasons.

A) Nickel distribution in dry season **B) Nickel distribution in post-rainy season**

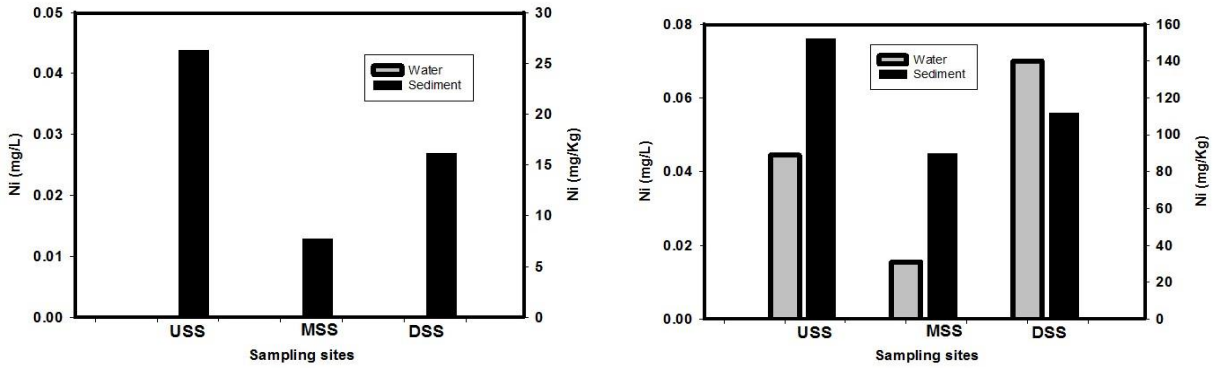

Figure 9: Nickel distribution in dry season(A) and in post-rainy season(B)

The concentrations of Cr in water samples (mg/L) of both seasons ranged from 0.018 of the USS in the dry season to 0.51 of the same site in the post-rainy season. The observed levels are mostly higher than those reported for AsgedeTsimbla River (15 -150 μg/L) by Zelealem and Sathishkumar (2020), In all the sampling sites of the river, the recorded values were below the permissible limit in the dry season, while all values were above the permissible limit in the post-rainy season. Cr concentrations in sediment samples (mg/kg) varied from 27.6 of the DSS in the dry season to 175.34 of the same site in the same season., These Cr levels are mostly lower than those in sediment samples of Awash River (10.0-712.67 mg/kg) reported by Niguse Bekele *et al* (2018). The mean concentrations of Cr in water followed a spatial trend of variations of the order MSS > DSS > USS in the dry season, and of the order USS > DSS > MSS in the post-rainy season. The spatial trend of variations in the mean concentrations of Cr in sediment samples was in the order MSS > USS> DSS in the dry season, and in the order DSS>USS>MSS in the post-rainy season.

A) Chromium distribution in dry season **B) Chromium distribution in post-rainy season**

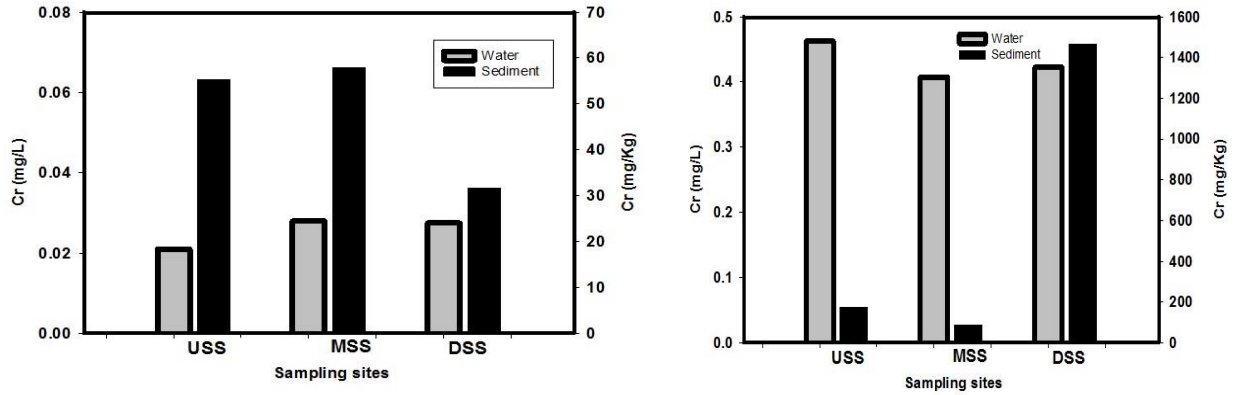

Figure 10: Chromium distribution in dry season (A) and in post-rainy season(B)

The concentrations of Cd in water samples (mg/L) of both seasons ranged from BDL of all sampling site in the dry season to 0.214 of USS in the post-rainy season, which are higher than Cd concentrations in Tsaeda Agam River of Mekelle (0.01 ± 0.00 to 0.015 ± 0.005 mg/L) reported by Mezgebe *et al* (2015). In all the sampling sites of the river, the values were below the permissible limit in the dry season, while they were above the permissible limit in the post-rainy season. Cd concentrations in sediment samples (mg/kg) varied between 1.4 of the DSS in the dry season and 227.88 of the USS in the post-rainy season. These Cd levels are largely higher than the Cd concentrations in sediment samples of Awash River (Not Detectable - 8.35) reported by Niguse Bekele *et al* (2018) and of Tekeze River (0.34 to 1.68 mg/kg) reported by Mulu Berhe *et al* (2012).The mean concentrations of Cd in water varied among the sampling sites following the order USS > DSS > MSS in the post-rainy season. The concentrations of Cd in all samples of the dry season were, however, below the detectable limit of the method of analysis. The mean concentrations of Cd in sediment samples varied among the sampling sites following the order MSS > USS > DSS in the dry season and in the order USS>DSS>MSS in the post-rainy season.

A) Cadmium distribution in dry season **B) Cadmium distribution in post-rainy seas**

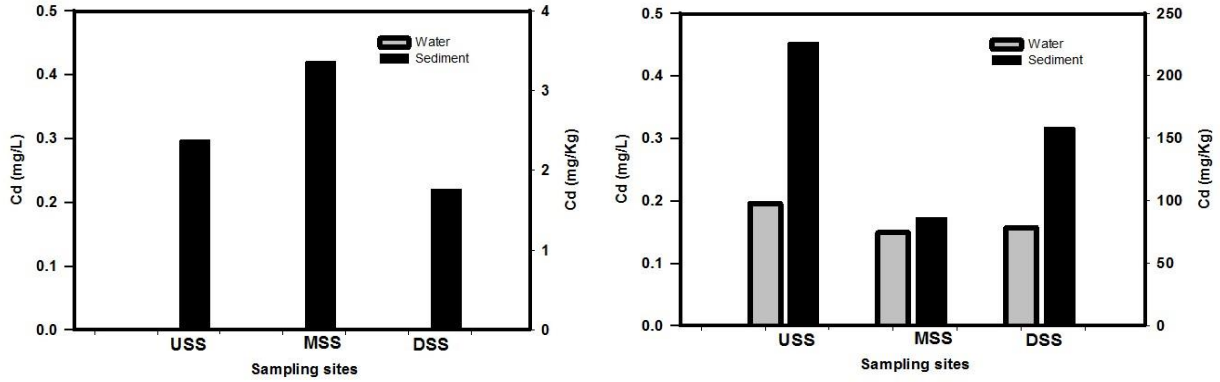

Figure 11: Cadmium distribution in dry season (A) in post-rainy season(B)

The concentrations of Hg in water samples (mg/L) of both seasons ranged from BDL of all sampling site in post-rainy season except one sample in MSS to 0.096 of the DSS in the dry season, which are lower than the Pb concentrations in Mojo River (1.324 – 1.86 mg/L) reported by Duressa Tamene and Seyoum (2015), and in Lake Beseka (0.434-0.916 mg/L) documented t by Abduro and Gelaneh (2017). In all the sampling sites of the river, all values were above the permissible limit in the dry season, while only one sample of MSS was above the permissible limit in the post-rainy season. Hg concentrations in the sediment samples (mg/kg) varied from 3.48 of the DSS in the dry season to 975 of the DSS in the rainy season. These levels of Hg are mostly higher than the Hg concentrations in sediment samples from Migori Gold Belt, Kenya (0.28–348 mg/kg) reported by Ogola *et al* (2002). The mean concentrations of Hg in water varied spatially following the decreasing trend, DSS > USS > MSS in the dry season. Hg concentrations were, however, below the detectable level in all samples except one sample from the MSS in the post-rainy season. The mean concentrations of Hg in sediments varied spatially following the decreasing trend, MSS > USS > DSS in the dry season and in order of DSS > USS > MSS in the post-rainy season.

A) Mercury distribution in dry season **B) Mercury distribution in post-rainy season**

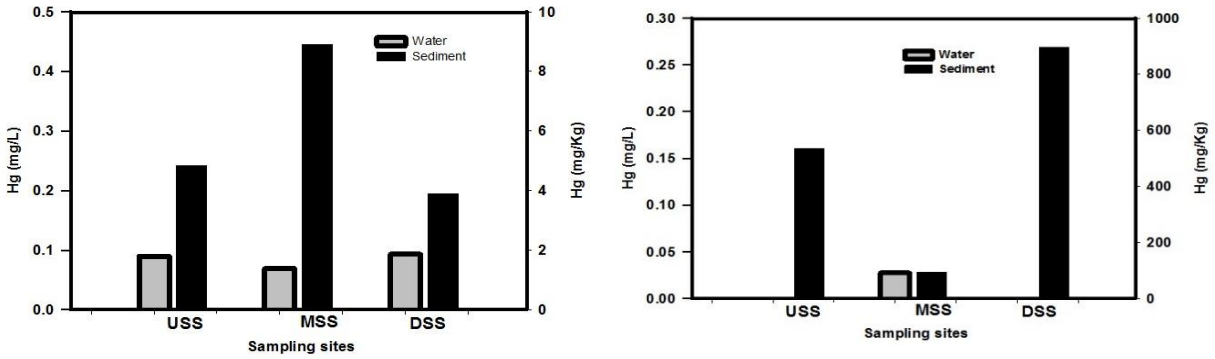

Figure 12: Mercury distribution in dry season (A) and in post-rainy season(B)

The concentrations of Pb in water samples (mg/L) of both seasons ranged from BDL of all sampling sites in dry season except one sample in MSS to 0.759 of the USS in the rainy season, which are lower than the Pb concentrations in AsgedeTsimbla River (8 -1100 µg/L) reported by Zelealem and Sathishkumar (2020), but are still largely higher than those of Togona River of Oromia (0.013 ± 0.01- 0.016 ± 0.02mg/L) reported by Fisseha *et a*l (2017). Pb concentrations in all samples of the dry seasons except one from the MSS were, however, below the detectable limit of the metal. In all the sampling sites of the river, the values were below the permissible limit in the dry season, while all values were above the permissible limit in the post-rainy season. Pb concentrations in sediment samples (mg/kg) varied from 22.08 of the USS in the dry season to 6513 of the MSS in the post-rainy season. These are largely higher than Pb concentrations in sediment samples from Akaki River and Aba Samuel reservoir (335.5–1833.4 mg/kg) reported by Kassegne *et al* (2018).The mean concentrations of Pb in water varied spatially in the order of USS > DSS > MSS in the post-rainy season, while the mean concentrations of Pb in sediment samples varied spatially in the order of MSS > DSS > USS in the dry season and in the order of USS > DSS > MSS in the post-rainy season.

A) Lead distribution in dry season **B) Lead distribution in post-rainy season**

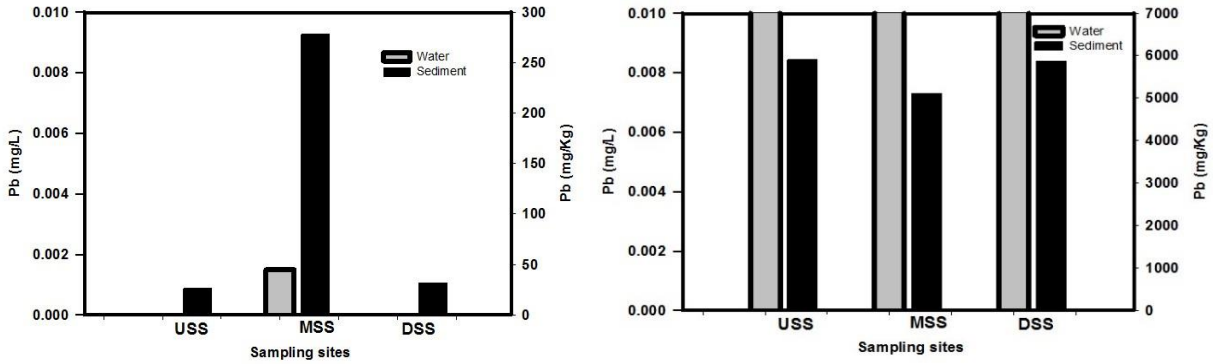

Figure 13: Lead distribution in dry season (A) and in post-rainy season(B)

The concentrations of As in surface water samples (mg/L) of both seasons ranged from 0.036 of the DSS in the dry season to 1.041 of the USS in the post-rainy season, which are mostly lower than the As concentrations in Mojo River (0.099 –1.28 mg/L) reported by Duressa Tamene and Seyoum, (2015),. The observed values are, however, mostly higher than those documented for Lake Beseka of the Main Ethiopia Rift (0.043-0.067mg/L; Abduro and Gelaneh, 2017). In all the sampling sites of the river, the values recorded were above the permissible limit during both seasons. As concentrations in sediment samples (mg/kg) varied from 8.96 of the DSS in the dry season to 5155 of the DSS in the post-rainy season. These levels are generally higher than those recorded for sediment samples from Lake Amponsah, Ghana (43.00 ± 16.26 – 87.67 ± 6.98 mg/kg; Hogarh *et al.*2016). The mean concentrations of As in water varied spatially following the decreasing order of DSS > USS > MSS in the dry season, and the order of MSS > USS > DSS in the post-rainy season. The mean concentrations of As in sediment samples varied spatially following the decreasing order of MSS > USS > DSS in the dry season, and in the order of USS >DSS > MSS in the post-rainy season.

A) Arsenic distribution in dry season **B) Arsenic distribution in post-rainy seas**

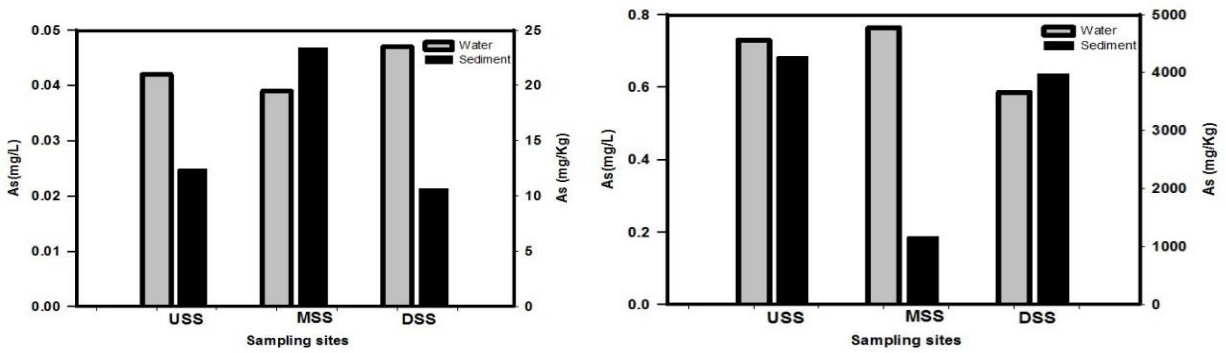

Figure 14: Arsenic distribution in dry season (A) and in post-rainy season(B)

The differences in HMs concentrations in water among sampling sites during both seasons were not marked except for Cu and Zinc in dry season. The differences in the concentrations of all HMs in water samples between seasons were marked. The concentrations of HMs in sediment samples varied markedly between the two seasons. The differences in HMs concentrations in sediments among sampling sites during dry seasons were marked for Cu, Zn, Pb and As while in post-rainy season, differences were not marked except for Ni and Pb.

In the dry season, only Mercury and Arsenic were above the WHO and Ethiopian standards (guideline values) for drinking water in all sampling sites, while Chromium, Cadmium, Mercury, Lead and Arsenic were above the WHO and Ethiopian standards for drinking water in all sampling sites, but for Nickel and Mercury, only one sample from DSS and MSS respectively was above WHO and Ethiopian standards for drinking water during the post-rainy season.

Although the differences in the levels of heavy metals among sampling sites seasons were not marked,

Copper, Zinc, Chromium, and Lead were relatively higher in water samples from MSS in the dry season, whereas Copper, Mercury and Arsenic were relatively higher in samples from the MSS during the post-rainy season suggesting that the levels of these metals were associated more with AGM pollution although the natural source cannot be overlooked because the mean concentrations of most of them were higher in the USS during the post-rainy season.

It was hypothesized that DSS is more or less impacted by the panning activity conducted at the mining site, which is in close proximity to the MSS. Furthermore, due to its geological features, natural source can also contribute to metal pollution of DSS, this is corroborated by the fact the trend of variations of most of the metal concentrations in the DSS is similar to either that in the USS or MSS depending on which effect is dominant.

In the dry season, all analyzed metals except Nickel were found to be more concentrated in sediment samples collected from MSS. However, the concentrations of all except Zinc and Lead were lower in the DSS compared to those in the USS. In the post-rainy season, all analyzed metals were found to be more concentrated in sediment samples from USS, followed by their levels in samples from the DSS, except for Mercury and Chromium, which were higher in sediment samples from the DSS. HMs concentrations were relatively lower in sediments from the MSS. The higher concentrations of HMs in sediments from USS during the post-rainy season might be associated with the release of metals through weathering processes and their transport via high runoff from agricultural lands, which are located on both sides of the USS considering the steep slopes and huge rocks that are characterized the site.

Mercury concentrations in water samples were higher in the dry season compared to those of the post-rainy season. This may be attributed to the high reactivity of Hg with organic materials, which are presumably higher during the post-rainy season, this may reduce the concentration of Hg in water. It can also be attributed to the dilution effect of precipitation, which occurred shortly before sampling. In the dry season, Mercury concentrations were markedly higher in water samples from the USS (about twice those of other sites), a finding, which is consistent with the results of Dorleko *et al* (2018) who reported highest peaks of Hg concentrations from non-mining sites. This suggests that Hg may have originated from natural sources.

In the post-rainy season, Mercury concentrations were below detectable limit except for a sample from the MSS as it was expectedly lower in sediment samples from the same site compared to other sampling sites. This suggests the association of the observed Mercury levels with pollution from the mining site. This was corroborated by the report of Cheepurupalli *et al* (2019) who conducted a study in the two most important mining woredas in Tigray including Adyabo mining site and confirmed the use of mercury in the mining processes although many respondents were reluctant to comment.

There is an increase in HMs concentrations both in water (except for Hg) and sediment samples (except for Zn) from the dry season to the post-rainy season. This temporal increase is likely to be due to the effect of runoff from mining activities and change in geochemical conditions. The results also show that in the dry season, metal concentration is more related to mining activities, whereas in the post-rainy season it is related more to natural and other sources. This may suggest that the contribution of pollution from weathering of rocks combined with other sources of pollution with metals in the post-raining season surpasses the contribution from mining activities to pollution with metals.

The results of our study show that the sediments are heavily polluted with heavy metals. During periods of sediment disturbance and/or changes in the geo-chemistry of sediments or climatic conditions, this is likely to cause a risk of secondary water pollution.

The limited data sets documented in the present study seem to suggest that both AGM and natural sources associated with the weathering of rocks have made contributions to the metal pollution of May Sieley River. This is consistent with the contention of Ahmed (2015) who conducted geological and geochemical investigation on low grade basement rocks in Shire and their health implication. He argued that health issues related to heavy metals in water and stream sediments of his study area generally emanated from the basement rocks upon weathering and stream waters draining through soil waste disposals from artisanal gold panning sites. These could contain high levels of contaminants and were supposed to be secondary source of water pollution in the area.

4.5. Human Health Risk Assessment (HHRA)

The HHRA was conducted based on the concentration of heavy metal elements measured in water samples. For each metal, the overall mean was calculated from the average of all means and it was used as Cw (Concentration of metal in water). The calculations were based on the following assumptions as recommended by USEPA that a mature adult weighing 60 kg consumes 2 L/day of water per day, while a child weighing 10 kg consumes 1 L/day of water per day, Exposure frequency = 350 days/year, Exposure duration (years) = 30 years for an adult, 6 years for a child, Averaging time (AT)= ED for noncarcinogenic effects, AT= ED*365 which equals 2190 days and 10950 days for children and adults respectively, while AT = 70 years (25550 days) for carcinogenic effects for both age groups. The oral reference dose (RfD) and oral slope factor (SF) were used.

Non-carcinogenic Risk Assessment

The table below summarizes the calculation of CDI by using (eq.1) for all analyzed heavy metals for both age groups.

Table 10: Calculation of CDI values of analyzed heavy metals for non-carcinogenic effects

		Adults						Children					
PARAMETER	**Overall mean (mg/L)**	**DI(L/day)**	**EF(days/year)**	**ED(years)**	**BW (kg)**	**AT(days)**	**CDI** (mg/kg/day)	**DI**	**EF**	**ED**	**BW**	**AT**	**CDI** (mg/kg/day)
Copper	0.02	2	350	30	60	10950	6.30E-04	1	350	6	10	2190	1.92E-03
Zinc	0.047	2	350	30	60	10950	1.50E-03	1	350	6	10	2190	4.51E-03
Nickel	0.043	2	350	30	60	10950	1.37E-03	1	350	6	10	2190	4.12E-03
Chromium	0.0228	2	350	30	60	10950	7.20E-04	1	350	6	10	2190	2.19E-03
Cadmium	0.167	2	350	30	60	10950	5.34E-03	1	350	6	10	2190	1.60E-02
Mercury	0.0465	2	350	30	60	10950	1.47E-03	1	350	6	10	2190	4.46E-03
Lead	0.28	2	350	30	60	10950	8.95E-03	1	350	6	10	2190	2.68E-02
Arsenic	0.36	2	350	30	60	10950	1.15E-02	1	350	6	10	2190	3.45E-02

The increasing order of CDI values in both age groups was as follows; Cu < Cr < Ni < Hg < Zn < Cd < Pb < As.

The hazard quotient for each heavy metal was calculated by using the Oral Reference Dose (RfD) of each metal (table 3) and its calculated CDI value by using (eq.2) The HQ values were obtained for adults were as follow; 1.58E-02, 5.00E-03, 6.85E-02, 2.40E-01, 1.07E+01, 8.10E+00, 2.56E+00, 3.84E+01 (mg/kg-day) for Cu, Zn, Ni, Cr, Cd, Hg, Pb and As respectively. For the children age group, the values of HQ were as follows; 4.79E-02,1.50E-02, 2.06E-01,7.29E-01, 3.20E+01, 1.49E+01, 7.67E+00, 1.15E+02 (mg/kg-day) for Cu, Zn, Ni, Cr, Cd, Hg, Pb and As respectively. It was found that in both age groups, the HQ values for As, Pb, Hg and Cd were at unacceptable non-carcinogenic health risk levels (HQ>1). As and Cd with HQ >10 pose high chronic risk in adults whereas As, Cd and Hg HQ values suggest the high chronic risk (HQ >10) for children age group. The concentration of the above-mentioned HMs (As, Pb, Hg and Cd) were above permissible limits set by the Ethiopian standards Agency (2013) and World Health Organization (2011). These are the four metals regarded to be highly toxic and do not have any beneficial effects to human health (Goyer *et al*., 2004). Cr concentration was above the standard limit; However, its HQ value does not show non-carcinogenic effect (HQ>1), but carcinogenic effect related to this metal was found. The increasing order of assessed metals based on their HQ values was Zn <Cu <Ni <Cr<Pb<Hg<Cd<As for both age groups.

Hazard Index (HI)

Based on the calculated HQ values of analyzed heavy metals, the Hazard Index was calculated for both age groups using(eq.3) to consider the additive effect of potentially toxic metals. The HI for adults was 6.13E+01mg/kg/day, while for children it was 1.71E+02 mg/kg-day. The Sum of HQs of analyzed metals was far greater than 1 for both age groups. Therefore, the HI results raise concern about the non-carcinogenic adverse health effects of drinking the river water in this area. HI values suggest that children have higher (almost three times) risk of non-carcinogenic health effects compared to adults. Similar results were reported by Bamuwamye *et al*(2017) and Awomeso *et al*(2017).

Carcinogenic Risk Assessment

The Incremental Lifetime Cancer Risk (ILCR) for Arsenic, Lead, Cadmium, Chromium and Nickel was calculated as they are potentially carcinogenic metals and their slope factor (SF) were available. The cancer risk was calculated based on the CDI values and their respective SF values by using (eq.4). The table below shows the CDI values for carcinogenic effect, where AT=70 years (25550 days).

Table 11: Calculated CDI values for carcinogenic effects

		Adults						Children					
PARAMETER	**Overall mean(mg/L)**	**DI(L/day)**	**EF (days/year)**	**ED (years)**	**BW (kg)**	**AT (days)**	**CDI** (mg/kg/day)	**DI**	**EF**	**ED**	**BW**	**AT**	**CDI** (mg/kg/day)
Nickel	0.043	2	350	30	60	25550	5.89E-04	1	350	6	10	25550	2.36E-04
Chromium	0.0228	2	350	30	60	25550	3.12E-04	1	350	6	10	25550	1.87E-04
Cadmium	0.167	2	350	30	60	25550	2.29E-03	1	350	6	10	25550	6.15E-04
Lead	0.28	2	350	30	60	25550	3.84E-03	1	350	6	10	25550	2.30E-03
Arsenic	0.36	2	350	30	60	25550	4.93E-03	1	350	6	10	25550	2.96E-03

The cancer risk assessment results for adults were found as follows; 0.000495, 0.012792, 0.013951, 0.032603, 0.007397 for, Ni, Cr, Cd Pb and As respectively. The cancer risk assessment results for children were found to be as follow; 0.000198, 0.007667, 0.003752, 0.019562, 0.004437 for Ni, Cr, Cd, Pb and As respectively.

This implies that 495 adults out of 1000000 are likely to get carcinogenic effects through chronic exposure to Nickel, 12792 adults out of 1000000 are likely to get carcinogenic effects through chronic exposure to Chromium, 13951 adults out of 1000000 are likely to get carcinogenic effects through chronic exposure to Cadmium, 32603 adults out of 1000000 are likely to get carcinogenic effects through chronic exposure to Lead, 7397 adults out of 1000000 are likely to get carcinogenic effects through chronic exposure to Arsenic.

The cancer risk assessment results for children imply that 198 children out of 1000000 are likely to get carcinogenic effects through chronic exposure to Nickel, 7667 children out of 1000000 are likely to get carcinogenic effects through chronic exposure to Chromium, 3752 children out of 1000000 are likely to get carcinogenic effects through chronic exposure to Cadmium, 19562 children out of 1000000 are likely to get carcinogenic effects through chronic exposure to Lead, 4437children out of 1000000 are likely to get carcinogenic effects through chronic exposure to Arsenic.

The results of cancer risk assessment for all assessed metals (As, Ni, Cr, Cd and Pb) in both age groups show that the carcinogenic effect associated with these metals should not be overlooked because they are not within the range recommended by USEPA (10^{-6}-10^{-4}). The strikingly similar result for carcinogenic risk was reported by Kavcar *et al* (2009), who found through deterministic approach that 91% of individuals had lifetime carcinogenic risks greater than 10^{-6} for Arsenic. The increasing order of carcinogenic effects of assessed heavy metals was Ni<As<Cr<Cd<Pb in adults and Ni<Cd<As<Cr<Pb in children. However, the carcinogenic risk for all metals was higher in adults compared to that of children. This is consistent with the results reported by Koki *et al* (2018) who concluded that the reason for the fact that the carcinogenic risk for children is less than that for adults lies in the shorter duration of exposure for children. However, children can be more vulnerable because of the fact that they have a weaker immunity.

Conclusion and recommendations

This study investigated the impact of artisanal gold mining on heavy metals pollution in May Sieley River and assessed the potential human health risk associated with continuous use of the river water by the local inhabitants. Sampling was conducted once during both dry and post-rainy seasons taking upstream as a reference site. In the dry season, Copper, Zinc, Chromium, and Lead were relatively higher in water samples from MSS, whereas Copper, Mercury and Arsenic were relatively higher in water samples from the MSS during the post-rainy season suggesting that their levels were primarily associated with pollution from AGM. In the dry season, all analyzed metals except Ni were found to be more concentrated in sediment samples from the MSS, which is closer to the mining site. However, levels of all metals except Zinc and Lead were lower in the DSS compared to those in the USS. However, the differences in HMs concentrations in water were not marked except for Cu and Zn in dry season. The differences in HMs concentrations in sediments among sampling sites during dry seasons were marked for Cu, Zn, Pb and As while in post-rainy season, differences were not marked except for Ni and Pb. During the post-rainy season, heavy metal concentration in the sediment was higher in the USS compared to those of other sites. Metal pollution in the river seems to be more related to mining activities in the dry season, with the natural source making more contribution during the post-rainy season. Our findings suggest that both AGM and natural source from weathering of rocks are responsible for metal pollution in May Sieley River.

The concentrations of HM were compared with WHO and Ethiopian standards, Hg and As were above WHO and Ethiopian standards for drinking water in all sites during the dry season, while Cr, Cd, Pb and As were above the WHO and Ethiopian standards for drinking water in all sites during the post- rainy season except, except Hg (in one sample of MSS) and Ni (in one sample of DSS). With regard to potential human health risk, it was found that in both adult and children groups, the HQ values for As, Pb, Hg and Cd were at unacceptable non-carcinogenic health risk level (HQ>1). The high values of As and Cd (HQ >10) suggest high chronic risk for adults and HQ values of As, Cd and Hg suggest high chronic health risk (HQ >10) for the children age group. The increasing order of assessed metals based on their HQ values was Zn <Cu <Ni <Cr< Pb <Hg<Cd <As for both age groups.

The Sum of HQ values (HI) of analyzed metals was far greater than 1 for both age groups, children being at greater risk of non-carcinogenic health effect, this raises concern about the non-carcinogenic adverse health effects of drinking the river water and using it for other household purposes. The Incremental Lifetime Cancer Risk (ILCR) for Arsenic, Lead, Cadmium, Chromium and Nickel was assessed and found that the carcinogenic effect associated with these metals is not acceptable. The study revealed that the river water is not safe because of HM pollution, AGM should be managed to reduce its contribution to the pollution of water bodies with metals. We strongly believe that the government needs to assist and empower the miners so that they may carry out their activities sustainably and in an environmentally friendly way. Monitoring of the impact of traditional gold mining on HM pollution by considering aquatic organisms in order to assess their bio-magnification along food chains is also recommended.

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APPENDICES

Appendix A. Questionnaire

Dear Sir/Madam,

The Masters student, from Africa Center of Excellence for Water Management (ACEWM) is carrying out a study on the **Assessment of the Effect of Artisanal Gold Mining on Heavy metals Concentrations in May Sieley River and Associated Potential Public Health Risk: The case of Shire, Tigray region, Ethiopia,** for his thesis. Your positive and constructive response in answering the following questions will enormously assist in making the study successful in terms of obtaining precise and reliable data and recommendations. The research findings will facilitate the formulation of policies and legislation as well as point out areas of intervention that will enhance mining activities in the region. Please fill in the appropriate answer for every question.

1. Gender: a. Male ☐

   b. Female ☐

2. Age of respondent:
   - a. Less than 18 ☐
   - b. Between 18-25 ☐
   - c. Between 26-40 ☐
   - d. Above 40 ☐

3. Level of education:
   - a. Primary school ☐
   - b. Secondary school ☐
   - c. Post-secondary school trainings ☐

4. Marital status
   a. Single ☐
   b. Married ☐
   c. Widowed ☐
5. How long have you been involved in Gold mining?
   a. Less than 1 year ☐
   b. Between 1-5 years ☐
   c. Between 6-10 years ☐
   d. Above 10 years ☐
6. Is Gold mining your only source of income?
   a. Yes ☐
   b. No ☐
7. If No, specify other sources of income
   a) ……
   b) …… …….
   c)……...
8. What are the materials that are used in gold mining process?
9. Have you had any awareness trainings from the government about Gold mining?
   a. Yes ☐
   b. No ☐
10. Do you use May Sieley River for drinking?
    a. Yes ☐
    b. No ☐

11. Do you use May Sieley River for household activities?

a. Yes ☐

b. No ☐

12. Do you use May Sieley River for watering livestock?

a. Yes ☐

b. No ☐

Thank you for your cooperation!!