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SCHOOL OF GRADUATE STUDIES

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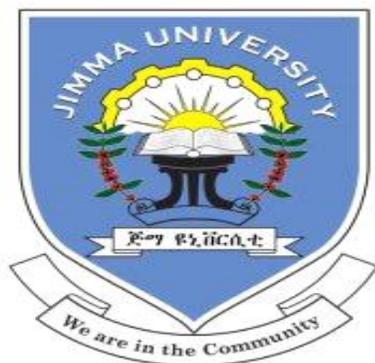
M.Sc THESIS ON

PHYSICO-CHEMICAL ANALYSIS AND DETRMINATION OF THE LEVEL OF SELECTED HEAVY METALS IN KOLATI RIVER, JIMMA ZONE

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PHYSICO-CHEMICAL ANALYSIS AND DETRMINATION OF THE LEVEL OF SELECTED HEAVY METALS IN KOLATI RIVER, JIMMA ZONE

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A THESIS SUBMITTED TO SCHOOL OF GRADUATE STUDIES JIMMA UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

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ABBREVIATION/ACCRONOMY

ANOVA   Analysis of variance

APHA   American public Health Association

EC   Electrical Conductivity

ESA   Ethiopian   Standard Agency

FAAS   Flame Atomic Absorption Spectroscopy

SD   Standard Deviation

SPADNS   Sodium-2,1,8, dihydroxy-3,6-naphtaline disulphate

SPSS   Statically package for the social science

TDS   Total dissolved solid

WHO   World Health Organization

Abstract

Water is the most abundant source that is essential for the survival of all known forms of life. But water pollution, particularly river water pollution problems mainly emanated from agricultural activities, municipal wastes and industrial wastes that can affect human being and domestic uses. The present study focuses on the analysis of Physicochemical characteristics like Temperature, PH, E.C, TDS, Salinity, turbidity, nitrate, nitrite, phosphate, sulphate, fluoride and heavy metal levels such as Cu, Zn, Cd, Pb, Co and Cr in water sample from kolati river systems at different site. Temperature, E.C, TDS and salinity were measured on site by thermometer and conductivity meter. The nitrate, nitrite, phosphate, sulphate and fluoride were determined by photometer. But the level of selective heavy metals was analyzed by FAAS. The range of all of the physicochemical parameter analyzed were: Temperature ($17.46\text{-}18.43^0C$), pH (8.03-8.45), EC (3409-9222.39μs/cm), TDS (1707-4607.06mg/L), Turbidity (111.44-234.4 NTU), Salinity (2007-6052.3mg/L), PO_4^{3-} (0.82-1.62mg/L), NO_3^-(5.06-14.53mg/L), NO_2^-(0.81-0.966 mg/L, F^-(0.89-0.96 mg/L), SO_4^{2-} (6.27-10.68 mg/L), Pb (0.07-0.12), Cu (0.042-0.056), Zn (0.037-0.113), Co (0.07-0.145) Cr (0.039-0.049) in mg/L. And the water sample taken from Kolati river at the site 4 recorded high value of all parameter since the site is influent discharge point. One-way ANOVA test(p≤0.05) showed that all measured values vary significantly across location. However, the result indicates that most of physio chemical parameter from Kolati river water system was within the WHO and ESA limit for drinking water standard. But TDS, Turbidity, salinity, E.C and Pb exceeded both WHO and ESA drinking water standard. This could be due to waste discharge flow farm nearby, municipal waste from the town, pesticides, Domestic waste, car wash, chemical from irrigation, waste from toilet. This study, therefore, recommended the government and other responsible authorities to take appropriate corrective measures.

Keyword*: - Kolati river, water quality, physicochemical, heavy metals level, FAAS.*

1. INTRODUCTION

1.1. Background of the Study

The normal functioning of a natural system depends entirely on the availability of adequate quantity and quality of water [1]. Without freshwater of adequate quality and quantity sustainable development will not be possible [2]. World Health Organization places great emphasis on the quality of drinking water and has recommended upper limits for a number of physical, chemical and biological parameters in water used for different activities. Springs and rivers are among the major sources of water used to supply major urban and rural communities.

In Ethiopia, human activities such as land use and modification, urbanization, human settlement and other practices associated with rapid population growth are the major water quality degrading factors [3]. Studies showed that there are increasing indications of water pollution, particularly river water pollution problems mainly emanated from agricultural activities, municipal wastes and industrial wastes that can affect human being and domestic uses [4]. In addition to this sustainable production is becoming an issue, due to the international competition in the Agricultural sector; by large usage of fertilizers are responsible for the environmental pollution. Farms use a lot of fertilizer that are largely washed off in the soil and enter into the water bodies. On the other hand, pesticides are major pollutants, because they introduce toxic metals in the environment. This is because of lack of information about how to use fertilizer and pesticides in a sustainable way at the farm level [5].

Physio-chemical parameters are highly important with respect to the occurrence and abundance of species. Chemical enrichment in river system are derived through a combined effect of both industrial and municipal effluents and runoffs from surrounding area or through solution effects from adjacent soil. The presence of nutrients in rivers may be attributed to the process of organic mineralization of nitrates and phosphates derived principally from surface runoffs from the immediate vicinity (forests, farms and settlement) and perhaps by in situ mineralization [6]. Soil erosion is closely linked with high surface runoffs and rapid siltation of surface water system resulting in subsequent decline in its portability. Eroded materials may exist in river systems as dissolved solids or suspended solids but within a particular regime of flow, river systems bear with them sediments, which constitute the byproducts of processes operating within the environment through which they flow. These are derived though leaching of soil profiles, surface runoffs, direct dumping of wastes (municipal and industry), soil erosion; atmospheric

fallouts etc. Heavy metals are toxic and can accumulate in a system without being noticed [7]. This makes them a source of concern. Sources of heavy metals includes industrial activates (mining, oil exploration activities, manufacturing and agricultural practices), domestics and commercial practices that generates wastes, and natural factors. Metal content in rivers may vary between the water column and bed sediments. However, variation in concentration of parameters depends on concentration from processes operating within the catchments.

Although there are no systematic and comprehensive water quality assessment programs in the country [8], 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. For this reason, due emphasis is given to the analysis of these contaminants. Heavy metals normally occurring in nature are not harmful to our environment because they are only present in very small amounts [9].

The use of kolati river water sources for irrigation and domestic uses is a common feature for many communities in Nono Benja woreda. The area is naturally rich in water resources which makes it favorable for agricultural activities mainly, cultivation of different crops like Teff, maize, sorghum, Pea, bean, wheat, vegetable and others (unpublished data, Nono Benja woreda Bureau of Agriculture,2007). All of these rivers are road side, which are susceptible to contamination from human activity and animal wastes. Among the different water resources in the area, kolati river is the one in which the livelihood of many farmers largely depend on. Additionally, the river passes near the town and in between flower farm. And some wastes are discharged to the river without any treatment from the farms. The river is only 500 m far from Nono town. It is also a dumping ground wastes from different human activity such as slaughter, car wash, and municipal wastes. Yet no baseline information is available at hand regarding the Kolati rivers water quality and classification. Because of this assessing its contaminant level is important.

1.2 Statement of the problem

As results of human activity Rivers in urban areas in many developing countries have water quality problems because of domestic and industrial wastes that are often discharged untreated into water bodies which lead to the increase in the level of potentially toxic elements concentrations and also in nature water acquires contaminants from its surrounding and those arising from humans and animals as well as other biological activities [1]. Kolati river is one of the major river in Nonno woreda that passes near the town and in between the farms. The farm around the area is used different chemicals and releases the wastes to the river without any treatment.   As the river runs along the side of the town (at the south west part), it could be fed with contaminants brought by run-off from the upload into the river at the peak of the floods, discharge from municipal wastes. At the effluent discharge site, the water is colored, turbid and the vegetation's along the river appears scorched despite the fact that water from this river is the major source in the area. Since there is no municipal water supply for the local communities living around the river, they rely on this untreated river water for drinking, irrigation and other household purposes. The environment damage caused by water pollution from municipal discharge effluent in Kolati River has not studied yet. These create an urgent need to assess the level of pollution of the river through the consideration of the impact of effluents from municipal discharge on water quality of the river. Therefore, the goal of this research is to generate baseline data on physio-chemical characteristics and selected heavy metals of the Kolati River. This also might initiate the researcher to conduct the study in this area from the point of view of water quality parameter

1.3. Objective

1.3.1. General Objectives

- The main objective of this study is to assess the physio-chemical parameters and heavy metals level of Kolati River.

1.3.2. Specific Objectives

- To determine the physic-chemical parameters (pH, temperature, Electrical conductivity, phosphate, nitrate, nitrite, sulphate, fluoride, salinity, TDS, Turbidity) of kolati Rivers.
- To determine the level of heavy metals (Cd, Zn, Pb, Cu,Cr and Co)of Kolati Rivers
- To compare the level water quality parameters with the national and international standard as well as reported literature values.

1.4 Significance of the study

The study outcome will provide preliminary information concerning pollution status of Kolati River and the acceptability for drinking, irrigation and other domestic purpose by comparing with national and international water quality standards set for different uses of water. Also it gives the baseline data on physio-chemical constituents and some heavy metals of the river water. Additionally, the results of the study serve as a source of information for further study who wants to conduct a research that Safe people of a community from contacting different kinds of diseases and used as a basis for management options of the river.

2. **LETRATURE REVIEW**

2.1. River water

Rivers carry water and nutrients to areas all around the earth. They play a very important part in the water cycle, acting as drainage channels for surface water. Rivers drain nearly 75% of the earth's land surface. Rivers provide excellent habitat and food for many of the earth's organisms. Many rare plants and trees grow by rivers. Ducks, voles, otters and beavers make their homes on the river banks. Reeds and other plants like bulrushes grow along the river banks. Other animals use the river for food and drink. Birds such as kingfishers eat small fish from the river. In Africa, animals such as antelopes, lions and elephants go to rivers for water to drink. Other animals such as bears catch fish from rivers. River deltas have many different species of wildlife. Insects, mammals and birds use the delta for their homes and for food. Rivers provide travel routes for exploration, commerce and recreation [1]. Water quality is defined in terms of the chemical, physical and biological contents of water. Water quality Guide lines provide basic scientific information about water quality parameters and ecologically relevant toxicological threshold values to protect specific water uses. Most of the rivers in the urban areas of the developing countries are the ends of effluents discharged from the industries. African countries and Asian countries experiencing rapid industrial growth and this are making environmental conservation a difficult task [10].

2.2. Physicochemical Parameters

Physicochemical parameter study is very important to get exact idea about the quality of water and we can compare results of different physicochemical parameter values with standard values. It is very essential and important to test the water before it is used for drinking, domestic, agricultural or industrial purpose. Physical and chemical properties are parameters that do not identify particular chemical Species but are used as indicators of how water quality may affect water uses. These are Temperature, electrical conductivity, total dissolved solids, hydrogen Ion concentration (measured as pH), salinity, and turbidity [11]. Water must be tested with different physic-chemical parameters. Selection of parameters for testing of water is solely depends upon for what purpose we are going to use that water and what extent we need its quality and purity. Water does contain different types of floating, dissolved, suspended and microbiological as well as bacteriological impurities. For Obtaining more and more quality and purity water, it should be tested for its trace metal, heavy metal contents and organic i.e. pesticide residue. It is obvious that drinking water should pass these entire tests and it should content required amount of mineral level. Only in the developed countries all these criteria are strictly monitored. Due to very low

concentration of heavy metal and organic pesticide impurities present in water it need highly sophisticated analytical instruments and well trained manpower. Following different physic chemical parameters are tested regularly for monitoring quality of water [1].   Table 1: Different analytical water quality parameters used for testing of quality of water and their source of occurrence and potential health effects with USEPA guidelines [37]

No	Parameter	Source of occurrence	Potential health effect	WHO* (2012)	ESA * (2012)
1	Temp.	Due to chemical reaction, hot waste water	Influence chemical, biochemical, biological of aquatic system, effect on solubility of essential gases	NM	NM
2	PH	Due to different dissolved gases and solid	Bitter test, corrosion, affect mucus membrane	6.5-9.5	6.5-9.5
3	E.C	Due to different dissolved solid	High conductivity increases corrosive nature of water	1200μs/cm	NM
4	Turbidity	Soil runoff	Higher level of turbidity are associated with disease causing bacteria	5NTU	7NTU
5	Total dissolved solid	From the Presence all dissolved salt	Undesirable taste, gastro-intestinal irritation, corrosion, or incrustation	1000mg/L	1500mg/L
6	Nitrate	Runoff from fertilizer use; leaking from septic tanks, sewage; erosion of natural deposits	Effect on Infants below the age of six months Symptoms include shortness of breath and blue-baby syndrome	50mg/L	50mg/L
7	Nitrite	NH3 compounds	Form nitrosamine's – carcinogenic	3mg/L	3mg/L
8	Phosphate	Waste water from detergent effluent, rocks	Stimulate microbial growth; rancidity mound growth; algal growth, eutrophication	5mg/L	5mg/L
9	Fluoride	Presence of mineral salts	Dental and skeletal flourish; non-skeletal manifestation	1.5mg/L	1.5mg/L
10	Sulphate	Due to dissolved Ca/Mg/Fe sulphate	Taste affect; gastro-intestinal irritation; calcium sulphate scale, laxative effect	500mg/L	NM

  Ref; [3-6]

2.3. Heavy Metal its Toxicity

Metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 [21]. Most of the heavy metals are dangerous to health or to the environment. Heavy metals in industrial wastewater include lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, silver, gold, and nickel. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO. 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. Children may receive higher doses of metals from food than adults, since they consume more food for their body weight than adults. Living organisms require trace amounts of some heavy metals, including cobalt, copper, iron, manganese, molybdenum, vanadium, strontium, and zinc. Excessive levels of essential metals, however, can be detrimental to the organism. Nonessential heavy metals of particular concern because of their toxicity are cadmium, chromium, mercury, lead, arsenic, and antimony [8]. Heavy metals are released to water streams from numerous sources. Typical sources are municipal wastewater-treatment plants, manufacturing industries, mining, and rural agricultural Cultivation and fertilization. There are two major types of sources, one is industrial and another one is agriculture [13].

2.3.1. Nature of Heavy Metals

Heavy metals have high solubility, and are having acidic or neutral PH. These heavy metals are generally present in very low concentration. Because of high solubility these are easily taken by living organisms and get accumulated in the body [14].

2.3.2 Heavy Metals Releasing from Agricultural Farms

Animal feedlots, Irrigation, Cultivation Pastures Dairy farming, Orchards Aquaculture, forestry releases phosphorus, nitrogen, metals, pathogens, sediment, pesticides, and some trace elements (e.g. selenium). Farmers use fertilizers and pesticides to promote growth and reduce insect damage the chemicals in these products may end up in water. Local environmental conditions (soil types, seasonal snow and rainfall) also affect this contamination. Many fertilizers contain forms of nitrogen that can break down into harmful nitrates. This could add to other sources of nitrates. Some

underground agricultural drainage systems collect fertilizers and pesticides. In Ethiopia, Sustainable production is becoming an issue, due to the international competition in the Agricultural sector; by large usage of fertilizers are responsible for the environmental pollution. Farms use a lot of fertilizer that are largely washed off in the soil and enter into the water bodies. On the other hand, pesticides are major pollutants, because they introduce toxic metals in the environment. This is because of lack of information about how to use fertilizer and pesticides in a sustainable way at the farm level [17].

Table .2 Summaries of some major source and health effect of heavy metals under the study.[37]

Sr.no	Pollutants	Major source	Effect of human health	Water quality guideline	
				ESA (mg/L) (2010)	WHO (mg/L) (2008)
1	Zn	Effluents from electroplating industries, sewage discharge, fertilizers, manufacture	Vomiting, diarrhea, liver and kidney damage, system dysfunctions	5	5
2	Cu	Copper electroplating, pesticide production, mining, common copper-bearing ores are S^{2-}, As, Cl^-, and CO_3^{2-}	Headache, nausea, vomiting, diarrhea, liver anemia, cirrhosis in patients, liver and kidney damage.	2	2
3	Pb	Paint, pesticide, lead storage batteries, crystal glass, preparation fertilizers	Cognitive impairment in children, cause blood and brain disorder, peripheral neuropathy in adults, developmental delay, decrease in hemoglobin production,	0.01	0.01
4	Cd	Rock, coal, petroleum, paint, pigments, electroplating, batteries production	Cd appears to accumulate with age, especially in the kidney and it is considered also as a cancer and cardiovascular diseases, fragile bones and damage to lungs, liver and blood	0.003	0.003
5	Cr	chromium arises from industrial sources and/or agriculture activities at the studied areas. Metal plating	for public health problems of cardiovascular disease, impaired glucose tolerance, elevated circulating insulin levels, and elevated serum cholesterol.	0.05mg/L	0.05mg/L
6	Co	Natural sources include wind-blown continental dust, seawater spray, volcanoes, forest fires, and continental and marine biogenic emissions.	Exposure to high levels of the non-radioactive cobalt results in lung and heart defect and dermatitis. The health effect of radioactive cobalt is known to cause cancer.	0.5	0.5

2.3.3 Copper

Environmental contamination due to copper is caused by mining, printed circuits, metallurgical, fiber production, pipe corrosion and metal plating industries [15]. The other major industries discharging copper in their effluents are paper, pulp, petroleum refining and wood preserving. Agricultural sources such as fertilizers, fungicidal sprays and animal wastes. Also lead to water pollution due to copper. Copper may be found as a contaminant in food, especially shell fish, liver, mushrooms, nuts and chocolates. Any packaging container using copper material may contaminate the product such as food, water and others. Cu is both an essential nutrient and a drinking water contaminant. Cu in a drinking water supply usually arises from the corrosive action of water leaching Cu from Cu pipes in buildings. Staining of sanitary ware and laundry may occur at Cu concentrations above 1mg/L. At levels above 5mg/L, Cu also imparts a color and an undesirable bitter taste to water. Although Cu can give rise to taste, it should be acceptable at the health-based guideline value of 2mg/L [2]. The adverse health effects caused by drinking water contaminated with copper are abdominal pain, vomiting, headache, nausea, and diarrhea. Copper in large doses is dangerous to infants and people with certain metabolic disorders. On the other hand, lack of copper intake causes anemia, growth inhibition, and blood circulation problems [16].

2.3.4 Zinc

The diet is normally the principal source of Zn. Zn is an essential trace element found in virtually all food and potable water in the form of salts or organic complexes. There are several sources of elevated Zn found the water bodies including industrial discharges, sewage effluents, domestic wastes, municipal wastes, mining, as well as natural chemical weathering of geological materials [17]. Due to its remarkable resistant to atmospheric corrosion; zinc is commonly used to protect iron from rusting, in the process called galvanization. Zinc is widely used for the manufacturing of zinc white and several useful alloys such as brass, German silver, delta metal, for the preparation of gold and silver in the cyanide method, for the desilverization of lead in parks process and as an anode material in galvanic cells. Various zinc salts are used industrially in wood preservatives, catalysts, photographic paper, and accelerators for rubber vulcanization, ceramics, textiles, fertilizers pigments, steel production and batteries drinking water containing Zn at levels above 3 mg/L may not be acceptable to consumers. Zn in large doses causes Depression, lethargy, neurological signs and increased thirst.

2.3.5 Lead

Lead is a dangerous element; it is harmful even in small amounts. Lead enters the human body in many ways. The main sources of lead contamination of the aquatic environment are the industrial discharges from smelters, paints and ceramics, through vehicular emissions, runoff from contaminated land areas, atmospheric fallout and sewage effluents. In some cases, lead is used to stabilize land pipes/plastic pipes and results in lead contamination of river water [2]. It can be inhaled in dust from lead paints, or waste gases from leaded gasoline. It is found in trace amounts in various foods, notably fish, which are heavily subject to industrial pollution. Some old homes may have lead water pipes, which can then contaminate drinking water. Most of the lead we take in is removed from our bodies in urine; however, there is still risk of buildup, particularly in children, Studies on lead are numerous because of its hazardous effects. Lead is considered the number one health threat to children, and the effects of lead poisoning can last a lifetime. Its toxicities are that damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system [18].

2.3.6 Cadmium

Cadmium is generally classified as toxic trace element. It is found in very low concentration in most rocks, as well as in coal and petroleum and often in combination with zinc. Geologic deposits of cadmium can serve as sources to groundwater and surface water, especially when in contact with soft, acidic waters [19]. The adsorption of Cd onto soils and silicon or aluminum oxides is strongly pH dependent, increasing as conditions become more alkaline. When the pH is below 6.5, Cd is desorbed from these materials. There is no evidence indicating its essentiality to humans. Galvanized steel is plated with zinc, which is normally contains about 1% Cd. Cd also has specific uses in paint, photography, and nickel-cadmium batteries. Some cases of cadmium poisoning are linked to cadmium-plated food utensils. It is introduced into the environment from paint and pigments, and plastic stabilizers mining and smelting operations and industrial operations, including electroplating, reprocessing cadmium scrap, and incineration of cadmium containing plastics. The remaining cadmium emissions are from fossil fuel use, Effluents from industries such as battery production, dye and manufacture of pigments fertilizer application, and Sewage sludge disposal [20]. Cadmium may enter drinking water as a result of corrosion of galvanized pipe. Landfill leachates are also an important source of cadmium in the environment. Cadmium that is taken into the body usually remains there. Inhaled cadmium is more hazardous than ingested cadmium. A major source of inhaled cadmium is tobacco smoke. Cd is chemically similar to Zn, an essential nutrient for plants and

animals; it is readily assimilated into the food chain. Plants absorb Cd from irrigation water. The recommended upper limit in irrigation water is 0.01 mg/L. Children are especially susceptible to lead because developing skeletal systems require high calcium levels. Lead that is stored in bone is not harmful, but if high levels of calcium are ingested later, the lead in the bone may be replaced by calcium and mobilized. Acute exposure of Cd can cause nausea, vomiting, diarrhea, muscle cramps, salivation, sensory disturbances, liver injury, convulsions, shock, and renal failure. Long-term exposure to low levels of Cd in air, food, and water leads to a build-up of Cd in the kidneys and possible kidney disease. Other potential long-term effects are fragile bones and damage to lungs, liver, and blood [36] USEPA [36] primary drinking water standard for Cd is 0.005 mg/L and WHO recommended guideline value for Cd in drinking water is 0.003 mg/L.

2.3.7 Chromium

Chromium is essential to animals and human. Chromium in excess amounts can be toxic especially the hexavalent form. Chromium is used in metal alloys and pigments for paints, cement, paper, rubber, and other materials. Electroplating can release chromic acid spray and air-borne Cr-trioxide, both can result in direct damage to skin and lungs, as well as chromium dust has been considered as a potential cause of lung cancer [33]. Sub chronic and chronic exposure to chromic acid can cause dermatitis and ulceration of the skin [36]. Long-term exposure can cause kidney and liver damage, and damage too circulatory and nerve tissue. Chromium often accumulates in aquatic life, adding also to the danger eating fish that may have been exposed to high levels of chromium.

3. MATERIALS AND METHODS

3.1 Description of the Study Area

The study area is located in Nonno Benja, Woreda, Jimma, Oromia regional state, Ethiopia and 432 Km south west of Addis Ababa and a longitude of 9°2′N 38°24′E. The altitude of the area ranges between 2,229and 2870 meter above sea level.

3.2 Selection of Study Area

There are a total of three known river water in this rural area, loko, lega hedu and KolatiRivers, all are flow to Gibe River. To investigate the quality of water in this area, Kolati River were purposively considered for physic-chemical parameters and selected heavy metals because of the potential sources of pollution, agricultural activities, population density and it is the backbone for eight kebele people. Kolati River was located in the catchment basin with intense human activities and characterized by deforestation, poor farming methods leading to soil erosion and siltation into water bodies and farming along river bank reserves. The degradation is due to the pollution from various institutions, agro-chemicals, urban effluent, car washing, soil erosion (siltation), and overgrazing. All these human activities lead to anthropogenic pollutants being transported to streams, rivers and other municipal drainage water systems; either dissolved in the water or attached to suspended matter and eventually gets into the Kolati river.
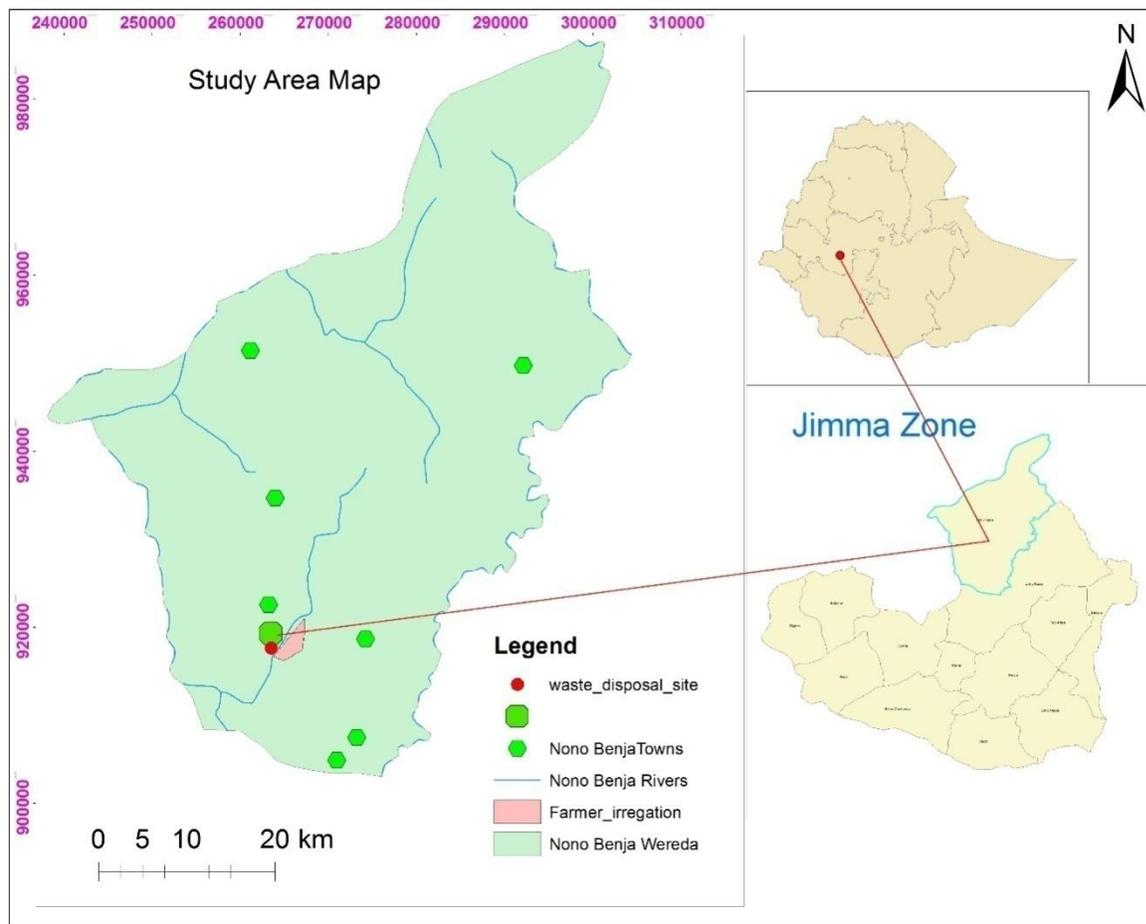
Figure1. Map of Ethiopia showing the five site of study area around Alga

3.3 Samples and sampling Techniques

Water samples were collected from five site of kolati River in August 2010. The river flows down from the upper river site through river site 1(upstream), Site2 (at vegetation land), Site3, Site 4(at waste disposal) and Site 5(downstream) across the villages and cultivated land. Sampling sites were selected based on the municipal waste, agricultural activities and population density. Standard procedures of [12] were followed for the collection of sample. A site in the upper river, was used as control to assess and compare contamination levels with the most utilized Site 2, Site 3, Site 4 and site5 of the river water. Trees and vegetation were present in the area. In all cases grab samples were used. Water temperature was measured in situ using thermometer and recorded in ℃ and Electrical

conductivity , Total dissolved solid and salinity were determined with field conductivity meter, PH was measured by PH meter, Turbidity was measured by portable turbidity meter.

Table 3. Five Sample station where selected at Kolati river from Site1 (Upstream) to Site5(downstream).

Site	Description of the sample site
1	Upstream of the water river located approximately at 500m from at vegetable farm.
2	At vegetable farm (Irrigation area or agricultural activity)
3	Sampling station site 3 was located at about approximately 200m from site2. And this site was at the end of irrigation activities
4	Located about 300m from site3 where the site at disposal waste (urban runoff , municipal waste)
5	Downstream from influent entry point (Lower stream of the river)

3.4   Sampling and Storage of Water

Water sampling was done according to the procedure described by Ndimele and Kumolu-Johnson [21]. Water samples from all sampling sites were collected into 1 L plastic bottles. Prior to sampling, the bottles were cleaned with 10% nitric acid and rinsed with distilled water. The bottles were rinsed three times with the river water at the time of sampling. Composite samples were collected by direct immersion of the sampling bottle into the river. For metal analysis after sample collection, 2 mL of nitric acid (Analytical grade) were added to the water samples to reduce adsorption of metals onto the walls of the plastic bottles. Sample bottles were then labeled to indicate date of sampling and the sampling site. Samples were transported in an ice-box to the laboratory and stored at 4 ^{0}C a waiting analysis.

3.5. Chemicals and Reagents

Commercially available 1000mg/L in 2% Nitric acid stock standard solution of Cu, Zn, Co, Cr, Cd and Pb were used. HN0$_3$ (65%UNI-CHEM(N472-4k) chemical reagent, HCl 37% GmbH.D.30926 Sigma-Aldrich, England) chemical reagent were used for sample digestion. Phosphate (PhosVer® chemical reagent, Germany) and Nitrate (Nitra Ver®5 nitrate reagent chemical, Germany), Reagent

Powder Pillows (Nitriver® 3 nitrite Reagent Set, Reagent Powder Pillow Sulfa ver® 4 Reagent Powder Pillow, SPANDS Reagent solution, buffer with pH- 4 standard solution and PH-10 Standard for calibration of pH meter and distilled water for preparations of solution.

3.6. Instruments and Apparatus

Polyethylene bottles, Ice-box, conductivity meter model (Elmetron-CC411), photometer (Model 7100, japan), Turbidity meter, pH-meter, mercury thermometer (0-50 ^{o}C), qualitative filter paper20-25µpore size Ø 9cm, Micro-wave digestion –Top wove control unit 912A743), Flame Atomic Absorption Spectroscopy (NOVAA400P analytiktijena, GERMANY) were used.

3.7. Sampling procedures

3.7.1. Cleaning sampling equipment

All poly ethylene bottles were washed with detergent, followed by repeated rinsing with distilled water and soaked in 10 % (v/v) HNO3 and finally rinsing three times with distilled water. Sample containers were kept dried until collection. The containers were rinsed with sample water prior to actual sample collection before being used for sampling [12].

3.7.2 Water Sampling, preservation and Transportation

The river water samples from sampling sites were collected with 1L-capacity polyethylene bottles by composites sampling technique, using the same sampling protocol at all sites. From each river sites one bottle of water samples were taken for all parameters being determined. The collected samples were stored in an ice-box to minimize volatilization and biodegradation between sampling and analysis periods and transported to the laboratory for analysis [12].

3.8. Sample preparation procedures for physicochemical analysis's

Physio-chemical properties are parameters that do not identify particular chemical species but have used as an indicator of how water quality may affect water uses [11]. Selection of parameters for testing of water quality is solely depends upon for what purpose we are going to use that water and what extent we need its quality and purity. The measurement of physicochemical parameter such as: temperature, Electrical conductivity, Total dissolved solid, Salinity was carried out at the site these values might change when transported to the laboratory. Water temperature was measured in-site using temperature analyzer 3 to 4 minute has recorded in °C.Electrical conductivity, Total dissolved solid and salinity were determined with conductivity meter. PH was measured digital PH meter. And

Turbidity was measured by turbidity meter. Nitrate, nitrite, phosphate, sulphate, and Fluoride was measured photometer

Table 4 Different analytical water quality parameters with their analytical technique and guideline values as per WHO and ESA guidelines

No	Parameter	Technique used
1	Temperature	Mercury thermometer
2	Electrical conductivity	Conductivity meter
3	PH	PH meter
4	Salinity	Conductivity meter
5	Turbidity	Turbidity meter
6	TDS	Conductivity meter
7	Nitrate	Photometer
8	Nitrite	Photometer
9	Phosphate	Photometer
10	Fluoride	Photometer
11	Sulphate	Photometer

3.8.1 Sample preparation procedure for NO_3^- , NO_2^-, PO_4^{3-}, F^-, SO_4^{2-} by photometer

Nitrate: -A sample cell was filled with 10mLof sample. Nitrate Ver Nitrate reagent powder pillow was added to the cell. Then sample cell was closed and shaked vigorously to dissolve the solid. The reaction time required 2 min and yellow color were developed due to the presence of nitrate. Then the instrument was calibrated by blank. Reading of nitrate was done by using photometer in mg/L[35].

Phosphate: -A sample cell was filled with 10mL of sample. Phosphate Reagent Powder Pillow was added to the cell. A blue color was developed due to the presence of phosphorus is in the sample. Then sample cell was closed and Shaked vigorously for 10 seconds. A 2-minute reaction time was required. Then the instrument was calibrated by blank. The result was taken from the photometer in mg/L [35].

Nitrite: -A sample cell was filled with 10 mL of sample. Nitrite reagent powder pillow has added to the cell. The sample cell closed and shaked to dissolve the solid. In 10 minute of the reaction time, a pink color was developed. Then the instrument was calibrated by blank. Then reading of nitrite was done by using photometer in mg/L [35].

Fluoride: - In the first sample cell, 10mLof distilled water has mixed with 2mLof SPADNS reagent. In the second sample 10mLof the water sample and 2 mL SPADNS reagent have mixed. Under the same condition both the sample and the blank have allowed to react the reagent for 1minute. The prepared blank has allowed to zeroing the reading on the instrument. Then the sample analyzed and reading on the instrument has recorded [35].

Sulphate(SO$_4^{2-}$):- One sulfa Ver ® reagent powder pillow has mixed with 10mLwater sample. The mixture has allowed reacting 5minute and shaked vigorously to dissolve the powder. The blank, in the second sample cell has inserted in to the cell holder to make the reading on the instrument zero. Then, the prepared sample in the first cell has allowed analyzing [35].

3.9. Sample preparation for Heavy metals

For digestion of water sample were done in triplicates using concentrated nitric acid and hydrochloric acid according method described by (37): 20mLwater sample were taken in to 100mLof digesting tube (Analytical Jena). To this water sample, 8mLof 3:1 ratio of nitric acid and hydrochloric acid were added. The solution was then digested in microwave digestion by adjusting temperature from 150-180 ℃ for boiling water and 50℃ for cooling for total 30 minutes. Then digested and cooled solution filtered with qualitative filter paper 20-25µ pore size Ø 9cm inserted in a 100mLpore filtration glass. Finally, the filtered was kept in refrigerator until the analysis time by GFAAS.

3.9.1. Heavy metals analysis procedures

The data qualities obtained from FAAS for heave metal analysis are highly affected by the calibration curve and standard solution prepared procedures. The calibration curve was established from five series working standard solution. The working solution for each selected heave metal (Zn, Cu, Pb, Cd, Co, Cr) were prepared freshly from intermediate standard solution (20mg/L) which was prepared by diluting stock standard solution (1000mg/L). After the instrument was calibrated; the sample solution aspired in Graphite furnace and absorbance of the sample was recorded. Then, the concentration of selected heave metals was obtained from the measured absorbance. Calibration curve

Appendix [7] showing Absorbance verses concentrated through direct analysis of five-point calibration standard   at specific wave length of the analyte. The calibration curve shows good correlation (R^2) greater than minimum acceptance value 0.995 [12]. This shows that there was a good linear relation between the concentration and instrument responses

Table .5. Instrument operation on parameter

Element (nm)	Wavelength (nm)	IDL (mg/L)	Oxidant (fuel)
Zn	213	$1x10^{-4}$	Air/C_2H_2
Cu	324	$1x10^{-4}$	Air/C_2H_2
Pb	283	$3x10^{-4}$	Air/C_2H_2
Cd	228	$7.5x10^{-5}$	Air/C_2H_2
Co	240	$1x10^{-6}$	Air/C_2H_2
Cr	357	5×10^{-6}	Air/C_2H_2

3.10. Methods of validation

3.10.1 Detection Limits

Method detection limits Method detection limit is defined as the minimum concentration of analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero [18]. Method detection limit for heavy metal may vary with wavelength selected and the spectrometer configuration and operation conditions.

Methods of detection Limit for water sample analysis was determine using reagent water blank with HNO3/HCl) that was digested in the same condition as the sample. In this study, after digestion of five blank solutions, seven reading have taken for each blank and the standard deviations of these have calculated. The method detection limit of each element has obtained by multiplying the standard deviation of the reading blank by three [18]

MDL= 3δblank

δblank is standard deviation of the blank reading

Limit of quantification (LOQ) – is the lowest concentration level at which measurement is quantitatively meaningful.

LOQ = 10δblank

3.10.2 Evaluation of analytical precision, Accuracy and recovery

The analytical method precision was assessed in terms of relative standard deviation (RSD) and standard deviations (SD) among measurements.

In this study, the precision of the results was evaluated by percentage relative standard deviation of the results of five samples (N=5) and triplicate readings for each sample.

$$\text{RSD} = \frac{SD}{\bar{x}} \text{X} 100$$

Where, RSD =Relative standard deviation, SD=standard deviation, $\bar{x}$ = mean value

Accuracy of analytical method has evaluated in terms of percent recovery by either the assay of known added amount of analyte in the sample or as the difference between the mean and the accepted true value together with the confidence intervals. In this study, the analytical accuracy of the procedures was determined by spiking experiment.

The resulted spiked samples have digested, diluted and analyzed for total heavy metals. The percentage recovery of each data has calculated as

$$\mathbf{R} = \frac{meanspikedvalue - unspikedvalue}{standardadded} \times \mathbf{100}$$

Where, R= Percent of recovery

4.RESULTS AND DISCUSSION

4.1. Instrumental calibration

Instrument was calibrated for each selected heavy metals using five series of their standard calibration before qualitative determination of them in the sample.

The calibration curve for were plotted as function of Absorbance verses concentration of the standard solution as showed in the table below.

The linearity for calibration line for Zn, Cu, Pb, Cd, Co and Cr showed correlation coefficient (r^2) of 0.9968, 0.9975, 0.9954, 0.9978, 0.9975, 0.9961 respectively which are greater than or nearly the minimum acceptance value of 0.995[12].

Table.6. Calibration curve Regression equation and correlation coefficient.

Metal	Standard concentration (mg/L)	Regression equation	Regression coefficient limit(r^2)
Zn	0.05; 0.1; 0.5; 1.5; 2.5	Y=0.6483x+0.0428	0.99683
Cu	0.05; 0.1; 0.5; 1.5; 2.5	Y=0.2275x-7E-05	0.99753
Pb	0.05; 0.1; 0.5; 1.5; 2.5	Y=0.032x+3E-05	0.99543
Cd	0.05; 0.1; 0.5; 1.5; 2.5	Y=0.485+0.0341	0.99783
Co	0.05; 0.1; 0.5; 1.5; 2.5	Y=0.0562x+0.0095	0.99573
Cr	0.05; 0.1; 0.5; 1.5; 2.5	Y=0.0551x-0.0176	0.99613

Therefore, the calibration curve was showed that there was linearity between the instrument response and prepared concentration which indicating the best working condition of the instrument. The calibration curves are given in Appendix [7]

4.2. Limit of detection and Limit of quantification

The Limit of detection and Limit of quantification for the analysis of metal using FAAS in river water for each selected heavy metal were determined experimentally by running blank samples and their values here given in the table 7. This was done to determine whether the blank sample contributes measurable quantities of the metal to be analyzed or contamination is introduced during digestion.

Table .7: The value IDL, LOD and LOQ (mg/L) of the methods

Metal	IDL	LOD	LOQ
Zn	1×10^{-4}	0.0105	0.0365
Cu	1×10^{-4}	0.0031	0.0105
Pb	3×10^{-4}	0.0008	0.0027
Cd	7.5×10^{-5}	0.0015	0.0051
Co	1×10^{-6}	0.0126	0.042
Cr	5×10^{-6}	0.0010	0.0034

4.3. Evaluation method performance

In this study Accuracy of the analytical methods has calculated percent of recovery. The percent calculated values have given in table 8**.** The recovery was within standard (80-120%) [12]**.** The recovery values in the above range are acceptable.

Therefore, the percentage recovery values have found between the lowest 82% to and highest 103.3% and all were within the required criteria. In addition, the RSD value is all below the standard limit Table 8. This confirms that the method has provided results within the required levels of accuracy and precision

Table .8. Mean percent recovery, Standard deviation and relative standard deviation of heavy metal.

Name metal	Site	Mean spiked value(mg/L)	Unspiked value(mg/L)	Amount of sample added (mg/L)	%Recovery	SD	%RSD
Zn	1	1.365	0.037	1.5	88.5%	0.001	0.59%
	2	1.427	0.050		91.9%	0.001	9.19%
	3	1.455	0.058		92.09%	0.0001	11.97%
	4	1.455	0.058		96.7%	0.001	1.20%
	5	1.462	0.055		93.79%	0.049	5.90%
Cu	1	1.410	0.039	1.5	91.3%	0.001	6.51%
	2	1.459	0.056		93.5%	0.002	14.40%
	3	1.506	0.038		97.5%	0.001	12.95%
	4	1.524	0.063		97.7%	0.001	10.26%
	5	1.436	0.057		91.8%	0.001	4.60%
Pb	1	1.879	0.065	2	90.7%	0.0002	10.74%
	2	1.880	0.078		90.7%	0.0002	8.22%
	3	1.934	0.090		92.3%	0.0003	11.37%
	4	2.151	0.113		101.8%	0.0002	5.17%
	5	2.172	0.092		103.3%	0.0002	6.78%
Co	1	2.119	0.066	1.5	102.22%	0.001	4.69 %
	2	2.122	0.089		102%	0.0046	3.07%
	3	2. 035	0.190		92.3 %	0.0001	0.66%
	4	1.678	0.153		82 %	0.001	3.65%
	5	1.656	0.016		82.03%	0.001	3.89%
Cr	1	2.137	0.401	2	86.8%	0.0002	6.65%
	2	2.142	0.042		85.9 %	0.0003	5.74%
	3	2.202	0.046		87 %	0.0005	6.5 %
	4	2.465	0.500		98.25 %	0.0007	6.8%
	5	2.275	0.043		92.13 %	0.0005	8.57%

The prepared concentration (standard concentration (mg/L) was ranging from 0.05- 2.5 mg/L and concentration equivalent of analyte added the fortify the sample (the amount of sample added) for each of selected heavy metals determined experimentally 1.5 and 2 mg/L. Therefore, the amount sample added was found between 0.05-2.5 mg/L.

4.4. Physic chemical parameters analysis Kolati river water sample

In percent study, comparative analysis of physical and chemical characteristics of Kolati river along water systems of five sites selected based on physical characteristics like Temperature, PH, TDS, Salinity, Turbidity, Electrical conductivity in conjugation with chemical characteristics such as, nitrate, nitrite, phosphate, sulphate, fluoride, Zn, Cu, Pb, Cd, Co, Cr the water quality has been assessed.

In this study the precision of the results was evaluated by standard deviation and relative standard deviation of the result of triplicate samples with triplicate measurement of each sample were used for the analysis of physicochemical parameter was sample. The precision of the analytical method has the method of detection calculated interims of relative standard deviation.

It can be seen in table 9 That the values of relative standard deviation (%RSD) are less 14.4% for all mean concentration of fortified matrix and triplicate samples. All of these values are below 15 %(Table 9). This shows that the precision of the result obtained in all methods acceptable [12]

Table.9. physio-chemical parameters of Kolati river water sample (Mean ± SD, n=3)

Parameters	Sites	Mean± SD	%RSD	Statically p–value	
				p-value	Significance(p=0.05)
Temp.℃	1	17.46±0.77	4.42	0.000	Significance different
	2	17.86± 0.20	1.02%		
	3	18.10± 0.70	3.91%		
	4	18.93± 0.49	2.58%		
	5	18.43 ± 0.56	3.03%		
PH	1	8.03± 0.06	0.74%	0.004	Significance different
	2	8.41± 0.015	0.17%		
	3	8.69± 0.10	1.13%		
	4	8.83± 0.03	0.339%		
	5	8.45± 0.03	0.35%		
Turbidity (NTU)	1	111.44± 0.34	0.3%	0.003	Significance different
	2	166.63±0.47	0.18%		
	3	175.8± 0.26	1.15%		
	4	244.56±0.83	0.34%		
	5	235.4±0.87	0.35%		

Electrical conductivity μs/cm	1	3409± 9.84	0.28%		
	2	4662± 2.51	0.05%	0.000	Significance different
	3	5185.66± 5.13	0.098%		
	4	9222.3± 5.13	0.13%		
	5	6944.33±5.13	0.074%		
TDS (mg/L)	1	1707± 2.08	0.12%		
	2	2471.33± 2.08	0.084%	0.000	Significance different
	3	2542.16± 1.89	0.074%		
	4	4603.06± 2.40	0.052%		
	5	3479.73± 0.46	0.013%		
Salinity(mg/L)	1	2007±2.64	0.13%		
	2	2790.93± 1.01	0.033%	0.000	Significance different
	3	3229± 1.73	0.053%		
	4	6052.36± 2.82	0.046%		
	5	4305.36± 4.79	0.112%		
Phosphate (mg/L)	1	0.82± 0.066	7.8%		
	2	1.643±0.041	2.49%	0.000	Significance different
	3	1.69±0.01	0.59%		
	4	1.87±0.02	2.87%		
	5	1.620±0.02	1.23%		

Nitrate(mg/L)	1	5.066±0.015	0.29%		
	2	8.453±0.136	1.61%	0.000	Significance different
	3	10.096±0.106	1.04%		
	4	14.536±0.077	0.523%		
	5	9.74± 0.04	0.41%		
Nitrite (mg/L)	1	0.810±0.012	1.85%		
	2	0.923±0.025	2.71%	0.000	Significance different
	3	0.900±0.01	1.11%		
	4	0.933±0.015	1.60%		

	5	0.790±0.01	1.26%		
Fluoride (mg/L)	1	0.890±0.017	1.91%	0.135	Not significance different
	2	0.903±0.006	0.63%		
	3	0.916±0.075	8.29%		
	4	0.97±0.08	5.90%		
	5	0.85±0.05	5.88%		
Sulphate (mg/L)	1	6.27±0.075	1.19%	0.000	Significance
	2	7.166±0.115	1.5%		
	3	10.5±0.440	4.19%		
	4	12.28±0.220	1.79%		
	5	10.68±0.300	5.66%		

Temperature: Temperature is measure with help of thermometer on site of sample collection. It is very important parameter because of this parameter the changes occur in the water. In current study, temperature vary from 17.53℃ at site1 (upstream) to 18.43℃ of the site 5 river water. One-way ANOVA test ($p \leq 0.05$) showed that the temperatures varied significantly among the river sites. In table 9 water temperature at Site 1(upstream) was lower than Site2, Site3, Site 4 and Site 5. This might to be the attribute to the fact that the site1 (upstream) is located relatively in the head of water, which have more shade and located at higher altitude and no foreign wastes and daily discharged to it. Even murky green water with lots of algae will be warmer than clear water. [18] Observed in study that water temperature fluctuates between 21°C to 29°C when toxic chemicals are discharged to the water. The variation in river water temperature usually depends on the geographic location, sampling time and chemical wastes discharges entering the water [27].

PH

pH is most important in determining the corrosive nature of water. Lower the pH value higher is the corrosive nature of water. pH will positively have correlated with electrical conductance and total alkalinity [26]. The mean pH value of Kolati River water ranged 8.03 minimum at Site1 to 8.16 maximum at site5 (downstream). These ranges are within the limit of Ethiopian and WHO guidelines for drinking. From the above results the pH of the rivers water is nearly slightly basic. One-way ANOVA test ($p \leq 0.05$) indicated that the pH is significantly different between and among each sample sites. Various factors bring about changes the pH of water. The higher pH

values observed suggests that carbon dioxide, carbonate-bicarbonate equilibrium is affected more due to change in physicochemical condition and water contamination with alkaline detergents from residential areas and release of bicarbonates and carbonate of calcium and magnesium in water from urban runoff [29]. This may be attributed to the alga population increase downstream of the river which can create alkaline condition by up taking CO_2.

In this study, the PH of the river different significantly ($p< 0.05$) betwen the selected site the river. Kolati River at site 3 and Site4 was probability influent discharge to it. Due to farmers use fertilizers used for agricultures (irrigation) and waste disposal.

Electrical Conductivity

The mean value was found between the minimum mean 3409µs/cm and the maximum mean 9222.3µs/cm, 6944.3µs/cm (Site 4, Site5) respectively. One-way ANOVA test ($p \leq 0.05$) showed that the conductivity varied significantly among and between each sample sites (Appendix 2) respectively. The difference among the sample sites indicative of discharge of some sources of pollution into the water body. Such as chloride, nitrate, sulfate, phosphate anions or sodium, magnesium, calcium, iron, and aluminum cations. But in the preset study, the main source was due to agro-industries chemicals and domestic waste near the river in going from site 1(upstream) to site 5(downstream). The highest value of electrical conductivity at influent discharge was municipal influent discharged from resident community and chemical applied to farm land. In this study, the PH of the river different significantly($p< 0.05$) between the selected site. Similarly, the finding of [30] also showed that the EC increases going downstream river apparently due to the accumulation of domestic, chemical and sewage wastewater and also to the enrichment of electrolytes from mineralization or weathering of sediment. These results agreed with the work of [28] on the assessment of water quality of river with the EC value of (335.7-610.1mg/L). According to his report the main reason behind fluctuation of mean EC values is dumping of huge volumes of toxic wastes into the river and industrial units and sewerage lines and agro-industries. This finding partly agrees with the current study, in which high concentration of EC site4 and site5. Conductivity increases with the increase of water temperature [12]. Low values are characteristic of high-quality, low-nutrient waters. High values of conductance can be indicative of salinity problems but also are observed in atrophic waterways where plant nutrients (fertilizer) are in greater abundance. Very high values are good indicators of possible polluted sites [2].

Total dissolved solids

The result of study ranges from1707 to 3479.73mg/L Site1to Site5(downstream). Higher TDS value were observed in the site4 and site5 (4603.06 and 3479.3) when compared to site1, site2 and site3(1707,2471.33, 2542.16) mg/L respectively site of the river. But all TDS values higher than the maximum acceptance value of ESA and WHO standard for drinking water. There is significance difference between site1 and higher value recorded in these site probably related to pollution (site4 and site5(downstream) of river water system ANOVA ($p \leq 0.05$) showed that indicating of mixing contamination in river from anthropogenic activities in and washed in materials from the catchment areas and erosion of the river bank, such as the mixing of sewerage, cloth washing, garbage dumping and waste water from town. Similarly, [29] reported that increase in value of TDS indicated pollution by extraneous sources (garbage dumping and chemicals from Agro-industry) and the high amount of dissolved, suspended and total solids of samples adversely affects the quality of running water and it is unsuitable for any other purpose irrigation and drinking.

Turbidity

The present study shows that turbidity for Site1(upstream), site2, site3, site 4 and lower stream were significantly different had the mean concertation values 111.4± 0.34mg/L, 166.63 ± 0.47mg/L, 175.8± 0.26mg/L, 244.56±0.84, 235.4±0.87mg/L respectively. Site1 is significantly different from site 2,3,4 and site 5. And Site4 (244.56±0.84) significantly different site5(235.4±0.87mg/L). This may be indicated that source of pollutant causes the river is not the same in the course of river. Highest value recorded at site 4, the indicated that waste where discharged from municipal waste and varies factory. It is observed that the turbidity concentration in all sites were above 5NTU permissible limits recommended by WHO. This indicate that the source of pollutant causes of river discharge from municipal, especially from domestic waste, waste water from town, car wash, garage toilet, chemical from irrigation (agricultural activity).

Salinity The mean concentration of salinity of the river under the study was ranging from a minimum of 2007.93 mg/L to a maximum of 6052.36 mg/L. One way ANOVA test ($p \leq 0.05$) river water under study showed that salinity varied significantly among the river site(Appendix2). Mean concentration of salt at site 1 (upstream) varies from sites2, site3, site4 and Site5(downstream); and

site 4 is also varying from site 5(downstream). This is due to the salts that released to the river or naturally, present in the river is not the same in proportion throughout the entire sites of the river. Higher salinity value has recorded at effluent entry site3 and site 4 due to the chemical effluent from agricultural activity and the municipal waste discharge that contain many organic as well as inorganic materials. A slight decrease from site 4 to site5 (downstream) has observed probably due to adsorption of many salts with the sediments at the bottom of the river course. But all salinity value higher than the maximum acceptance value of WHO and ESA standard for drinking water. As the result water from the river cannot utilized for irrigation, drinking and house hold purpose.

Nitrate The average of concentration of nitrate in the studied river water was varied from at Site1 5.066±0.015mg/L, site2 8.4533 ± 0.136mg/L, site3 10.096±0.106mg/L, site4 14.536±0.07mg/L and site5 (downstream) 9.74± 0.04mg/L. The comparison of NO_3^- levels in the studied river waters was below the permissible limit with the WHO and Ethiopian recommended value (50mg/L), indicated the suitability for house hold purpose and irrigation. But, site4 and site5 (downstream) of the river had the highest mean concentration value than site1 and site2 and site3. The major expected value source nitrate is from the use of nitrogen containing fertilizers domestic sewage, municipal discharge, animal manure used in crop land and naturally from atmospheric deposition. And high nitrate site4 the studied river was due to agricultural runoff from farm (irrigation).   One-way ANOVA test ($p \leq 0.05$) showed that the nitrate varied significantly among the river sites (Appendix 2). Most of the nitrates are intercepted or retained on the upper part of soil strata or taken up by plant roots for growth while percolating with water vertically through open spaces and the porous media of different soil horizons (might be due to leaching of nitrate from nearby agricultural field). These results agreed with the work on [30].

Phosphate

Phosphate was estimated from all five samples. The lowest phosphate means concentration value of 0.82±0.0664 was observed at site1(upstream) and the highest phosphate value were observed at site-3, site-4 and site-5(downstream), (1.69±0.01 mg/L), (1.87±0.02mg/L) and (1.62 ±0.02mg/L) respectively. The highest phosphate values indicate that the farmers along the river bank use fertilizers, which has potential of being leached or washed in the river. In this study, the maximum mean concentration of phosphate was recorded at influent discharged point (site of site4) due to

discharge from fertilizers runoff, detergent use, and domestic waste and biological process. High levels of both phosphates and nitrates can lead to Eutrophication, which increases algal growth and ultimately reduces dissolved oxygen in the water and the common source of phosphate and nitrate which were increased activity of washing, detergent use, fertilizer runoff, and wastes from Agro-industry [34]; [11]**.** On way ANOVA test (p≤ 0.05) show that the phosphate varied significantly among the five river sites. The comparison with the WHO standard and Ethiopian standard, the mean concentration of the phosphate in the river sites were below permissible limit. This indicates that in the cause of phosphate the river water is not polluted in all sites.

Nitrite

Nitrite was estimated from all the five samples. Mean concentration of nitrate in the studied river varied significantly (P≤ 0.05) across the selected sites (Appendix 2). The lowest nitrite value of 0.81±0.02mg/L was observed at site1 and the maximum value 0.923±0.025mg/L, 0.9±0.01mg/L, 0.933±0.015mg/L at site2, site3, site4 and to started decrease at site5(downstream), (0.79± 0.01) due to at downstream absorption of many salt with sediments at the bottom of river course. All values measured did not exceed surface water standard set ESA and WHO(3mg/L) at the enters site. However, the maximum concentration is at the site3 and site4. Due to the source of nitrite ion is in the river can be from nitrogen containing organic compound, farmers use fertilizes from irrigation and farm land release to water without any treatment.

Sulphate

The mean sulphate concentration in the five site studied ranges from site1 (6.27±0.05mg/L) to site5 (10.68±0.22mg/L). But the maximum mean concentration of sulphate was recorded at influent discharge in point of site of midstream4 (12.28±0.22) was might to be the cause adverse effects on aquatic ecosystem. In the entire sites, the values were below the limit of the standard WHO (500 mg/L) and ESA standard. One way ANOVA (P≤ 0.05) result show that the mean concentration of sulphate at site1 differ significantly site2, site3, site4 and site5 (downstream). This might that the major source of sulphate can be the decomposition plant and animal and agricultural runoff

Fluoride

Naturally, fluoride has found in low concentration in water and foods. Water with underground sources is more likely to have higher levels of fluoride. Fresh water supplies generally contain between 0.01-0.3 mg/L. The mean concentration of fluoride at site 1(upstream), site2, site3, site4 and site5 (downstream) were 0.89 ±0.017 mg/L, 0.903±0.06mg/L, 0.916±0.075mg/L, 0.96±0.057mg/L and 0.85±0.05± respectively. It has seen that the mean concentration fluoride at site 3 and 4 higher than site1and site5 (downstream). Due to the fluoride level of site4 can be increased by contamination fertilizers, road salt, as well as human and animal waste. In all the entire sites, the values measured were below   the maximum limit set by ESA and WHO (1.5 mg/L) standards for surface water

4.4. 1. Correlation between physic-chemical parameters

Pearson correlation coefficient was used examine the relationship between the various physic-chemical parameters in the water sample from all the sample sites. Table 10 shows the correlation matrix of the relation between the physic-chemical parameter concentrations of river water samples. In previous study reported at high correlation coefficient (near +1 or -1) means good relationship between two variable and its concentration around zero means no relation between them at significant level of 0.05%l it can be strong correlated , If r>0.7, whereas r value between 0.5 and 0.7 shows moderate correlation between two different parameters. Therefore, Pearson correlation coefficient matrixes among the determined physio chemical parameter are present in table (10)

Table.10. Correlation between physic-chemical parameters among the selected sites of Kolati River

	Temp	PH	E.C	TDS	Turbidity	Salinity	NO_3^-	NO_2^-	PO_4^{3-}	SO_4^{2-}	F^-
Temp	1										
PH	.288	1									
E.C	.056	.776**	1								
TDS	.046	.775**	.999**	1							
Turbidity	.040	.783**	.999**	.999**	1						
Salinity	.120	.724 **	.945**	.945**	.926*	1					
NO_3^-	.166	.929**	.938*	.734 *	.862*	.944	1				
NO_2^-	.472	.644**	297	.297	.167	.180	.621	1			
PO_4^{3-}	.403	.905**	.742**	.739**	.797**	.738**	.874**	.593*	1		
SO_4^{2-}	.036	.875**	.893**	.884**	.859**	.895**	.907**	.253	.772*	1	
F^-	.439	.488	.322	.378	.150	.342	.444	.638*	. 275	320	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

In present study, Pearson correlation coefficient Temperature of the river water was weakly correlated with PH(r=.028), E.C(r=.056), TDS(r=.046), salinity(r=.120), turbidity(r=.040), nitrate(r=.166), nitrite(r=.472), phosphate(r=.403), sulphate(r=.036) and fluoride(r=.439) (r<.5). The PH water river between the selected site strongly correlated with E.C(r=.776), TDS(r=.775), turbidity(r=.783), salinity(r=.724), nitrate(r=.929), phosphate(r=.905), sulphate(r=.875) (r> 7) and weakly correlated with fluoride(r=.488). This indicates that the same source (similar) input. The E.C. of the river was also strongly correlated with The PH (r=.776),TDS(r=.999), turbidity(r=.999), salinity(r=.945), nitrate(r=.938), phosphate(r=.742), sulphate(r=.893) (r> 7) and weakly correlated with fluoride(r=.322) and nitrite(r=.297). Therefore, E.C. of the water is the number charge of ion in the solution, it is another measured of dissolved materials. TDS strongly correlated with turbidity(r=.999), salinity(r=.945), nitrate(r=.743), phosphate(r=.739), sulphate(r=.884) and weakly correlated with nitrite and fluoride (r=.297, .378) respectively. This indicated that more soluble salt has dissolved in the river salt. Pearson correlation coefficient nitrate strongly correlated with PH, E.C, TDS, turbidity and salinity (r=.929, .938, .734, .862, .944) respectively and weakly correlated fluoride(r< .5) (Table 10)

4.6. Heavy   Metal Analysis

Heavy metals concentrations in surface water and sediments is influenced by impute from

Source, character of sediment, organic materials, temperature and sometimes the mineral composition of underlying rock in the area where the surface water situated. Thus, spatial and temporal variation in heavy metals concentration in sediments and especially in water should be naturally expected [34].

In the present study, significant variations have indicated by the concentration of the metals with higher concentration shown at effluent discharge site except for few. Table.11 contains the results of the laboratory analysis conducted on the water samples from River Kolati and their detail discussions have given in the following section

Table.11. Concentration of heave metal (mg/L), mean ± SD (n=3) in Kolati river water.

Selected metal		Site 1	Site 2	Site 3	Site 4	Site 5	Statically p-value	
							p-V (p≤0.05	Significance
		mean± SD	mean± SD	mean± SD	mean± SD	mean± SD		
Zn		0.037± 0.001	0.063±0.001	0.077±0.002	0.113±0.002	0.062±0.007	0.000	Significance Deferent
	%rsd	1.62%	1.5%	2.5%	1.8%	10.96%		
Cu		0.042± 0.003	0.044± 0.008	0.045±0.006	0.056±0.006	0.055±0.003	0.030	Significance Deferent
	%rsd	6.4%	17.5%	13.3%	10.35%	5.2%		
Pb		0.07± 0.008	0.084±0.008	0.093±0.010	0.120±0.003	0.10±0.007	0.000	Significance Deferent
	%rsd	10.7%	8.21%	10.75%	2.5%	6.8%		
Cd		BDL	BDL	BDL	BDL	BDL	-	-
Co		0.079±0.012	0.098±0.008	0.19±0.002	0.156±0.003	0.145±0.012	.000	Significance Deferent
	%rsd	14.55%	8.16%	1.2%	2.05%	8.27%		
Cr		0.039±0.005	0.041±0.005	0.044±0.001	0.045±0.001	0.0496±0.005	0.000	Significance Deferent
	%rsd	12.8%	12.1%	1.8%	8.2%	9.8%		

BDL= Below Detection Limit

Zinc

The mean concentration values of zinc obtained in the study area were 0.037 ± 0.0006 mg/L at site1 0.063 ± 0.00118 mg/L at site2 0.0077 ± 0.017 mg/L at site3, 0.113 ± 0.0021 mg/L and 0.062 ± 0.00687 mg/L at site5 (downstream) respectively. This is much less than the recommended upper limit for Zn in drinking water set by the WHO and the Ethiopian standard in all samples. Hence no health concern in the cause of Zn. As result water from the river can be utilized for irrigation and drinking their cattle. But at site3 and site4 of the river were exposed to Zn metal compared to site1 and site2. The One-way ANOVA result ($p \leq 0.05$) indicated that the Zn Concentrations between the water samples varied significantly (Appendix 5). This is may be waste discharged from municipal waste.

According to [17] the main sources of Zn were industrial discharges, sewage effluents, agro-industries, fertilizers, domestic wastes, municipal wastes, as well as natural chemical weathering of geological materials.

Copper

The concentration of copper in water samples of the river obtained in the study area were 0.042 ± 0.0027mg/L at Site 1, 0.044 ± 0.0078mg/L at Site 2, 0.0045 ± 0.006mg/L at Site3, 0.056 ± 0.0058mg/L and 0.055 ± 0.0026mg/L at site5 respectively. The WHO and Ethiopian guideline for Cu in domestic water supply is 2 mg/L. Therefore, Cu is not supposed to be a problem for domestic use and no health problems associated with Cu for domestic use and Irrigation. But Site 4 and Site 5(downstream) is site of the river were exposed to Cu metal compared to Site1 and Site2. This due to the source of Cu compound in the river can be from agricultural chemicals of Cu compound when farmer use irrigation. In the previous study reveals that the amount of Cu in Little Akaki River was reported in the range of 0.001 to 0.021 mg/L using ICP-MS instrumentation [32] which were low concentration

The One-way ANOVA result ($p \leq 0.05$) indicated that the Cu Concentrations between the water samples varied significantly (Appendix5) which is could cause the variation of Cu among the water river.

Lead

The concentration of lead in the study area varied from, 0.07 ± 0.0075, 0.084 ± 0.0069, 0.093 ± 0.01, 0.120 ± 0.003 and 0.10 ± 0.0068 mg/L from Site1(upstream) to Site5(downstream) of the river water respectively. The highest concentration was observed in site3, site4 and site5 and the lowest concentration was observed at site1 (upstream) of the river water. The value Pb concentration increase from Site1 to lower stream of the river water. The acceptable limit of lead reported by WHO and Ethiopian standard in drinking water is 0.01mg/L. The values obtained in all the analyzed samples were above this limit. This could be due to poor environmental control, runoff from contaminated land area, atmospheric fallout and sewage influent and car wash. The One-way ANOVA result ($p \leq 0.05$) indicated that the Pb Concentrations between the water samples varied significantly which could cause the variation of Pb among the river water. The mean Pb concentrations obtained in this work was also much higher than previously reported of 0.096 mg /L at [32]. Lead is considered the number one health threat to children, and the effects of lead

poisoning can last a lifetime. Its toxicities are that damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system [18].

Cadmium

The concentration of Cd in water sample of the river is very low which is below detection Limit. The WHO and Ethiopian guideline for Cd in domestic water supply is 0.003mg/L. The concentration of Cd in of Kolati river water does not exceed this level; therefore, Cd is not supposed to be a problem for domestic use and no health problems associated with Cd for drinking their cattle and Irrigation.

Cobalt

Cobalt: Measured mean concentration of Co ranges from a minimum value of 0.079±0.0115 mg/L at site 1 to a maximum value of 0.19 ± 0.0023 mg/L at Site3 and at Site4 0.15±0.0032mg/L. In all selected site of the river, the value of record was below minimum permissible limit of ESA and WHO (0.5mg/L). Therefore, no problem using the river for domestic and for irrigation activities water for Kolati River. But at site3 and site4 of the river were exposed to Co metal compared to site1 and site2. The One-way ANOVA result ($p \leq 0.05$) indicated that the Co Concentrations between the water samples varied significantly which could cause the variation of Co among the river water (Appendix 5). This is may be originated either from natural or anthropogenic sources.

Chromium

Chromium was estimated from all five samples. The lowest chromium means concentration value of 0.039±0.005 was observed at site1 and the highest chromium value were observed at site4 and site5 (downstream) (0.045±0.0012mg/L) and (0.0496±0.004 mg/L) respectively. The highest chromium values indicate that the farmers along the river bank use fertilizers (agricultural activities). Chromium is essential to animals and human. Chromium in excess amounts can be toxic especially the hexavalent form. Chromium is used in metal alloys and pigments for paints, cement, paper, rubber, and other materials. Electroplating can release chromic acid spray and air-borne Cr-trioxide, both can result in direct damage to skin and lungs [18] as well as chromium dust has been considered as a potential cause of lung cancer [33]). Sub chronic and chronic exposure to chromic acid can cause dermatitis and ulceration of the skin

4.6.1 correlation between heave metal analysis

Pearson correlation coefficient was used to examine the relation between the various heavy metal in the water from all sample site. Table 12 shows the correlation matrix of the relation between

heavy metal concentration of river water sample [36] reported at high concentration coefficient (near+ or -1) means good relationship between the two variable and its concentration around zero means no relationship between them at significant level of 0.05% level, it can be strong correlated , If r> 0.7, whereas, r value between 0.5 and 0.7 show moderate correlation between two different parameters

Table.12. correlation between measured metal from the selected sites of Kolati River

Name of metal	Zn	Cu	Pb	Co	Cr
Zn	1				
Cu	.877**	1			
Pb	.498	.595*	1		
Co	.633 **	.315*	.637*	1	
Cr	.489	713**	.718*	.630*	1

**. Correlation is significant at the 0.01 level (2-tailed).

 *. Correlation is significant at the 0.05 level (2-tailed)

At it shows in the table12 Zn is strongly correlated with Cu (r=0.877) and weakly correlated with Cr (r= 0.498) (Appendix 6). This may be a result of precipitation of element as hydrous metal oxides. The Cu in the river is strongly correlated with Cr(r=.713) and weakly correlated with Co(r=.315). This may be the source of metal Cu and Cr is the same and presence of the one can affect the other.

4.7. Comparison of Heave metal level in Kolati River water samples with different standard

There are some reports from different countries on the analysis of the metal contents of the river water. It is important to compare the result obtained from the analysis of the water sample in this study with the values sited in other countries and WHO guideline values. Currently, all of the concentrations of heavy metals that are determined in this study were in the permissible range of the international guidelines listed below.

Table 13. Comparison between the average heavy metal content of river water of this study with that of literature and WHO values

Parameter	Site	Mean ± SD	Drinking water standard		
Zn			WHO	ESA	USEPA
	1	0.037±0.001			
	2	0.063±0.012			
	3	0.077±0.017	3mg/L	5mg/L	5mg/L
	4	0.113±0.002			
	5	0.062±0.007			
Cu	1	0.042±0.003			
	2	0.044±0.008	2mg/L	2mg/L	1.3mg/L
	3	0.045±0.006			
	4	0.056±0.006			
	5	0.055±0.003			
Pb	1	0.07±0.008			
	2	0.084±0.007	0.01mg/L	0.01mg/L	0.015mg/L
	3	0.093±0.01			
	4	0.12±0.003			
	5	0.10±0.007			
Cd	1	BDL			
	2	BDL	0.003mg/L	0.003mg/L	0.003mg/L
	3	BDL			
	4	BDL			
	5	BDL			
Co	1	0.079±0.0115			
	2	0.098±0.008	0.5mg/L	0.5mg/L	0.5mg/L
	3	0.19±0.0023			
	4	0.156±0.0032			
	5	0.14±0.012			
	1	0.039±0.005	0.05mg/L		
	2	0.041±0.005			
	3	0.044±0.001			
Cr	4	0.045±0.001			
	5	0.049±0.005			

4.8. Statistical analysis

Result of water sample analysis were compared against standard set by WHO, ESA and obtain data were analyzed using SPSS soft were (version25) and Microsoft Excel 2016. Descriptive data have generated for all variables and have presented as means ± standard deviation ($\bar{x}\pm$ SD). The mean variations in data between the five sites have analyzed using One-way ANOVA. The parameters have correlated against each other to determine their relationship using Pearson's correlation. Significance has considered at 95% confidence interval.

5. Conclusion and Recommendation

The main goal of this paper was to generate baseline data on physic-chemical characteristics and selected heave metals in Kolati river. All samples were analyzed for physio- chemical parameters (Temperature, PH, TDS, E.C, Turbidity, salinity, nitrate, nitrite, phosphate, sulphate, fluoride) and six heavy metal using standard procedures. The result shows that the values of E.C, TDS, Turbidity, salinity and concentration of heavy metal of Pb in the samples, were higher than the recommended set by WHO and Ethiopian (ESA) standard. This is an indication weak during water treatment practices in these areas which in turn, have implication on the health of the people. The results from present study clearly pointed out that river water are highly polluted at the site2, site3, site4 and site 5(downstream) sites when compared to that of the site 1 (upstream) site. The study provides an informative data and helps to understand the contamination of water in the Kolati River due to the discharge of influent from flow farm nearby, municipal waste from town, pesticides, domestic wastes, car wash, and chemical from irrigation waste from toilets. This indicated the need of further investigation on the source of stringent.

5.2. Recommendation

This study, recommended the government and other responsible authorities to:

- Municipality should be preventing any kinds of waste disposal in to river, canals or any reservoirs that supply's domestic river water.
- Educate the people to have better water storage practice
- Government should be educated the people how to use the fertilizers and pesticides in sustainable way at farm levels.
- Support further study to be conducted on the other physical and chemical parameters significant health concern and identification of potential source Contaminants including heavy metals contaminants.

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Appendix 1. Mean ± SD values for physio chemical parameters

Para		TEM	PH	TDS	EC	SALI
One	Mean	17.5333	8.0300	1707.0000	3409.0000	2007.0000
	Std. Deviation	.77675	.06245	1.00000	9.84886	2.64575
Two	Mean	19.4667	8.4133	2332.6667	4662.3333	2790.9333
	Std. Deviation	.20817	.01528	2.08167	2.51661	1.00664
Three	Mean	17.8667	8.6967	2542.1667	5185.6667	3229.0000
	Std. Deviation	.70946	.10599	1.89297	5.13160	1.73205
Four	Mean	18.6667	8.8300	4603.0667	9222.3333	6052.3667
	Std. Deviation	.49329	.03000	2.40069	12.01388	2.82902
Five	Mean	18.436	8.4533	3479.7333	6944.3333	4305.1333
	Std. Deviation	.56862	.03055	.46188	5.13160	4.79618
Total	Mean	18.100	8.4847	2932.9267	5884.7333	3676.8867

Report

Para		TURB	Nitrat	Nitrite	Phosphate	Sulphate	Fluoride
One	Mean	111.4400	5.0667	.8133	.8267	6.2700	.8900
	Std. Deviation	.34176	.01528	.01528	.06429	.07550	.01732
Two	Mean	166.6333	8.4533	.9233	1.6433	7.1667	.9033
	Std. Deviation	.47258	.13614	.02517	.04163	.11504	.00577
Thre	Mean	175.8000	10.0967	.9000	1.6900	10.5000	.9167
	Std. Deviation	.26458	.10017	.01000	.01000	.44441	.07638
Four	Mean	244.5667	14.5367	.9333	1.8767	12.2833	.9667
	Std. Deviation	.83865	.07767	.01528	.02517	.22546	.05774
Five	Mean	235.3000	9.7633	.7900	1.6200	10.6833	.8500
	Std. Deviation	.81854	.01528	.01000	.02000	.53873	.05000
Total	Mean	186.7480	9.5833	.8720	1.5313	9.3807	.9053
	Std. Deviation	50.49166	3.15771	.06247	.37779	2.37510	.05705

Appendix 2: One- way ANOVA test Result for all parameters among the water sample sites

ANOVA

		Sum of Squares	Df	Mean Square	F	Sig.
TEM	Between Groups	144.747	4	36.187	105.398	.012
	Within Groups	3.433	10	.343		
	Total	148.180	14			
PH	Between Groups	1.131	4	.283	82.193	.000
	Within Groups	.034	10	.003		

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	Total	1.165	14			
TDS	Between Groups	15312800.363	4	3828200.091	1285205.939	.000
	Within Groups	29.787	10	2.979		
	Total	15312830.149	14			
EC	Between Groups	61123612.267	4	15280903.067	254399.052	.000
	Within Groups	600.667	10	60.067		
	Total	61124212.933	14			
SALI	Between Groups	29434909.077	4	7358727.269	875621.998	.000
	Within Groups	84.040	10	8.404		
	Total	29434993.117	14			
TURB	Between Groups	35688.145	4	8922.036	25013.185	.000
	Within Groups	3.567	10	.357		
	Total	35691.712	14			
Nitrate	Between Groups	139.492	4	34.873	4476.223	.000
	Within Groups	.070	9	.008		

	Total	139.562	13			
Nitrite	Between Groups	.052	4	.013	50.038	.000
	Within Groups	.003	10	.000		
	Total	.055	14			
Phosphate	Between Groups	1.984	4	.496	354.317	.000
	Within Groups	.014	10	.001		
	Total	1.998	14			
Sulphate	Between Groups	77.860	4	19.465	174.574	.000
	Within Groups	1.115	10	.111		
	Total	78.975	14			
Fluoride	Between Groups	.022	4	.005	2.247	.136
	Within Groups	.024	10	.002		
	Total	.046	14			

Appendix 3- Correlation Between physico chemical parameters some selected river Correlations

		Tem	PH	E.C	TDS	Turbidity	Salinity	nitrate	nitrite	phosphate	sulphate	Fluoride
Tem	Pearson Correlation	1	.288	.046	.056	.120	.040	.166	.472	.403	.036	.439
	Sig. (2-tailed)		.298	.870	.843	.669	.886	.555	.076	.136	.899	.101
	N	15	15	15	15	15	15	15	15	15	15	15
PH	Pearson Correlation	.288	1	.775**	.766**	.724**	.782**	.929**	.644**	.905**	.875**	.488
	Sig. (2-tailed)	.298		.001	.001	.002	.001	.000	.010	.000	.000	.065
	N	15	15	15	15	15	15	15	15	15	15	15
E.C	Pearson Correlation	.046	.775**	1	1.000**	.945**	.999**	.938**	.297	.742**	.893**	.322
	Sig. (2-tailed)	.870	.001		.000	.000	.000	.000	.282	.002	.000	.243
	N	15	15	15	15	15	15	15	15	15	15	15
TDS	Pearson Correlation	.056	.766**	1.000**	1	.946**	.999**	.934**	.297	.739**	.884**	.318
	Sig. (2-tailed)	.843	.001	.000		.000	.000	.000	.283	.002	.000	.247
	N	15	15	15	15	15	15	15	15	15	15	15
Turbidity	Pearson Correlation	.120	.724**	.945**	.946**	1	.933**	.862**	.169	.797**	.859**	.150

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	Sig. (2-tailed)	.669	.002	.000	.000		.000	.000	.548	.000	.000	.595
	N	15	15	15	15	15	15	15	15	15	15	15
Salinity	Pearson Correlation	.040	.782**	.999**	.999**	.933**	1	.944**	.314	.738**	.895**	.342
	Sig. (2-tailed)	.886	.001	.000	.000	.000		.000	.255	.002	.000	.213
	N	15	15	15	15	15	15	15	15	15	15	15
nitrate	Pearson Correlation	.166	.929**	.938**	.934**	.862**	.944**	1	.558*	.874**	.907**	.444
	Sig. (2-tailed)	.555	.000	.000	.000	.000	.000		.031	.000	.000	.097
	N	15	15	15	15	15	15	15	15	15	15	15
Nitrite	Pearson Correlation	.472	.644**	.297	.297	.169	.314	.558*	1	.593*	.253	.638*
	Sig. (2-tailed)	.076	.010	.282	.283	.548	.255	.031		.020	.363	.010
	N	15	15	15	15	15	15	15	15	15	15	15
phosphate	Pearson Correlation	.403	.905**	.742**	.739**	.797**	.738**	.874**	.593*	1	.772**	.275
	Sig. (2-tailed)	.136	.000	.002	.002	.000	.002	.000	.020		.001	.321
	N	15	15	15	15	15	15	15	15	15	15	15
sulphate	Pearson Correlation	.036	.875**	.893**	.884**	.859**	.895**	.907**	.253	.772**	1	.320

	Sig. (2-tailed)	.899	.000	.000	.000	.000	.000	.000	.363	.001		.246
	N	15	15	15	15	15	15	15	15	15	15	15
Fluoride	Pearson Correlation	.439	.488	.322	.318	.150	.342	.444	.638[*]	.275	.320	1
	Sig. (2-tailed)	.101	.065	.243	.247	.595	.213	.097	.010	.321	.246	
	N	15	15	15	15	15	15	15	15	15	15	15

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Appendix 4. Mean ± SD values for Metal Analysis

Report

SITE		Zn	Cu	Pb	Co	Cr
ONE	Mean	.03713816	.04243223	.07090625	.07983393	.039758016
	Std. Deviation	.000618026	.002783266	.007522298	.011511415	.005185399
TWO	Mean	.06329374	.04698901	.08416667	.09875445	.041627344
	Std. Deviation	.0011886933	.0078461936	.0069333933	.0081009274	.005553459
HRE	Mean	.07755669	.04558242	.09302083	.19157770	.044404114
	Std. Deviation	.0017190816	.005560570	.010672382	.002369512	.000818376

F O U R	Mean	.11344851	.05632234	.12093750	.15676157	.046866304
	Std. Deviation	.002157111	.005811736	.006319921	.003202847	.009706367
FI V E	Mean	.06239498	.05578022	.10000000	.14596679	.049612825
	Std. Deviation	.006855060	.002601960	.006853660	.012113156	.004941459
T ot al	Mean	.07076641	.04942125	.09380625	.13457888	.044453721
	Std. Deviation	.0027191978	.0073389224	.0018493635	.042405199	.0036933617

Appendix -5 One way of ANOVA for metal Analysis

ANOVA

		Sum of Squares	Df	Mean Square	F	Sig.
Zn	Between Groups	.009	4	.002	23.969	.000
	Within Groups	.001	10	.000		
	Total	.010	14			
Cu	Between Groups	.000	4	.000	4.199	.030
	Within Groups	.000	10	.000		
	Total	.001	14			
Pb	Between Groups	.004	4	.001	17.093	.000
	Within Groups	.001	10	.000		
	Total	.005	14			
Co	Between Groups	.024	4	.006	84.701	.000
	Within Groups	.001	10	.000		
	Total	.025	14			
Cr	Between Groups	.019	4	.005	132.345	.000
	Within Groups	.000	10	.000		
	Total	.019	14			

**Appendix 6- Correlation of metal analysis**

Correlations

		Zn	Cu	Pb	Co	Cr
SITE	Pearson Correlation	.542*	.719**	.752**	.657**	.989**
	Sig. (2-tailed)	.037	.003	.001	.008	.000
	N	15	15	15	15	15
Zn	Pearson Correlation	1	.498	.877**	.633*	.498
	Sig. (2-tailed)		.059	.000	.011	.059
	N	15	15	15	15	15
Cu	Pearson Correlation	.877**	1	.595*	.315	.713**
	Sig. (2-tailed)	.059		.019	.253	.003
	N	15	15	15	15	15
Pb	Pearson Correlation	.498	.595*	1	.637*	.718**
	Sig. (2-tailed)	.000	.019		.011	.003
	N	15	15	15	15	15
Co	Pearson Correlation	.633*	.315	.637*	1	.630*
	Sig. (2-tailed)	.011	.253	.011		.012
	N	15	15	15	15	15
Cr	Pearson Correlation	.498	.713**	.718**	.630*	1
	Sig. (2-tailed)	.059	.003	.003	.012	
	N	15	15	15	15	15

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Appendix -7GFAAS standard calibration graph for Heavy Metal

calibration curve of zn metal

$y = 0.6483x + 0.0428$
$R^2 = 0.9968$

calibration curve of Cu metal

$y = 0.2375x - 7E-05$
$R^2 = 0.9975$

Calibration curve of Pd metal

$y = 0.032x + 3E-05$
$R^2 = 0.9954$

Calibration curve of Cd metal

$y = 0.485x + 0.0341$

$R^2 = 0.9978$

Calibration curveof Co metal

$y = 0.0562x + 0.0093$

$R^2 = 0.9957$

Calibration curve of Cr metal

$y = 0.0551x - 0.0176$

$R^2 = 0.9961$

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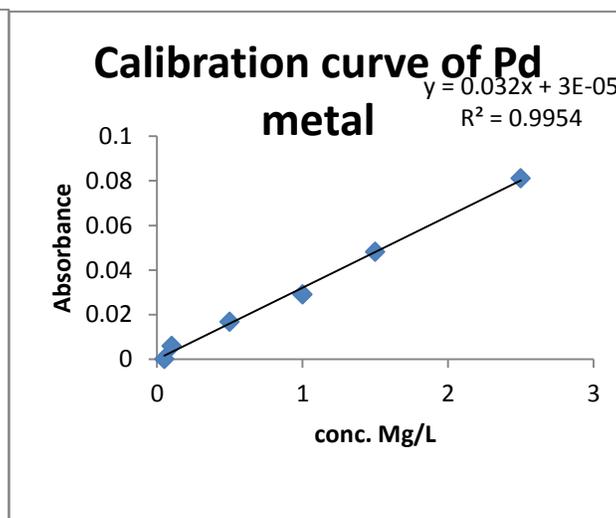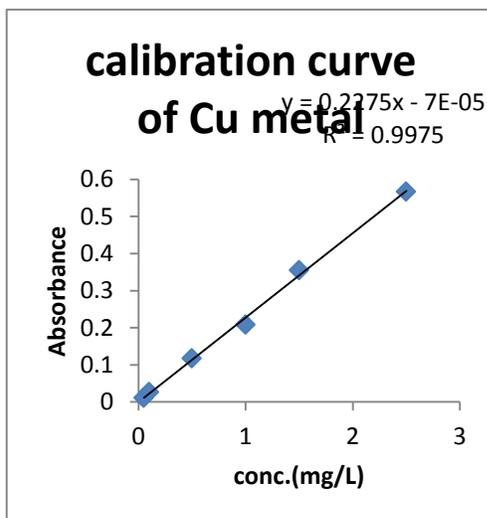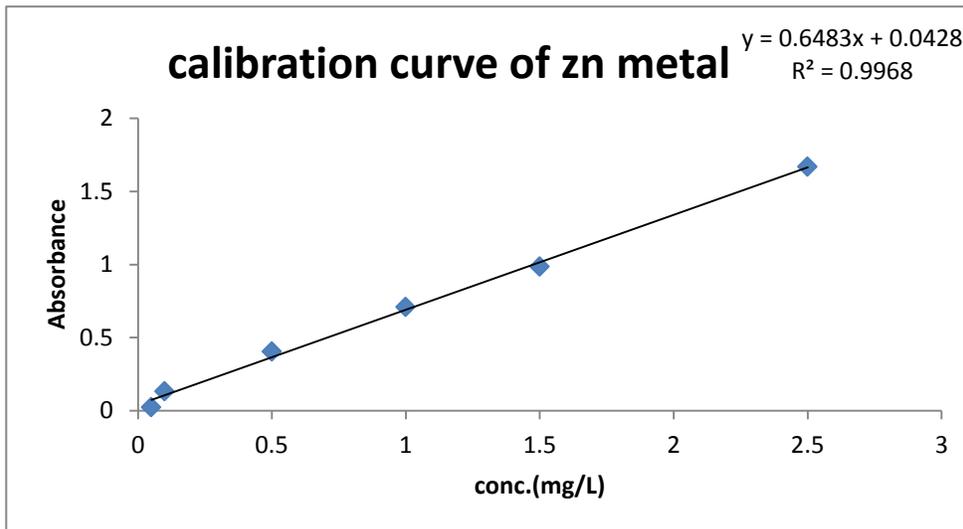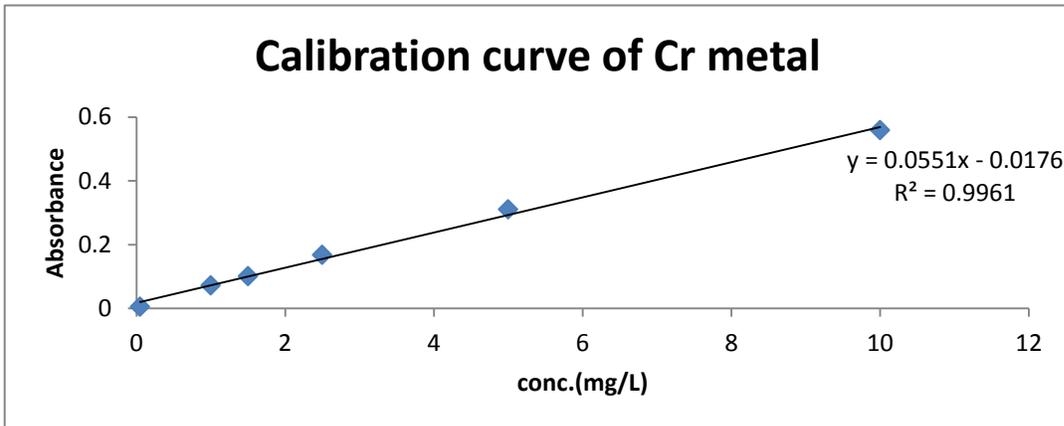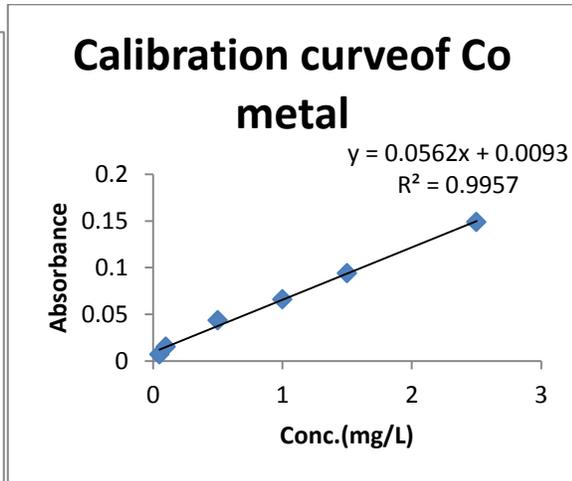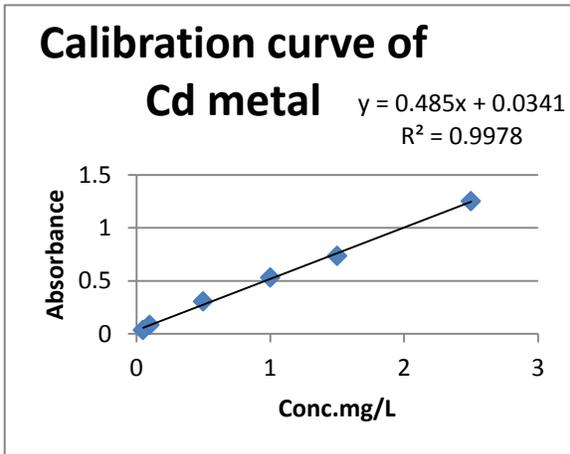
Appendix- 8The five sample of site of river water

Site 1

Site 2

Site 2

Site 3

Site 4(At influent point)

Site 5

Appendix -9-Image showing physio chemical parameter measurement

Appendix 10 Sample digestion procedure

Digesting tube

Micro wave digestion

Sample filtration

Sample after filtration

GFAAS

Reading from computer