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COLLAGE OF NATURAL AND COMPUTATIONAL SCIENCES
DEPARTMENT OF CHEMISTRY

A

M.Sc. THESIS ON

Investigation of the Level of Selected Physicochemical Parameters and Heavy Metals on Ketar River Water in Ziway Dugda Woreda, East Arsi Zone ,Oromia Region, Ethiopia.

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DECLARATION

This is to certify that the thesis prepared by Teshome Lemma entitled*:* Investigation of The Selected Physicochemical Parameters and Concentration of Some Heavy Metals on Ketar River Water in Sheled kebele, Ziway Dugda Woreda, East Arsi Zone, Oromia Region, Ethiopia is my original work and has not been presented for any other award, and that all sources of materials used in this thesis are duly acknowledged. This thesis was carried out under the advisor of Hulugirgesh Degefu (Ph.D.), Department of Chemistry, College of Natural and Computational Sciences, Debre Berhan University in the academic year of 2019-2021.

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APPROVAL ON

Investigation of the Selected Physicochemical Parameters and Heavy Metals on Ketar River Water in Ziway Dugda Woreda,East Arsi Zone, Oromia Region, Ethiopia.

BY

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A thesis submitted in partial fulfillment of the requirement for the degree of masters in Chemistry.

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LIST OF ACRONYMS

ANOVA	Analysis of Variance
APHA	American people health association
EC	Electrical Conductivity
DNA	Deoxyribo Nucleic Acid
EPA	Environmental Protection Agency
ICPOES	Inductively Coupled Plasma Optical Emission Spectrometry
LOQ	Limit of Quantization
LSD	Least Significant Difference
MDL	Method Detection Limit
Ppm	parts per million
RSD	Relative Standard Deviation
RNA	Rib Nucleic Acid
SD	Standard Deviation
SPSS	Statistical Package for Social Science
TDS	Total Dissolved Solids
TH	Total Hardness
UNESCO	United Station Environmental Science and Cultural Organization
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

ABSTRACT

Water is the most important in shaping the environment and regulating the climate. Water bodies are used for drinking and other purposes. However, they are easily polluted by different chemicals such as pesticides, herbicides, fertilizers that are used to grow crops, wastewater that flows from villages, town and factories. Due to this reason, the pollution of water bodies deteriorates from time to time. The quality of water is described according to its physical, chemical and biological characteristics. The main objective of this study was to examine the levels of selected physicochemical properties and heavy metals content of Ketar River water. In the study, three sampling sites along the river course have chosen based on the objectives of the study. After processed with acid digestion methods for heavy metals determination, the physicochemical parameters were analysed using standard analytical methodologies and selected heavy metals using inductively coupled plasma/optical emission spectroscopy (ICP/OES). The accuracy and precision of the optimized procedure was evaluated by analyzing the digest of the spiked samples and the percentage recoveries obtained varied from 87.70 to 101.8%. The levels of physicochemical parameters and heavy metals determined in mg/L were in the ranges TH (32.50 ± 0.67 - 35.00 ± 0.67), TDS (242.77 ±1.71 -445.46 ± 2.28), Cl^- *(0.94 ± 0.11 - 1.10 ± 0.36), pH (6.19 ± 0.05 -7.17 ± 0.01), EC (0.11 ± 0.01 - 0.13 ± 0.01), Cd (0.010 ± 0.00 - 0.03 ± 0.002), Cr (0.03 ± 0.00 - 0.041 ± 0.007), Pb (0.081 ± 0.012 - 0.288 ± 0.05) and Zn (0.070 ± 0.003 - 0.095 ± 0.015) were found to be the highest and the least concentration of the physicochemical parameters and heavy metals, respectively. One way ANOVA at 95% confidence level indicated that there are a significant difference in the level of TH and Pb and no significant difference in the levels of TDS,* $Cl,^-$ *pH, EC, Cd, Cr, and Zn in all the samples and the results of Pearson correlation revealed that there is strong/weak and/or moderate positive/negative correlation between physicochemical parameters and heavy metals with each other. The obtained values of each parameter were compared with the standard values set by the world health organization (WHO), (2008) and Ayers and west cot, FAO, (1976, 1994) drinking water quality standard.*

Key words*:-heavy metals, physicochemical parameters, Ketar River.*

CHAPTER ONE

1.1. Background of the Study

Water is essential for life on earth because of its importance in various fields. The pattern of human settlement throughout history has often been determined by availability of water. Next to oxygen, water is the most important substance for human existence. Water is the most abundant substance on the earth's surface that is essential for the survival of all known forms of life. Water plays an important role in the world economy, as it functions as a solvent for a wide variety of chemical substances, industrial cooling, transportation and agriculture. More than 70% of freshwater is consumed for agriculture [Baroni *et al.,* 2007].

Water on earth is one of the most abundant natural resources, but only about 1% of that resource is available for human consumption [Grey *et al*., 2013; Adeleye *et al*., 2016]. It is estimated that over 1.1 billion people lack supply of adequate drinking water due to the rising cost of potable water, growing populations, and variety of climatic and environmental concerns [WHO, 2015].The major challenge in water supply chain is continuous contamination of freshwater resources by a variety of organic and inorganic pollutants [Schwarzenbach *et al*.,2006]. Aquifers around the world are depleting and being polluted due to multiple problems of saltwater intrusion, soil erosion, inadequate sanitation, contamination of ground/surface waters by algal blooms, detergents, fertilizers, pesticides, chemicals, heavy metals, and so forth. Increasing industrialization has been accompanied throughout the world by the extraction and distribution of mineral substances from their natural deposits. Unlike many other pollutants associated with the environments, metals are non-biodegradable and can undergo bio magnifications in living tissues **[**Oti Wilberforce and Nwabue, 2013]. Uptake and accumulation of heavy metals by plants is either via the roots or foliage surfaces [Sawidis *et al*., 2001]. Some factors which affect metal uptake include soil pH, metal solubility, conductivity, stages of plant growth and plant species [Sharma *et al*., 2006; Ismail *et al*., 2005].

Environmental contamination by heavy metal through industrial waste is one of the main health problems in industrial countries. Metal contaminants can easily enter the food chain if contaminated water, soil or plants are used for food production. The industrial compounds generally may contain organic compounds, inorganic complexes and other non-degradable substances [Huguet *et al*., 2009]. Most agricultural lands in Ethiopia and in globe are suffering from major constraints to agricultural production. All vegetable and other crops are cultivated under moisture stress in the Central Rift Valley areas of the country during the main rainy season and using irrigations during following dry seasons [Edossa *et al*., 2013]. Many people could be at risk of adverse health effects from consuming vegetables cultivated in contaminated soil. Many researchers have shown that some vegetables are capable of accumulating high levels of metals from the soil [Garcia *et al*., 1981]. Heavy metals are one of a range of important types of contaminants that can be found on the surface and in the tissue of fresh vegetables. Heavy metals, such as cadmium, copper, lead, chromium and mercury, are important environmental pollutants, particularly in areas under irrigated with wastewater [Bigdeli and Seilsepour, 2008]. Contaminants such as bacteria, heavy metals, nitrates and salt have found their way into water supplies due to inadequate treatment and disposal of waste from human and livestock, industrial discharges, and over-use of limited water resources [Singh and Mosley, 2003]. This is highlighted recently in Bangladesh where natural levels of arsenic in groundwater were found to be causing harmful effects on the population [Anawara *et al*., 2002].

Water quality and suitability for use are determined by its taste, odor, color, and concentration of organic and inorganic matters [Dissmeyer, 2000]. Contaminants in the water can affect the water quality and consequently the human health. The potential sources of water contamination are geological conditions, industrial and agricultural activities, and water treatment plants. These contaminants are further categorized as microorganisms, inorganics, organics, radionuclides, and disinfectants [Nollet, 2000]. The inorganic chemicals hold a greater portion as contaminants in drinking water in comparison to organic chemical [Azrina, 2011]. A part of inorganics are in mineral form of heavy metals. Heavy metals tend to accumulate in human organs and nervous system and interfere with their normal functions. [WHO, 2011].

A number of scientific procedures and tools have been developed to assess the water contaminants [Dissmeyer,2000].These procedures include the analysis of different parameters such as pH, turbidity, conductivity, total suspended solids (TSS), total dissolved solids (TDS), total organic carbon (TOC), and heavy metals. These parameters can affect the drinking water quality, if their values are in higher concentrations than the safe limits set by the World Health Organization (WHO) and other regulatory bodies [WHO, 2011]. Therefore, the investigation of the drinking water quality by researchers and governmental departments has been performed regularly throughout the world [Tuzen and Soylak, 2006; Heydari and Bidgoli, 2012].

In Ethiopia, the dominant source of drinking water used to supply major urban and rural communities is from wells, rivers, lakes and springs [Aschalew Demeke, 2009]. Even though, there are no systematic and comprehensive programs in the country, there are increasing indications of water contamination problems in some parts of the country. The major causes of this contamination could be soil erosion, domestic waste from urban and rural areas and industrial wastes [Stagnitti *et al*., 1998].

The main sources of pollution that enter surface water bodies are industries, municipal solid waste and oily wastes from garages and fuel stations. Most of the water resources are gradually becoming contaminated due to the addition of foreign materials from the surroundings. These include organic matter of plant and animal origin, land surface washing and industrial and sewage effluents. Rapid urbanization and industrialization with improper environmental planning often lead to discharge of industrial and sewage effluents into rivers [Lokeshwari and Chandrappa, 2006].

There were no reports in the literature on the study of some composition of wastewater out from industries, municipal solid, oily wastes from garages and fuel station, domestic waste discharged from Assela Town. The proposed study of some composition of wastewater was expected to deliver a base line data on the composition in wastewater that discharged from Asella Town. Because the waste matter mentioned above mixed with small rivers that crossed Asella town and at the end entered Ketar River. Due to this reason, emphasis was given to the determination of the level of pH, Electrical Conductivity (EC), total dissolved solid (TDS), total hardness (TH), Chloride (Cl^-), and selected heavy metals (Cd, Cr, Pb, Zn) composition present in Ketar River. Therefore, determination of level of some physiochemical parameters and metal composition in the Ketar River was very important to ensure individuals health status level of metals depending on the reported result under the discussion and recommendation parts by comparing the analyzed parameters with WHO and FAO drinking water quality standards. Furthermore, the result of this study may help for regular monitoring and control contamination of Ketar River.

1.2. Statement of the Problem

Saf**e** drinking water is a fundamental right of human being. However, is the water that we drink safe? The answer is obviously no. Water bodies usually consist of different bio-assimilation and bio-accumulation of metals in aquatic organisms which have long term potential implications on human health and ecosystem. People have the right to know the quality of water that they perceive to be pure.

Clean water is one of the understood basics for the health of humans and plants. Nowadays, water bodies are used for drinking and other purposes. However, they are easily polluted by different chemicals such as pesticides, herbicides, fertilizers that are used to grow crops, wastewater that flows from villages, town and factories. Due to this reason, the pollution of water bodies deteriorates from time to time.

Among the water bodies of Arsi zone, Ketar River is one of the largest rivers and it is located in the south western part of the zone. This river finally enters the Lake Ziway by crossing Lemmu Bilblo, Digelu, Tiyo and Ziway Dugda districts. The people who live around it, they use this river for different purposes. For example, drinking, cooking food, cleaning, irrigation, for their cattle's, as well. As the other rivers, Ketar is polluted in the following ways:

- When farmers used pesticides, herbicides and fertilizers to improve the quality of their crops, these chemicals were easily mixed to the river by rain.
- By washing cars, served motor oils and disposal of lead batteries from garages, the work of welding, plating, painting and wastewater which was released from factories, domestic waste, municipal solid and petrol stations were directly entered four rivers by crossing Asella town. Finally they entered Ketar River.

Consequently, the reasons that mentioned above, the river reduced its cleanness alarmingly. So, the researcher was motivated to conduct the study identifying the level of toxic heavy metals and some physicochemical parameters whether they were greater or not as they expected in the river standard.

1.3. Objectives of the Study

1.3.1. General Objective

The main objective of this study is to investigate the level of selected physicochemical parameters and heavy metals on Ketar River water for drinking and irrigation purposes.

1.3.2. Specific Objectives

- To determine concentration of heavy metals Cd, Cr, Pb and Zn in Ketar River water sample.
- To determine the levels of selected physicochemical parameters like Chloride, EC,TH, pH and TDS in Ketar River water sample.
- To compare the results with WHO and FAO.

1.4. Significance of the Study

The study on water has a great significance in helping alleviate certain problems which can pose risk to human health. The study was designed to conduct the investigation of selected heavy metals from the river and some physicochemical parameters of Ketar River water for drinking and irrigation purposes.

It is believed that the result of this study may have the following importance for its users. Firstly, when the level of toxic heavy metals known properly, the people who live around the Ketar river might be beneficial. Secondly, this study might be motivating other researchers to conduct a research further on this area and to protect the river from contamination of waste matters and the increasing level of heavy metals.

Generally, the people who live in cities and towns have little knowledge how to protect the environment and the river. They usually release house hold wastes, toilets, oily substances and grease from garages and washing cars carelessly. So, if the researcher conducts this study in advance, he might be shows the dangerous and health problems that the people face around the river. Moreover, the researcher tries to find solutions how to reduce the contamination of environment and the river.

1.5. Scope of the Study

The study was delimited to Ketar River water that found in Sheled kebele, Ziway Dugda woreda, East Arsi zone, Oromia region, Ethiopia. The researcher believes it was better if the study covers all physicochemical parameters and assess large number of heavy metals concentration in Ketar River water on different area at different time but due to various constrains particularly time and budget the study was restricted to assess some physicochemical water quality parameters such as pH, Chloride, total dissolved solid (TDS), Electrical Conductivity (EC), total hardness (TH), and selected heavy metals such as cadmium, chromium, lead and zinc content of River Ketar. The study was conducted in dry time due to the factors such as floods which can affect the physical, chemical and biological behavior of the river water.

CHAPTER TWO

2. REVIEW OF RELATED LITERATURE

2.1. Introduction

Minerals are usually classified in to two main groups on the basis of their relative amounts in the body. One of the groups is macro elements or macro minerals occurring in relatively larger amounts and needed in quantities of 100mg or more per day which include calcium, magnesium, sodium and potassium. Minerals occurring in small amounts and needed in quantities of a few milligrams or less per day are called microelements or trace elements, which include iron, zinc, copper, manganese, cobalt, nickel, chromium and boron. Other trace metals like aluminum, lead, cadmium, mercury and arsenic are till now recognized as potentially harmful. Actually, all essential elements may also be toxic in animals and humans if ingested at sufficiently high level and for a long enough periods [WHO, 1996; Sanger *et al*., 2005].

2.2. Heavy Metals

The term Heavy Metals refer to any metallic element that has a relatively high density and is toxic or poisonous at low concentration [Lenntech, 2004]. Heavy Metals are a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm^3, or 5 times or more, greater than water [Syman and Huton,1986; Nriagu,1988; Hawks,1997]. And also heavy metals are defined as those elements with a specific density at least five times the specific gravity of water. Heavy metals include Cadmium (Cd), Copper (Cu), Lead (Pb), Zinc (Zn), Mercury (Hg), Arsenic (As), Silver (Ag), Chromium (Cr), Iron (Fe) and Platinum group elements, Copper and Zinc are essential trace elements for living organisms at low concentration (< 10mg/L). However, they become toxic at high concentration (>10mg/L). Most of these metal ion (Cd, Cu, Zn, Hg, As, Ag, Cr and Fe) can be released from the industries are in simple cationic forms [Volesky, 1995].   The characteristics of heavy metals are described by [Wang, 2006]. Toxicity that can last for a long time in nature. Heavy metals cannot be degraded including bio treatment and are very toxic even at low concentration (1.0-10.0mg/L).Heavy Metals are dangerous because they tend to bio accumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemicals concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (Metabolized) excreted [Tsoumbarist *et al*., 1994]. World Health Organization (WHO) has established levels of metals in foods above which, they should not be consumed. For this reason, the levels of trace metals in our food should be of much importance and concern to us.

2.3. Heavy Metals in Water

Water is considered as most suitable medium to clean, disperse, transport and dispose of wastes. These activities have undesirable effects on the natural environment. Also uncontrolled land uses, urbanization, deforestation, unauthorized release of chemical substances and discharge of untreated wastes have impacted negatively on the quality of water resources [UNESCO, 2003]. Heavy metals pollution of water is most significant environmental problems of recent times. Water can be regarded polluted when gets changed in composition either naturally or by human activities that make less suitable for drinking, domestic, agricultural, industrial, recreational, wildlife and other uses. Water pollution also take form of sediment eroded from stream banks, large booms of algae low levels of dissolved oxygen or abnormally high temperatures [Calhoun, 2005 and Goal, 2009].

The contamination of waters with wide pollutants becomes a great concern over the last few dedcades. Discharge of heavy metals to rivers or other aquatic environment can change both aquatic species diversity and ecosystems due to their toxicity and accumulative behavior [Al-We her, 2008]. Heavy metals dissolved in water endanger the lives of public who use it for drinking and irrigation. When used for irrigation heavy metals have the danger of being incorporated in food chain and ingested by the public [Wogu and Okaka, 2011].

2.4. Source, Use and Health Effects of Heavy Metals

Human activity like industrial production, mining, agricultural fertilizers and transportation are the main source of heavy metal contamination in the environment. These different sources increase heavy metal concentration that is serious hazard in water, soil, plants and animals of systems. When compared to other water pollutants, heavy metals pollution is less visible but its impact on ecosystem and human are intensive and extensive. Diseases like edema of eyelids, tumor, congestion of nasal mucous membrane and pharynx ,stuffiness of head, gastrointestinal, muscular, reproductive, neurological and genetic malfunctions are caused by heavy metals like Pb, Cd, Cr and Zn intake of toxic metals cause several harm to the body ranging from acute to chronic disease such as allergies, asthma, hypertension, anemia and immune system dysfunction. Aluminum, mercury, and lead are known to attack the nerves and brain causing hyperactivity in children, liver and kidney dysfunction [Alzheimer's, 2010]. Heavy metals significantly contribute to human environment pollution due to impossibility of their biodegradation, and because some of them have cumulative toxic properties. Due to the high toxicity the stability of Lead, Cadmium, Chromium and Zinc it is necessary to determinate their content in materials, food, water, soil and other samples to estimate their contamination level [Biljana, 2011].

2.4.1. Lead (Pb)

Lead is rarely found as the free metal in nature, but it is present in several minerals, principally in Galena (PbS) the main source for lead production. It is also found as Anglesite (PbSO4) and Cerrusite (PbSO3). Lead is one of the most commonly used non-ferrous metals. It has many applications; its largest use is in making storage batteries, most of which are recycled. As a result of its resistance to corrosion and malleability, it finds use in building constructions, storage tank lining and corrosive liquid containers. Other uses of the metal are for radiation shielding, ammunition, solder, cable sheathing and pipe work. Lead compounds are used as pigments in paints and ceramics, catalysis, antibacterial substances and wood preservatives. Lead exists in the oxidation states Pb2+ and Pb4+, with the divalent form being the more stable in most aquatic environments. The speciation of lead compounds in water is complicated and depends up on a number of factors, principally pH, dissolved oxygen and concentration of other organic and inorganic compounds. And concentration of lead in waters is usually limited by the solubility of PbCO3, and by adsorption on to particulate matter [Dojlido and Best 1993].

During physicochemical process of bones tissue remodeling part of the Pb(II) ions by migration through the oral and other biological fluids reach other remote organs ,hence the brain, kidneys and the liver [Biljana, 2008;Uauy. 1998]. Everyone is exposed to trace amount of Lead through air, soil, household dust, food, drinking water and various consumers. Inorganic Lead arising from a number of industrial and mining sources like pigments, anticorrosion coatings, lead smelter, alloys, and batteries occurs in water in the +2 oxidation state [Tavallali, 2010; Morsi, 2011].

It is easily deposited in blood, kidney, reproductive system, nervous system and brain so as results fatal diseases. Acute lead poisoning in humans causes severe damage in the kidneys, liver, brain, reproductive system and central nervous system, and even causes death. Its mild poisoning cause anemia, headache and sore muscles and the victim may feel fatigued and irritable. Chronic exposure to lead causes nephritis, scaring and the shrinking of kidney tissues [Tan, 2010; Nazari, 2011]. Moreover, lead and its compounds are reasonably anticipated to be human carcinogens based on limited evidence of carcinogenicity from studies in humans and sufficient evidence of carcinogenicity from studies in experimental animals [Methods, 2011]. Most victims of lead poisoning are children with low socioeconomic status, such as children living in slums [Amitai, 2008]. Lead exposure accounts for about 1% of the global burden of disease and sympathetically most exposure affects children in developing countries. 15- 20% mental retardation could be caused by exposure to lead. High blood lead levels in children may cause permanent deficiencies in growth [Amitai, 2008; Tong, 2000].

2.4.2. Cadmium (Cd)

Cadmium is usually present as complex oxides, sulfides, and carbonates in zinc, lead and copper ores. Cadmium in several aspects is similar to zinc and therefore, it is always associated with zinc in mineral deposits. Cadmium is extremely toxic to most plants and animal species particularly in the form of free cadmium ions. The major sources of cadmium include metallurgical industries, municipal effluents, sewage sludge and mine wastes, fossil fuels and some phosphorus containing fertilizers. Cadmium can potentially harm human health depending upon the form of cadmium present, the amount taken in, and whether the cadmium is eaten or breathed [Cruz, 2013]. It has many applications: its largest use is electroplating, fertilizers, mineral processing and battery manufacturing [Sharma, 1995].

The human health implications of cadmium related to bone and renal disease caused by populations exposed with industrially contaminated drinking water. Lung renal dysfunction is reported in industrial workers exposed to air-borne cadmium. In low doses, it produces coughing, headaches, and vomiting. In larger doses, it can accumulate in the liver and kidneys that replace calcium in bones, leading to painful bone disorders and to a renal failure. The kidney is one of critical target organ in humans chronically exposed to cadmium by ingestion [USEPA, 1999]. In addition to its extraordinary cumulative properties, cadmium is also a highly toxic metal that can disrupt a number of biological systems, usually at doses that are much lower than most toxic metals [Nordberg *et al*, 2007].

2.4.3. Chromium (Cr)

Chromium is one of the known environmental toxic pollutants in the world. The main sources of chromium contamination are tanneries, steel industries and sewage sludge application and fly ash. Besides these, chromium plating and alloys in motor vehicles are considered to be more probable sources of chromium [McGrath and Smith, 1990 and Shaheen, 1975] at an elevated concentration it could be toxic for plants and animals. Concentrations between 5-30 mg/kg are considered critical for plants and could cause yield reductions. The problems that are associated with chromium exposure are skin rashes, upset stomach, ulcers, respiratory problems, weakened immune systems, kidney and liver damage, alteration of genetic material, lung cancer and ultimately death [McGrath and Smith 1990 and Pendias *et al*., 1984].

Among the different heavy metals, Chromium is a common and very toxic pollutant introduced in to natural waters from a variety of industrial wastewaters. The two main forms of Chromium, (chromate and dichromate) pose significantly higher levels of toxicity than the other valence states [Krejpcio, 2001; Agaje, 2007; Qaiser *et al*., 2009]. The two common oxidation states of chromium have different chemical, biological and environmental characteristics. Trivalent chromium (Cr (III)) is relatively insoluble and required by microorganisms in small quantities as an essential trace metal nutrient, while hexavalent chromium (Cr (VI)) is a great concern because of its toxicity even in trace amount, leads to carcinogenic disorders, more hazardous and mutagenic to living organisms, and as a result of this, couple with its threat to the environment, it is included in the priority list of 21 hazardous substances. [Ozgunay, 2007; Rengaraj, 2001].

Wastewaters those generated during dyes and pigments production, film and photography, galvanometer, metal cleaning, plating and electroplating may contain undesirable amounts of chromium (VI). Concentration present in industrial effluent streams are in range of 50-200 mg/L. The permissible limit of Cr (VI) determined by WHO for discharge into inland surface waters is 0.1 mg/L and in potable water are 0.05 mg/L. Ethiopian Environmental Protection Authority (EPA) also set a minimal standard to be 0.1 mg/L for hexavalent chrome containing industrial effluent. It has been reported that excessive intake of chromium by human leads to hepatic and renal damage, capillary damage, gastrointestinal irritation and central nervous system irritation. [Rengaraj, 2007; Karthikeyan, 2005]. Chromium (Cr) below toxic limit balances blood sugar levels, regulates hunger, reduces cravings protect DNA and RNA improves heart function, helps control fat and cholesterol levels in the blood [Krejpcio, 2001].

2.4.4. Zinc (Zn)

Zinc (Zn) is a ubiquitous trace element. It is one of the most important trace elements in the body, and it is indispensable to the growth and development of microorganisms, plants, and animals. It is found in all body tissues and secretions in relatively high concentrations, with 85% of the whole body zinc in muscle and bones, 11% in the skin and the liver, and the remaining in all the other tissues, with the highest concentrations in the prostate and parts of the eye. The average amount of Zn in the adult body is about 1.4–2.3 g Zn [Calesnick and Dinan, 1988; Stefanidou *et al.;* 2006; Bhowmik *et al*.; 2010]. It is the second most abundant transition metal ion in living organisms, after iron; however, if hemoglobin-bound iron is not considered, then Zn becomes the most abundant transition metal [Vasak and Hasler 2000]. Zinc is the only metal that is a cofactor to more than 300 enzymes [Rink and Gabriel, 2000]

In contrast to other transition metal ions, such as copper and iron, zinc does not undergo redox reactions due to its filled d shell. It is a biologically essential trace element and critical for cell growth, development, differentiation, homeostasis, connective tissue growth and maintenance, DNA synthesis, RNA transcription, cell division, and cell activation. It is also critical in wound healing, taste acuity, immune system function, prostaglandin production, bone mineralization, proper thyroid function, blood clotting, cognitive functions, fetal growth, and sperm production. It regulates body fluid pH, it promotes the formation of collagen to make hair, skin, nails, and it helps to enhance memory and improves mental development, it maintains the normal function of the prostate, and it has important implication in testosterone secretion [Bhowmik *et al.;* 2010]

Deficiencies in Zn also accompany many diseases such as gastrointestinal disorders, renal disease, sickle cell anemia, alcoholism, some cancer types, AIDS, burns, aging, and others [Keen and Gershwin 1990; Mocchegiani and Fabris 1995; Fraker *et al.*. 2000; Mocchegiani and Muzzioli 2000a]. In pregnant women, zinc deficiency may lead to fetal brain cells decrease and may affect their development. Children's zinc deficiency may hinder normal growth, intellectual development, and reproductive system health. In adult males, zinc deficiency may lead to prostatic hyperplasia, affecting the reproductive function and fertility. Nevertheless, zinc supplementation is a powerful therapeutic tool in managing a long list of illnesses [Bhowmik *et al.;* 2010].

The toxicity of Zn is as a result of excessive absorption which suppresses copper and iron absorption while free Zn^{2+} ion in solution is highly toxic to plants, invertebrates, and even fish. Zinc salts are intestinal irritants and can cause nausea, and abdominal pain [FAO/WHO, 2011]. The efficacy of Zn supply seems to be strictly related to the dose and length of the treatment. Long treatment or high doses of Zn may provoke a Zn accumulation with subsequent damage on immune efficiency [Mocchegiani *et al.;* 2001]. Modest immune modifications are observed in old people treated with high doses of zinc for short periods, as well as with physiological zinc doses for long periods of 1 year. Zinc accumulation might exist in both conditions, causing toxic effects. After zinc physiological supplementation, immune recovery has been observed in elderly, in cancer, in infections, as well as in patients with sickle cell disease, since it decreased oxidative stress and generation of inflammatory cytokines[(Mocchegiani and Muzzioli 2000a].

Zinc is an essential trace element for plants, animals and humans which found in all food and potable water as salts or organic complexes. Although drinking water seldom contains zinc above 0.1 mg/L, levels in tap water can be considerably higher because of the zinc used in plumbing material [Swami Nathan *et al.*, 2011]. The solubility of zinc is highly dependent on the compounds, for example zinc phosphate is insoluble and zinc nitrate is very soluble. In general zinc is considered to be very mobile. Its presence in environment and subsequent up take by human's causes pulmonary manifestation, fever, chills and gastroenteritis [Tortora, 1997]

2.5. Water Sources

Water is one of the basic substances that help for all forms of living things (animals and plants) [Lokeshwari and Chandrappa, 2006] and water is usually obtained from two major types of natural sources. These are surface water such as fresh water, lakes, rivers, streams…etc. And the other one is ground water such as borehole water and well water [Jay, 2000]. Water has exceptional properties due to its polarity and hydrogen bonds which mean it is able to dissolve, absorb, adsorb or suspend many different compounds [Wang and Christie, 2003]. Thus, in nature, water is not clean as it obtained pollutants from its environment and those arising from humans and animals as well as other biological and physical activities [Sharma and Marshall, 2008a].

2.6. Drinking Water Quality

Water quality refers the chemical, physical and biological characteristics of water with respect to its suitability for particular purpose (drinking, industry, agriculture). It involves the process of evaluation of the physical, chemical and biological nature in relation to natural quality, human effects and intended uses, particularly uses affect human health and aquatic system. Water quality depends on the local geology and ecosystem, as well as human uses that water bodies as sink [Johnson *et al.*, 1997].

The quality of water, whether it is used for drinking, irrigation or recreational purposes, is significant for health in both developing and developed countries. In early days, water was primarily used for domestic needs like drinking, washing, bathing, cooking and etc. But due to industrial and urban development requirement of water for these activities has increased along with domestic purpose. Quality of water can be described by its physical, chemical and microbial characteristics [WHO, 2001].Water quality guidelines provide basic scientific information about the water quality parameters and physicochemical parameters. These parameters will not identify particular chemical species but have used as an indicator of how the water quality may affect water uses [Weiner, 2008]

2.7. Determination of Some Physicochemical Parameters

Water has a wide range of physical and chemical characteristics that affects its quality and treatability [Hutton, 1996]. Physical and chemical testing of drinking water is necessary to assure that treated water is safe and palatable and to monitor the various water treatments for safe drinking water supply. Physicochemical testing of raw water is also helpful to determine treatment techniques and chemical dosage [Avcievala, 1991; Eaton, 1998].

Physicochemical quality parameters of water are important not only in the assessment of the degree of pollution but also in the choice of the best source and treatment needed. The discharge of industrial effluents to the nearby water bodies in particular and environment in general is a major treat to deteriorate the water quality for its intended purposes. Physical properties of the elements are measured easily even some may readily be observable by the layman [Akoto and Adiyiah, 2007].

The parameters considered as part of this study are discussed below:-

2.7.1. The pH of River Water

The pH is determined using pH meter. It indicates the intensity of acidity and alkalinity and measures the hydrogen ion concentration in water. pH is used in determining the corrosive nature of water. Lower pH value higher is the corrosive nature of the water. Decrease the pH value can cause the increase in the amount of organic carbon and carbonate. It is important parameter of water body since most of the aquatic organisms are adapted to an average pH and do not with stand abrupt changes. pH blow 6.5 cause’s corrosion [Denek. I, 2006].

One important water quality parameter, the pH of water, affects the biochemical process in water [Chapman, 1996]. The WHO guide level for pH in drinking water quality is 6.5 to 8.5 [WHO, 1993]. The pH values of most natural water are in the range of 6.5-8.5 [Chapman, 1996]. Most drinking water have a pH from 4 to 9 and the majority are slightly alkaline due to carbonates and bicarbonates of calcium and magnesium dissolved in water with variable pH are most likely contaminated and indicating the introduction of industrial wastes [Hutton, 1996]. Waters with pH lower than 4 have a sour taste and above 8.5 an alkaline bitter taste. In addition to these, low pH levels can increase corrosive characteristics resulting in contamination of drinking-water and adverse effects on its taste and appearance [Sawyer and McCarty, 1978].

2.7.2. Electrical Conductivity (EC)

Water capability to transmit electric current is known as electrical conductivity and served as a tool to assess the purity of water [Murugesan *et al.*; 2006]. It is an excellent indicator of TDS which is a measure of salinity that affects the taste of potable water [WHO, 1993]. Solutions of most inorganic compounds are relatively good conductors. Conversely, molecules of organic compounds that do not dissociate in aqueous solution conduct a current very poorly, if at all. Significant changes in conductivity can be an indicator that a discharge or some other source of pollution has entered the water. Conductivity meter (sensor) is used to measure the conductivity of water [APHA, 1999].

Electrical conductivity in water is a measure of the ion-facilitated electron flow through it. Water molecules dissociate into ions as a function of pH and temperature and result in a very predictable conductivity. Some gases, most notably carbon dioxide, readily dissolve in water and interact to form ions, which predictably affect conductivity as well as pH. For the purpose of this discussion, these ions and their resulting conductivity can be considered intrinsic to the water. Water conductivity is also affected by the presence of extraneous ions. The extraneous ions used in modeling the conductivity specifications are the chloride and sodium ions [USP, 2007].

2.7.3. Total Hardness (TH)

Water that has high mineral content is known as hard water. Hard water contains bicarbonate, chlorides and sulphates of calcium and magnesium. When treated hard water with soap, it gets precipitated in the form of insoluble salts of calcium and magnesium. Hardness of water is a measure of the total concentration of the calcium and magnesium ions expressed as calcium carbonate. There are two types of hardness. Temporary hardness and permanent hardness. Temporary Hardness is due to the presence of bicarbonates of calcium and magnesium. It can be easily removed by boiling. Permanent Hardness is due to the presence of chlorides and sulphates easily removed by using an ion exchange column [APHA, 1999]. Water hardness is an aesthetic quality of water, and is caused mostly by the minerals calcium and magnesium. Hardness is a natural characteristic of water which can enhance its palatability and consumer acceptability for drinking purposes. Health studies in several countries in recent years indicate that mortality rates from heart diseases are lower in areas with hard water [EPA EU, 2001].

2.7.4. Total Dissolved Solid (TDS)

Total dissolved solid is a measure of the combined content of all inorganic and organic substances contained in liquid, in molecular, ionized or micro-granular (colloidal sol) suspended form. Generally the operational definition is that the solids must be small enough to survive filtration through a filter with two-micrometer (nominal size or smaller) pores. Total dissolved solids are differentiated from total suspended solids (TSS), in that the latter cannot pass through a sieve of two micrometers and yet are indefinitely suspended isolations.

The term "settle able solids" refers to material of any size that will not remain suspended or dissolved in a holding tank not subject to motion, and excludes both TDS and TSS. Settle able solids may include larger particulate matter or insoluble molecules [USEPA, 1991].High levels of total dissolved solids do not correlate to hard water, as water softeners do not reduce TDS. Water softeners remove magnesium and calcium ions, which cause hard water, but these ions are replaced with an equal number of sodium or potassium ions. This leaves overalls unchanged [USEPA, 1991].

2.7.5. Chloride (Cl^-)

Chloride in the form of the Cl^-ions is one of the major inorganic anions or negative ions in saltwater and freshwater. It originates from the dissociation of salts such as sodium chloride or calcium chloride in water. These salts and their resulting chloride ions originate from natural minerals saltwater intrusion into estuaries and industrial pollution. These are many possible sources of manmade salts that may contribute to elevated chloride readings. Sodium chloride and chloride and Calcium chloride used to salt roads contribute to elevated chloride levels in streams. Chlorinated drinking water and sodium chloride water softeners often increase chloride levels in wastewater of a community. In drinking water the salty taste produced by chloride depends upon the concentration of the chloride ion. Water containing 250 mg/L of chloride may have a detectable salty taste if the chloride came from sodium chloride [Vernier, 2013]. Chlorides are widely distributed as salty of calcium, sodium and potassium in water and wastewater. In potable water, the salty taste produced by chloride concentrations is variable and dependent on the chemical composition of water. The major taste producing salts in water are sodium chloride and calcium chloride. The salty taste is due to chloride anions and associated cat ions in water. In some water which is having only 250 mg/L of chloride may have a detectable salty taste if the cat-ion present in the water is sodium. On the other hand, a typical salty taste may be absent even if the water is having very high chloride concentration for example 1000mg/L. This is because the predominant cat-ion present in the water is not sodium but either calcium or magnesium may be present [Method, 1994].

A normal adult human body contains approximately 81.7g chloride. On the basis of a total obligatory loss of chloride of approximately 530 mg/day, a dietary intake for adults of 9mg of chloride per kg of body weight has been recommended (equivalent to slightly more than 1g of table salt per person per day). For children up to 18 years of age, a daily dietary intake of 45 mg of chloride should be sufficient [Ottawa, 1978]. Chloride toxicity has not been observed in humans except in the special case of impaired sodium chloride metabolism, e.g. in congestive heart failure [Wesson, 1969]. Chloride increases the electrical conductivity of water and thus increases its corrosivity. In metal pipes, chloride reacts with metal ions to form soluble salts [WHO, 1978], thus increasing levels of metals in drinking-water. In lead pipes, a protective oxide layer is built up, but chloride enhances galvanic corrosion [Gregory, 1990].

2.8. Heavy Metal Analysis

Metal content of samples were determined by a wide different of analytical methods, with the choice often based on the precision and sensitivity required. Both macro and trace elements can be determined by different spectroscopic or chromatographic methods, such as Atomic Absorbance Spectrometry using Flame (FAAS) or Graphite Furnace (GFAAS) atomization, Atomic Emission Spectrometry (AES), Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Inductively coupled plasma/optical emission spectroscopy (ICP/OES), Inductively Coupled Plasma Mass Spectrometry (ICPMS), X-ray Fluorescence (XRF), and Ion Chromatography (IC) [Welz, B; Sperling, M. 1999].

2.9. Inductively Coupled Plasma/ Optical Emission Spectroscopy (ICP/ OES)

Inductively coupled plasma/optical emission spectroscopy (ICP/OES) is a powerful tool for the determination of metals in a variety of different sample matrices. With this technique, liquid samples are injected into a radiofrequency (RF)-induced argon plasma using one of a variety of nebulizers or sample introduction techniques. The sample mist reaching the plasma is quickly dried, vaporized, and energized through collisional excitation at high temperature. The atomic emission emanating from the plasma is viewed, collected with a lens or mirror, and imaged onto the entrance slit of a wavelength selection device. Single element measurements can be performed cost effectively with simple monochromator/photomultiplier tube (PMT) combination, and simultaneous multi element determinations are performed for up to 70 elements with the combination of a poly chromator and an array detector [Charles *et al.*, 1997]. The analytical performance of such systems is competitive with most other inorganic analysis techniques, especially with regards to sample throughput and sensitivity.

The principle used in the inductively coupled Plasma Optical Emission Spectroscopy is When plasma energy is given to an analysis sample from outside, the component elements (atoms) are excited [Thomas J. *et al.,* 2012]. When the excited atoms return to low energy position, emission rays (spectrum rays) are released and the emission rays that correspond to the photon wavelength are measured. The element type is determined based on the position of the photon rays, and the content of each element is determined based on the rays' intensity [Thomas J. *et al.,*]. To generate plasma, first, argon gas is supplied to torch coil, and high frequency electric current is applied to the work coil at the tip of the torch tube. Using the electromagnetic field created in the torch tube by the high frequency current, argon gas is ionized and plasma is generated. This plasma has high electron density and temperature (10000K) and this energy is used in the excitation-emission of the sample. Solution samples are introduced into the plasma in an atomized state through the narrow tube in the center of the torch tube [Rodolfo *et al.,* 2005].

An important part of any ICP/OES instrument is the computer control incorporated into the instrument. The majority of automated functions of an ICP/OES instrument are directly controlled by an on-board computer. At the simplest level of multi element ICP/OES instrumentation, a computer is needed to handle the massive amounts of data that such an instrument generates. While virtually every commercial ICP/OES instrument available today uses some type of computer to control the spectrometer and to collect, manipulate, and report analytical data, the amount of computer control over other functions of the instrument varies widely from model to model [Zander *et al.,* 1999].

A lot of studies on heavy metals in water, soil, plants and animals used flam atomic absorption spectrophotometer. The study carried out by [Begum.*et.al*, 2009] in the analysis of lead, iron, zinc, nickel and copper in soil and plants employed this method for analysis. Similarly [Radulescu *et al.,* 2014] in the analysis of Pb, Cd, Cr, Ni, Mn, Zn and Fe in surface water, depth water and therapeutic mud used flam atomic absorption spectrophotometry in their analysis in Romania. [Rahmanian *et al.,* 2015] employed FAAS method in analysis of Cu, Zn, Fe, Cd, Pb, Cr, As, Hg, and Sn in drinking water in Malaysia. [Bizualem, 2017] analyzed levels of Cd, Cu, Pb and Zn in Guder River and [Mekonnen *et a*l, 2018] analysis level of Fe, Pb, Cu, and Mn in River Rebu using FAAS method in Ethiopia.

For current study in [2020] researcher use inductively coupled plasma/optical emission spectroscopy (ICP/OES). ICP/OES is a chemical method used for the detection of trace-level elements based on inductively coupled plasma producing excited atoms and ions, which emit electromagnetic radiation at element specific wavelengths. The intensity of the characteristic emission lines allows determining the concentration (atoms per volume) of the element with in the sample [Charles *et al*, 1997]. Most of these diagnostics however, being essentially based on excite analysis are time consuming and require a proper sampling preparation atomic absorption spectroscopy (AAS). ICP/OES essentially involves collecting sample for subsequent analysis [Charles *et al.,* 1997; Thomas J *et al.,* 2012]. The main analytical advantages of the ICP over other excitation sources originate from its capability for efficient and reproducible vaporization, atomization, excitation, and ionization for a wide range of elements in various sample matrices [Rodolfo *et al.,* 2005]. Hence due to also to particular applications, there is a need promote the development application of suitable on line and/or time resolved analytical techniques. A powerful and challenging analytical technique well suited for online elemental analysis or aerosol is laser induced

2.10. Some Work on Physicochemical and Heavy Metals of River Water

Various research papers on water quality have been presented at different years. Related works on levels of selected physicochemical properties indicators and heavy metals content in different rivers due to excessive industries effluent, municipal discharge, agricultural activities and natural process carried out by different researches are summarized below.

[Jain *et al*. 2014] have studied the "Comparative Review of Physicochemical Assessment of Pavana River". They studied the water quality from 2005 to 2013 and the physicochemical parameter such as pH, dissolve oxygen, chemical oxygen demand and biological oxygen demand. It was observed that the water is highly polluted at many places. There was decrease in COD, BOD contents in the water

The study carried in Nigeria-delta coast on river Ethiope Showed River Ethiope is highly contaminated with pollutants discharged from industries sited along its bank, sewage, market municipal solid waste and surface run-off. Many research studies have conducted in Nigeria, in Niger Delta coast because of increasing river water pollution. The results obtained by researchers show that effects of effluents include high BOD, dissolved TDS, low DO and pH and the presence of inorganic elements. Besides, excessive contamination of river water will be led to increased algae growth, resulting in eutrophication reduced transparency and photosynthesis affecting growth of fishes, aquatic plants and animals, death of fishes and production of odors and color, increased turbidity, conductivity, temperature and heavy metals toxicity increased microbial group [Aisien *et al.*, 2003].

[Gupta *et al*., 2009] analyzed water samples from 20 sampling points of Keitel for physicochemical characteristics. Analysis of pH, colors, Odors, hardness, chloride, alkalinity, TDS. On comparing the results against drinking water quality standards laid by Indian Council of Medical Research (ICMR) and WHO, it is found that some of the water samples are non-potable for human being due to high concentration of physicochemical parameters.

As shown in [Bizualem, 2017] studied of physicochemical parameters and some heavy metals for water quality assessment of Gudar river for drinking purpose, in Ethiopia using purposive sampling method was employed pH, turbidity, EC, Alkalinity, Potassium, Phosphate, Chloride, Carbonate, TH, TDS and heavy metals (Cd, Pb, Cu, Zn, and Ag) using FAAS were determined. However, the increasing values of some physicochemical water quality parameters indicates that the river water located near the site of collection is not safe for drinking purpose but it can be used for agricultural activities such as irrigation purpose. The quality of river Gudar is getting contaminated especially by heavy/trace metals.

CHAPTER THREE

3. MATERIALS AND METHODS

3.1. Site of Study Area

The study was conducted on Ketar River water which is found in Sheled kebele, Ziway Dugda Woreda, East Arsi Zone, Oromia Region, Ethiopia. 20km distance from Assela Town at 195km from Addis Ababa. The River originated from Highland of Galema Mountain of south eastern part of the zone. This river finally enters the Lake Ziway by crossing Lemu Bilblo, Digelu, Tiyo and Ziway Dugda districts.

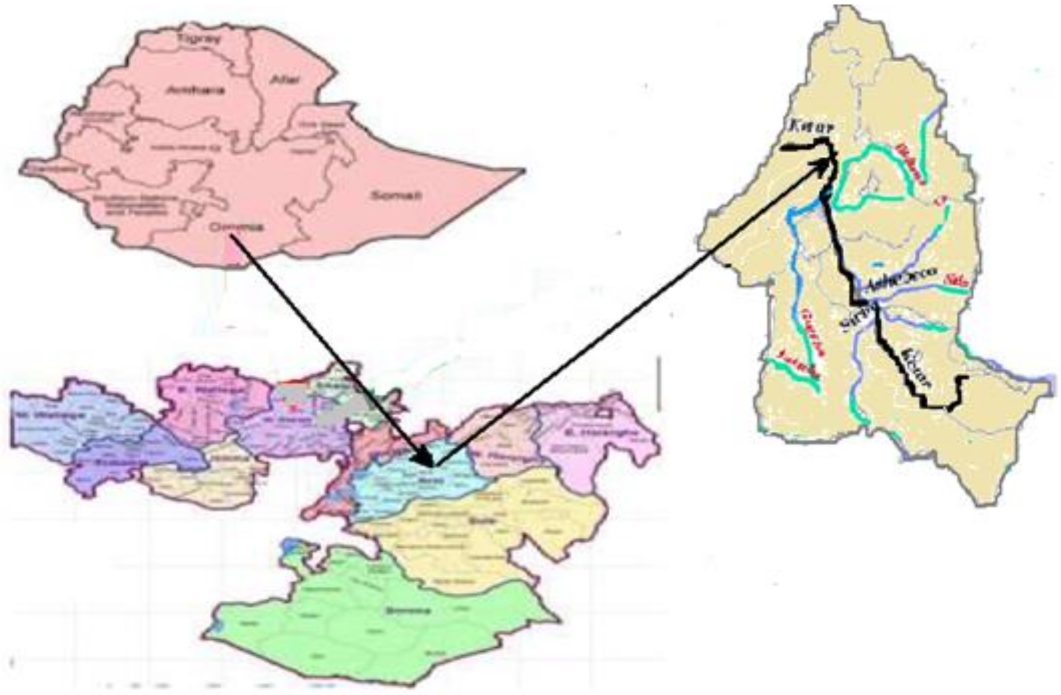

Figure 3.1 Location of Ketar River

3.2. Instruments and Apparatus Used for the Study

Inductively coupled plasma/optical emission spectroscopy (ICP/OES) (Arcos SOP -ICP-OES, Model ARCOS FHS12, Germany**)**, pH meter (Model Starter 2100 –OHRUS, Germany) used for determination pH of water sample. EC, conductor meter (EC-93 NIEUWKOOP BV instrument made in Holland) used for determination of conductivity of sample, **(**Titronic Basic Boom BV meppel is made in Holland) used for determination of chloride of sample, TDS was determined by oven dry. The common laboratory apparatus used during the study included fume hood and different sized beakers, Erlenmeyer flasks, funnels, graduated cylinders, volumetric flasks, and block digester, centrifuge, shaker, droppers, glass pipettes, gloves, stirrer, what man filter paper, test tubes (different size), plastic bottles, were used.

3.3. Chemicals and Reagents Used for Study

Reagents and chemicals used for the laboratory works were all analytical grade. Potassium chromate indicator solution, detergents, silver nitrate solution,EDTA solution, NH_4OH, buffer solution, KCl solution, deionized water was used for all dilutions throughout the study, Nitric acid, (69-70% HNO_3) (Labochemie**,** India), and hydrochloric acid, (35.4% HCl) (Labochemie**,** India) reagents were used for analysis of the selective heavy metals.

3.4. Physicochemical Parameters Experimental Procedures

3.4.1. Determination of Total Hardness(TH)

The total hardness of the water sample was measured by titration method. For measuring the total hardness of water, 0.01M (0.02N) EDTA solution was used as chelating agent and as a titrate (titrant) (i. e. 3.722gm of EDTA was dissolved in 1000mL of distilled water) 100mL of the EDTA solution was poured in to the burette. 50mL of sample water was placed in the beaker. 2mL of NH_4OH was used as a buffering agent to adjust the pH of the sample water. One drop of Eric chrome Blank was added into the sample water with spatula and used as indicator. The change in volume of the titrate (EDTA solution) consumed was recorded from the burette reading (mL) as the color of the sample water changes from wine red to light blue. The titration has been repeated three times and the average value of the titrant solution consumed has been taken [APHA, 1999].

The formula that has been used in the calculation of total hardness is as follows:

$$\text{Total hardness} = \frac{\text{Average Volume of EDTA} \times \text{N of EDTA} \times \text{Equivalent weight of } CaCO_3 \times 1000\text{mL/L}}{\text{Volume of sample taken}}$$

3.4.2. pH

The pH meter was calibrated with pH = 4.01 and rinsed with distilled water and again calibrated with pH = 7.00 buffer and then rinsed with distilled water. The sample was placed in a beaker and the electrode was rinsed with distilled water lowered into the sample. The reading has been taken after three minutes of stability. (i. e. after allowing the pH meter to adjust its reading to the water pH for a few minutes) [WHO, 1996].

3.4.3. **Total Dissolved Solid (TDS)**

Appropriately washed 200ml capacity porcelain evaporating dish were dried in an oven at a temperature of $105C^0$ for 1hr , cooled, stored in desiccators and weighed before use. 50 ml of water sample was pipette off using a pipette, quantitatively transferred to the filter paper. Then the filtrate was quantitatively transferred into the pre-weighed dry evaporating dishes. Then the sample was boiled at $105C^0$ to dryness. At last the evaporating dish with dry residue was cooled in desiccators and weighed [APHA, 1992]. Finally, TDS was determined using the following formula;

$$\text{TDS mg/L} = (A - B) \times 1000/\text{L of sample}$$

Where, A = weight of dish + weight of residue after filtrate (mg) B = weight of dish (mg)

3.4.4. Electrical Conductivity

Conductivity meter was used to measure the conductivity of the water sample. The conductivity meter was calibrated using 0.001M KCl reference solutions before taking electrical conductivity. The electrode was rinsed with distilled water and lowered into the water sample continued in the plastic container .The conductivity in µS/cm of the sample was recorded [UNEP/WHO, 1996]

3.4.5. Chloride

Chloride was measured by titration method. 50mL of sample in a conical flask was taken. 2mL of potassium chromate was added to the sample solution. It was titrated against 0.02N silver nitrate until a persistent brick red color was appeared which was the end point of the titration. A blank by placing 50mL of chloride free distilled sample water also conducted. Finally, chloride was determined using the following formula:

$$\text{Chloride (mg/L)} = \frac{(A - B) \times N \times 35.5 \times 1000\text{mL/L}}{V \text{ of the sample in mL}}$$

Where, A =Volume of titrant (silver nitrate) for the sample

B = Volume of titrant (silver nitrate)for bank

V = Volume of the sample in mL

N = Normality of silver nitrate

3.5. Sample Collection and Preparation

3.5. 1. Water Sample Collection

The samples were collected for assessing of selected physicochemical properties like pH, EC, TH, TDS, Chloride and heavy metals (Cd, Cr, Pb & Zn) concentration in Ketar River water of three different sites using standard methods in dry time. The samples were labeled for each site as (S_1, S_2 and S_3) and transported to laboratory stored in refrigerator at about 4 ºC before analysis. Samples were collected in cleaned, dry polyethylene bottles. The containers were initially washed with detergent, rinsed three times with distilled water and at the point of Samples were taken where the water was visibly flowing and well mixed. From six bottles or liters sample, the three bottles were immediately acidified with 5mL nitric acid, for later analysis of metals concentration. The purpose of the acid was to keep the metals in solution and to avoid adsorption to the container walls [APHA, 1999].

3.6. Digestion of Water Samples

The water samples from each sampling bottle were mixed thoroughly by shaking. A 50 mL aliquot of water sample was pipetted into a digestion flask. The metal percentage found in water was estimated by digestion of the water sample in 4mL concentrated (69 -70%) HNO_3 and 1mL concentrated (35.4%) HCl at 250^0c maximum temperature for 3 hours until a clear solution was observed. The digested samples were cooled. The solutions filtered through what man filer paper N<u>o</u> 1 and the clear solution was diluted to 50 mL volumetric flask [Sanayei *et al.,* 2009]. The digest heavy metals were analyzed by using ICP/OES.

3.7. Preparation of Standards Solution

Standard solution which is given in (Brands of Germany). Stock solution of 1000ppm of each metal ion was prepared by dissolving calculated amounts of each metal salt in 100mL of distilled water and diluted to 100mL. Eight standard solutions was prepared by serial dilution of each stock solution. Calibration curves were prepared to determine the concentration of the metals in the sample solution. The instrument was calibrated using eight series of working standards. The working standard solutions of each metal were prepared from the 10mg/L intermediate standard solutions of their respective metals.

The selected heavy metals were cadmium, chromium, lead and zinc. Calibration curves for each of the selected metals were prepared using eight standard solutions. The usual procedure in quantitative analysis method was to prepare a series of standard solution over a concentration range suitable for the sample being analyzed i, e. such that the expected sample concentrations were within the range established by the standard. These standards prepared by dilution from 1000ppm stock solution were as follows: 0.028ppm, 056ppm, 0.084ppm, 0.112ppm, 0.14ppm, 0.168ppm, 0.196ppm and 0.224ppm for cadmium, chromium and lead. 0.056ppm, 0.112ppm, 0.168ppm, 0.224ppm, 0.28ppm, 0.336ppm, 0.392ppm and 0.448ppm for cadmium. Calibration curves were drawn for Cd, Cr, Pb and Zn by plotting intensity versus metal ion concentration as Figure 3.2 with (R^2 Pb = 0.9967, Cr = 0.9999, Cd = 0.9998 and Zn = 0.9994) values.

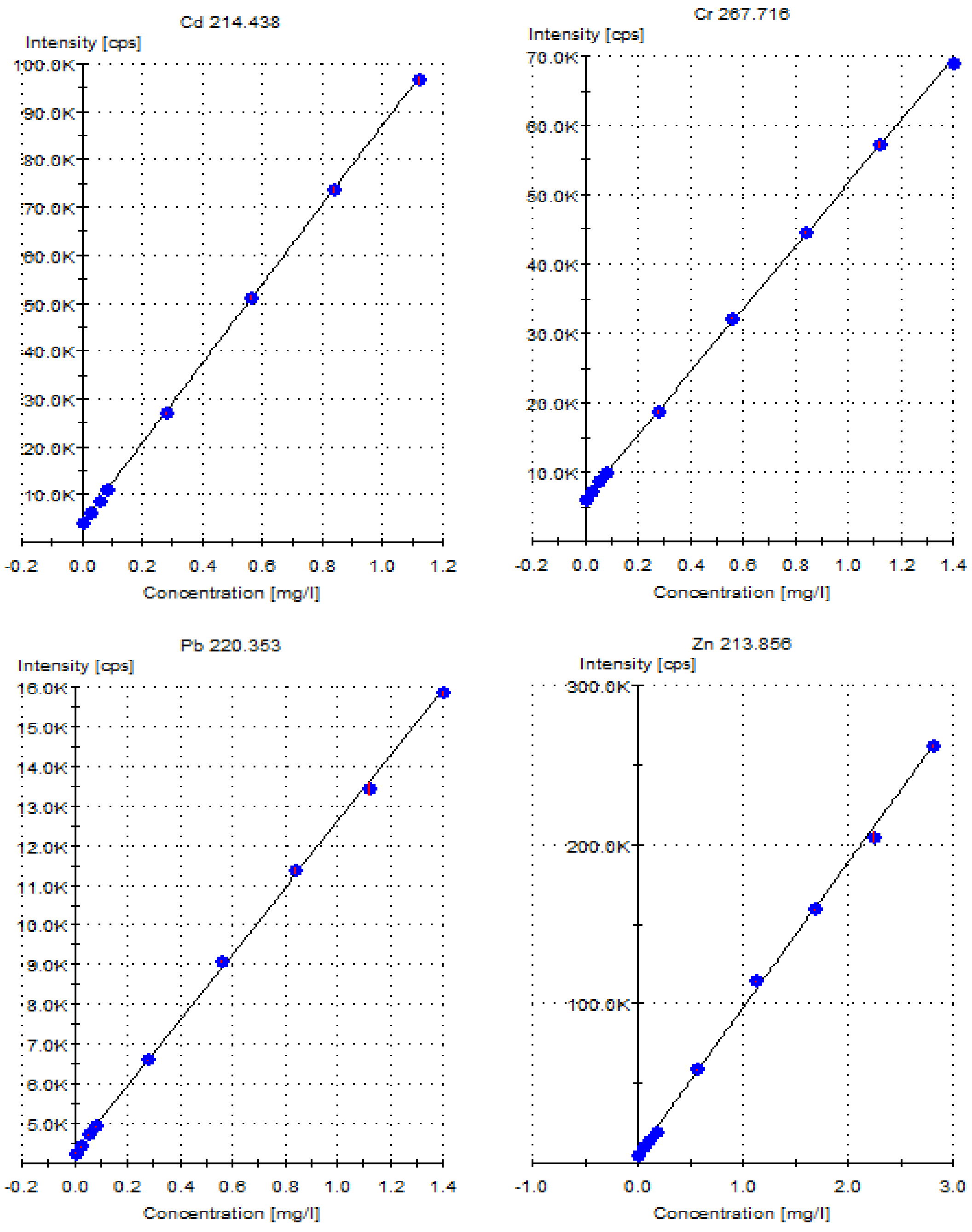

Figure3.2: Calibration curve of Cadmium, Chromium Lead and Zinc standard solution.

3.8. Heavy Metals Analysis

Selected heavy metals such as Cd, Cr, Pb and Zn were analyzed from collected samples of water, using ICP/OES after appropriate digestion had been made at Horticoop Ethiopia (Horticulture) Analytical Laboratory PLC, Bishoftu, Ethiopia. Per Standard solutions were used. All data were recorded in triplicate. The instrumental working condition and method detection limit for ICP/OES is given in Table (3.1).

Table 3.2 The working condition, method detection limit and ICP/OES instrument detection limit, for heavy metals analysis of Water sample of Ketar River.

Elements	Cd	Cr	Pb	Zn	Flame system
Wave length in (nm)	214.4	267.7	220.2	213.8	Plasma
Instrumental detection limit (mg/ L)	0.009	0.001	0.001	0.001	Plasma
Water MDL (method detection limit)	0.009	0.007	0.001	0.01	plasma
Back ground correction	on	on	on	on	Air

3.9. Method of Optimization Process

The optimum condition is the one which required minimum reagent volume consumption, minimum digestion time reflection and clear digestion solution, ease of simplicity and absence of undigested water sample. In this study, to prepare a clear colorless sample solution that is suitable for the analysis using ICP/OES different digestions were carried out using HNO_3 and HCl acid mixtures by varying parameters such as volume of the acid mixtures, digestion time and digestion temperature. From the optimization procedure the acid mixture of 4mL of (69-72%) HNO_3 and 1mL of (35.4%) HCl, digestion time of 3 hours and digestion temperature of $250^{O}C$ were found to be the optimal conditions for digestion of 50mL water samples.

3.10. Method Validation

3.10.1. Precision and Accuracy

Accuracy and precision are probably the most often quoted terms to express the extent of errors in a given analytical results. Analytical results must be evaluated to decide on the best values to report and to establish the probable limits of errors of these values [Kikuchi *et al*., 2002].The analyst will thus be concerned with the question of precision (repeatability of results), that is, the agreement between a set of results for the same quantity and also with accuracy, that is the difference between the measured value and the true value of the quantity, which is determined [Dean, 1997]. In this study, the precision of an analytical procedure is usually expressed as the variance, relative standard deviation and percentage relative standard deviation of a series of measurements [Matusiewicz and kopras, 1997]. The precision of the results was evaluated by percentage relative standard deviation of the results of three samples (n=3) and triplicate readings for each sample giving a total of nine measurements for a given sample.

$$\% \text{ RSD} = \left(\frac{SD}{\bar{X}}\right) \times 100$$

Where: RSD= represent relative standard deviation SD = Standard deviation and $\bar{X}$ = Mean value. On the other hand, the accuracy and validity of the measurements were determined by analyzing spiked samples.

3.10.2. Method Detection Limit (MDL)

Method Detection Limit (MDL) defined as the minimum concentration of substance that can be measured and reported with 95% confidence that the analyte concentration is greater than zero, and is determined from analysis of a sample in a given matrix containing the analyte [Theodore D, 2003].Three replicate blank samples were digested following the same procedures utilized for digesting of water samples. Each blank was assayed for its metal contents (Cd, Cr, Pb and Zn) by ICP/OES. The standard deviation (SD) of the three replicate blanks were calculated to determine the MDL and LOQ. Method detection limit (MDL) was calculated as three times the standard deviation (MDL = 3SD) and limit of quantitation (LOQ) was calculated as ten times the standard deviation (LOQ = 10SD) [David and Terry, 2008].

In present study due to the absence of certified reference materials or water samples in laboratory, the validity of the digestion procedure, precision and accuracy of ICP/OES was assured by spiking water samples with standard of known concentration. The spiked and non-spiked water samples were digested following the same procedure employed in the digestion of the respective samples and analyzed in similar condition. Then the percentage recovery of the analyte was calculated by: [Deribachew *et al.*, 2015; Kedir, 2015].

$$\text{recovery (R)} = \left(\frac{CM \text{ in the spik samples} - CM \text{ in the non spik sample}}{Amount \text{ added}}\right) x \ 100\,\%$$

Where, CM = concentration of metal of interest

3.11. Data analysis

Samples data were analyzed in triplicate using SPSS software (version 20). Descriptive data have generated for all variables and presented as means±SD.The results of the physicochemical parameters and heavy metals concentration analyzed from sampling sites were compared with WHO (2008) and Ayers and Westcot, FAO(1976, 1994) standards for surface water guideline permissible for drinking, domestic use and irrigation purposes and interpreted whether it is acceptable or not. The mean variations in data between three sites were analyzed using One-way ANOVA. The correlation of each parameter's relationship was determined using Pearson's correlation. Significance has considered at 95% confidence interval, differences in mean values obtained.

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1. Levels of Physicochemical Parameters of Water Sample

Physicochemical variables measured for the investigation of Ketar River include: pH, electrical conductivity (µS/Cm), total hardness (mg/L), total dissolved solid (mg/L), and chloride (mg/L).

The analyzed laboratory result taken from three sampling points was evaluated based on the average mean values of the three replicates for each physiochemical water quality parametric values and was compared with the WHO, (2008) and Ayers and West cot, FAO (1976, 1994) of drinking water quality standards, and interpreted in accordance with the result obtained from the laboratory analysis with the maximum WHO allowable limits. The interpretations of the result of physicochemical values were based on the summarized table (4.1) below.

Table 4.1 Levels of concentration of physicochemical Parameters of Water Sample of three sites, (Mean ±SD, n=3, mg/L and (µS/Cm) in Ketar River water sample

Parameters	Site-1	Site-2	Site-3	WHO	Ayers&Westcot, FAO
TH	32.50 ± .67	35.00 ± 0.67	34.33 ±0.68	300	NA
TDS	445.46 ±2.28	248.94 ±5.89	242.77 ±1.71	500	2000
Chloride	0.94 ± 0.11	1.10 ± 0.23	0.94 ± 0.12	250	400
pH	6.19 ± 0.05	6.31 ± 0.02	7.17 ± 0.01	6.5-8.5	6.5-8.5
EC	0.11 ± 0.01	0.13 ± 0.01	0.11 ± 0.01	750	3000

Source: WHO, (2008) for drinking water, Ayers and West cot, FAO (1976, 1994) for domestic use, drinking cattle, irrigation water, SD-standard deviation, NA-not available.

Total Hardness (TH): Water that has high mineral content is known as hard water. Hard water contains bicarbonate, chlorides and sulphates of calcium and magnesium. When treated hard water with soap, it gets precipitated in the form of insoluble salts of calcium and magnesium [APHA, 1999].

The result of mean concentration of TH in Ketar River water samples was in ranged from (32.50 ± 0.67 – 35.00± 0.67 mg/L) with minimum and maximum value, which was below

300 mg/L of (WHO, 2008) permissible guideline for drinking water, domestic usage. The statistical analysis of one way ANOVA mean comparison of TH of water at 95% confidence levels show significant difference ($p < 0.05$) in all between and within groups of sampling site (Appendix-1). Pearson mean correlation shows TH was strongly correlated with EC (= 0.679*, $p < 0.05$), negatively strongly correlated with TDS (r = -0.796*, $p < 0.05$), negatively corralled with chloride (r = -0.004, $p > 0.05$), pH (r = -0.212, $p > 0.05$) (Appendix-3). Negative correlation is a relationship between two variables in which one variable increases as the other decreases and vice versa. Positive correlation is a relationship between two variables in which both variables move in random that is in the same direction. A positive correlation exists when one variable decreases as the other variable decreases or one variable increases while the other increases.

Total Dissolved Solids (TDS): is a measure of the combined content of all inorganic and organic substances contained in a liquid in molecular, ionized or micro-granular (colloidal sol) suspended form [USEPA, 1991]. A higher TDS causes change on taste of water and not good for metallic pipelines used for transportation of water inside homes [Ramesh and Seetha, 2013].

The result of mean concentration of TDS in Ketar River water samples was ranged from (242.77± 1.71 – 445.46 ± 2.28 mg/L) with minimum and maximum result which was below 500 mg/L of (WHO, 2008) and 2000 mg/L of Ayers and westcot, FAO (1976, 1994) permissible guideline. The statistical analysis of ANOVA mean comparison of TDS of water at 95% confidence level shows not significant difference ($p > 0.05$) in all between and within groups of sampling site (Appendix-1). Pearson mean correlation shows TDS was positively correlated with pH (r = 0.054, $p > 0.05$) negatively correlated with chloride (r = -0.148, $p > 0.05$), EC (r = -0.265, $p > 0.05$) (Appendix-3)

Chloride: chloride in the form of the Cl^-ions is one of the major inorganic anions or negative ions in saltwater and freshwater. In drinking water the salty taste produced by chloride depends upon the concentration of the chloride ions. Water containing 250 mg/L of chloride may have a detectable salty taste if the chloride came from sodium chloride [Vernier, 2013]. Chloride toxicity has not been observed in humans except in the special case of impaired sodium chloride metabolism, e.g. in congestive heart failure [Wesson, 1969]. Chloride increases the electrical conductivity of water and thus increases its corrosivity. In metal pipes, chloride reacts with metal ions to form soluble salts [WHO, 1978].

The result of mean concentration of chloride in Ketar River water samples was ranged from (0.94 ± 0.11 -1.10 ± 0.36 mg/L) with minimum and maximum result which was below 250 mg/L of (WHO, 2008) and 400 mg/L of Ayers and west cot, FAO (1976, 1994) permissible guideline. The statistical analysis of one way ANOVA mean comparison of chloride of water at 95% confidence level shows not significant difference ($p > 0.05$) in all between and within groups sampling site (Appendix-1). Pearson mean correlation shows chloride was negatively correlated with pH ($r= -0.326$, $p > 0.05$), EC ($r= -0.125$, $p > 0.05$), (Appendix-3). The excessive concentration of chlorine in drinking water gives a salty test of the water that cannot satisfy thirsty but lower concentration affects the treatment process [WHO, 2014].

pH: pH is classed as one of the most important water quality parameters because it will decide whether the water is suitable for drinking purpose. Measurement of pH relates to the acidity or alkalinity of the water. A sample is considered to be acidic if the pH is below 7.0. It is alkaline if the pH is higher than 7.0. Acidic water can lead to corrosion of metal pipes and plumping system. Alkaline water shows disinfection in water. The pH values of most natural water are in the range of 6.5-8.5 [Chapman, 1996].

The result of mean concentration of pH ranged (6.19 ± 0.05 – 7.17± 0.01) with minimum and maximum value which slightly below (6.5-8.5) of (WHO, 2008) and (6.0-8.5) of Ayers and West cot, FAO (1976, 1994) permissible guideline for drinking water, domestic usage and irrigation purposes. The statistical analysis of one way ANOVA at 95% confidence level of pH shows not significance different ($p > 0.05$) in all between and within groups of sampling site (Appendix-1). Pearson mean correlation shows negatively strongly correlated with EC ($r = - 0.721^*$, $p < 0.05$), (Appendix-4).

Electrical Conductivity (EC): water capability to transmit electric current is known as electrical conductivity and served as a tool to assess the purity of water [Murugesan *et al.*; 2006]. Solutions of most inorganic compounds are relatively good conductors. Conversely, molecules of organic compounds that do not dissociate in aqueous solution conduct a current very poorly, if at all [APHA, 1999].

The result of mean concentration of EC of Ketar River was ranging from (0.11 ± 0.01 – 0.13 ± 0.01 µs/Cm) with minimum and maximum value which was below 750 µs/Cm of WHO, (2008) and 3000 µs/Cm of Ayers and Westcot, FAO (1976, 1994) permissible guideline for drinking water, domestic use and irrigation purposes. The statistical analysis of one way

ANOVA mean comparison of EC of water at 95% confidence levels shows not significant difference ($p > 0.05$) in all between and within groups of sampling site (Appendix-1).

4.2. Levels of heavy metals in the water samples

Concentration of heavy metals (Cd, Cr, Pb, and Zn) was determined using inductively coupled plasma/optical emission spectroscopy (ICP/OES) at their corresponding wave length 214.4, 267.7, 220.2 and 213.8 nm respectively. The concentrations of these metals were obtained in mg/L. The percentage recoveries of the analytes were calculated by the use of the equation:

$$\%\ \text{recovery (R)} = \left(\frac{CM\ in\ the\ spik\ samples - CM\ in\ the\ non\ spik\ sample}{Amount\ added}\right) x\ 100$$

Where: CM is concentration of metal of interest

According to the standard, 80-120% recovery and ≤ 20% RSD can have used as starting for assessment of accuracy and precision [APHA, 1999]. Finally, the results of recovery analysis were listed in (Table 4.2) and the percentage recoveries lie within the range 87.70 – 101.8%. Therefore, the percentage recoveries for Ketar River water samples were within the acceptable range for all the metals.

Table 4.2 Validation of Analytical Method That Shows Recovery Test in (ppm)

Heavy metals	Concentration after spike	Concentration before spike	Amount added	%Recovery
Cd	1.962	0.014	2.00	97.40
Cr	2.070	0.034	2.00	101.80
Pb	2.184	0.149	2.00	101.75
Zn	1.832	0.079	2.00	87.65

The precision of an analytical procedure expresses the closeness or agreement (degree of scatter) between a series of measurements obtained from multiple sampling of the same homogeneous sample [Yohannes, 2018]. The precision of the results were evaluated by the relative standard deviation of the results of triplicate digests. Values of relative standard deviations (% RSD) were less than ≤ 20% for all of the mean concentrations of metals. The mean values were determined from triplicate analysis of each sample and the accuracy and obtained for each sample in terms of mg/L with values for standard deviation were shown in

(Table 4.3) below.

Table 4.3 Levels of heavy metals concentration (Mean ± SD, n=3, mg/L) in Ketar River water of different sites.

Metals	Site-1	Site-2	Site-3	WHO	Ayers & West cot, FAO
Cd	0.03 ± 0.002	0.010 ± 0.00	0.010 ± 0.00	0.003	0.01
Cr	0.041 ± 0.007	0.038 ± 0.004	0.03 ± 0.00	0.05	0.1
Pb	0.081 ± 0.012	0.288 ± 0.050	0.083 ± 0.012	0.01	5
Zn	0.095 ± 0.015	0.073 ± 0.014	0.070 ± 0.00	3	2

Source: WHO (2008) for drinking water, Ayres and West cot, FAO (1976, 1994) for domestic use, drinking cattle, irrigation water.

Cadmium (Cd): is highly toxic metal that disrupt a number of biological systems, usually at doses much lower than most toxic metals [Nordberg *et al.*, 2007]. In low doses, it produces coughing, headaches, and vomiting. In larger doses, it can accumulate in the liver and kidneys that replace calcium in bones, leading to painful bone disorders and to a renal failure. The kidney is one of critical target organ in humans chronically exposed to cadmium by ingestion [USEPA, 1999].

The mean concentration of Cadmium metal in Ketar River water sample was ranged from (0.010 ± 0.00 - 0.03 ± 0 .002mg/L) with minimum and maximum value which was above 0.003 mg/L of WHO (2008) and maximum value (in site-1, 0.03mg/L) which was above 0.01mg/L Ayers and West cot, FAO (1976, 1994), permissible guideline for drinking water, domestic use and irrigation purposes. The statistical analyses of one- way ANOVA at 95% confident level shows not significance different ($p > 0.05$) between and within the groups of sampling site (Appendix 4). Pearson mean correlation shows Cd was strongly correlated with Zn ($r = 0.702^{*}$, $p < 0.05$), positively correlated with Cr ($r= 0.135$, $p > 0.05$) negatively correlated with Pb ($r = -0.240$, $p > 0.05$) (Appendix-6). Although the values recorded at the three sites, concentration of site-1 > site-2 and site-3 . This showed that Ketar River more polluted at site-1.Similarly higher level of Cadmium above the permissible limit concentrations was reported in previous studies by Bizualem, (2017). Farmers use pesticides, herbicides and fertilizers to improve the quality of their crops and paint pigments and incineration of cadmium containing plastics, nickel-cadmium batteries and PVC plastics activities practiced around the river might be contributed to the observed high levels of cadmium.

Chromium (Cr): Among the different heavy metals, Chromium is a common and very toxic pollutant introduced in to natural waters from a variety of industrial wastewaters Qaiser *et al*., 2009]. Trivalent chromium (Cr (III)) is relatively insoluble and required by microorganisms in small quantities as an essential trace metal nutrient, while hexavalent chromium (Cr (VI)) is a great concern because of its toxicity even in trace amount [Ozgunay, 2007]. Excessive intake of chromium by human leads to hepatic and renal damage, capillary damage, gastrointestinal irritation and central nervous system irritation. [Rengaraj, 2007]

The measured mean concentration of chromium in Ketar River was ranging from minimum of (0. 03 ± 0.00mg/L) to the maximum of (0.041 ± 0.007mg/L) which was below 0.05 mg/L of WHO (2008) and 0.1 mg/L Ayers and West cot, FAO (1976, 1994), permissible guideline for drinking water, domestic use and irrigation purposes. The statistical analyses of one- way ANOVA at 95% confident level of Cr metal shows not significance different ($p > 0.05$) between and within the groups of sampling sites (Appendix 4). Pearson mean correlation shows Cr was positively correlated with Pb ($r = 0.289$, $p > 0.05$), Zn ($r = 0.609$, $p > 0.05$). (Appendix-6). The values recorded at the three sites showed concentration below the standard recommended for fresh surface water. The low values observed in the river provide an indication that there was a low usage of Cr containing materials and potential contamination by this metal within the sampling sites is minimal.

Lead (Pb): Seriously, hazardous species found in the river of the studied sites is lead. It is easily deposited in blood, kidney, reproductive system, nervous system and brain so as results fatal diseases. Acute lead poisoning in humans causes severe damage in the kidneys, liver, brain, reproductive system and central nervous system, and even causes death [Tan, 2010; Nazari, 2011].

The measured mean concentration of lead metal in Ketar River water sample was ranged from (0.081 ± 0.012 - 0.288 ± 0.050 mg/L) with minimum and maximum value which was above 0.01 mg/L of WHO (2008) permissible guideline for drinking water and domestic uses and minimum and maximum value which was below 5 mg/L of Ayers and west cot, FAO (1976, 1994) permissible guideline for drinking water, domestic use and irrigation purposes. The statistical analyses of one-way ANOVA at 95% confident level shows significance different ($p < 0.05$) between and within the groups of sampling site (Appendix-4). Pearson mean correlation shows Pb was positively correlated with Zn ($r = 0.084$ $p > 0.05$). (Appendix- 6). Although the values recorded at the three sites, concentration of site-2 > site-3 > site-1 . This showed that the river more polluted at site-3.In all the entire selected sites of the river, the values recorded were above the maximum permissible guideline. Higher level of lead above the permissible limit concentration was reported in previous studies such as those by Bizualem, (2017) in River Gudar and Tibebu *et al.*, (2017) in Hora natural mineral water. Washing cars, served motor oils and disposal of lead batteries from garages, the work of welding, plating, painting and wastewater which was released from factories, domestic waste, municipal solid and petrol stations were directly entered the rivers cross Asella Town and finally entered the Ketar River was probably contributed to increases of Pb concentration.

Zinc (Zn): is a ubiquitous trace element. It is one of the most important trace elements in the body, and it is indispensable to the growth and development of microorganisms, plants, and animals [Stefanidou *et al.;* 2006]. It is also critical in wound healing, taste acuity, immune system function, production, bone mineralization, proper thyroid function, blood clotting, cognitive functions, fetal growth, and sperm production. It regulates body fluid pH [Bhowmik *et al.;* 2010]. The toxicity of Zn is as a result of excessive absorption which suppresses copper and iron absorption while free Zn^{2+} ion in solution is highly toxic to plants, invertebrates, and even fish. Zinc salts are intestinal irritants and can cause nausea, and abdominal pain [FAO/WHO, 2011].

The measured mean concentration of Zinc in Ketar River was ranging from minimum of (0.070 ± 0.00 mg/L) to the maximum of (0.095 ± 0.015mg/L) which was below 5mg/L of WHO (2008) and 2mg/L Ayers and Westcot, FAO (1976, 1994), permissible guideline for drinking water, domestic use and irrigation purposes. The statistical analyses of one- way ANOVA at 95% confident level of Zn metal shows not significance different ($p > 0.05$) between and within the groups of sampling site (Appendix-4). The values recorded at the three sites shown concentration below the standard recommended for fresh surface water, there were indications of the presence of this metal in the river. This shown that the metal concentration in the water were generally low. Based on the values recorded, pollution level of toxic heavy metals on the three sites of the river might be assumed with the sequence, site- 2 > site-1 > site-3.

CHAPTER FIVE

5. SUMMARY, CONCLUSION AND RECOMMENDATION

5. 1. Summary and Conclusion

In this study, the investigation of Water quality on Ketar River was conducted based on selective water quality parameters namely; pH, electrical conductivity (EC), total hardness (TH), total dissolved solid (TDS), chloride (Cl-) and the levels of heavy metals (Cd, Cr, Pb and Zn) concentration which were relevant to indicate the suitability of water for drinking and other purposes. The analyzed results taken from three sampling points was evaluated compared with the WHO, (2008) and the Ayers and west cot, FAO, (1976, 1994) drinking water quality standards and interpreted in accordance with the result obtained from the laboratory analysis.

The analyzed results of (EC,TDS, TH and chloride) were shown below maximum permissible guideline but the amounts of pH value slightly in acidic range. The mean of heavy metals concentration of Cd and Pb in water sample of all sites were above WHO (2008) and below Ayers and west cot, FAO (1976, 1994) permissible guideline for drinking, domestic use and irrigation purposes except Cd in site-1 above permissible guideline. The levels of Cr and Zn were below maximum permissible guideline. From obtained result, It can be concluded that the increasing value of acidity, Cd and Pb concentration indicates that the Kater River water was not safe for drinking purpose but it can be used for agricultural activities such as irrigation purpose.

As it was investigated in this river; the domestic wastes, deteriorating household paints, car wash, disposal of lead batteries from garage and the agricultural activities practiced around the river had contributions to the observed acidic pH, higher level of cadmium and lead.

5.2. Recommendation

The value of pH and heavy metals content showed that the Ketar River water was unsafe for drinking purpose. Based on the obtained results and conclusions of this study, the following recommendations were formulated:-

- To protect the river, the community and concerned body should take the controlling mechanism such as proper treatment of urban and rural sewage before discharging it into the river.
- Awareness should be often given to the residents of urban about the disposal of solid and liquid wastes by the responsible bodies.
- Awareness should provide to the owners of factories how solid and liquid wastes can be recycled.
- The study was conducted with in one season, on selected physicochemical parameters and heavy metals content. So, it showed lack of comprehensiveness. Further studies should be conducted in different seasons considering other water quality parameters such as biological water quality parameters and other water quality parameters for drinking and irrigation purposes.

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APPENDIXES

Appendix 7: ANOVA mean comparison of physicochemical parameters in Ketar River water sample

		Sum of Squares	Df	Mean Square	F	P-value
TH (mg/L)	Between Groups	94.389	5	47.960	1.154	.023
	Within Groups	4.167	3	.694		
	Total	98.556	8			
TDS (mg/L)	Between Groups	59087.580	5	11817.516	1.698	.352
	Within Groups	20884.182	3	6961.394		
	Total	79971.762	8			
Chloride (mg/L)	Between Groups	.085	5	.017	.183	.951
	Within Groups	.280	3	.093		
	Total	.365	8			
pH	Between Groups	.587	5	.117	.662	.680
	Within Groups	.532	3	.177		
	Total	1.119	8			
EC(µs/Cm)	Between Groups	.001	5	.000	2.150	.281
	Within Groups	.000	3	.000		
	Total	.001	8			

Appendix 8: Mean comparison of physicochemical parameters in Ketar River water sample

Parameters	Site-1	Site-2	Site- 3
	Mean ± SD	Mean ± SD	Mean ± SD
Total hardness (mg/L)	32.50 ± 0 .67	35. 00 ± 0.67	34.33 ± 0.68
Total dissolved solid(mg/l)	445.46 ± 2.28	248.94 ± 5.89	242.77 ± 1.71
Chloride (mg/L)	0.94 ± 0.11	1.10 ± 0.23	0.94 ± 0.12
pH	6.19 ± 0.05	6.31 ± 0.02	7.17 ± 0.01
Electrical conductivity (µs/Cm)	0.11 ± 0.01	0.13 ± 0.01	0.11 ± 0.01

Appendix 9: Linear Pearson Correlation among the Physicochemical Parameters in Ketar River water sample in (mg/L) & (µs/Cm).

		TH	TDS	Chloride	pH	EC
TH	Correlation	1	-.796*	-.004	-.212	.679*
	P-value		.010	.992	.585	.044
TDS	Correlation		1	-.148	.054	-.265
	P-value			.704	.889	.491
Chloride	Correlation			1	-.326	-.125
	P-value				.391	.748
pH	Correlation				1	-.721*
	P-value					.028
EC	Correlation					1
	P-value					

Appendix 10: ANOVA mean comparison of Heavy Metals in the Ketar River water sample

		Sum of Squares	Df	Mean Square	F	Sig.
Cd (ppm)	Between Groups	.001	5	.000	1.800	.333
	Within Groups	.000	3	.000		
	Total	.001	8			
Cr (ppm)	Between Groups	.001	5	.000	3.067	.193
	Within Groups	.000	3	.000		
	Total	.001	8			
Pb (ppm)	Between Groups	.358	5	.072	1841.000	.000
	Within Groups	.000	3	.000		
	Total	.358	8			
Zn (ppm)	Between Groups	.002	5	.000	2.067	.292
	Within Groups	.001	3	.000		
	Total	.003	8			

Appendix 11: Mean comparison of Heavy metals in Ketar River water sample

Metals	Site-1	Site-2	Site-3
	Mean ± SD	Mean ± SD	Mean ± SD
Cd (ppm)	0.03 ± 0.002	0.010 ± 0.00	0.010 ± 0.00
Cr (ppm)	0.041 ± 0.007	0.038 ± 0.004	0.03 ± 0.00
Pb (ppm)	0.081 ± 0.012	0.288 ± 0.050	0.083 ± 0.012
Zn (PPm)	0.095 ± 0.015	0.073 ± 0.014	0.070 ± 0.00

Appendix 12: Linear Pearson Correlation of heavy metals in Ketar River water sample.

Metals		Cd (ppm)	Cr (ppm)	Pb (ppm)	Zn (ppm)
Cd (ppm)	Correlation	1	.135	-.240	.702*
	P-v alue		.729	.533	.035
Cr (ppm)	Correlation		1	.289	.609
	P-value			.450	.082
Pb (ppm)	Correlation			1	.084
	P-value				.829
Zn (ppm)	Correlation				1
	P-value				