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DEPARTMENT OF CHEMISTRY

M.Sc. THESIS ON

PHYSICOCHEMICAL CHARACTERISTICS AND INVESTIGATION OF SOME SELECTED HEAVY METALS IN WATER SAMPLES OF EJERSA RIVER WOLISO, ETHIOPIA.

November, 2018

JIMMA, ETHIOPIA

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A THESIS SUBMITTED TO JIMMA UNIVERSITY, SCHOOL OF GRADUATE STUDY, COLLEGE OF NATURAL SCIENCE, DEPARTMENT OF CHEMISTRY IN PARTIAL FULFILLMENT FOR THE REQUIREMENTS OF THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY.

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APPROVAL SHEET

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ABBREVIATIONS

ANOVA	Analysis Of Variance
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
EC	Electrical Conductivity
EDWQ	Ethiopian Drinking Water Quality
EPA	Environmental Protection Authority
FAAS	Furnace Atomic Absorption Spectroscopy
IDL	Instrumental Detection Limit
LOD	Limit of Detection
LOQ	Limit Of Quantification
MDL	Method Detection Limit
RSD	Relative Standard Deviation
SD	Standard Deviation
TDS	Total Dissolved Solid
TSS	Total suspended Solid
TQWR	Tentative Quality South African Target Water Range
WHO	World Health Organization

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ABSTRACT

Water is the most abundant substance on the earth's surface that is essential for the survival of all known forms of life. The present study is undertaken to investigate the water quality of Ejersa river interms of physicochemical characteristics and some selected heavy metals by considering effluent discharged from municipal wastes, Abattoir, prison and flooding.In the study, four sampling sites along the river course were selected. Composite sampling technique were used to collect the water samples and analyzed for some physicochemical parameters on site and heavy metals were analyzed in the lab by using GFAAS. The instrument was calibrated by using de-ionized water and standard solution by following standard procedures. The obtained results range (pH 5.7±0.15 to 6.51± 0.25, TDS 1686 ±6.22 to 3523±8.26 mg/L, EC 3340 ±6.05 to 6996 ±4.18 µS/cm, T° 18.7 ±0.15 to 19.56 ±0.41 ^{o}*C,* NO_3^- *36.6±0.5 to59.33±0.05 mg/L, Color 21.66±0.57to 30.66±1.15 HU, Salinity 2046 ±3.55 to 4406±4.63 mg/L, Turbidity 141.66 ±1.52 to 233.66±1.5 NTU, Nitrite 0.47±0.02 to 0.96±0.01, Phosphate 0.46±0.01 to 0.84±0.02) were recorded minimum and maximum at site A and Site C respectively. The level of heavy metals was found to be in the range (Zn 0.134±0.03 to 0.833±0.06 mg/L, Cu 0.062±0.01 to 0.529±0.02 mg/L, Co 0.173±0.07 to 0.239±0.04 mg/L, Cr 0.156±0.04 to 0.188±0.01 mg/L, Cd 0.077±0.02 to 0.0819±0.04 and Pb 0.321±0.04 to 0.404± mg/L) were recorded minimum and maximum at sites A and C respectively. These results however implicated site C to be the most polluted site, probably being the point of discharge. A comparison of the measured parameters with the national and international standards set by EDWQ (2010) and WHO (2008) shows that all the parameters measured (except* PO_4^{3-}*,* NO_2^-*, Cu and Zn) were above the standards. This indicates that the river water was significantly contaminated and therefore not suitable for domestic, agricultural and industrial uses. The concentrations of each parameter (except Cd) among the selected sites were significantly different (ANOVA,* $p \leq 0.05$*). The findings indicate that, there is a need to protect the quality of the river system. Therefore, it recommended that the government and other responsible authorities have to take appropriate corrective action and should support further study has to be conducted on other physical, chemical and untested biological parameters of significant health concern and identification of potential source of the contaminants of the river*

Index Terms:-*Physicochemical, heavy metals level, FAAS, Ejersa River*

1. INTRODUCTION

1.1 Background of the Study

Water is the most abundant substance on the earth's surface that is essential for the survival of all known forms of life [1]. It is always the vital commodity for humans, used for drinking, cooking, agriculture, transport and recreation, among other purposes. Nevertheless, most important is the fact that water is a major constituent of all living matter, comprising up to two-thirds of the human body. In addition, water plays an important role in the world economy, as it functions as a solvent for a wide variety of chemical substances, industrial cooling and transportation. It also serves as a receptor of industrial waste, domestic waste and wastewater resulting from other uses of water [2].

Water obtained from two principal natural sources: Surface water such as fresh water, lakes, rivers, streams, etc. and ground water such as borehole water and well water [3].They are open dynamic ecosystems whose physical, chemical and biotic characteristics can greatly influenced by different activities taking place within their drainage basins. Urban centers put huge amount of organic and synthetic waste in to rivers with little or no treatment. With-ever increasing population and industrialization, however, human societies affect rivers and their ecosystem structure and function in an ever-alarming way. In general, the effect of human activities in rivers and their ecosystem affect one or more of the five attributes of watersheds and streams; Water quality, habitat structure, stream flow patterns, sources of energy and nutrients, and biotic interaction. Today, a number of rivers and streams flow-through urbanized areas across the world, were profoundly impact by changes associated with urbanization. Continuous economic growth, urbanization and high human population growth rate are some of the contributors to the rapid increase in volume and variety of both industrial and household waste generated in many rapidly growing urban centers, especially in developing countries [4]. In Ethiopia, the dominant source of drinking water used to supply major urban and rural communities is from river, wells and springs. Although there are no systematic and comprehensive assessment programs on the quality of the water in the country [5]. The major causes of this contamination could be soil erosion, domestic waste from urban and rural areas, agricultural activities, industrial wastes, inadequate treatment, and over-use of limited water resources [6]

Many researchers conducted an analysis to evaluate the quality of river water in the country. Their results have compared with international water quality standards like EPA and WHO. However, because of rapid urbanization, industrialization, old agricultural practice, over uses of chemicals, etc. Direct discharge of waste material from different sources to river and open lands, leakage of the rivers are still not in control. This study examines the water quality parameters and heavy metals content of Ejersa River in relation to WHO guidelines for surface water. It also aimed at on the investigation and potential source of contaminants of the river water under the consideration of effluents from Abattoir, prison in the area under the study.

1.2 .Statement of the problem

Ejersa River is one of the rivers found around Woliso town. As the river runs along the side of the town it could be feed with contaminants brought by run-off from the upload into the river at the peak of the floods, discharge from municipal wastes, Abattoir and prison. The Abattoir and prison release directly the wastes to the river without any treatment. But the community live around and downstream of this untreated river water used for different activities, irrigation and other household purposes. The environmental deterioration caused by water pollutant from municipal discharge, abattoir and prison effluent in Ejersa River has not studied yet. So that it requires to investigate the quality of the river through the consideration of the impact of these effluents discharge on water quality of the Ejersa River. The main victims of this river water are the urban communities, which live near to the river and rural communities found in Badessa Koricha, Obi Koji, and Fodu Gora Kebeles. Many villages at downstream of the river, uses the river water for domestic consumptions, drinking their cattle and used for irrigation purposes.

1.3. Objective

1.3.1. General Objective

The general objective of this study was to investigate physicochemical characteristics and the level of some selected heavy metals in water samples collected from Ejersa River

1.3.2. Specific Objectives

- To determine the physicochemical properties (pH, EC, Turbidity, Temperature, Nitrate, Nitrite, phosphate , Color, salinity and TDS) of Ejersa river
- To analyze the concentrations of heavy metals (Cd, Pb, Zn, Cu, Co, Cr) in water samples of Ejersa River.
- To analyze the status of water for drinking, irrigation and other household purposes according to WHO and EDWQ

1.4 Significance of the Study

The significances of this study is to provide information on the pollution status of Ejersa river by investigating some selected heavy metals and the acceptability for household, drinking, irrigation and other domestic purpose by comparing with different guideline of water quality standards set for different uses of water. The study result will be used for the relevant authorities in designing appropriate preventive measure to ensure that the water quality in the river is improve. Also it gives the baseline data on physicochemical constituents and some heavy metals of the river water. Finally the result of the study serves as a source of information for further study.

2. LETRATURE REVIEW

2.1. The use of river water

Rivers drain nearly 75% of the earth's land surface. Rivers provide excellent habitat and food for many of the earth's organisms. They play a very important part in the water cycle, acting as drainage channels for surface water. Rivers carry water and nutrients to areas all around the earth. 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 [7]. 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 [8].

2.2. Physicochemical Characteristics

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. It is very essential and important to test the water before it is used for drinking, domestic, agricultural or industrial purpose. Physicochemical characteristics 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. These are Temperature, electrical conductivity, total dissolved solids, Turbidity, hydrogen Ion concentration (measured as pH), Salinity, color and different ions [9]. Water must be tested with different physicochemical 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's 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 physicochemical parameters are tested regularly for monitoring quality of water [7].

2.2.1. pH

pH can be viewed as an abbreviation for power of hydrogen or more completely, power of the concentration of hydrogen ion. pH is most important in determining the corrosive nature of water. Lower the pH value higher is the corrosive nature of water [10]. The reduced rate of photosynthetic activity the assimilation of carbon dioxide and bicarbonates which are ultimately responsible for increase in pH, the low oxygen values coincided with high temperature during the summer month. 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 [11].The pH of pure water at 25^{o}C is 7.0, but the pH of environmental waters is affected by dissolved CO_2 and exposure to minerals [7].

2.2.2. Temperature

Temperature is an important in controlling the rate of all chemical reaction and biological reactions. Water temperature is one of the controlling factors for the dynamics of aquatic environments; because it interferes in the organism's metabolism, influencing the reproduction, accelerating the reactions' speed and increasing the degradation rate of organic matter [7]. Cool water is generally more palatable than warm water, and temperature have an impact on the acceptability of a number of other inorganic constituents and chemical contaminants that may affect taste. High water temperature enhances the growth of microorganisms and may increase problems related to taste, odor, color and corrosion [12]. The variation in river water temperature usually depends on the geographic location, season, sampling time and temperature of wastewater discharges entering the stream [13].

2.2.3. Electrical Conductivity

One of the physicochemical parameter is electrical conductivity (µs/cm). This is influenced by dissolved salts. This parameter is playing a role as a proxy of ion content in the river. Electrical conductivity (EC) is the measure of the ability of water to conduct an electric current and depends upon the number of ions or charged particles in the water. EC determinations are useful in aquatic studies because they provide a direct measurement of dissolved ionic matter in the water. 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 eutrophic water ways where plant nutrients (fertilizer) are in greater abundance. Very high values are good indicators of possible polluted sites. The main reason behind fluctuation of mean EC values in is dumping of huge volumes of toxic wastes into the river and city's many of industrial units and sewerage lines and agro-industries [13]. Conductivity often is used to estimate the amount of TDS rather than measuring each dissolved constituent separately [14].The EC increases going down river apparently due to the accumulation of domestic and sewage wastewater and also to the enrichment of electrolytes from mineralization or weathering of sediment [15].

2.2.4. Total Dissolved Solids

Total dissolved solids indicate the salinity behavior of river water. The composition of solids present in a natural body of water mainly depends upon the nature of the bedrocks and the soil developed from it. The term total dissolved solid (TDS) refer to materials that are completely dissolved in water and the physicochemical factors, which govern the chemistry of salts in water, may also influence the composition [16]. Dissolved solids in natural waters may consist of carbonates, bicarbonates, chlorides, sulfates, phosphates, nitrates, magnesium, sodium, iron, manganese and other substances. Determination of the "solids" content is important for both aesthetic and practical reasons; drinking water with high solids content can have a disagreeable palatability. The palatability of water with a TDS level of less than about 600 mg/L is generally considered to be good; drinking-water becomes significantly and increasingly unpalatable at TDS levels greater than about 1000 mg/L. Taste problems in water often arise from the presence of high TDS levels with certain metals present, particularly iron, copper, manganese, and zinc [17] reported that increase in value of TDS indicated pollution by extraneous sources. 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.

2.2.5 Turbidity

Turbidity is a measure of the clarity of the water. It is related to the scattering of light by fine and suspended particles that cause water to have a cloudy appearance. Turbidity is an optical property of water measured by a turbidity meter, or neuphelometer, as the intensity of light scattered at one or more angles to an incident beam of light. Turbidity is mainly caused by suspended matter or impurities such as clay, silt, organic and inorganic matter [18].

2.2.6. Salinity

All natural waters contain soluble salts. The concentration of the salts determines whether the water is of high quality (drinkable or usable for irrigation without need for special precautions) or of low quality (brackish or saline). Water in the soil also contains soluble salts (sometimes called free or nonattached salts). The amount of salts in the root zone (or the salt concentration in the soil solution) determines whether the soil is “normal” or “salt-affected” (saline, sodic, or salinesodic). Salinity becomes a concern when an “excessive” amount or concentration of soluble salts occurs in the water, either naturally or as a result of mismanaged irrigation water. Worldwide, salt-affected most abundant in arid regions, and in irrigated lands the formation of salt-affected is the most important process of chemical soil degradation. Salinity is more of a concern in irrigated shoreline areas where groundwater supplies are influenced by intrusion of sea water. Sediments dredged from salt-laden deposits are also chronic problems, particularly when used as fill on which vegetation is attempted. Salinity is generally a cyclical problem related to water availability from rainfall; it is aggravated in dry years and relieved in wet years. Fortunately, most have physical and structural qualities that impart behavioral resilience and prevent salts from imposing irreversible soil degradation [19].

2.3. Major Chemical Parameters

2.3.1. Nitrate

Nitrate is attributed mainly to anthropogenic activities such as runoff water from agricultural lands, discharge of household and municipal sewage from the market place and other effluents containing nitrogen specie [20]. High nitrate concentrations in domestic water supplies can be toxic to human life. Nitrate is used mainly in inorganic fertilizers. In soil, fertilizers containing inorganic nitrogen and wastes containing organic nitrogen are first decomposed to give ammonia, which is then oxidized to nitrite and nitrate. Most natural water are deficient in nitrate having a concentration usually below 5 mg/L, but certain polluted surface water and ground water may have substantially higher quantities. Drinking water standards for nitrate are strict because the nitrates can be reduced to nitrites, which oxidize iron in blood hemoglobin from ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}). The resulting compound, called met hemoglobin, cannot carry oxygen. The resulting oxygen deficiency is called methemoglobinemia. It is especially dangerous in infants (blue baby syndrome) because of their small total blood volume.

2.3.2. Phosphate

Increase in concentration of phosphate indicates that there is mixing of industrial effluents, sewage water and waste water in the river water. Higher concentration of Phosphates leads to eutrophication and this result in deficiency of dissolved oxygen (DO) which kills fishes and other aquatic fauna. Toxicity of $PO4^{3-}$ in humans includes impaired renal function, rhabdomyolysis and tumorolysis Syndrome. Sewage, detergent use and fertilizer runoff are common sources. Phosphorus is also a constituent of animal wastes [21]. Compounds containing phosphorus that are of interest to water quality include Orthophosphates (all contain $PO4^{3-}$), tri sodium phosphate (Na_3PO4), disodium phosphate (Na_2HPO4), monosodium phosphate (NaH_2PO_4), and ($(NH_4)_2HPO4$). Orthophosphates are soluble and are considered the only biologically available form. To measure total phosphate, all forms of phosphate are chemically converted to orthophosphates or hydrated forms [9].

2.4. Heavy Metal Toxicity, Nature and Source

2.4.1 Heavy Metal Toxicity

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 [9].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 [23].

2.4.2. 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 [24].

2.4.3. Sources of Heavy Metals in River Water

The two main sources of heavy metals in water and wastewater are natural and anthropogenic. Naturally, heavy metal pollutants enter into river water through ore-bearing rocks, wind-blow dust, forest fires and vegetation. In addition, urban run offs and aerosol particles are natural source of heavy metals of water bodies. It has reported that volcanic eruptions produce hazardous impacts to the environment, climate and health of exposed individuals. Apart from the deterioration of social and chemical conditions and the gases released, various organic compounds as well as heavy metals have released during eruptions. Soil erosion has indicated to be a natural source of heavy metal pollution in water. The two main agents of soil erosion are wind and water. During rainfall, sediment-bound heavy metals have distributed to the soil. Water containing agrochemicals with toxic metal concentration drop this sediment bound metal in the soil even as it causes erosion [25]. Some of the anthropogenic sources of heavy metals in water and wastewater effluents are industrial discharge, domestic sewage, urban storm, non-point source runoff and atmospheric precipitation, landfills, inputs from rural areas. In addition, metal finishing and electroplating, mining and extraction operations are also included in anthropogenic sources of heavy metals. In some cases, textile industries have indicated to be major sources of heavy metal pollutants in water. This has said to be mostly originate from the dyeing process, which is a major process in such industries. The compounds used for these dyeing processes (coloration) include copper, chromium, nickel and lead which is very toxic and carcinogenic [26].

Although heavy metals are naturally present in small quantities in all river water, it is almost exclusively through human activities that these levels have increased to toxic levels. The heavy metals, therefore, find their way into natural water bodies originated from both natural and anthropogenic sources, which accumulate in the media and subsequently enter the human bodies.

Table 1. The major sources and significance of pollution in aquatic eco-systems [27]

Class of pollutant	Effects and Significance
Trace Elements	Health, aquatic biota, toxicity
Heavy metals	Health, aquatic biota, toxicity
Inorganic pollutants	Toxicity, aquatic biota
Algal nutrients	Eutrophication
Acidity, alkalinity, salinity (in excess)	Water quality, aquatic life
Trace organic pollutants	Toxicity
Polychlorinated biphenyls	Possible biological effects
Pesticides	Toxicity, aquatic biota, wildlife
Sewage, human and animal wastes	Water quality, oxygen levels
Biochemical oxygen demand	Water quality, oxygen levels
Pathogens	Health effects
Detergents	Eutrophication, wildlife, esthetics
Chemical	carcinogens Incidence of cancer

2.4.4. Industrial Effluents Discharged to River

Industrial effluents are the major source of pollution of water and air in the environment. Depending on the industry and their water use, various levels of pollutants have discharged in to the aquatic environment directly or indirectly through public sewer line. Wastewaters are generated by many industries because of their operation and processing. The waste water discharged from the industries contain suspended solids, both degradable and non-biodegradable organics, oils and greases, heavy metal ions, dissolved inorganic, acids, bases and coloring compounds which have capability to pollute nearby rivers [28]. The impact of industrial toxic and hazardous wastes on the aquatic life including microorganism cannot be over-stressed. Consequently, up on the industrial revolution, many production and manufacturing companies have due to improper waste management techniques, added toxic and hazardous wastes including synthetic compounds into the aquatic environment. Despite a variety of alternatives available for industrial waste management, many industries continue to degrade the most precious but scarce natural resources especially water. Industrial effluents have characterized by their abnormal turbidity, conductivity, chemical oxygen demand (COD), total suspended solids (TSS) and total hardness. The river residential environment in any industrial effluent site is always under considerable stress due to the prevailing harsh environment conditions, especially high temperature and salinity, restricted benthic fauna diversity and over all development of a fragile intertidal ecosystem [28]. Most of the rivers in the urban areas of the developing countries are the ends of effluents discharged from the industries. African and Asian countries experiencing rapid industrial growth and this are making environmental conservation a difficult task [8]. One of the three people in developing countries does not access to safe drinking water and some 123 fresh water animal species have gone to extinction in North America [29]. A number of industries in developing countries still use outdate or the least practicable technologies due to economic constrain. Majority of the industries in Ethiopia are old and use out dated technology. Despite the fact that their number is few, their impact in terms of pollution is enormous. Moreover, a great majority of these industries discharges their waste in the form of liquid, dust particles and smoke without treatment [30].

2.4.5. Wastes discharged from Abattoir and Prison

Specific use have different quality needs and water supply in one way is considered more acceptable if it produces better results or causes fewer problems than an alternative water supply; for example, good quality river water which can be sued successfully for irrigation may be unacceptable for municipal use without treatment to remove the sediment because of its sediment load. Similarly, snowmelt water of excellent quality for municipal use may be too corrosive for industrial use without treatment to reduce its corrosion potentials. The ideal situation is to have several supplies from which to make a selection, but normally only one supply is available. In this case, the quality of the available supply must be evaluated to see how it fits the intended use. Most of the experience in using water of different qualities has been gained from observations and detailed study of problems that developed following use. Toxicity problems occur if certain constituents (ions) in the soil or water are taken up by the plant and accumulate to concentration high enough to cause crop damage or reduced yield. The degree of damage depends on the uptake and the crop sensitivity. The permanent, perennial type crops (tree crops) are the more sensitive. Damage often occurs at relatively low ion concentrations for sensitive crops. It is usually first evidenced by marginal leaf born and interveinal chlorosis plants, while in human there were reported cases of liver and kidney related problems. Toxicity can also occur from direct absorption of the toxic substances through leaves wet. As concentrations increase in the applied water damage develops more rapidly and becomes progressively more severe. Pollution of general environment has increasingly gathered a global interest. In this respect, contamination of agricultural soils with heavy metals has always been considered a critical challenge in scientific community [28]. Heavy metals are generally present in agricultural soils at low levels. Due to their cumulative behavior and toxicity however, they have a potential hazardous effect not only on crop plants but also on human health. With the increasing awareness of risk assessment of heavy metals in food crops, monitoring of these metals in agricultural soils is therefore critical as it gives information in nutritional planning and provides data for epidemiological studies. Information about the movement of metals through ecosystem as well as their bioaccumulation, tropic transfer, and potential toxicological effects is provided by measure of the concentrations in soils and biota. The persistence, biomagnifications, and distribution of trace metals in terrestrial food webs have been investigated in studies patterns of uptake and bioaccumulation have been studied by investigation of the relationship between metal concentration in soils and several parts of plant tissues. Both abattoir waste water and municipal sledge waste has led to multi-elements concentration of soils. Elevated concentration of certain trace elements, when mobile, can cause great environmental concern by accumulating and contaminating soils, vegetation, animals or surface and ground water.

2.5 Importance, Sources and Health Effects of Some Heavy Metals and Physicochemical

Some water pollutants have needed in trace amounts for plants and microorganisms as micronutrients, however, they become extremely toxic in high concentrations. Copper, Lead, zinc, Cadmium, boron and phosphorus, for example, can be toxic or may otherwise adversely affect aquatic life when present above certain permissible limits. However, their presence in low amounts is essential to support and maintain functions in aquatic ecosystems. Other trace metals naturally, found in the body at low concentrations and are essential for human health. Iron, for example, prevents anemia, and zinc is a cofactor in over 100 enzyme reactions. However, some heavy metals such as cadmium, chromium, and lead have no known physiological activities, but they have proved detrimental beyond a certain limit. In aquatic ecosystems, heavy metals greatly depress the number of living organisms. They have negative effect on the growth of aquatic organisms [31].

Table 2 Source, effect, importance of trace element in natural water and physicochemical Parameters [27].

Elements	Sources	Effects and significance
Arsenic	Mining byproduct, chemical waste	Toxic, possibly carcinogenic
Beryllium	Coal, industrial waste	Toxic
Chromium	Metal plating	Essential as Cr(III), toxic as Cr(VI)
Copper	Metal; plating, mining, industrial	toxic to waste
Lead	Industrial waste, mining, fuels	Toxic, harmful to wildlife
Zinc	Industrial waste, metal plating,	Essential element, toxic to plants
pH	Due to dissolved gases and solid	Bitter test, corrosion
Temp.	Due to chemical rxn, hot waste water	effect on solubility of essential gases
EC	Due to dissolved solid	increases corrosive nature of water
Turbidity	Soil runoff	Higher level causing bacteria
TDS	From dissolved salt	bad taste, irritation, corrosion
Color	Dissolved salts	Consumer acceptance decreases
Nitrite	NH_3 compounds	Form nitrosamine's - carcinogenic
Nitrate	Runoff, fertilizers	Effect on infant
phosphate	Waste water, rocks	rancidity mould growth

2.6. Heavy metals

2.6.1 Cadmium:

The major intentional uses of cadmium are Ni-Cd batteries, cadmium pigments, cadmium stabilizers, cadmium coatings, cadmium alloys and cadmium electronic compounds such as cadmium telluride (CdTe). The major classes of products where cadmium is present as an impurity are non-ferrous metals (zinc, lead and copper), iron and steel, fossil fuels (coal, oil, gas, peat and wood), cement, and phosphate fertilizers. Cd is toxic by whatever route it is administered and some of the changes produced may result from its metabolic antagonism to Cu, Zn, and Fe: these include anaemia, hypertension and skin changes [32]. Cadmium emissions to the environment are normally transported continually between the three main environmental compartments, air, water and soils, but a steady state flux is probably achieved and the general levels can reasonably well be established. Cadmium is a natural, usually minor constituent of surface and groundwater. It may exist in water as the hydrated ion, as inorganic complexes such as carbonates, hydroxides, chlorides or sulphates, or as organic complexes with humic acids. Cadmium may enter aquatic systems through weathering and erosion of soils and bedrock, atmospheric deposition, direct discharge from industrial operations, leakage from landfalls and contaminated sites, and the dispersive use of sludge and fertilizers in agriculture. Much of the cadmium entering fresh waters from industrial sources may be rapidly adsorbed by particulate matter, and thus sediment may be a significant sink for cadmium emitted to the aquatic environment.

Rivers containing excess cadmium can contaminate surrounding land, either through irrigation for agricultural purposes, dumping of dredged sediments or flooding. It has also been demonstrated that rivers can transport cadmium for considerable distances, up to 50 km, from the source [33].

2.6.2. Copper

Copper is a reddish metal that occurs naturally in rock, soil, water, and air. Its unique chemical and physical properties have made it one of the most commercially important metals. Since copper is easily shaped or molded, it is commonly used to make pennies, electrical wiring, and water pipes. Copper compounds are also used as an agricultural pesticide, and to control algae in lakes and reservoirs. Copper also occurs naturally in plants and animals. It is an essential element for all known living organisms, including humans. However, very large single or long-term intakes of copper may harm health. Someone may be exposed to copper by breathing air, eating food, or drinking water containing copper or may also be exposed by skin contact with soil, water, or other copper-containing substances. Most copper compounds found in air, soil, and water are strongly attached to dust or embedded in minerals, and cannot easily enter the body. These forms are not likely to affect health. Other forms become dissolved in water and are not attached to other particles [34]. However, drinking water may contain higher levels of a dissolved form of copper. High levels of copper occur if corrosive water comes in contact with copper plumbing and copper-containing fixtures in the water distribution system. The level of copper in drinking water increases with the corrosivity of the water and the length of time it remains in contact with the plumbing. Immediate effects from drinking water which contains elevated levels of copper include vomiting, diarrhea, stomach cramps and nausea [34].

2.6.3 Cobalt

Cobalt is a metal that may be stable (non-radioactive as found in nature), or unstable (radioactive, man-made). The most common radioactive isotope of cobalt is cobalt-60.The non-radioactive cobalt is a naturally occurring element found in rocks, soils, water, plant, and animals in small amount. The largest uses of non-radioactive metallic cobalt are for production of pigments in glass, ceramics, and paints; as catalysts in the petroleum industry; as paint driers; as trace element additives in agriculture and medicine. The major biological role of cobalt is as a continent in vitamins B_{12}. It is an essential element, required for good health in animals and humans, and therefore, it is important foodstuffs to contain enough amount of cobalt. The major sources in diet are meat, milk and liver. Shortage of cobalt results in deficiency of vitamin B_{12}, which is common in vegetarians due to low vitamin B_{12} intake from their diets.

Sources of cobalt in the atmosphere are both natural and anthropogenic. Natural sources include wind-blown continental dust, seawater spray, volcanoes, forest fires, and continental and marine biogenic emissions [33]. Cobalt that realize in to the water will stick to particles in the water column or to the sediment at the bottom of the body of water in to which it was realized, or remain in the water column in ionic form. Eventually, most parts of it end up in the soil or sediment. Exposure to high levels of the non-radioactive cobalt results in lung and heart defect and dermatitis. Liver and kidney effects have also been observed in animals. The health effect of radioactive cobalt is known to cause cancer. Therefore, exposures to gamma radiation from cobalt-60 result in an increased risk of cancer.

2.6.4. Lead

Lead, a very soft, blue-gray, metallic element has been used since antiquity. Because it is so soft, lead is usually alloyed with other elements. Combined with other elements, it forms a variety of interesting and beautiful minerals, all of which are heavy due to their lead content. The most significant lead mineral is galena (PbS, lead sulfide). PbCO3 and PbSO4 are two other lead-based minerals. Lead had been recognized as an industrial hazard before it was appreciated that house dust is a profile source of the elements from paint, the street, old batteries, solder from cans and toothpaste tube. Lead has no known nutritional and physiological function and it is usually toxic for organisms [35]. Lead may occur in drinking water either by contamination of the source water used by the water system, or by corrosion of lead plumbing or fixtures. Corrosion of plumbing is by far the greatest cause for concern. All water is corrosive to metal plumbing materials to some degree. Grounding of household electrical systems to plumbing may also exacerbate corrosion.

2.6.5 Zinc

Zinc is one of the most common elements in the earth’s crust. It is also an essential element for all living things. Pure zinc is a bluish-white, shiny metal. Zinc has many commercial and industrial uses. A large proportion of all zinc, perhaps more than a third, is used to galvanize metals such as iron so as to prevent corrosion. Zinc metal is used for dry batteries, roof cladding, and to protect iron structures from corrosion by attaching zinc as sacrificial anodes [32]. Zinc is one of the most abundant trace elements in the human body. It is typically taken in by ingestion of food and water, although it can also enter the lungs by inhaling air, including that contaminated with zinc dust or fumes from smelting or welding activities. Zinc is an essential element in our diet, but too little or too much can be harmful. Eating large amounts of zinc can cause stomach cramps, nausea, and vomiting. Zinc is found throughout the environment in air, soil, and water, and it is present in all foods. Natural processes, but most results from human activities can release it. Releases to air, water, and soil are common in areas where ores are mined, processed, and smelted for zinc. Because cadmium and lead are commonly present in zinc containing ores, they are also typically released during these processes and so areas are often jointly contaminated. Surface water can be impacted by discharges of metal manufacturing and chemical industry wastes, and also by run-off following precipitation on soils high in zinc, either due to the natural setting or human applications, including use of zinc fertilizer on agricultural soils [32].

2.6.6 Chromium

Chromium is not essential for plants but is essential for animals and may be deficient in human food. Because plants do not easily absorb chromium, regulations allow for higher concentrations of chromium in soils than occur naturally. It is required for carbohydrate metabolism as it potentiates the action of insulin. However, Chromium deficiency should also be considered as one of several nutritional factors that influence three recognized risk factors for public health problems of cardiovascular disease, impaired glucose tolerance, elevated circulating insulin levels, and elevated serum cholesterol. In addition, inadequate maternal chromium intake is known to cause premature birth and intra-uterine growth retardation and in males it has been linked with infertility [36].

3. MATERIALS AND METHODS

3.1 Study Areas

Woliso is one of the towns in Oromia regional state of Ethiopia, which was established in 1919 E.C. Woliso town is located a distance of 114 Km to the south west from the capital of Ethiopia and one of the Oromia state administrative town and is the capital of south west shoa zone. The town is located at 8.31^{0}60$^{''}$North latitude and 37.58^{0}60" East longitudes. The elevation of the town ranges from 1900 to 2000 meters above sea level. The mean temperature of the town is 22.5 ℃ and the mean annual rainfall is 1200 mm. Climate: The lowest and the highest annual average values of temperature are between 10 and 25 ^{o}C. The main rainy season, which is characterized by intense rainfall of short duration, is responsible for 70% of the annual average rainfall of 1400 mm [37]. Rivers like Ejersa, Walga, Kala, and Rebu, which are serving the local communities for domestic consumption and irrigation purpose, have found around the town. The town is bounded up with Ejersa River at the West and Rebu River at the East.

The study was conducted on Ejersa River which is about 0.5 Km far from the center of Woliso town. The river has originated from the highland, which is located at the western part of Woliso town. Flowing South west direction of the plain of the town, the river is finally joined Walga river basin. The criteria for consideration of sampling sites in the river are based on different waste sources, accessibility of the sampling site, and purpose of the study [38].

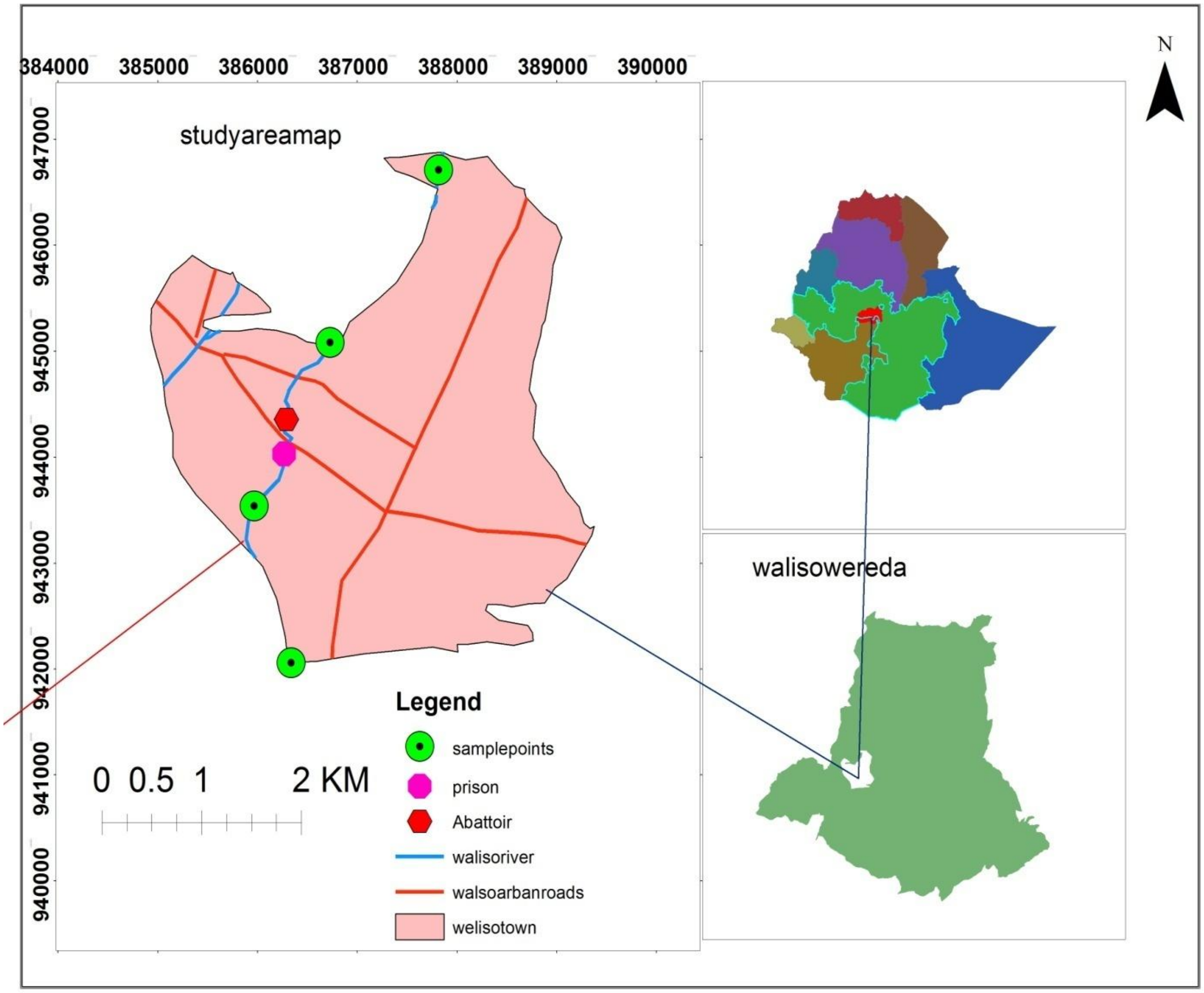


Figure 1 Study Area

3.2 Selection of Study Area

Ejersa River is 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 variuos 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[37]. Either dissolved in the water or attached to suspended matter and eventually gets into the Ejersa river. That is why this river is choosen.

3.3. Sampling and Sampling strategies

The sample sites of the river were identified by considerations of efluent discharged to the river water. The water samples of the river were collected from four cites by using composite Sampling method [39,40]. Sample site A (upstream), sample site B (municipal wastes),Sample site C (at efluent of both prison and Abattoir) and sample site D (downstream).

Wastes directly discharged from Abattoir to Ejersa River

Figure 2 showing wastes discharged from Abattoir and prison

3.4 Sampling and Storage of Water

Water sampling was done according to the procedure described by WHO and EPA.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. Immediately 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 [7].

3.5. Chemicals and Reagents

Chemical reagents and solvents including, ultra-pure HNO_3 65% (UNI-CHEM,N43725), HCl 37% standard solutions of selected heavy metals (Pb, Cd, Zn, Cr, Cu, and Co) and distilled water were utilized in the study. Reagent Powder Pillows Nitriver 3 nitrite, Reagent Set, Nitriver 5 nitrate Reagent Powder Pillow, High Reagent Reactive Phosphorus were standards used to analyse nitrite,nitrate and phosphate ions in water sample.

3.6. Instruments and Apparatus

In this study, Atomic Absorbsion Spectroscopy (GFAAS NOVAA 400P, Germany) equipped with Acetyleen air background correctors,Qualitative filter paper 20-25µ porose size Ø9 cm with vacuum filtration set up,Microwave Digester (TopWave Controll unit 912A743, Germany) were used for heavy metals determination. And Photometer (Wagtech 7100),Conductivity meter (CC-411 Elemelron), Turbidity meter (Wegtech International), pH Testr 30 (Double Junction Wegtech international pH-4 & pH-10 standard buffer solution), Comparator were used for physicochemical parameters.

3.7. Laboratory Analysis

3.7.1. Stock and Working Standard Solutions

Stock standard solutions containing 1000 mg $L^{-1}$of (Pb, Cd, Cr, Cu, Zn and Co) were purchased (Analytical Grade). Working standards for all the metals were prepared from the stock solutions by serial dilutions in distilled water.

3.7.2. Calibration of Instrument

Calibration was done by preparing working standard solutions of known and certified standard chemical within working range of instruments for six points of calibration curve for each metal. By following the read out device (computer) the working standards, the GFAAS constructs a suitable calibration curve of response /absorbance verses concentration. The GFAAS was used suitable graph and determined concentrations of unknown analyte (Appendix 7) showings the absorbance versus concentration has constructed through direct analysis of five-point calibration standards at specified wavelength of the analytes. The calibration curve shows good correlation coefficient (R^2) greater than the minimum acceptance value 0.995 [40] This shows that there was a good linear relationship between the concentration and instrument responses.

Table 3. Standard Concentration for metal analyzed

Metals	concentration of standards (mg/L)
Pb	0.05, 0.5, 1.0, 1.5, 2.5, 4.0
Zn, Cu, Cd, Co	0.05, 0.1, 0.5, 1.0, 1.5, 2.5
Cr	0.05, 1.0, 1.5, 2.5, 5.0, 10

Table 4. Instrument operation condition for GFAAS

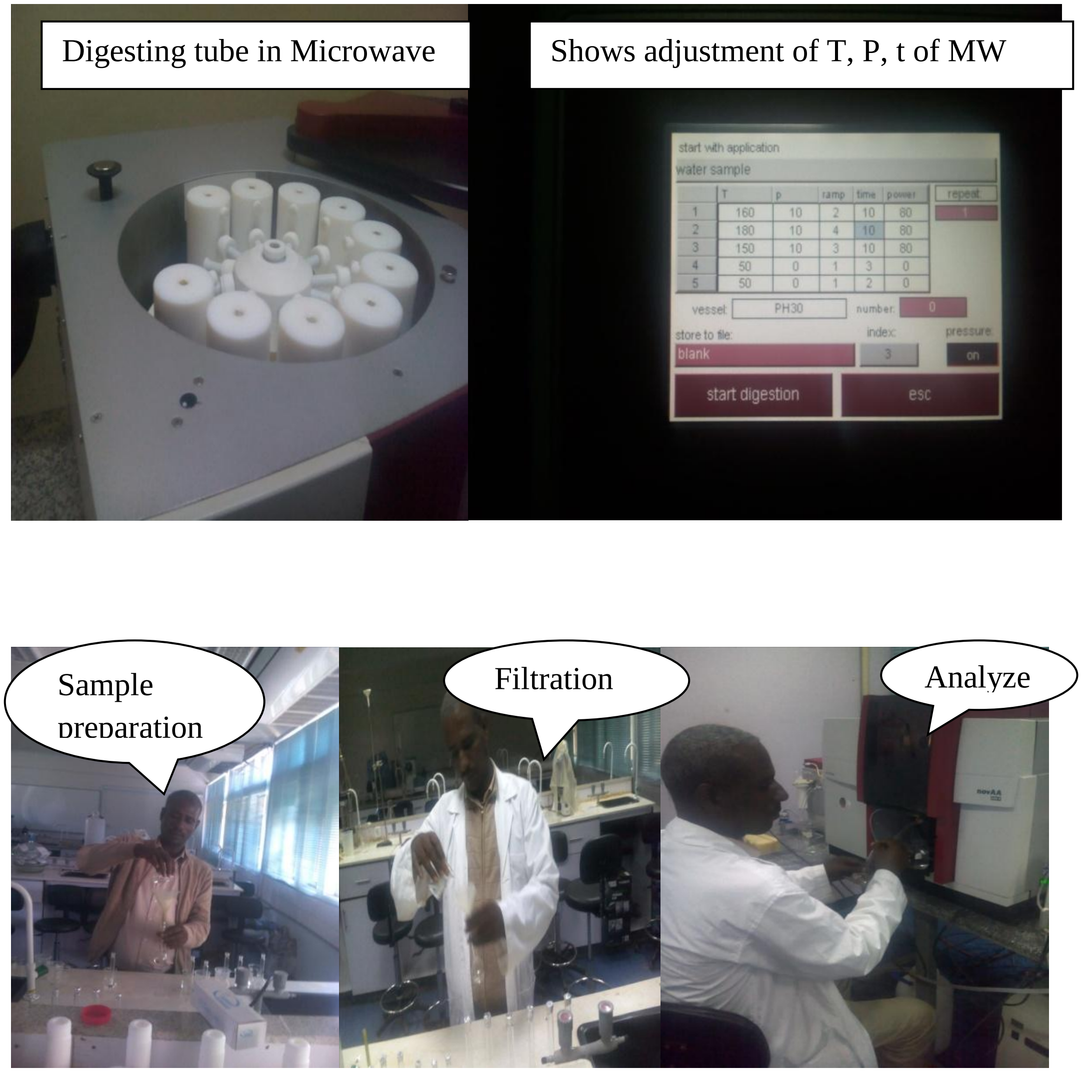
Element	Wave length (nm)	IDL(mg/L)	Silt width (nm)	Current(mA)	Energy(eV)	Flame
Zn	213	0.0001	0.7	2	100	Air-Acetylene
Cu	324	0.0001	0.7	2	74.5	Air-Acetylene
Pb	283	0.0003	0.7	2	71.8	Air-Acetylene
Cd	228	$0.075x10^{-3}$	0.7	2	86	Air-Acetylene
Co	240	$0.01x10^{-4}$	0.2	2	78	Air-Acetylene
Cr	357	$0.05x10^{-4}$	0.7	2	82	Air-Acetylene

3.7.3. Digestion of Water Samples for Metal Analysis

Digestion of the water samples were done in triplicates using concentrated nitric acid and hydrochloric acid 3:1 ratio according to method described by [36]. A mixture of concentrated nitric acid and hydrochloric acid (8 ml) was added to 20 ml of water samples in a Digesting tube (Analytik Jena) were inserted in the microwave digester and then it was adjusted as temperature 150-180 ^oC, pressure 10-15 atm, and time up to 35 min for digestion; and also temperature 50 ^oC, pressure zero, time 8min for cooling. Displayed the instrument until the samples were digested and cooled for 40-43 min. And then the solution filtered using Qualitative filter paper 20-25 µ pores size Ø9 cm inserted in a 100 mL milli pore filtrations glass. A blank solution had been similarly prepared.

Table 5. Microwave digestion adjustment

Temp (^oC)	160	180	150	50	50
Pressure (atm)	20	10	10	0	0
Time (min)	10	15	10	5	3



start with application

water sample

	T	p	ramp	time	power
1	160	10	2	10	80
2	180	10	4	10	80
3	150	10	3	10	80
4	50	0	1	3	0
5	50	0	1	2	0

repeat: 1

vessel: PH30

number: 0

store to file: blank

index: 3

pressure: on

Figure 3 Picture showing Digestion,filtration and reading

3.7.4. On site Measurement

The measurement of physicochemical parameters such as temperature, electrical conductivity, total dissolved solid, turbidity, pH, salinity and color were carried out at the site as these values might change when transported to the laboratory. Water temperature was measured in-situ, using temperature analyzer probe by dipping in water for about 2 to 3 minutes and has recorded in degree Celsius. Electrical conductivity, total dissolved solid and salinity were determined with field conductivity meter. pH was measured using portable digital pH meter. Turbidity has measured by portable turbidi meter and color was measured using comparator.

3.7.5. Anions analysis procedures

Each anion (nitrite, nitrate, and phosphate) were determined separately using photometer (Wagtech 7100) by using Reagent Powder Pillows. Reagent Powder Pillows Nitriver 3, Reagent Set, Nitriver 5 nitrate Reagent Reagent Powder Pillow, High Reagent Reactive Phosphorus were standards used to analyse nitrite, nitrate and phosphate ions in water sample

Nitrite (NO_2^-):

Two sample cells were prepared. The first sample cells, was filled with 10 mL sample water. The content of one NitraVer 3 Nitrite Reagent Powder Pillow has added to the cell and swirled to dissolve. In 20 minutes of reaction time, a pink color was developed. The second sample cell has filled with about 10 mL de-ionized water, which serves as a blank. This has used to calibrate the instrument to 0.0 mg/L NO_3^-. Then, the prepared sample in the first sample cell has inserted into the photometer and a direct reading of the concentration of NO_2^- has recorded.

Nitrate (NO_3^-):

A content of one NitraVer 5 Nitrate reagent powder pillow has added to 10 mL sample water in the first sample cell and shaken vigorously for one minute, and allowed to stand for 5 minutes for anamber color development. In the second sample cell, about 10 mL of de-ionized water have filled. This has used as a blank to calibrate the instrument to 0.0 mg/L NO_3^-. Then, the sample prepared in the first sample cell has inserted into the photometer; a direct reading of the concentration of NO_3^- has recorded.

Phosphate (PO43-):

two test tube vials were prepared and using a TenSette pipet, 5 mL of deionized water has mixed with reactive High Range Phosphorus in the first test tube vial. Into the second test tube, one Reactive High Range Phosphorus has added to 5.0 mL of the water sample. The two test tube vials have allowed react for seven minutes. The blank in the first test tube has used to calibrate the photometer reading to 0.0 mg/L. Finally, the sample prepared has analyzed to determine the concentration of phosphate.

3.8 Method Validation

3.8.1 Evaluation of analytical precision, accuracy, recovery and quality control

Precision

The precision of an analytical procedure has usually expressed as the variance, relative standard deviation and percentage relative standard deviation of a series of measurements. In this study, the precision of the results was evaluated by percentage relative standard deviation of the results of three samples (N=4) and triplicate readings for each sample giving 12 measurements for a given bulk sample.

RSD= =CVx**100**--(3.1)

Where SD = standard deviation, X= mean value, RSD = relative standard deviation,

CV =coefficient of variance

Accuracy

Accuracy of analytical method has evaluated in terms of percent recovery by added known 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

$$\%R=\frac{Cs-C}{S}\text{---(3.2)}$$

Where Cs =concentration of spiked sample, C= concentration of unspiked sample

S= concentration of added (spiked), %R= percentage recovery.

Method detection limit

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 [41]. Method detection limit for heavy metal may vary with wavelength selected and the spectrometer configuration and operation conditions.

Method detection limit for water sample analysis was determined using reagent water blank with HNO3/ HCl that was digested in the same condition in the condition as the sample. In this study, after digestion of three blank solutions, seven readings have taken for each blank and the standard deviations were calculated for a 99% confidence level was taken for (Cd, Pb, Zn Cu Co and Cr).

The method detection limit of each metals has obtained by multiplying the standard deviation of the reagent blank by three.

MDL=3xδblank ---(3.3)

Where δ blank = standard deviation of the blank readings

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

LOQ=10 x δblank--(3.4)

Data Analysis

Data were analyzed using Microsoft Excel 2007. Descriptive data have generated for all variables and have presented as means ± standard deviation ($\bar{X}$ ± SD). The mean variations in data between the four sites have analyzed using One-way ANOVA (by IBM SPSS statistics software, version 25). The parameters and selected heavy metals have correlated against each other to determine their relationship using Pearson’s correlation (Table 9, 11). Significance has considered at 95% confidence interval. Differences in mean values obtained were considered significant if calculated p-values were<0.05 (Table 8, 10). The mean difference is significant at the 0.05 level.

4. RESULTS AND DISCUSSIONS

4.1 Results of Method Validation

Method Detection Limits

The method detection limit (MDL) of the analytical method for each analytes was determined from seven replicate of blank with target analyte. The calculated values represent the measured minimum concentration of the analytes and the values reported with 99% confidence that the analyte concentration greater than zero.

Table 6. Regression equation, Correlation coefficient and Detection limit

Analyte	Regression equation	Correlation coefficient	Detection limits		
			IDL^{x} (mg/L)	LOD (mg/L)	LOQ (mg/L)
Zn	Y=0.047x+0.0035	0.9989	1 x10^{-4}	0.022	0.073
Cu	Y=0.227x-0.00007	0.9978	1 x10^{-4}	0.016	0.052
Pb	Y=0.021x-0.0003	0.9969	3x10^{-4}	0.019	0.064
Cd	Y=0.485x+0.034	0.9978	7.5x10^{-5}	0.018	0.06
Co	Y=0.056x0.009	0.9959	1x10^{-6}	0.0087	0.029
Cr	Y=0.067x+0.012	0.9977	5x10^{-6}	0.009	0.031

^{x}Results are obtained from the manual of the instrument

Recovery Testes

The precision and accuracy of the analytical method has calculated in terms of relative standard deviation and percent recovery using equation 3.1 and 3.2 respectively. The recovery and relative standard deviation were within the standard / required limit; 80-120% for recovery and < 20 % for RSD [40]. Recovery values in the above range are acceptable for environmental investigations and the digestion procedure is believed to remove metals fractions associated with carbonates, sulphides, soluble salts, organic matter [42]. According to the standard, 80-120% recovery and ≤ 20% RSD [40] unless other criteria are provided by a chosen laboratory. Therefore, the percentage recovery values have found between the lowest 80 % to and highest 120 % and all were within the required criteria. In addition, the RSD value is the standard limit (Table 6). This confirms that the method has provided results within the required levels of accuracy and precision.

Table 7. Percentage Recoveries, Standard Deviation (SD) and Relative Standard Deviation (RSD of heavy metals

Metal	Site	Add value(mg/L)	Unspiked value(mg/L)	Spiked value(mg/L)	%RECOVERY	SD	RSD(%)
Zn	A	1.5	0.134	1.888	116.9	0.006	4.47
	B		0.137	1.436	86	0.003	2.18
	C		0.833	1.999	80.6	0.02	2.4
	D		0.199	1.665	97.7	0.007	3.5
Cu	A	1.5	0.062	1.284	81.7	0.001	1.61
	B		0.078	1.322	82.9	0.002	2.56
	C		0.529	1.855	88.4	0.02	3.78
	D		0.066	1.301	82.3	0.002	3.03
Pb	A	2	0.31	1.989	83.9	0.008	2.5
	B		0.34	1.999	82.9	0.01	2.9
	C		0.41	1.999	80.6	0.02	4.4
	D		0.35	1.999	82.4	0.02	
Cd	A	2	0.077	1.884	90.3	0.004	5.19
	B		0.081	1.921	92	0.008	9.87
	C		0.088	1.945	93,2	0.002	2.27
	D		0.078	1.912	91.7	0.006	7.69
Co	A	1.5	0.17	1.739	104.6	0.005	2.94
	B		0.22	1.798	105.2	0.012	5.45
	C		0.25	1.823	104.8	0.004	1.6
	D		0.23	1.801	104.7	0.007	3.04
Cr	A	2	0.15	1.994	92.4	0.011	7.33
	B		0.17	1.999	91.4	0.004	2.3
	C		0.19	1.999	90.4	0.006	3.15
	D		0.18	1.999	90.9	0.01	5.5

A=Upstream=Only Municipal wastes=Municipal, Abattoir, and Prison wastes, D=downstream

The standard concentration is in the within the linear dynamic range (LDR).

4.2 Physicochemical Analysis of water sample

4.2.1. The mean variation of physicochemical parameters by using one-way ANOVA

Physicochemical variables measured for the determination of Ejersa River include: pH, temperature (℃), electrical conductivity (µS/cm), turbidity (NTU), total dissolved solid (mg/L), salinity (mg/L), color (HU), nitrite (mg/L), Nitrate (mg/L) and phosphate (mg/L).

Table 8. Results of physicochemical parameters of water samples collected from Ejersa River and Statistical P-values (the values were expressed as X±SD, n=3

Parameters	Site A	Site B	Site C	Site D	Guideline(mg/L)		
					P-valu	WHO	EDW
pH	6.51±0.25	6.4±0.26	5.7±0.15	6.01±0.15	0.0001	6.5--------8.5	
T (^{O}C)	18.7±0.15	19.16±0.25	19.56±0.41	18.93±0.25	0.035	-	-
EC(µS/cm)	3340±6.05	6933±5.09	6996±4.18	6356±5.16	0.002	500	500
TDS(mg/L)	1686±6.22	3453±4.41	3523±8.26	3490±3.1	0.0001	1000	1000
Turbi(NTU)	141.66±1.52	173±1.53	233.66±1.5	162±2.34	0.0002	5	7
Salini(mg/L)	2046±3.55	4320±6.05	4406±4.63	3926±4.41	0.0001	-	-
Color (HU)	21.66±0.57	29.66±0.55	30.66±1.15	25.66±0.53	0.0002	15	15
NO_3^-(mg/L)	36.6±0.5	44±1.21	59.33±0.5	52±1.14	0.0003	50	50
NO_2^-(mg/L)	0.47±0.02	0.55±0.01	0.96±0.01	0.75±0.05	0.001	3	3
PO_4^{3-}(mg/L)	0.46±0.01	0.49±0.02	0.84±0.02	0.6±0.01	0.0002	5	-

Site A = water sample from upstream of river;

Site B = water sample from only municipal waste discharge point;

Site C = water sample from effluent of all waste discharge point;

Site D= downstream of the river.

- Except Nitrite and Phosphate all parameters are above the recommended level in all site by WHO and EDWQ.
- All the measured values are significantly different.

pH: is a simple parameter but extremely important, since most of the chemical reaction in aquatic environment are controlled by any change in its value. In this study, the pH of the water sample at the four sites range from 5.7±0.15 (site C) to 6.51±0.25 (site A). The value in site C, D, and B is below the minimum limit (6.5-8.5) of EDWQ (2010) and WHO (2008) guideline ranges. The lower pH values observed suggests that because of acidic character of the effluent site, equilibrium has affected more due to change in physicochemical condition [10]. The presence of different metals decrease the pH because of interaction between carbonates and bicarbonates formed from the dissolved CO_2 and stabilized CO_2. In this study, the pH of the river differed significantly ($P<0.05$) between the selected sites of the river (Table 8) and strongly correlated with dissolved solid, color, salinity and $NO3^-$(Table 9/Appendix 2). Site C was not significantly different from site D ($P> 0.05$), but significantly different from site A and B. Site A and B is significantly differing from site D ($P<0.05$) (Appendix 1). The major contributor for the decrease in the pH value of the Ejersa River at site C was probably the effluent discharged from the Prison and Abattoir, fertilizers used for agricultural activities. Water with pH value of about 5.7 is exceptional and may reflect contamination by acid. Low pH tends to facilitate the solubility of salts and heavy metals.

Temperature: The present investigation reveals that the temperature of the river varied from a minimum of 18.73 ^oC at site A to a maximum of 19.56 ^oC at site C (Table 8), water temperature at site A was lower than that of site C. This might be attribute to the fact that site A is located relatively in the headwater, which have more shade and located at higher altitude and no foreign wastes are daily discharge to it. The maximum temperature recorded at site C may be attributing to exothermic reaction taking place between the ionic species discharged from the effluents discharged from Abattoir, Prison and municipal wastes. The water temperature during sampling period across the sampling sites was significantly different (ANOVA, $P<0.05$) among the sites of the studied river (Appendix 1).

The fluctuation in river water temperature usually depends on season, geographic location, sampling time, and temperature of effluent entering the stream. All aquatic life forms have characteristic temperature preference and tolerance limits. Any increase in the average temperature of a water body can have ecological impacts. It can elevate the metabolic oxygen demand which in conjugation with reduced oxygen solubility, affect many species. Increase in temperature also increases the rate of microbial activity.

Electrical Conductivity (EC): EC of the water sample ranging from the minimum of 3340µS/cm (site A) to a maximum of 6996 µS/cm (site C). The highest concentration value of electrical conductivity recorded were probably associated with the effluent discharge from dissolved substance from Prison, Abattoir and municipal effluent discharged from resident community and chemicals applied to farm land. This value was started to decrease downstream of the river (Table 8) due to dilution effect. This may also be a sign that ions responsible for the conductivity were precipitate out or settling on the riverbed or being absorbed by aquatic plants. The mean concentration values of electrical conductivity of the river varied significantly ($P \leq 0.05$) among the sampling sites (Appendix 1). Since, the conductivity of the water is a function of the number of charged ion in solution; it is another measure of dissolved materials.

Total Dissolved Solid (TDS): is an important parameter in evaluating the suitability of water for irrigation, since the solid might clog both pores and components of water distribution system. The observed mean total dissolved solid concentration in the river water currently measured varied between a minimum mean values of 1686 ± 26.22 mg/L (site A) to a maximum mean values of 3453 ± 40.41 mg/L (site Band C). The values at all the sites were above the minimum permissible limit set by both EDWQ and WHO. The high values recorded at sites B and C probably related to pollution through discharge of effluent from Prison, Abattoir, municipal and sewage wastewater discharge into the river. The mean total dissolved solid values varied significantly ($p \leq 0.05$) among the selected sites of the river. The dissolved salt present in the water, affect its aesthetic value as well as its physicochemical properties. High content of dissolved solid elements, affect the density of water, influences osmoregulation of freshwater in organisms, reduces solubility of gases (like oxygen) and utility of water for drinking, irrigation and industrial purposes. Total dissolved solid greater than 1200 mg/L may be objectionable to consumers and could have impacts for those who need to limit their daily salt intake example severely hypertensive, diabetic, and renal dialysis patient. High concentration of total dissolved solid also reduce water clarity, contribute to a decrease in photosynthesis, combine with toxic compound and heavy metals, and lead to an increase in water temperature. Primary sources for higher TDS in the river water might be due to agricultural runoff, discharge of domestic waste from the town and other human activities like washing of different vehicle at and around the river [46].

Salinity: is a measure of dissolved salts in river. The mean concentration of salinity of the river under the study was ranged from a minimum of 2046 mg/L to a maximum of 4406 mg/L. Higher salinity value was recorded at effluent entry site (site C) due to the chemical effluent from the prison, abattoir and municipal waste discharge that contain many organic as well as inorganic materials. A slight decrease from site C to site D is observed probably due to adsorption of many salts with the sediments at the bottom of the river course. Salinity values of the river water under the study differed significantly ($P<0.05$) (Appendix 1). Mean concentration of salt at site A varies from sites B, C and D; and site B is also varying from site C and D. 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.

Conductivity is a good measure of total amount of salts in water and this is commonly used to determine salinity. In natural water ions usually originate from inorganic compounds present in water [47]. High salinity may influence the growth of aquatic vegetation. Salt may decrease osmotic pressure, causing water to flow out of the plant to achieve equilibrium. Less water can be absorbed by plant, causing stunted growth and reduce yield. High salt concentrations my cause leaf tip and marginal leaf burn, leaching or defoliation.

Turbidity: Turbidity is the measure of the suspended particulate matter in a water body that interferes with the passage or dispersion of a beam of light through the water. The mean turbidity values of water sample measured at the selected sites were differed significantly ($P \leq 0.05$) across the selected sites of the river (Appendix 1). The results obtained from the river under the study shows that the maximum turbidity value of 233.66 NTU (site C) and minimum turbidity value of 141.66 NTU (site A) were recorded. In all the sites the values obtained were extremely greater than the minimum permissible value of WHO (5 mg/L) and EDWQ (7 mg/L) standards for surface water, is significantly different. This might be due to daily disturbance of the river by washing of different vehicles and surface runoff. Site A is significantly different from sites B, C and D; and site C significantly differ from site D indicating that the source of pollutant causes the river to turbid is not the same through out of the courses of the river. High value recorded at site C, indicate that wastes were discharged from the effluent site. Turbidity increases the total available surface area of solids in suspension in which bacteria can grow. High turbidity reduces light penetration; therefore, it impairs photosynthesis of submerged vegetation and algae. In turn, the plant growth may suppress fish productivity. Turbidity interferes with the disinfection of drinking water and is aesthetically unpleasant.

Color: is the measure of dissolved coloring compounds in water. The color of water sample measured ranging from 21.66± 0.57 HU (site A) to 30.66 ± 1.11HU (site C). In the studied river, it has observed that there is a gradual decrease in the value of color of the river water from the effluent discharge point to downstream of the river. The maximum color of the river at site C due to coloring materials discharge from the effluents and vegetation origin such as algae and weeds that found around the course of the river. Color intensity increases with increase in pH. Results from the four selected sites were significantly different ($P<0.05$) among the sites (Appendix 1).

Color in drinking water may be due to the presence of organic matter such as humic substances, metals such as iron and manganese, or highly colored industrial wastes. Drinking water should ideally be colorless. Increase in color may interfere with the passage of light thereby impeding photosynthesis. Colored water is not aesthetically acceptable to the public. The high color value of Ejersa River may probably due to discharge from prison, abattoir and municipal wastes and dissolved vegetation found around the course of the river.

Nitrite: The mean nitrite concentration measured shows the maximum value of 0.96 ± 0.02 mg/L (at site C) and a minimum value of 0.47 ± 0.05 mg/L (at site A). All the values measured did not exceed surface water standard set by EDWQ and WHO (3.0 mg/l) at the entire sites. However, the maximum concentration is recorded at site C, which has started to decrease downstream, is probably from agricultural chemicals and nitrogen containing chemical. The mean concentration of nitrite among the sites differed significantly ($P<0.05$). Mean concentration of nitrite at site C is significantly varies from site A and significantly varies from site B. Site C is not differ significantly from site D (Appendix 1) which shows that the sources of nitrite ion in the river course is not the same at the four sites. Site C has more exposed to the source of nitrite ion. Expected source of nitrite in this river can be from nitrogen containing organic matter, commercial fertilizers, and naturally from mineral rocks decomposition. Many effluents, including sewage, are rich in ammonia, which in turn can lead to increased nitrites concentration. High level of nitrite in river water may indicate pollution. It has used as a source of nutrients for plants. At high pH and high ammonia, the toxicity effect of nitrite is increases.

Nitrate: Nitrate represents the most oxidized form of nitrogen and the product of oxidation of nitrogenous matters and its concentration may depend on the nitrification and de-nitrification activities of microorganisms. Nitrate mean concentration range from a minimum of 36.6 ± 0.5 mg/L (site A) to a maximum of 59.33 ± 0.05 mg/L (site C). The values in the site C was above the permissible limit of WHO and EDWQ (50 mg/L) as shown in (Table 8).. The major expected source of nitrates are from the use of nitrogen containing fertilizers, domestic sewage, municipals discharge, animal manure used on cropland, and naturally from atmospheric deposition and the oxidation of ammonia [44]. Mean concentration of nitrate in the studied river varied significantly ($P\leq 0.05$)

across the selected sites (Appendix 1). The presence of nutrients (nitrate, ammonia and phosphate) in the river has attributed to the processes of organic mineralization of nitrates and phosphates derived principally from the surface runoff from the immediate vicinity (forest, farm and communities) perhaps by in situ mineralization [44]. The high concentration of nutrients like nitrate and nitrites could deplete the amount of dissolved oxygen in water. This in turn affects the biomass and species diversity of aquatic organism.

Phosphate (PO_4^{3-}): Phosphate determination is useful in measuring the water quality since it is an important plant nutrient and may play a role of limiting factor among all other essential plant nutrients. The concentration of PO_4^{3-} in the studied river varies from the minimum of 0.47 ± 0.01 mg/L (site A) to the maximum of 0.84 ± 0.01 mg/L (site C). In all the entire site, the concentration of phosphate is below the maximum limit set by WHO as well as EDWQ (5 mg/L) standard. In this study, the maximum mean concentration of PO_4^{3-} was recorded at site C was might be due to the discharge from fertilizers, domestic wastes and biological process [45]. When phosphate detergents are used, disposal of the wastewater is an issue. Mean concentration of phosphate differed significantly ($P \leq 0.05$) among the sites of the river (Appendix 1). the values of phosphates in the studied river, Ejersa River, increased toward the discharge point and started to decrease downstream. Elevated concentration of PO_4^{3-} ion in the river is characteristic of natural contact with minerals, domestic and municipal sewage water. The decomposition of plant materials, which have potential to release phosphate, could explain the higher concentration. The breakdown of phosphorus complexes in detergent wastewater (and other household products, as well as human and industrial wastes that contain phosphate) creates freely available phosphates; these can contribute to an oversupply of phosphate in waterways and cause imbalance of the aquatic ecosystem. This result in excessive algal growth and increasing the number of decomposer organism that requires oxygen, which can deplete the amount of oxygen dissolved in the water. Excessively large number of decomposers may reduce the oxygen levels to the extent that other aquatic organisms die from lack of oxygen [43].

4.2.2. Correlation among physicochemical parameters

Pearson correlation coefficient matrixes among the determined physicochemical parameters are present in (Table 9). There was a strong correlation between the EC, Salinity and TDS (r=0.999), TDS, Turbidity, Salinity and color (r=0.905, 0.913, 0.921), between Nitrate and Nitrite (r=0.966), EC, TDS, Salinity, Nitrate, Nitrite and Phosphate (r=0.891, 0.895, 0.886, 0.940, 0.974 respectively).

And there was weak correlation between T, Turbidity, Color, Nitrate (r=0.375, 0.411, 0.472 respectively).

Table 9. Correlation between physicochemical parameters among the selected sites of Ejersa River Correlations (pearson correlation 2-tailed)

	pH	T	EC	TDS	Tur	Salin	Color	NO_3^-	NO_2^-	PO_4
pH	1									
T	.637	1								
EC	.694	.621	1							
TDS	.687	.625	.999	1						
Turb	.849	.781	.687	.670	1					
Salin	.707	.639	.999	.997	.704	1				
Color	.643	.762	.913	.905	.821	.921	1			
NO_3^-	.668	.375	.738	.744	.411	.728	.472	1		
NO_2^-	.792	.433	.777	.781	.560	.773	.551	.966	1	
PO_4^{3-}	.775	.525	.891	.895	.618	.886	.700	.940	.974	1

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

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

In this study, the **pH** of the river differed significantly ($P<0.05$) between the selected sites of the river and strongly correlated with dissolved solid, color, salinity and $NO3^-$(Table 9) Site C was not significantly different from site D ($P> 0.05$), but significantly different from site A and B. Site A and B is significantly differing from site D ($P<0.05$) (Appendix 3). The major contributor for the increase in the pH value of the Ejersa River at site C was probably the effluent discharged from the Prison and Abattoir, fertilizers used for agricultural activities. Water with pH value of about 9.63 is exceptional and may reflect contamination by bases. High pH tends to facilitate the solubility of salts and heavy metals.

Temperature of the river water was strongly correlated with pH (r=0.637), turbidity (r=0.781), TDS (r=0.625), color (r=0.762), salinity (r=0.639), EC (r=0.621), NO2-(r=0.62), and weakly with NO_3^- (r=0.375) (Table 9/Appendix 2).

The **conductivity** of the water is a function of the number of charged ion in solution; it is another measure of dissolved materials. This can be indicated from the strong correlation (r=0.999) values of total dissolved and salinity recorded. EC of the river was also strongly correlated with pH(r= 0.87), color (r=0.913), NO2- (r=0.818), NO3- (r=0.738) and PO_4^{3-} **(**r=0.891) (Table 9/Appendix 2).

The mean total dissolved solid (**TDS**) values varied significantly ($p \leq 0.05$) among the selected sites of the river and strongly correlated (r=0.999) with EC, salinity, and color (r>0.9) (Table 9/Appendix2). This can indicate that more colored basic salts have dissolved in the river.

Salinity of the river water is strongly correlated to TDS (r=0.997) and strongly with pH (r=0.707), EC (r=0.999), and color (r=0.921) values of the river indicating that, large quantities of salts were dissolved in the river.

Turbidity values of the river were strongly correlated with pH (r=0.849), color (r=0.821) and T (r=0.781) and weakly correlated with NO_4^{3-} (r=0.411) indicating the maximum turbidity values recorded of the river especially at the effluent discharge point.

Color correlated with other measured parameters the values of color of the river were strongly correlated with EC (r=0.913), TDS (r=0.905), salinity (r=0.921) and NO3- (r=0.472 weakly correlated).

Nitrite is strongly correlated with nitrate (r=0.966) and phosphate(r=0.974) measured physicochemical parameters, except temperature(r=0.433 weakly correlated) (appendix 2). This shows that the presence of nitrite could indicated by the increase in the concentration of nitrate .

The **Nitrate** correlation coefficient value shows that the nitrate concentration is strongly correlated with all the measured physicochemical parameters (r>0.9) and weakly correlated with Temperature, Turbidity and color (Table 9/Appendix 2).

Phosphate concentration is strongly correlated with EC (r=0.891), with Nitrite(r=974), Nitrate(r=0.940) and moderately correlated with temperature (r=0.525)

4.3. Concentration Level of the Measured Metals of the Water Sample

4.3.1. The mean variation of heavy metals by using one-way ANOVA

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 10) contains the results of the laboratory analysis conducted on the water samples from Ejersa river and their detail discussions have given in the following section.

Table 10. Results of mean concentration of selected metals of water sample of Ejersa River from upstream to downstream and Statistical P-value (the values were expressed as X±SD, n=3

	Site A mg/L	Site B mg/L	Site C mg/L	Site D mg/L	Guidelines		
					p-value	WHO(mg/L)	EDWQ(mg/L)
Zn	0.134±0.03	0.139±0.01	0.833±0.06	0.199±0.07	0.022	0.2	5
Cu	0.062±0.015	0.066±0.04	0.529±0.02	0.078±0.03	0.001	0.1	2
Pb	0.321±0.04	0.339±0.03	0.404±0.01	0.347±0.02	0.002	0.01	0.01
Cd	0.077±0.02	0.0774±0.08	0.0819±0.04	0.0786±0.06	0.994	0.0003	-
Co	0.173±0.07	0.208±0.05	0.239±0.04	0.222±0.01	0.04	0.001	-
Cr	0.156±0.04	0.169±0.01	0.188±0.01	0.174±0.06	0.05	0.02	-

Site A= water sample from upstream of Ejersa river;

Site B= water sample from the only domestic discharge point;

Site C= water sample from all effluent discharge;

site D=water sample from downstream.

Zinc: Zinc is one of the important trace elements that play a vital role in the physiological and metabolic process of many organisms. It is an essential trace element for bacteria, plants and animals including humans. It also plays an important role in protein synthesis and is a metal, which show low concentration in surface water due to its restricted mobility from the place of rock weathering or from natural source [48]. The measured concentration of zinc in the studied river was ranging from minimum of 0.134± 0.003 mg/L (Site A) to the maximum of 0.833 ± 0.06 mg/L (site C). In the entire site, the concentrations recorded were higher than WHO (0.2 mg/L) permissible level for surface water, but lower than the EDWQ (5.0 mg/L) guideline. An increase in the concentration of Zn at site C, which followed with decrease downstream, has observed. The increase in mean concentration of Zn at site C might be due to formation of some soluble salts with certain anions that might be discharge from the effluent [49].

In the studied river the average concentration of Zn has observed to decrease downstream. The mean concentration of Zn among the four sites of the river (ANOVA, $P<0.05$) was varied significantly (Table 10). This may be a result of precipitation of the element as hydrous metal oxide. A very high concentration of zinc has known to be harmful to the body. It causes phytotoxicity and affects many function of the body such as reproduction, skin health, sense of smells and tastes, brain function and growth. The frequent intake of zinc supplements can cause copper deficiency, because zinc inhibits absorption of copper in the body.

Copper (Cu): The concentration of copper in the water sample under the study ranges from a minimum of 0.062 ± 0.0015 mg/L (site A) to a maximum of 0.529± 0.001mg/L (site C). Shows that below the recommended limit set by EDWQ (2 mg/L) and above the recommended limit set by WHO (0.1 mg/L) guidelines. Therefore there are indications of the presence of this metal in the river. This shows that the metal concentration in the water were generally low. However, it was observed that sample collected from the sites of effluent discharge point (site C), shows higher value of Cu. Across the sampling sites, the concentration of Cu was differing significantly (ANOVA, $P<0.05$) (Table 10). The low values observed in the river provide an indication that there is a low usage of Cu containing materials and potential contamination by these metals within the sampling sites is minimal. Considering the guideline, the river water can considered wholesome with respect to copper content. This implies the river water may be safe from this metal pollution. The source for the presence of copper in the river can be from agricultural chemicals of copper compounds, corrosion of copper containing alloys in pipefitting, may introduce measureable amounts of copper into water in a pipe system [49]. Cu is more of essential trace element, but toxic to plants and algae at higher level. It also impairs an undesirable taste to water.

Lead (Pb): Seriously, hazardous species found in the river of the studied sites is lead. The values of lead ranging from a minimum 0.321 ± 0.032 mg/L (site A) to a maximum 0.404± 0.01 mg/L (site C).

In all the entire selected sites of the river, the values recorded were above the minimum permissible limit of EDWQ and WHO (0.01 mg/L). Statistical ANOVA results (Table 10) shows that, among the sampling sites the mean concentration of Pb was significantly different ($P<0.05$) (Appendix 4). Most of the lead we take has removed from our bodies in urine; however, as exposure to lead is cumulative over time, there still risk of buildup, particularly in children. Lead concentrations have effect on three human systems: blood forming system, nerve system and renal system. 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 [50].In the studied river, car wash, domestic waste, deteriorating household paints, disposal of lead batteries from garage, which have discharged through small tributaries that passing through the center of the town has probably attributed to the increase in Pb concentration. The agricultural activities practiced around the river may also contributed to the observed high levels of lead, since this metal can occur as impurities in fertilizers and metal based pesticides and compost and manure.

Cadmium: The mean concentration of Cadmium in the study area was minimum 0.0771±0.02 mg/L (site A) and maximum 0.0819±0.04 mg/L at site C. The concentration Cd values recorded from four sites are much more than the recommended upper limit for Cd in drinking water of 0.003mg/L set by the WHO and the Ethiopian Standards in all samples, hence the water was polluted in case of Cd. One-way ANOVA ($p \geq 0.05$) indicated that the Cd Concentration among the water samples not varied significantly which could not cause the variation of Cd among the water river. Cd is a poisonous metal and can cause serious health problems even if ingested in small amounts. 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 [9].

Cobalt: cobalt concentration ranges of the studied sites were from 0.173±0.07 mg/L) to 0.239± 0.04 mg/L. Cobalt concentrations were above the recommended limit at all sampling sites (Table 9). The WHO guideline for Co is 0.001 mg/L in water for domestic use. The limit was above in river and therefore Co is a problem of using the river for domestic purpose, and for the irrigational and livestock watering activities water of Ejersa River.

Chromium: concentration of chromium of the study area is above the minimum limit, from 0.156±0.04 to 0.188 ± 0.01(Table 10). There is strong correlation among chromium and all the heavy metals studied in the river water (Table 11). Because of the higher concentration of Cr in all sites of the studied area there is a problem. Many industrial wastes are discharged into water regularly. Most of these wastes are degraded slowly by living organisms into smaller harmless molecules; however some are not easily broken down by them instead they accumulate to levels which could pose serious health hazards to organisms. Some heavy metals in low concentrations are essential for life but at high concentration they cause toxicity, carcinogenicity, allergenicity and sometimes they also inhibit the activity of sensitive enzymes. Chromium (Cr) is one of the major industrial wastes produced from many industries like textiles, tanneries, electroplating, metallurgical which causes health issues in humans and animals and also affects marine life [37]

4.3.2. Correlation among measured heavy metals

Pearson correlation coefficient matrix among the selected heavy metal is present in (Table 11). Significant correlation between the heavy metals Zn and Cu (r = 0. 538), Cr and Co (r = 0.684), Zn and Pb (r=0.613), Cu and Pb (r=0.696), Cu and Co (r=0.773)., and strongly correlate of Pb and Co (r= 0.920), this shows that there is a direct relationship between the two metals, Cu and Cr (r = 0.676), Cr and Pb (r = 0.736) could indicate the same or similar source input was there. And there was a weakly correlation between Cd and Zn (r = 0.153), Cu and Cd (r=0.343), Pb and Cd (r=0.423), Cd and Co (r=0.223), this means there is inverse relation between these two metals.

Table 11.Correlation between measured metals from upstream to downstream of Ejersa River

	Zn	Cu	Pb	Cd	Co	Cr
Zn	1					
Cu	.538	1				
Pb	.613*	.696*	1			
Cd	.153	.343	.423	1		
Co	.575	.773**	.920**	.223	1	
Cr	.558	.676*	.736**	.722**	.684*	1

*. Correlation is significant at the 0.05 level (2-tailed).
**. Correlation is significant at the 0.01 level (2-tailed).

Zinc is strongly correlated with lead (r=0.613) but, weakly correlated with the other metals analyzed (Table 11). This may be a result of precipitation of the element as hydrous metal oxide. A very high concentration of zinc has known to be harmful to the body.

The **copper** in the river is strongly correlated with Co (r=0.773) and weakly correlated with Cd (r = 0.343). This is a good indication that the source of the metals Cu, Zn and Co is the same and the presence of the one can affect the other.

Lead (Pb) concentration strongly correlated with Co (r=0.920) and weakly correlated with Cd (r=0.432) (Table 11).

Cadmium (Cd): concentration strongly correlated with Cr (r=0.722) and weakly correlated with all the five metals (Zn, Cu, Pb, and Co (r=0.153, 0.343, 0.423,and 0.223) (Table 10).

Cobalt: concentration strongly correlated with Pb (r=0.920) and Co (r=0.773), weakly correlated with Cd (r=0.223) and moderately correlated with Zn (r=0.575) and Cr (r=0.684) (Table 10)

Chromium: concentration strongly correlated with Pb (r=0.736), Cd (r=0.722) and moderately correlated with Zn (r=0.558), Cu (r=0.676) and Co (r=0.684) (Table 11).

5. CONCLUSION AND RECOMMENDATION

5.1. CONCLUSION

The investigation and characteristics of water sample for physicochemical parameters and heavy metals from water samples of Ejersa river showed a significant variation among the different sites in most of the measured parameters. The variation was due to the difference in the sources of effluent discharged to the river where site B and C were with more significant variation than the other two sites. Generally, the following conclusions have drawn from this study:

It can be seen that the concentration of different studied physicochemical parameters such as pH, EC, TDS, salinity, color, turbidity, NO_3^-, were above the permissible limit set by EDWQ, 2010 and WHO, 2008. With respect to the parameters there was quite high level of water pollution especially, at effluent discharge site, site C. This may be due to direct discharge of effluent from Prison, Abattoir, agricultural chemicals and municipal discharge. High values of nutrients such as NO_3^-, also attributed from the natural decomposition of plant matter

Based on the values recorded, pollution level of the four sites of the river may be assumed with the following sequence, site C> D>B>A. Even though, the sample water tested were found to be rich in plant nutrients required for plant growth, but due to the presence of high level toxic heavy metal Pb, the river water may not good for irrigation as well as domestic purpose.

It has seen from this work again the decrease in the level of pollution downstream of the river were due to dilution of the effluent discharged, capability of some ions to form precipitation, volatility tendency of some parameters, and absorbability of some ions with aquatic plants and animals are some expected reasons.

5.2. RECOMMENDATION

The continued discharge of effluents into river, apart from making the river unsightly, rendered the water useless for domestic usage, instilled undesirable effects on the biotic community. This investigation revealed that there was an extreme adverse impact of effluent from Prison, Abattoir and municipal discharge. As this river water used to community for different activities like drinking, irrigation, domestics and household purpose they take action to control and keep the river water by cleaning their environment. The institutions (Abattoir and Prison) also take remedial action to treat the river water by controlling their wastes from direct discharge.

Finally, government and any responsible authorities should support further study that has conducted on other physical, chemical and untested biological parameters of significant health concern and on identification of potential sources of the contaminants of this river.

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Appendixes

Appendix 1. One-way ANOVA values for physic-chemical parameters

		Sum of Squares	df	Mean Square	F	Sig.
pH	Between Groups	2.767	3	.922	20.494	.0001
	Within Groups	.360	8	.045		
	Total	3.127	11			
T	Between Groups	1.153	3	.384	4.756	.035
	Within Groups	.647	8	.081		
	Total	1.800	11			
EC	Between Groups	27097266.667	3	9032422.222	5922.900	.002
	Within Groups	12200.000	8	1525.000		
	Total	27109466.667	11			
TDS	Between Groups	6485729.333	3	2161909.778	851.593	.0001
	Within Groups	20309.333	8	2538.667		
	Total	6506038.667	11			
Turbidity	Between Groups	14097.583	3	4699.194	1944.494	.0002
	Within Groups	19.333	8	2.417		
	Total	14116.917	11			
Salinity	Between Groups	10998500.000	3	3666166.667	2618.690	.0001
	Within Groups	11200.000	8	1400.000		
	Total	11009700.000	11			
color	Between Groups	152.250	3	50.750	87.000	.0002
	Within Groups	4.667	8	.583		
	Total	156.917	11			
NO3	Between Groups	182.667	3	60.889	91.333	.0003
	Within Groups	5.333	8	.667		
	Total	188.000	11			
NO2	Between Groups	.424	3	.141	679.080	.001
	Within Groups	.002	8	.000		
	Total	.426	11			
PO4	Between Groups	.255	3	.085	393.064	.0002
	Within Groups	.002	8	.000		
	Total	.257	11			

Appendix 2. Correlation between physicochemical parameters among the selected sites

Correlations

		pH	T	EC	TDS	Turbid	Salin	color	NO3	NO2	PO4
pH	Pearson Corr	1	.637*	.694*	.687*	.849**	.707*	.643*	-.668*	-.792**	-.775**
	Sig.		.026	.012	.014	.000	.010	.024	.018	.002	.003
	N	12	12	12	12	12	12	12	12	12	12
T	Pearson Corr	.637*	1	.621*	.625*	.781**	.639*	.762**	-.375	-.433	-.525
	Sig.	.026		.031	.030	.003	.025	.004	.230	.160	.080
	N	12	12	12	12	12	12	12	12	12	12
EC	Pearson Corr	.694*	.621*	1	.999**	.687*	.999**	.913**	-.738**	-.777**	-.891**
	Sig.	.012	.031		.000	.014	.000	.000	.006	.003	.000
	N	12	12	12	12	12	12	12	12	12	12
TDS	Pearson Corr	.687*	.625*	.999**	1	.670*	.997**	.905**	-.744**	-.781**	-.895**
	Sig.	.014	.030	.000		.017	.000	.000	.005	.003	.000
	N	12	12	12	12	12	12	12	12	12	12
Tur	Pearson Corr	.849**	.781**	.687*	.670*	1	.704*	.821**	-.411	-.560	-.618*
	Sig.	.000	.003	.014	.017		.011	.001	.184	.058	.032
	N	12	12	12	12	12	12	12	12	12	12
Sal	Pearson Corr	.707*	.639*	.999**	.997**	.704*	1	.921**	-.728**	-.773**	-.886**
	Sig.	.010	.025	.000	.000	.011		.000	.007	.003	.000
	N	12	12	12	12	12	12	12	12	12	12
Color	Pearson Corr	.643*	.762**	.913**	.905**	.821**	.921**	1	-.472	-.551	-.700*
	Sig.	.024	.004	.000	.000	.001	.000		.122	.063	.011
	N	12	12	12	12	12	12	12	12	12	12
NO3	Pearson Corr	-.668*	-.375	-.738**	-.744**	-.411	-.728**	-.472	1	.966**	.940**

	Sig.	.018	.230	.006	.005	.184	.007	.122		.000	.000
	N	12	12	12	12	12	12	12	12	12	12
NO2	Pearson Corr	-.792**	-.433	-.777**	-.781**	-.560	-.773**	-.551	.966**	1	.974**
	Sig.	.002	.160	.003	.003	.058	.003	.063	.000		.000
	N	12	12	12	12	12	12	12	12	12	12
PO4	Pearson Corr	-.775**	-.525	-.891**	-.895**	-.618*	-.886**	-.700*	.940**	.974**	1
	Sig.	.003	.080	.000	.000	.032	.000	.011	.000	.000	
	N	12	12	12	12	12	12	12	12	12	12

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

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

Appendix 3. One-way ANOVA values of the measured metals

ANOVA

		Sum of Squares	Df	Mean Square	F	Sig.
Zn	Between Groups	.101	3	.034	5.727	.022
	Within Groups	.047	8	.006		
	Total	.148	11			
CU	Between Groups	.000	3	.000	38.637	.001
	Within Groups	.000	8	.000		
	Total	.000	11			
Pb	Between Groups	.000	3	.000	1690.747	.002
	Within Groups	.000	8	.000		
	Total	.000	11			
Cd	Between Groups	.000	3	.000	.123	.944
	Within Groups	.000	8	.000		
	Total	.000	11			
Co	Between Groups	.000	3	.000	10.008	.004
	Within Groups	.000	8	.000		
	Total	.000	11			
Cr	Between Groups	.000	3	.000	4.059	.050
	Within Groups	.000	8	.000		
	Total	.000	11			

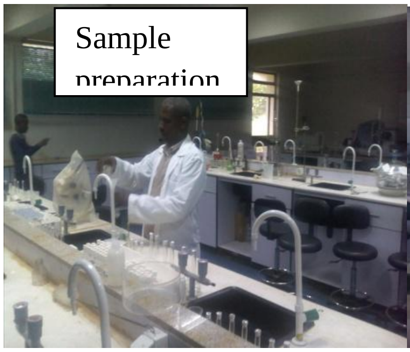
Appendix 4. Correlation between measured metals among the four sample sites

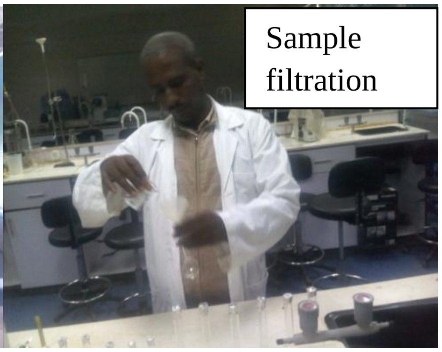
Correlations

		Zn	Cu	Pb	Cd	Co	Cr
Zn	Pearson Correlation	1	.538	.613*	.153	.575	.558
	Sig. (2-tailed)		.071	.034	.636	.050	.060
	N	12	12	12	12	12	12
Cu	Pearson Correlation	.538	1	.696*	.343	.773**	.676*
	Sig. (2-tailed)	.071		.012	.275	.003	.016
	N	12	12	12	12	12	12
Pb	Pearson Correlation	.613*	.696*	1	.423	.920**	.736**
	Sig. (2-tailed)	.034	.012		.171	.000	.006
	N	12	12	12	12	12	12
Cd	Pearson Correlation	.153	.343	.423	1	.223	.722**
	Sig. (2-tailed)	.636	.275	.171		.485	.008
	N	12	12	12	12	12	12
Co	Pearson Correlation	.575	.773**	.920**	.223	1	.684*
	Sig. (2-tailed)	.050	.003	.000	.485		.014
	N	12	12	12	12	12	12
Cr	Pearson Correlation	.558	.676*	.736**	.722**	.684*	1
	Sig. (2-tailed)	.060	.016	.006	.008	.014	
	N	12	12	12	12	12	12

Appendix 5 . Image showing Sampling Sites of Ejersa River

Appendix 6. Image showing laboratory analysis

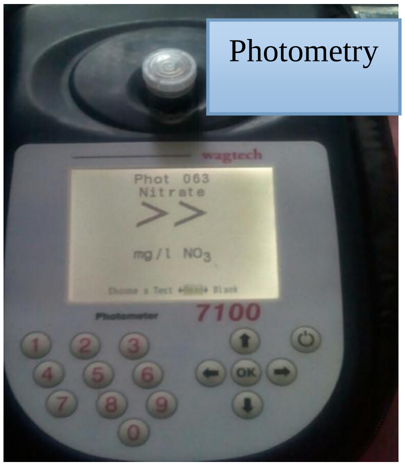

Sample preparation

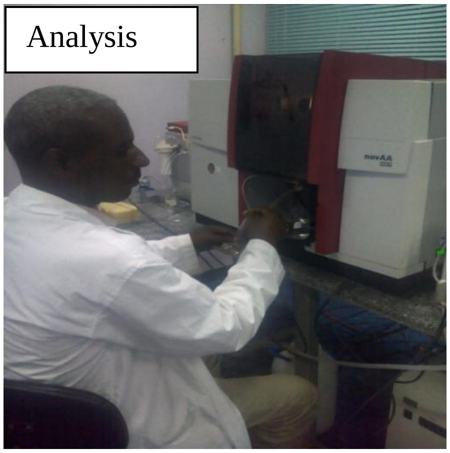

Sample filtration


Prepared sample for GFAAS

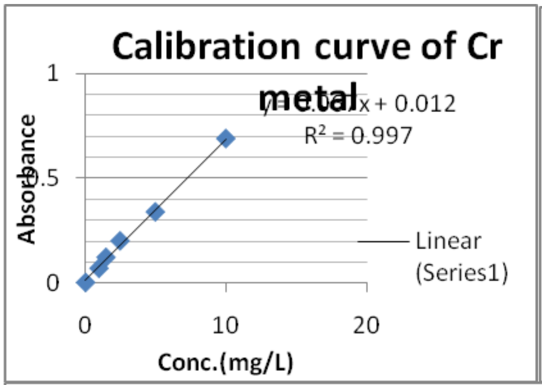

Adjust for digestion

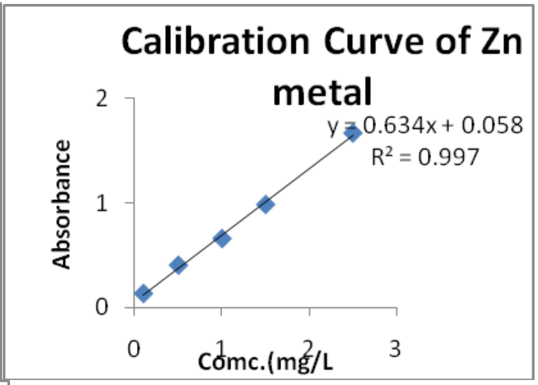

Insert sample in MW

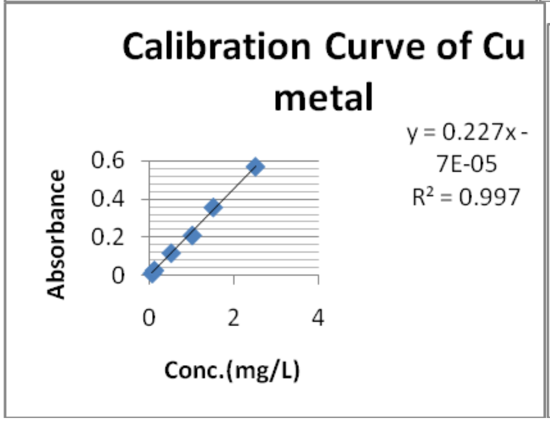

Photometry

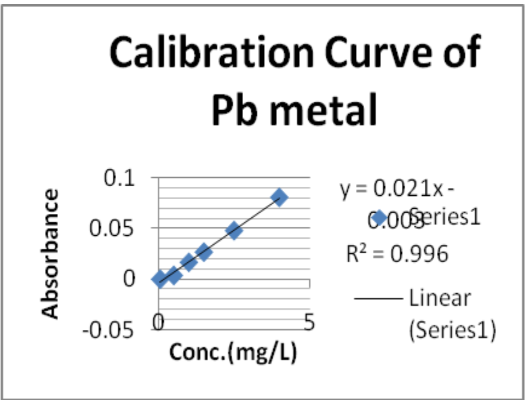

Analysis

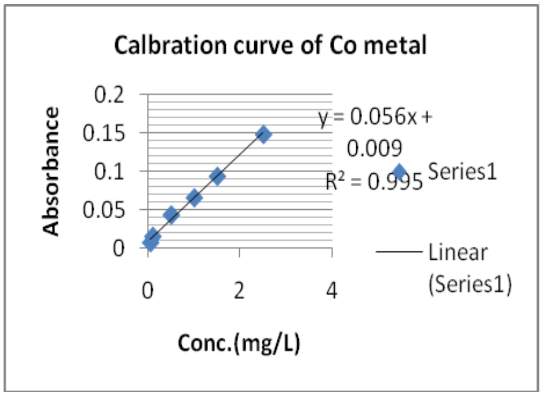
Appendix 7. Calibration curve for standard solution of the analyzed

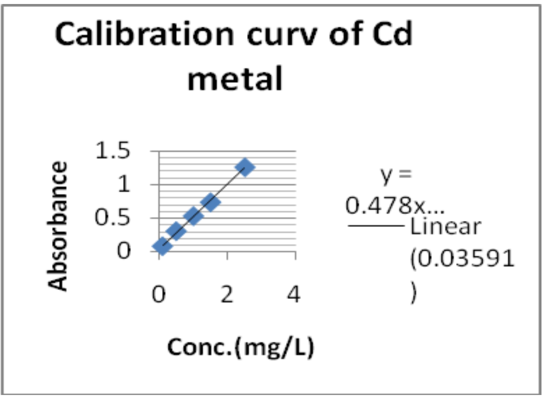

Calibration curve of Cr metal


Calibration Curve of Zn metal


Calibration Curve of Cu metal


Calibration Curve of Pb metal


Calbration curve of Co metal


Calibration curv of Cd metal