JIMMA UNIVERSITY

COLLEGE OF NATURAL SCIENCE

DEPARTMENT OF CHEMISTRY

ASSESSMENT OF SELECTED HEAVY METALS AND SOME PHYSIOCHEMICAL PARAMETERS FROM ATEBELA RIVER SEBETA, ETHIOPIA

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RESEARCH TITLE: ASSESSMENT OF SELECTED HEAVY METALS AND SOME PHYSIOCHEMICAL PARAMETERS FROM ATEBELA RIVER SEBETA, ETHIOPIA

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Abbreviations

AAS Atomic Absorption Spectroscopy

ANOVA Variance Analysis

CART: Centre Agro-Ruler Technologies

CSA: Central statistical Agency of Ethiopia

EC: Electrical Conductivity

EPA: Environmental protection Agency

FAO: Food and agricultural organization

IDL: Instrumental detection Limit

LOD: Limit of detection

LSD: Least significant difference

LSDL: Least significant difference level

MDL: Method Detection Limit

MOE: Ministry of Environment

WHO: World Health Organization

US EPA: United States Environmental protection Agency

Abstract

This study was intended to investigate the concentration of selected heavy metals such as: Cr, Cu, Zn, Cd, and Pb; and also physicochemical parameters of water sample from Atebela River. Water samples were collected from four sampling points along the river impacted by discharges from different sources of Sebeta City using purposive sampling technique and the concentration of heavy metals in the river was analyzed by using Flame Atomic Absorption Spectroscopy. Thus, the mean concentration of Cu at sites of A, B, C, and D was 0.072 ± 0.004 mg/L, 0.088 ± 0.01 mg/L, 0.069 ± 0.005 mg/L and 0.080 ± 0.005 mg/L, respectively whereas the mean concentration of Zn at sites of A, B, C, and D was 0.037 ± 0.003 mg/L, 0.062 ± 0.003 mg/L, 0.048 ± 0.003 mg/L and 0.05 ± 0.003 mg/L, respectively. Physiochemical parameters of the river such as turbidity, pH and electrical conductivity were found as: 15. 78 ± 0.23 NTU, 31.66 ± 0.5 NTU, 33.05 ± 0.2 NTU, 50.33 ± 0.58 NTU; 7.45 ± 0.23, 6.67 ± 0.01, 7.04 ± 0.11, 7.06 ± 0.12 and 0.162 ± 0.026 mS/cm, 0.945 ± 0.02 mS/cm, 0.820 ± 0.00 mS/cm and 0.830 ± 0.01 mS/cm, respectively for sites of A, B, C, and D as in their order written . The level of metals studied found below the minimum concentration limit of WHO and FAO standard for irrigation.

***Key word**: Heavy metals, physiochemical parameters, Atebela River*

1. Introduction

Water resources in the world have been greatly influenced over the last years by human activities, by which the world is currently facing critical water supply and drinking water quality problems. Pollution of water bodies from technological activities such as industrial effluents and agricultural chemicals is considered a minor threat in developing countries like Ethiopia, but urban water pollution is growing at alarmingly faster rates [1]. Pollutants are directly or indirectly discharge in to water bodies without any treatment; harmful compounds cause water pollution which affects plants and organisms living in water. Damage is not only to individual species and populations, but also to the natural biological communities [2].

Industrialization is among the major cause of surface water pollution in Ethiopia, particularly in urban areas. Addis Ababa is well known by its numerous industries and most of the industries are located around of this city. Accelerated pollution and eutrophication of rivers, streams, springs and other water reservoirs because of anthropogenic activity in Africa particularly Ethiopia is a case, since as developing counties lack and have not stringent regulations that have been implemented to restrict the discharge of untreated wastewater into rivers, streams and other water bodies [3].

River water has been and is still being used for many purposes, which include drinking, irrigation, animal farming, recreation and serves as habitat for numerous organisms, including human being. The availability of good quality water is an indispensible feature for preventing diseases and improving the quality of life [4]. River water contains some types of impurities whose nature and amount vary with source of water may be effluent from industries, urban runoff, sewage discharge, mining, soil erosion [5]. From the environmental pollutants there are a series of metals, most of them unusual, some very common and many rather has little importance for the environment. Since these metals may become environmentally damaging, not the least since they react with the components in living cells [6]. Among environmental pollutants heavy metals are of particular concern due to their potential toxic effect and ability to bio-accumulate in aquatic Ecosystem [4]. The growth of industries and urban causes accumulation of trace metals, especially heavy metals in the water ways. Many dangerous chemical elements accumulate in the environment and in the sediments of water bodies [7].

Lead is particularly toxic to the brain, kidney, and reproductive system and cardiovascular system because acute and chronic exposure, this poses serious threat to human health. They cause the irregularity in blood composition, badly hurt vital organ such as lung, kidney and liver. Heavy metals such as Cu, Cr, Cd etc are poisonous to plants at higher concentration can cause considerable amount of environmental degradation and ecological damage to water, soil and air [8].Thus, it is important to protect the soil, water and the environment in general to make it free of heavy metal contaminations. Sebeta is City found 26 Km from Addis Ababa, due to the expansion of great anthropogenic activities in the City, effluents, and wastes are deposed to stream and rivers, because of this river play great role to transport discharged waste and runoff. So, Atebela River is assumed to be one of the victims of aforementioned pollutants. Therefore, this study was aimed to investigate the concentration of the selected heavy metals (Cd, Cr Cu, Pb and Zn) and some physicochemical parameters of Atebela River.

1.1 The statement of the problem

Toxic heavy metals such as Pb, Cr, and Cd can be differentiated from other pollutants in that they can be accumulated in living organisms and causes various diseases, even relatively at low concentration**.** These chemical elements never degrade or metabolized to harmless compounds, such as water and carbon dioxide. They can be part of a waste, stored in landfills and carried to different part of water body such as lake, river etc. Water quality also influenced by physicochemical parameter like turbidity, pH electrical conductivity etc. for its particular use. Therefore determination of heavy metal concentration and physicochemical parameters are helpful in preventing water pollution.

Atebela River situated in Sebeta City in Ethiopia twenty six kilo meter (26 km) from Addis Ababa, Ethiopian Capital City, around this area there is great anthropogenic activities like beverage and liquor, textile, horticulture, tanning industries were built around the river. Residual from industries and domestic wastes as indicate on the map are discharged to this river. The river is now the main public concern due to its extreme pollution. The communities use it for different purposes; for irrigation of lands, house hold activities, drinking of domestic animals. Even though studies on heavy metal determination have been done during the last decade in different parts of Ethiopia, there is no previous report on the analysis of heavy metals; Cd, Cr, Cu, Pb and Zn and physicochemical parameters of the Atebela River, Sebeta, Ethiopia.

1.1.2 Objectives of the study

1.1.3 General objective

To investigate the concentration of selected heavy metals and physicochemical parameters, from Atebela River water.

1.1.4 Specific objectives

- To determine the levels of heavy metals (Cd, Cu, Pb, Zn, Cr) in Atebela river at different points along the river.
- To compare the level of heavy metals along the river in sampling points
- To compare the level of heavy metals with national and international standards for drinking and irrigation purposes.
- To determine the physicochemical parameters (pH, turbidity and electrical conductivity) of Atebela river in Sebeta city.

1.2 The significance of the study

This study would have significant contribution in understanding the levels of Cd, Cr, Cu, Pb and Zn, and some physicochemical parameters of Atebela River. It also will give adequate information for the society so as to keep the quality of river water. The fact that no analysis was made on the level of these toxic metals in this river, it will make this work significant and initiate another people for further research work. The findings of the research work may also help concerned government or non-governmental officials regarding the quality Atebela river water that the people of the area are using for irrigation purpose. The result of this study will also assist the relevant industries and authorities in designing appropriate preventive measure to ensure that the water quality could improve.

1.3 The scope of the study

The study focus on determination of five selected heavy metals (Cd, Cr, Cu, Pb, and Zn) that were considered prevalent in the area; and some physicochemical parameters like pH, turbidity and electrical conductivity. Atebela River is a river which crosses Sebeta City in between and passes in to the South West of Addis Ababa, which extends to East Shoa zone inters to Awash River. The study was started in August 2019 by taking triplicate samples from four different site in the river in areas where suspected to contamination.

2. Review of related literature

2.1 Water pollution

Water pollution is a worldwide problem affecting developed and developing countries in a similar way. Heavy metal contaminants are one prevalent type of water pollutant. They are persistent in the environment once discharged and removal from source water is necessary to ensure clean drinking water supply. The problem of heavy metal pollution arises from several sources. Heavy metal such as Zn can naturally exist in ground water; Lead can be present as result of lead solder piping. Mercury and Cadmium can be as result of power plant emission [9].

Additionally a variety of industrial processes can produce problematic heavy metal concentration in discharge water from factories that are harmful to human and can contaminate agricultural land. Although heavy metals are naturally occurring elements that are found throughout the Earth's crust, most environmental contamination and human exposure results from anthropogenic activities such as mining and smelting operations, industrial production ,domestic, agricultural use of metals and metal containing compounds [10].

The present use of metals in society has in many cases turned out to severely damage the environment. Toxic heavy metals most importantly Mercury, Lead and Cadmium constitute one major Category of environmental threats [10]. In most of this man made environment, there are places where those heavy metals are naturally so abundant that they reach toxic levels and the places themselves are dangerous for humans. Metals appear in several forms often with vastly different biological effects. Aquatic environment gets contaminated with a variety of pollutants generated from diverse sources (industries, agriculture and domestic). Among the pollutants heavy metals are the major cause of aquatic environment because of their toxicity, persistency and tendency to accumulate in organisms [11].

The contamination of river by heavy metal is serious problem worldwide in general and particularly in Ethiopia very problematic some of them like Cr, Cd and Pb are non-degradable and toxic. Heavy metals are essential to maintain various biochemical and physiological functions in living organisms when in very low concentrations; however they become harmful when they exceed certain threshold concentrations [8].

Heavy metals are relatively high density (specific gravity greater than about 5) or of high relative atomic weight especially these poisonous, such as, mercury or lead [10].The term heavy metal was in use as far back as 1817, at the time of elements divided into nonmetals, light metals heavy metals. “It is impossible to come up with consensus”. to concluded that any idea of defining “heavy metals” on the basis of density must be abandoned yielding nothing but confusion [12].

Water quality influences its suitability for a particular use, i.e. how well the quality fulfills the requirement of the user. Water quality deals with the physical, chemical and biological characteristics of water in relation to all other hydrological properties. For example, river water having good quality with sediment load can be applied for irrigation successfully but may be objectionable for municipal use without treatment. Similarly, snowmelt water is acceptable for municipal purpose and may not be applicable for industrial due to its corrosion potential. The characteristics of water quality have become important in water resources planning and development for drinking, industrial and irrigation purposes [13].

The agriculture success is highly dependable on the quality of water applied in an agriculture area. Due to the application of poor or hazardous quality water the agriculture land/soil is affected and damages the crop yield in several ways. The accumulation of salts in root zone, limited the availability of water and plant can take up lesser water which resulted in high plant stress and decreased crop yields. The presence of metals in irrigation water also has adverse effects on crop production. Also, high concentration of salts can change the plant nutrients balance in the soil meanwhile some salts are toxic to certain plants [13].

Water in agricultural activities is an important component that is supplied by a network of irrigation channels. Rivers, lakes, and spring water are sources of irrigation water that are facing pollution problems. Agricultural water sources may be of poor quality because of natural causes, contamination, or both. Rivers are polluted due to the discharge of untreated sewage and industrial effluents. The poor water quality of rivers and spring water has an effect on irrigation water quality. In the last century, surface water resources have been polluted to such levels that they could no longer be used in agricultural irrigation [14].

2.2 Toxicity of heavy metals

Most of the industries discharge their waste directly without any treatment into the stream, Lakes, Oceans as well as in the open land and contaminate the ground water. Environmental contamination and exposure to heavy metals such as mercury, cadmium and lead is a serious growing problem throughout the world. Human exposure to heavy metals has risen dramatically in the last 50 years as a result of an exponential increase in the use of heavy metals in industrial processes and products [15].

Heavy metals cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases death. Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to join disease such as rheumatoid arthritis and disease of the kidney, circulatory system, nervous system and damaging of the fetal brain. At higher doses heavy metal can cause irreversible brain damage. Children may receive higher doses metals from food than adults, since they consume more food from their body weight than adults [16].

The contamination of natural water is a worldwide distributed problem which deserves a large attention not only its environmental hazardous effects but also for the risks involved to human health as well as economic damage it produce [17]. Nowadays the environmental pollution with many pollutants such as heavy metals becomes one of the critical problems. Water, fruits vegetables and medical plants which are in touch with the pollution sources like air, soil and water are the most the subjected food for pollution with these pollutants, where the pollutants reaches these kind of food during growing, transportation, and viewing for sales in open places (public markets) [18].

It has been largely recognized that heavy metal concentration are much higher than in urban or industrial areas in natural environment. Consequently the possibility of heavy metal incorporation in drinking water or trophic webs exists, and so the potential generation of deleterious effects of human population. Toxicity also varies according to the environmental condition that controls the chemical speciation of metals.

The distribution of trace elements differs depending on hydrologic conditions, partly because of the dilution of upstream inputs during the flood periods through the process of precipitation, sedimentation and variety factors such as chemical reactivity, land use pattern and biological productivity. Some of heavy metals that are introduced in aquatic system are deposited in the sediment of aquatic plant and organisms [19]. Within the European community the 13 elements of the highest concern are As, Cd, Co, Cr, Cu, Hg, Mn, Pb, Tn, Th, the emission of which are regulated in waste incinerators some of these elements are actually necessary for humans in minute amount (Co, Cu, Cr, Ni, Mn) while others are carcinogenic or toxic [20].

2.3 The source of heavy metals

Since the beginning of industrialization, a great variety of anthropogenic chemical compounds have been synthesized for countless uses. The two main source of heavy metal in soil are natural and anthropogenic. The natural factors include soil erosion ,volcanic activities, urban runoffs aerosol particles while the anthropogenic factor include metal finishing and electroplating process, mining extraction operations, textile industries and nuclear power. Volcanic eruption produces hazardous impacts to the environment, climate and health of exposed individuals. The presence of these heavy metals in the soil and water bodies is known to significantly deteriorate the quality of such soil and water [21].

2.3.1 Cadmium

Cadmium distributed in the earth's crust in a very small amount. In the earth's crust, it is uniformly distribute but normally estimated to be present at an average concentration of between 0.15 and 0.2 mg/kg [22]. Food is the main source of cadmium intake for non-occupationally exposed people. Crops grown in polluted soil or irrigated with polluted water may contain increased concentrations, as may be meat from animals grazing on contaminated pastures [23].

Cadmium is considered one of the hazardous metals to human health. Cadmium acute exposures may lead to inflammation followed by cough, dryness and irritation of the nose and throat, headache, dizziness, chest pain, pneumonitis, and pulmonary edema. Long-term exposures to cadmium may turn carcinogen in humans, where normal epithelial cells transform to malignant cells inhibiting the biosynthesis of DNA, RNA, and proteins [24].

2.3.2 Chromium

Chromium (Cr) is a silvery white transition metal with atomic number of 24, relative atomic mass of 52.99 g/mol, and lies between iron and nickel. The main benefit of this chemical element is in alloys, forms inert protective oxide on the surface of oxidizing environment, at low concentration, Cr is involved in natural human lipid and in protein metabolism, so that very small amount of are needed for normal life function. Human exposure to sufficiently high chromium concentrations would result in potential harm through its toxic harm genotoxic and carcinogenic effects [25].

2.3.3 Copper

Copper is indeed an essential trace mineral that is vitally important for physical and mental health. But due to wide occurrence of copper in our food, hot water pipe, nutritional deficiencies table and birth control pills increase chance of copper toxicity. Copper is not poisonous in its metallic state but some of its salts are poisonous. Copper is a powerful inhibitor of enzymes. It is needed for a body for a number of enzymes but sometimes copper salts are poisonous for human organ system. Copper toxicity is increasingly becoming common these days. It is a condition in which an increase in the copper retention in the kidney occurs. Copper first start depositing in the liver and disrupts the liver's to ability detoxify elevated copper level in the blood thus adversely affect the nervous system, reproductive system, adrenal function, connective tissue, learning ability of new born baby etc [26].

2.3.4 Lead

Lead, a ubiquitous and versatile has been used since prehistoric times. It has become widely distributed and mobilized in the environment, and human exposure. At high level of human exposure there is damage to almost all organs and organ systems, most importantly the central nervous system, kidneys and blood system, male reproductive system, pregnancy, bone tissue heart, killing at excessive level [27].

2.3.5 Zinc

In the periodic table of the elements, zinc found in group IIB, together with the two toxic metals cadmium and mercury Compared to several other metal ions with similar chemical properties, zinc is relatively harmless. Only exposure to high doses has toxic effect. There are three major routes of entry for zinc into the human body; by inhalation, through the skin, or by ingestion. Each exposure type affects specific parts of the body. The most widely known effect of inhaling zinc-containing smoke is the so-called metal fume fever, which is mainly caused by inhalation of zinc oxide [28].

2.4 Some physicochemical parameters of water

Water quality influences its suitability for a particular use, i.e. how well the quality fulfills the requirement of the user. Water quality deals with the physical, chemical and biological characteristics of water in relation to all other hydrological properties. For example, river water having good quality with sediment load can be applied for irrigation successfully but may be objectionable for municipal use without treatment. Similarly, snowmelt water is acceptable for municipal purpose and may not be applicable for industrial due to its corrosion potential. The characteristics of water quality have become important in water resources planning and development for drinking, industrial and irrigation purposes [29].

The water quality used for irrigation is essential for the yield and quantity of crops, maintenance of soil productivity, and protection of the environment. For example, the physical and mechanical properties of the soil, ex. soil structure (stability of aggregates) and permeability are very sensitive to the type of exchangeable ions present in irrigation waters. The determination physicochemical parameters like electrical conductivity, pH and turbidity were important in the study [30].

2.4.1 pH of water

The pH is the concentration of hydrogen ions (H^+) and hydroxyl ions (OH^-) in the water. It is used to determine the acidic, basic or neutral behaviors of water. The pH values ranges from 1 to 14, which means, if pH of water is less than 7, then it is called acidic water whereas, pH equal to 7 as neutral and more than 7 is called the basic nature water. The pH of water and soil could not harm the plant growth directly. pH highly affects the efficiency of coagulation and flocculation process[30].

The main use of pH in a water analysis is for detecting abnormal water. The normal pH range for irrigation water is from 6.5 to 8.4. An abnormal value is a warning that the water needs further evaluation. Irrigation water with a pH outside the normal range may cause a nutritional imbalance or may contain a toxic ion [31]. The US EPA recommends the appropriate pH range to be 6.0–9.0, Israel 6.5–9.5, Italy 6.0–9.5, and Portugal 6.5–8.4. The MOE sets the pH standard for direct wastewater reuse as 5.8–8.5, the lower limit being somewhat low compared to the standards of other countries. Low pH values affect the mobility of heavy metals in the soil and can be absorbed by crops and contaminate water bodies [32].

Although pH usually has no direct impact on consumers, it is one of the most important operational water quality parameters. Careful attention to pH control is necessary at all stages of water treatment to ensure satisfactory water clarification and disinfection with chlorine, the pH should preferably be less than 8; however, lower-pH water (approximately pH 7 or less) is more likely to be corrosive. The pH of the water entering the distribution system must be controlled to minimize the corrosion of water mains and pipes in household water systems according to WHO.

2.4.2 Electrical conductivity (EC)

The electrical conductivity (EC) of water is defined as the capacity of water to transmit the electric current. It depends on the dissolved ions in the water and their charge and movement. Because it is a good solvent, water dissolved mineral salts in the form of ions, which hold the electric current due to ionic conduction. When the EC of water is high, it shows that there is high concentration of ions in the water.

The EC indicates the number of total solids in water and is dependent on the temperature of water. The electrical conductivity of water also affects the plant growth. The measurement of EC at 25 ^{o}C temperature is considered as reference [29]. Generally, if the EC of irrigation water is below 0.7 mS/cm, it does not affect crop growth; when above 3.0 mS/cm, it can cause severe damage. Israel and Italy aim for unrestricted irrigation and have EC standards for wastewater reuse of 1.4 and 3.0 mS/cm, respectively. Portugal has a fairly strict EC standard of 1.0 mS/cm. In South Korea, the MOE sets the EC standard for direct wastewater reuse differently for food crops and processed food crops; the standards are 0.7 and 2 mS/cm, respectively [32].

2.4.3 Turbidity

The amount of cloudiness in the water is known as turbidity which is caused by dissolved or total suspended solids and most of the time those are invisible to the naked eye as smoke in air. Turbidity, typically expressed as nephelometric turbidity units (NTU); it is important parameter to measure for water quality. Turbidity can be caused by i.e. Silt, sand and mud; Chemical precipitates [33]. Turbidity can interfere with disinfection and provide a medium for microbial growth. High turbidity may indicate the presence of disease causing organisms. These organisms include bacteria, viruses, and parasites that can cause symptoms such as nausea, cramps, diarrhea, and associated headaches [30].

A high level of turbidity can affect the performance of the irrigation facility, and can lower the hydraulic conductivity of the soil and in turn pollute the soil surface through surface flow. The standard for turbidity can be set up based on the turbidity’s influence on the irrigation facility performance, or vegetables which are vulnerable to germ infection. In the case of indirect wastewater reuse, a strict standard of 2 NTU can be applied for directly consumed crops, and, for indirectly consumed crops, a specific standard that can prevent the adverse effects is needed. Increasing turbidity reduces the clarity of water to transmitted light. Below4 NTU, turbidity can be detected only using instruments, but at 4 NTU and above, a milky-white, muddy, red-brown or black suspension can be visible [30].

3. Materials and methods

3.1 General description of the study area

Sebeta is a town located in the Oromia Special Zone Surrounding Finfinne of the Oromia Region. This town has latitude and longitude of 8°54′40″N 38°37′17″E and an elevation of 2,356 meters (7,730 feet) above sea level. The climate in Sebeta is warm and temperate. In winter, there is much less rainfall than in summer. The average annual temperature in Sebeta is 17.4 °C. The rainfall here averages 1073 mm [34].

Atebela river basin originated from South East Shoa zone at particular place Atebela kebele in Sebeta Awash woreda. It passes in to the West of Sebeta city, which extends to east Shoa zone inters to Awash River having an approximate total length of 65 km starting from its origin to the margin of East Shao. There are important tributaries joining from Sebeta City to Atebela River.

3.2 Sampling site selection

A preliminary survey of sampling stations was done carefully to select the appropriate sampling site during the month of September, 2019 and potential areas were identified. Based on these, four sampling sites were selected by considering the relative sources of pollution to the river. Site A was approximately 1.2 Km located out of the city up the stream and assumed as a control sample; at this point the river was relatively free from the waste disposal, because it was out of the City, and where less anthropogenic activities taking place; some of the residents use the water for house hold purposes. The land around the river is a farmland and partly covered with some indigenous trees and grasses. The sampling site B was located in the downstream of the first site at effluent entry point in the city. The site was where effluents discharged from different factories like alcoholic, textile, horticulture, tanning, domestic and sanitary waste materials of inhabitants of the community and municipal wastes mixed with Atebela River through canals. In this site, the water surface appears blackish during sampling time. The sampling site C was located out of the city at about 1000 m (1 Km) down the river from the discharge entry point (sample site B). The land around the river has covered with grasses, shrubs and eucalyptus trees. Agricultural activities are intense including river water abstraction for irrigation purpose. The land around the site is marshy.

The sampling site D was located out of the city down the stream from sample C. This site is rural area where great agricultural activities going on and the societies use the water for different purpose.

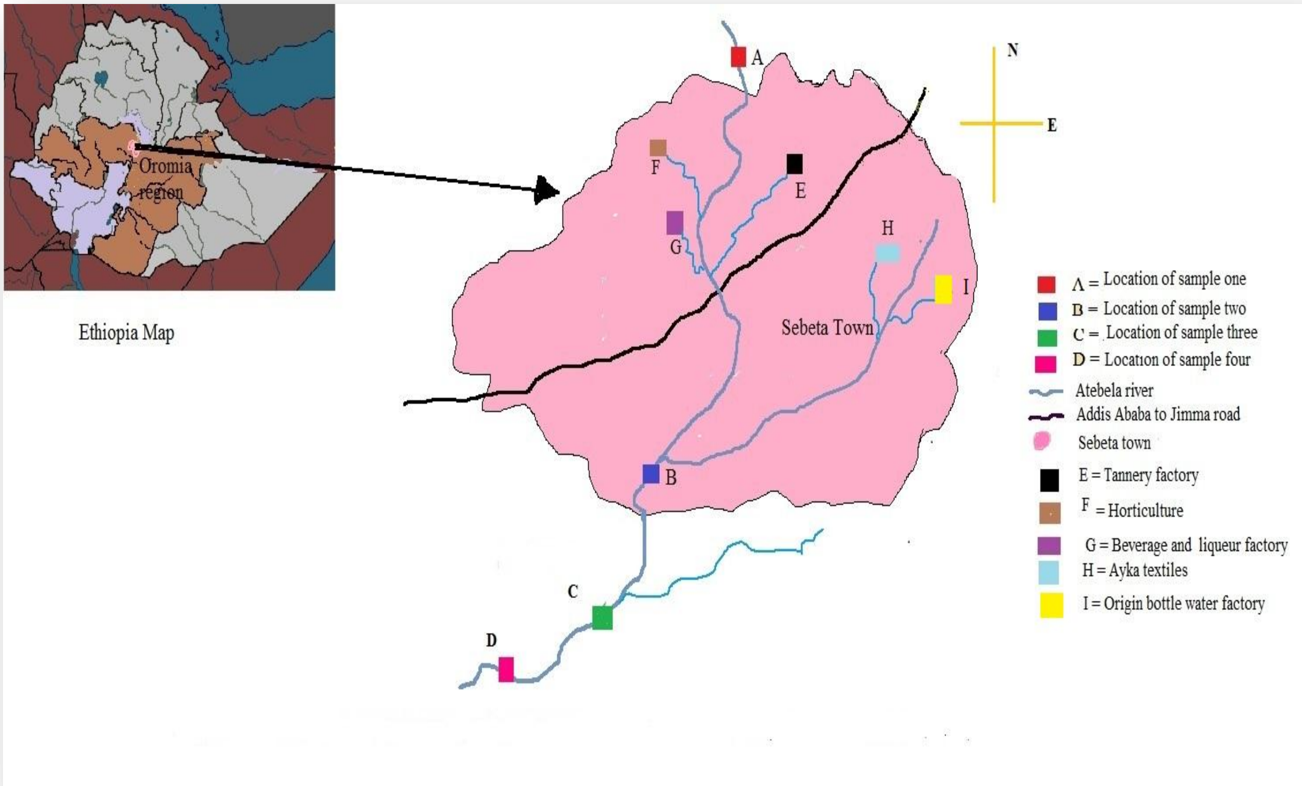

Figure 1: Map of Ethiopia showing the sampling sites of Atebela River, in Sebeta city Oromia, Ethiopia, Mokennen et.al (2007).

The above map shows the map of Ethiopia and Sebeta city the specific study area. It explains that Atebela River which found in Sebeta city was victims of many waste disposals from different industries such as Tannery, Horticulture, beverage and liqueur, Ayka Textiles and Origin water factory.

3.2.1 Chemicals, reagents and instruments

All chemicals, HNO_3, HCl, (Pentokeyorgany, India LTD), standard solutions of each metal (Cd, Cr, Cu, Pb, and Zn) and reagent were purchased (Merck KGaA 64271 Darmstadt, Germany) in the form of standard solution. Reagents; HNO_3 and, HCl and solvents used were reagent grade. De-ionized water was used during the study. The polyethylene containers cleaned by de-ionized water prior to use. Heavy metals analysis was carried out using Atomic absorption Spectroscopy (AAS) (Jena, Germany). Atomic absorption spectrometry is very common and reliable technique for detecting metals and metalloids in environmental samples. For the physiochemical; turbidity meter was used for measuring turbidity, Bante portable multi parameter (900 P) was used for measuring electrical conductivity and pH.

3.2.2 Sampling techniques

Four representative River water samples were collected using purposive sampling method by looking particularly points of possible contamination and the sites were chosen based on locations of industries, agricultural activities, population density from the Atebela River, before the water inters the city, in between the City , and from two points after the water pass from the City. Triplicate water sample from each site was taken using polyethylene plastic bottle, equal portion of the water sample were added to make as composite and homogenized sample according to literature [35].

3.2.3 Pretreatment of the samples

The sampling bottles were soaked in 10% HNO_3 for 24 hrs and rinsed several times with double distilled water (DW) prior to use. Samples were preserved with the addition of ultrapure HNO_3 (up to pH less than 2) to prevent precipitation of metal hydroxide or adsorption of metal ions on the wall of the container. Water samples (1000 mL) were collected and immediately acidified with pure nitric acid (0.5 mL HNO_3 + 100 mL DW). The samples thus were refrigerated and preserved at 4 ℃ in sampling kits to minimize microbial activity. In the lab water samples were filter through whattman no 42 µm filter paper to remove particulate matter [17].

3.2.4 Sample digestion procedure

100 mL from each acid preserved water sample was taken in separate 250 mL Erlenmeyer flasks and mixed with a 2 mL (69% -71%), mixture of $HNO_{3,}$ and 1.0 mL of HCl (37%) solution. The samples were heated on hot plate under a fume hood to not more than 85℃. After the digestion has completed, these samples was evaporated on to the lowest possible volume (about 20 mL). The flasks were covered with a watch glass to prevent sample contamination from the fume hood environment. And then the digested samples were cooled and filtered using whattman number 42 µm filter paper into 50 mL volumetric flasks and diluted to the mark with distilled water. A blank solution was similarly prepared. Three replicate measurements were carried out on each sample [30].The digested samples have preserved in refrigerator for analysis. These solutions have then used for the elemental analysis in Arba Minch University.

3.3 Method validation

The results were validated by the following criteria

3.3.1 Linearity

Using calibration curves, y = ax + b, the unknown concentration the largest analytes from water samples were determined. The linearity of the calibration curve was considered acceptable when the correlation factor R > 0.995 [36].

3.3.2 Recovery test

The efficiency and accuracy of the method was evaluated by analyzing the digests of spiked sample, which was taken from stock solution of each metal an spike in 250 mL Erlenmeyer flask containing 1 mL sample [37].

$$\%\text{Recovery} = \frac{\text{amount after spiked} - \text{amount before spiked}}{\text{amountadded}} \text{x}100 \text{ [38]}$$

Table1: Recovery test of the selected samples

No	Element	sample type	Amount added (mg/L)	amount after spiked (mg/L)	amount before spiked	Percentage recovery
1	Cd	2	1.5	1.375	0	91.7%
		4	1.5	1.21	0	80.10%
2	Cr	2	1.5	1.77	0	118%
		4	1.5	1.502	0	100 %
3	Cu	2	1.5	1.53	0.088	96.10%
		4	1.5	1.33	0.08	83.30%
4	Pb	2	1.5	1.78	0	118.60%
		4	1.5	1.595	0	106.3%
5	Zn	2	1.5	1.73	0.062	111.20%
		4	1.5	1.26	0.05	80.10%

Sample type 2 = sample site two (B), Sample type 4 = sample site four (D)

3.3.3 The efficiency and accuracy of the method

Recovery testes**:** The accuracy of the analytical method has been evaluated in terms of percent recovery equations. The percent calculated values have given in Table1. The recovery was within the standard / required limit; ranged from 80-120%. Recovery values in the above range are acceptable for environmental investigations. To obtain the recoveries of the sample selectively sample four and two were spiked. The table shows all the recovery results lie with the acceptable range (80-120%) in between 80.1% to 118.6 %. Thus, good recoveries were obtained for all metals validating that the optimized procedure has had good accuracy [34].

3.3.4 Precision

"Precision" is a measure of the confidence you can have in your measured results, the lower percent of the Relative Standard Deviation (RSD) of the results, the higher the confidence[39].The relative standard deviation (RSD) = $\frac{100X\sigma}{\bar{X}}$ where $\bar{X}$ is the mean value measured result and σ is standard deviation of sample. Thus, the relative standard deviation was calculated to know the precision [40].

3.3.5 Statistical analysis

The data were analyzed by one way analysis of variance (ANOVA) for comparison using SPSS. Least significant level (LSD) test was used for means of comparison. The level significance for means comparison $p < 0.05$ was considered**.** The level of significance for means comparison for copper was $p < 0.05$, the sample means is significant. The level of significance of means comparison for turbidity, pH and Electrical conductivity was $p < 0.05$; significant variation was observed on the physicochemical parameters of the water samples that collected from different sites.

3.3.6 Determination of cadmium, chromium, copper, lead, zinc, using FAAS

FAAS instrument Analytik Jena® ContrAA 300 was operated under the following flame parameters: burner gas: C_2H_2/ air, and burner height: 6 mm. Acetylene output pressure was adjusted at 80-100 kPa while air pressure was set at 300-600 kPa. Ten milliliters sample solution was then introduced to the sample tube and analyzed.

3.3.7 Method detection limit and limit of quantification

Method validation was assessed by determining several analytical data namely linearity, percentage recovery, precision sensitivity which is expressed by determination of limit of detection (LOD) and limit of quantification, and accuracy. The method detection limits and limits quantification of each element in four samples sites in Atebela River was given in (Table 2). LOD was calculated as the mean concentration of the blank plus three times standard deviation of the blank. LOQ was calculated as the mean concentration of the blank plus ten times standard deviation of the blank [41].

$LOD = x_b + 3S_b$ & $LOQ = x_b + 10S_b$ Where, Xb is the mean conc. of the blank and S_b is the standard deviation of the blank. For more accurate analysis the values of x_b and s_b are obtained from a regression line equation. i.e., assume the equation. $y = bx + a$, $a = x_b$ Where '$s_{y/x}$' residual standard deviation & 'a' is y-intercept, $S_b = s_{y/x}$ [42]

$$S_{y/x} = \sqrt{\frac{\sum_i (y-\hat{Y})^2}{n-2}} \qquad [43]$$

Table 2: Limit of detection and Limit of quantification in Atebela River at four Sample sites (n=4).

Metals	Limit of detection (mg/L)	Limit of quantification (mg/L)
Cd	0.061	0.1221
Cr	0.0079	0.020
Cu	0.016	0.043
Pb	0.002	0.008
Zn	0.013	0.023

3.4. Preparation of standard solution

The working standard solutions containing 1000 mg/L of Pb, Cd, Cu, Cr and Zn were purchased. Working standards for all the metals were prepared from the stock solutions by serial dilutions in distilled water and the correlation coefficient (R^2) obtained from calibration curves were drown. The validity of the developed method was evaluated by establishing analytical figures for determination of Cd, Cr, Cu, Pb, and Zn in Atebela River.

4. Results and discussion

Selected heavy metal concentrations of the Atebela River were presented in Table3.Comparison of the analyzed heavy metals with international standard was also indicated.

Table 3: The concentration of selected heavy metals (Cd, Cu, Pb, Zn, and Cr), in Atebela River at different sampling sites.

No	Parameters	($\bar{X} \pm$ SD) mg/L	For irrigation FAO Recommended max. limit (mg/L)
1	Cd		
	A	BDL	
	B	BDL	0.01
	C	BDL	
	D	BDL	
2	Cr		
	A	BDL	
	B	BDL	
	C	BDL	0.1
	D	BDL	
3	Cu		
	A	0.072 ± 0.004	
	B	0.088 ± 0.01	0.2
	C	0.069 ± 0.005	
	D	0.080 ± 0.005	
4	Pb		
	A	BDL	
	B	BDL	5
	C	BDL	
	D	BDL	
5	Zn		
	A	0.037 ± 0.003	
	B	0.062 ± 0.003	
	C	0.048 ± 0.003	2
	D	0.05 ± 0.003	

BDL = below detection limit, A=Site one, B = Site two, C = Site three, D = Site four, $\bar{X}$ = Mean, SD = Standard deviation

4.1. Selected Heavy metal concentration in Atebela River

Heavy metals Cd, Cr, Cu, Pb, and Zn were analyzed for total content. The level of heavy metals significantly varies in Atebela River in four sampling sites which is presented in (Table 3). The concentration Cd, Cr, and Pb found in the upstream cross section was not generally detected but The mean concentration of copper in Atebela River in each sites was in the order of B > D > A > C. The mean concentration of Cu at point A (before water entering Sebeta City) was 0.072 mg/L, the mean concentration of Cu at point B (in the middle of the City) was 0.088 mg/L, the concentration of Cu at point C (after the water pass out from the City) 0.069 mg/L, the concentration of Cu at point D which was 1000 m from point C (after the water Pass from the City) was 0.080 mg/L.

The result shown that there was an increment in concentration of Cu at the middle than at point A, this could be due to the increment of the level of Cu at point could be from chemical weathering, steel production, electrical industry, and sewer sludge or could be the case that the soil contents of heavy metals [44]. Point C is the lowest of all concentration which was 0.069 mg/L. The fractions of heavy metals in the water vary with the origin of the metals, availability, their forms of occurrence and mobility. It is usually determined based on the relative amount of the metal in water soluble, exchangeable as well as bound to carbonates fraction [45].On the upper steam point A the total metals may be the water soluble, exchangeable, and bound to carbonates or reducible form this might be the reason for increment at site A, B and D. The reason for decreasing of concentration C the existence of copper might be in silicate and sandy form which cannot be easily soluble and analyzed. Another reason might be due to dilution of the river from different tributaries. This regression model found that main drivers of high copper concentrations are also high clay content, high pH and heavy summer rainfall. The influence of geology is limited to certain parent materials such as tephra and acidic volcanic rocks (high copper concentration) while sedimentary rocks and fluvial deposits have lower copper levels [46]. Therefore the location of sample site C might be sedimentary rock.

The mean concentration of Zinc in Atebela River in each sites in the order of B > D > C > A. The concentration of Zn at point A (before water entering Sebeta City) was 0.037 mg/L, the mean concentration of Zn at point B (in the middle of the City) was 0.062 mg/L, the concentration of Zn at point C (after the water pass out from the City) 0.048 mg/L, the concentration of Zn at point D which was 1000 m from point C (after the water Pass from the City) was 0.050 mg/L.

The result shown that there was an increment in concentration of Zn at the middle than at point A; this was because the increment of the level of Zn at point B from wastes. Due to diffusion, heavy metal abundant waste and tailings penetrate into the river, becoming pollution sources [47]. Other cause for increment of zinc at site B, C and D, zinc is common industrial metal. Owing to its relatively high mobility, it is likely that anthropogenic inputs will be important close to urban areas and land fill sites. A potential source of zinc is the metal fittings on pumps and pipe work making it difficult to discount on anthropogenic origin in pumped ground water. The commonest ways of domestic sources for zinc to inter small water supply systems is via dissolution from pluming fitting or pipes. Many fittings contain brass and galvanized steel water pipes are common, these will readily leach zinc metal **[**48]**.** Even though the study reveals that there is an increment of zinc at site C, B, and D compared with site A in Atebela River the concentration is lesser extents in the samples when compared to WHO and FAO standard. The results demonstrate there is no risk irrigating the farm land with Atebela River. The accumulation zinc heavy metal was substantially lower values and considered safe for irrigating purpose.

4.1.2 Cadmium in Atebela River

Cadmium in Atebela River was not detected. It is a naturally occurring toxic metal with common exposure in industrial workplaces, plant soils, and from smoking. Due to its low permissible exposure in humans, overexposure may occur even in situations where trace quantities of cadmium are found [49]. The recommended maximum concentration of cadmium elements is 0.01mg/L.

4.1.3 Copper in Atebela River

Copper is a metal that is naturally present in the environment, but the level of contamination can be increased around, near smelting facilities, phosphate fertilizer plants. There are also significant amount of copper released from waste water treatment plants, which could lead to problems downstream for a community that uses this river as their source of irrigation purpose [26]. The world health organization has established a 2.0 mg/L of copper as maximum permissible guidance for drinking water supply. But FAO has established the maximum concentration limit for irrigation 0.2 mg/L because Toxic to a number of plants at 0.1 to 1.0 mg/L in nutrient solutions [49].

The most common health effects of the excessive consumption of copper bearing would be: nausea, vomiting, diarrhea, upset stomach, and dizziness [25]. If extreme intake of copper occurs, kidney and liver damage is also possible. Accordingly the laboratory result of the study shown in table 3 was less than the maximum permissible limit guidance level i.e. 2 mg/L which is set by WHO and 0.2 mg/L of copper as the standard level, which set by FAO, at all points of the sample location. Therefore there in no health effects regarding to this parameters upon usage for irrigation.

4.1.4 Chromium in Atebela River

Natural occurrence of chromium is in ore, but chromium arises in surface water discharges from electroplating, tanning, textiles, paint and dyeing of plants [50]. Regards to health significance, chromium is toxic, to a degree which varies with the form it occurs, the element is essential nutritional requirement in limited amounts and its deficiency can lead to glucose metabolism. Certainly, it has been reported that chromium deficiency is greater nutritional concern than over exposure. However, it is considered that the element is carcinogenic at high concentrations. The result of watering in chromium contaminated water might be death of livestock. According to the world guidance level WHO, the maximum permissible limit for drinking water supply is 0.05 mg/L of Chromium. The permissible limit of chromium metal by Agricultural food organization (FAO) for irrigation purpose is 0.1 mg/L [49].

Therefore, as the laboratory results of the study were shown no chromium detected in all sample locations. This result indicates that there is no health effect on the users. First it were suspected that the chromium was to be found that there is a tannery which were releasing effluents directly to Atebela River, but now the study result shown as no chromium was detected, his is due the fact that the government decided to close the tannery in 2011 E.C because of the public compliance.

4.1.5 Zinc in Atebela River

Zinc is one of the important trace elements that play a vital role in physiological and metabolic process of many organisms. Nevertheless higher concentration of zinc can be toxic to the organisms. it plays an important role in protein synthesis is a metal which shows fairly low concentration in surface water due to its restricted mobility from the place of rock weathering or from the natural sources [51]. Zinc is an essential trace element found in virtually all food and potable water in the form of salts or organic complexes. The diet is normally the principal source of zinc. Although levels of zinc in surface water and groundwater normally do not exceed 0.01 and 0.05 mg/L, respectively.

The derivation of a formal guideline value is not required at this time. However, water containing zinc at levels above 3 mg/L may not be acceptable to consumers according to WHO. The Mean concentration of zinc in Atebela River was 0.049 ± 0.003 mg/L. The permissible limit of zinc in water according to WHO standard is shouldn't be greater than 3 mg/L. In all the four sample sites concentration Zinc was recorded below the permissible limit.

4.1. 6 Lead in Atebela River

Lead is a heavy metal of anthropogenic origin. Lead is a pollutant that accumulates in soils, sediments, and water and extremely persistent in the environment. Lead has no biological function and it is toxic to living organisms even at low concentration. Although lead is not an essential element, some plant species proliferate in lead contaminated area and accumulate different parts of the plants [52].According to the world guidance level WHO, the maximum permissible limit for drinking water supply is 0.01 mg/L for lead. The permissible limit of Lead metal by Agricultural food organization (FAO) for irrigation purpose is 5 mg/L [48].Therefore, as the laboratory results of the study were shown no Lead detected in all sample locations. This result indicates that there is no health effect on the users.

4.2 Heavy metals in irrigation water

The mean concentration of selected heavy metals in irrigation water samples collected from four sampling sites of Atebela River, Sebeta, Ethiopia, the metal concentration were far below the recommended maximum limit for irrigation water set by FAO [53]. The mean concentration of Copper, and zinc were 0.077 ± 0.003 mg/L, and 0.049 ± 0.006 mg/L respectively. This was below the recommended maximum limit for irrigation. The concentration of three elements Cd, Cr, and Pb were undetected, Even though as consequence of some number industrial activities low level of metals in irrigation water samples were recorded. This is due to the dilution of the waste water within the Atebela River.

Similar findings stated that the minimum level of lead was detected in sampling sites that are found in the upper catchment, sites such as Burayu Gefersa, Tinzizwonze around France embassy and Yeka Abado [3]. And reported that the level of Pb, Cd and Cr around Burayu area were below the detection limit, whereas the current investigation has shown 1-3-fold higher concentration of lead, however the value is within the standard limit.

The majority of the heavy metals that enter the river systems are removed from the liquid phase within a few minutes, mainly through precipitation and adsorption. This reveals that sediment pollution with heavy metals is mainly affected by nearby land use systems. The Wonji area has gentle slopes, slow water flow, and high sedimentation, which might have contributed to the high concentrations of metallic contaminants. EF values of Zn for all sampling sites ranged between moderate and significant enrichment levels. Many of the sites with significant Zn enrichment were in rural areas where floriculture farms and cereal crop agriculture are dominant. Therefore, runoff from agriculture fields (artificial fertilizers, pesticides, and animal manure) could be the major source of Zn [54].

4.3 Physiochemical analysis

The measurement of physicochemical parameters; electrical conductivity, pH and turbidity were carried out off the site. Turbidity of water samples were measured by international portable turbidity meter (model wag- WT 3020) by using replicate measurements. For its analysis the instruments were calibrated at standards of 0, 10,500 which is recommended by manufacturers'. 250 mL of water sample was added to 500 mL of beaker. Electrical conductivity and pH, measuring instruments; Bante portable multi parameter (model 900P) water quality meter were calibrated by dipping in water samples until the stable measurements value were observed.

Table 4: Showing the triplicate measurements of the physicochemical parameters

			For irrigation		
Parameters	**The sample site**	**Values**	**FAO**	**WHO**	**US-EPA**
Turbidity in (NTU)		Mean ± SD	-	-	Food crops < 2 For processed crops < 5
	A	15.78 ± 0.23			
	B	50.33 ± 0.58			
	C	31.66 ± 0.57			
	D	33.05 ± 0.21			
pH			6.5- 8.4	6.5- 8.5	6.0-9.0
	A	7.45 ± 0.23			
	B	6.67 ± 0.01			
	C	7.04 ± 0.11			
	D	7.06 ± 0.12			
Electrical Conductivity in (mS/cm)					
	A	0.162 ± 0.026			
	B	0.945 ± 0.02	< 1.5	-	-
	C	0.820 ± 0.00			
	D	0.830 ± 0.01	1.5- 2.7	-	-
			> 2.7	-	-

NB: Samples for physicochemical analysis were collected in January, 2020.

4.3.1Turbidity

A high level of turbidity can affect the performance of the irrigation facility, and can lower the hydraulic conductivity of the soil and in turn pollute the soil surface through surface flow. The World Health Organization; WHO establishes that the turbidity of drinking water shouldn't be more than 5 NTU, and should ideally be below 1 NTU but didn’t establish standard for irrigation purpose. For food crops irrigation turbidity should be ≤ 2 NTU in average and for processed crops < 5 NTU [32]. In the case of indirect wastewater reuse, a strict standard of 2 NTU can be applied for directly consumed crops, and, for indirectly consumed crops, a specific standard that can prevent the adverse effects is needed [32]. According the result obtained on the Table 4 above the turbidity results were ranged from 15.78 ± 0.23 NTU to 50.33 ± 0.58 NTU the increment of turbidity at point B, C and D relative A due to may be waste disposal, chemical (heavy metal) precipitate from the city, which shows that the water was very turbid, And undesirable for neither dinking nor irrigation purpose with regard to this parameter.

4.3.2 pH

The US EPA recommends the appropriate pH range to be 6.0–9.0 for agricultural purposes and the MOE sets the pH standard for direct waste water reuse 5.8-8.5 [29]**.**The WHO and FAO organization recommend the permissible limit of pH to be 6.5- 8.5 and 6.5-8.4 respectively [32].At the sites A, B, C and D of the Atebela river pH recorded were 7.45 ± 0.23, 6.67 ± 0.01, 7.04 ± 0.11 and 7.06 ± 0.12, respectively. Therefore the results of the study shows that pH ranged from 6.67 ± 0.01 to 7.45 ± 0.23 which is within acceptable range of pH. Thus the pH of the river is within normal range.

4.3.3 Electrical conductivity (EC)

Electrical conductivity (EC) which is a measure of water's ability to conduct an electric current is related to the amount of dissolved minerals in water, but it does not give an indication of which element is present but higher value of EC is a good indicator of the presence of contaminants such as sodium, potassium, chloride or sulphate**.** The conductivity values had a significant positive relationship with all heavy metals [34, 55].

At site A, B, C, and D the electrical conductivity recorded to be 0.162 ± 0.026 mS/cm, 0.945 ± 0.02 mS/cm, 0.820 ± 0.00 mS/cm and 0.830 ± 0.01 mS/cm respectively. It signifies the amount of total dissolved salts. Thus increasing of conductivity values at point B, C and D relative control sample A, may indicate that the presence of heavy metal ions. Permissible limits of electrical conductivity for classes of irrigation water are in the range 1.5 mS/cm to 2.7 mS/cm [56].

FAO permissible limit for irrigation of electrical conductivity less than 1.5 m S/cm none harm the crops, 1.5 mS/cm to 2.7 mS/cm moderately harm, the crops above 2.7 mS/cm severely harm the plant (Electrical conductivity less 1.5 mS/cm can directly applied for irrigation, 1.5 mS/cm to 2.7 mS/cm is usable after dilution and greater than 2.7 mS/cm is harmful for irrigation) according to FAO. The recorded EC values for the studied sites were ranged from 0.162 ± 0.026 mS/cm to 0.945 ± 0.02 mS/cm lower than the permissible limit which is set by FAO for irrigation purposes at point B, C and D, and therefore with regard to electrical conductivity cannot harm the plants. Thus, the result indicated that the river receive high amount of dissolved inorganic substances in ionized form from their surface catchments. The lower the EC, water is available to plants [57].

5. Conclusion

The findings of Atebela River revealed that, the concentration Cd, Cr, and Pb found in the upstream cross section was not generally detected, but for Cu and Zn the concentration varies with small quantity at each sampling site. The mean concentration of copper in Atebela River in each sites was in the order of B > D >A > C and the mean concentration of zinc in Atebela River was in the order of B > D >C > A. Even though the study reveals that there is an increment of zinc and Cu relative to control sample A at site C, B, and D in Atebela River, the concentration is lesser extents in the samples when compared with WHO and FAO standards. Results of turbidity obtained were 0.162 ± 0.026 NTU, 50.33 ± 0.58NTU, 31.66 ± 0.57 NTU, and 33.05 ± 0.21NTU at sites A, B, C, and D, respectively. The pH was ranged from 6.67 ± 0.01 to 7.45 ± 0.23; the electrical conductivity ranged from 0.162 ± 0.026 mS/cm to 0.945 ± 0.02 mS/cm. The control sample A was lower than the rest of the result which indicate there were factors contribute to increments these physicochemical (electrical conductivity and turbidity) parameters at point B, C, D. Wastes and effluent from the city were the cause for the increments of physicochemical parameters at these points.

5.1 Recommendation

Atebela River was found to be not under high impact with respect to studied heavy metals. Since, the river water is used for a variety of purposes such as irrigation, cattle drinking and domestic purposes; it is advisable to further study with seasonal variation data to confirm the safety of the water for the intended use. In fact, the physiochemical parameters analysis indicated the river is not to the standard for drinking considering the dry season information of the Atebela River.

6. References

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6.1 Appendix

6.1.1 List of Figures

Figure 2:

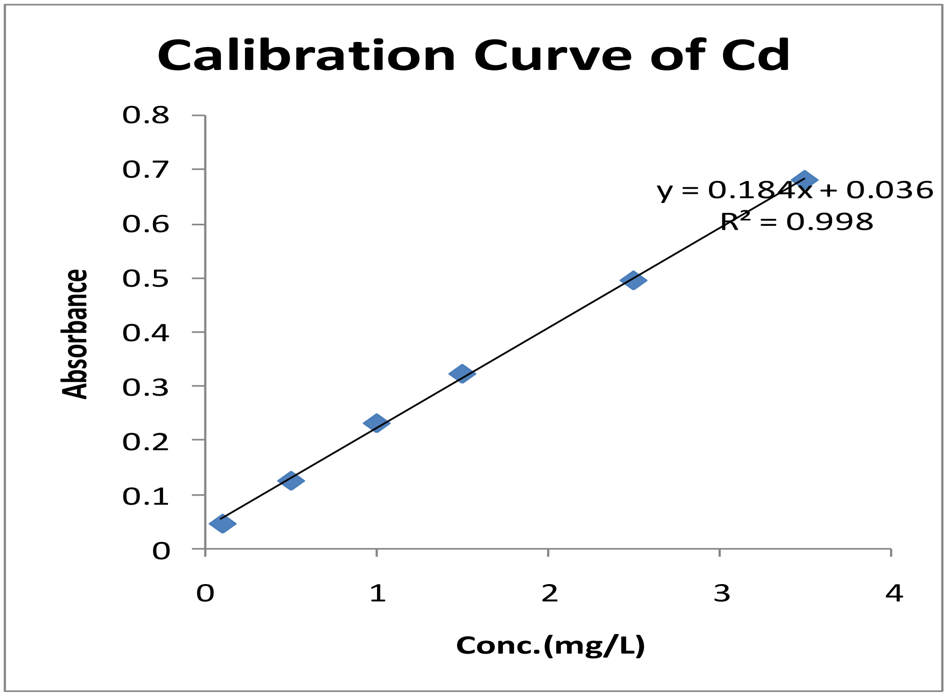

Figure 3:

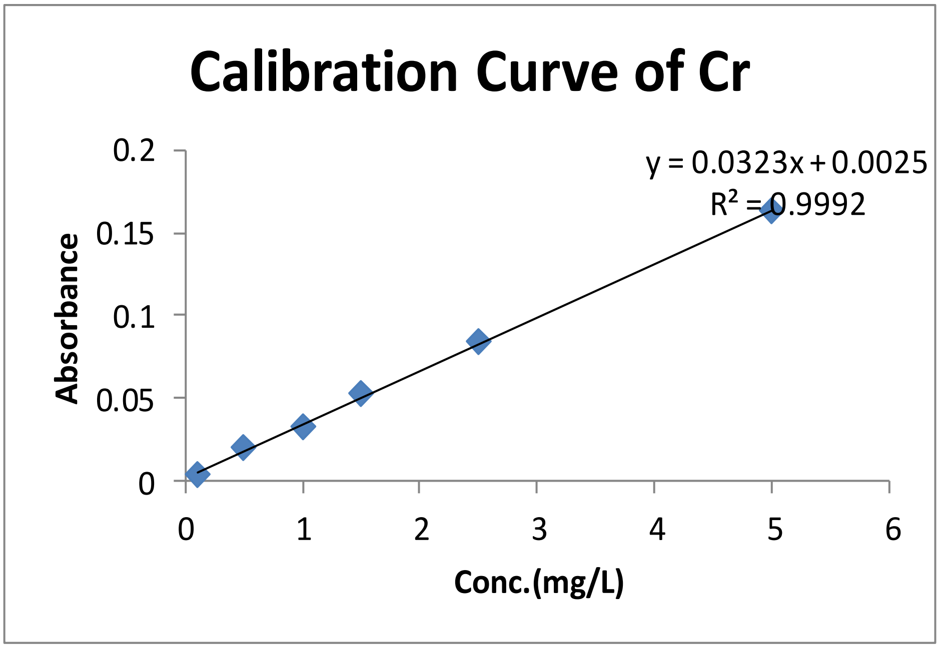

Figure 4:

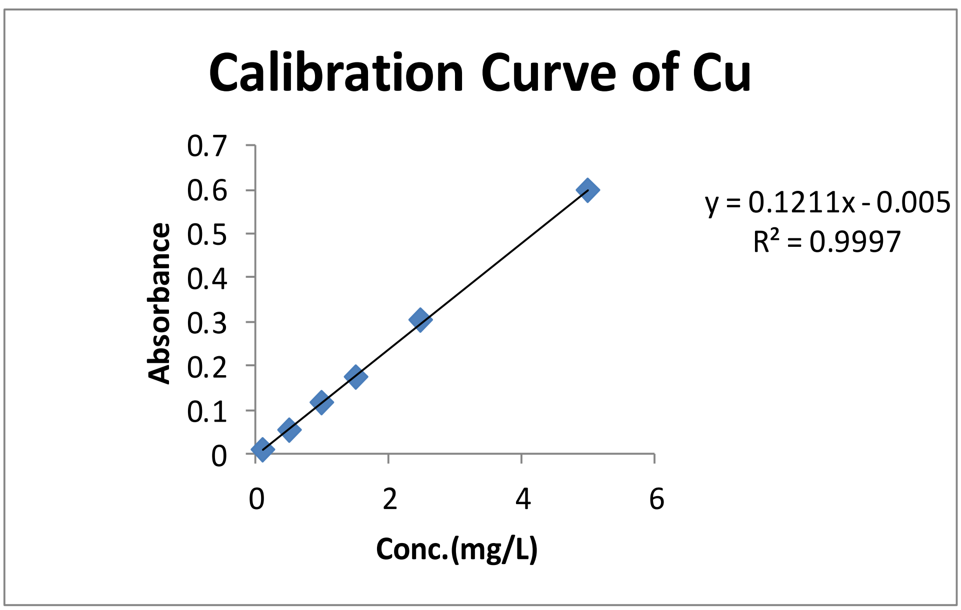

Figure 5:

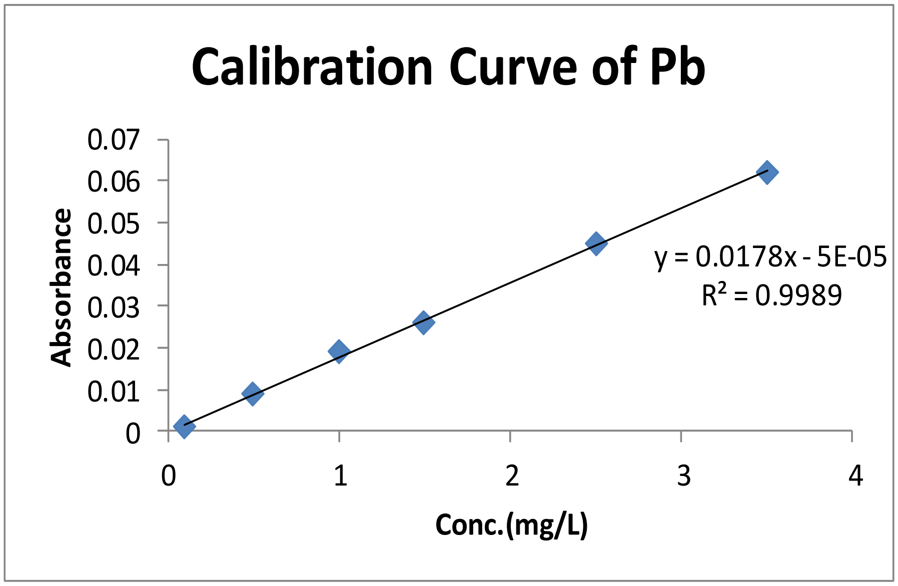

Figure 6:

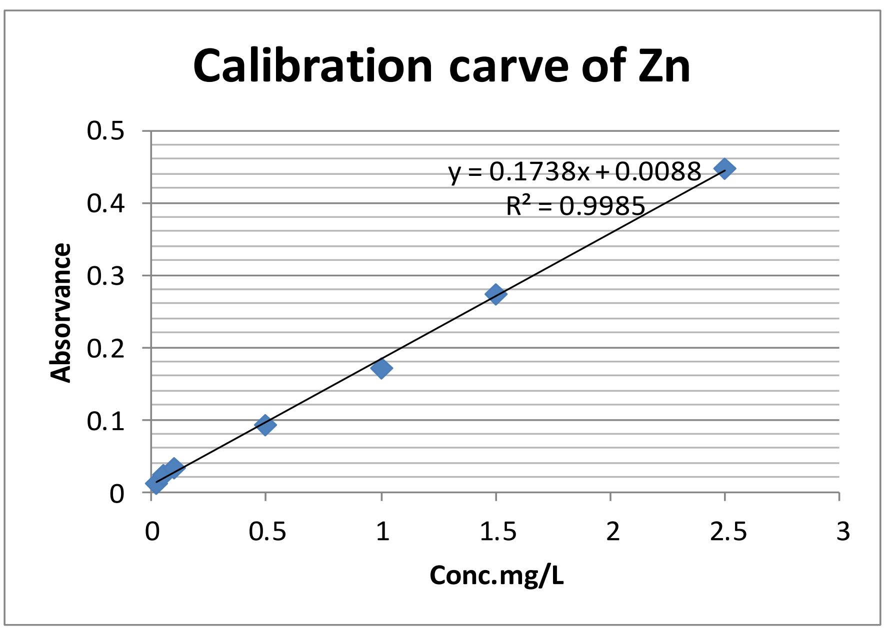

Table 5: Linear equations and correlation coefficients of the calibration curves for the respective metal's

Metals analyzed	Correlation coefficients(R^2)	Wave length (nm)	Regression equation
Cd	0.998	228.9	y=0.184 + 0.036
Cr	0.999	357.9	y=0.032x + 0.002
Cu	0.999	324.7	y=0.121x-0.005
Pb	0.998	283.2	y=0.017x-0.00005
Zn	0.998	213	y=x0.173x- 0.008

Table 6: mean comparison of copper

ANOVA: one side

SUMMARY

Groups	Count	Sum	Average	Variance
Column 1	3	0.22	0.073	1.3E-06
Column 2	3	0.265	0.088	8.5E-05
Column 3	3	0.206	0.069	2.1E-05
Column 4	3	0.24	0.08	0.000

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.001	3	0.000	6.5	0.02	4.07
Within Groups	0.000	8	3.38e-05			
Total	0.001	11				

Figure 7: positions of samples sites

** collected in September 2019**

Table 7: ANOVA: one sided for Turbidity

SUMMARY

Groups	Count	Sum	Average	Variance
Column 1	3	47.4	15.8	0.05
Column 2	3	151	50.3	0.33
Column 3	3	94.97	31.7	0.32
Column 4	3	99.14	33.05	0.05

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1794.95	3	598.32	3156.79	1.2E-12	4.07
Within Groups	1.52	8	0.19			
Total	1796.5	11				

Table 8: ANOVA: one sided For Ph

SUMMARY

Groups	Count	Sum	Average	Variance
Column 1	3	22.3	7.45	0.05
Column 2	3	20	6.67	3.3E-05
Column 3	3	21.1	7.04	0.01
Column 4	3	21.2	7.06	0.01

ANOVA

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	0.91	3	0.30	15.7	0.001	4.07
Within Groups	0.16	8	0.02			
Total	1.07	11				

Table 9:ANOVA: one sided for Electrical conductivity

SUMMARY				
Groups	**Count**	**Sum**	**Average**	**Variance**
Column 1	3	0.482	0.16	0.0007
Column 2	3	2.835	0.945	0.0002
Column 3	3	2.461	0.820333	1.3E-06
Column 4	3	2.489	0.829667	0.0002

ANOVA						
Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	1.15	3	0.38	1301.6	4.30E-11	4.07
Within Groups	0.002	8	0.0003			
Total	1.15	11				

Figure 8: Bante portable multi parameter and a turbidity meter

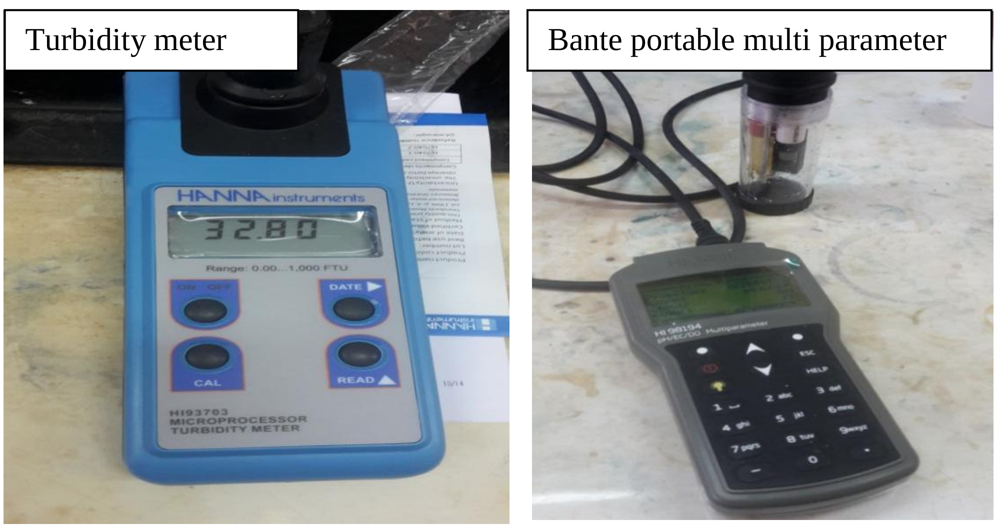

Figure 9: Quick calibration solution Bante portable multi parameter