JIMMA UIVERSITY
COLLEGE OF NATURAL SCIENCES
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MSc Thesis on

Assessment of Physico-chemical parameters and Some Selected Heavy Metals in Dal River water, Gachit District, West Omo Zone, Ethiopia

By: Melaku Barunie

Advisor: Abera Gure (PhD)

Co-advisor: Feyisa Wodajo (MSc)

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This is to certify that the thesis prepared by Melaku Barunie, entitled with **"Assessment of Physico-chemical parameters and Some Selected Heavy Metals in Dal River water, Gachit District West Omo Zone, Ethiopia"** and submitted in partial fulfillment of the requirements for the Degree of Master of science in chemistry (Analytical) complies with the regulation of the university and meets the accepted standards with respect to originality and quality signed by the Examining Committee.

Submitted by:

____________________ ______________ _____________

PG Candidate Signature Date

Approved by:

____________________ ______________ _____________

Name of Thesis Advisor Signature Date

____________________ ______________ _____________

Name of Co-Advisor Signature Date

___________________ ______________ _____________

Name of External Examiner Signature Date

____________________ ______________ _____________

Name of Internal Examiner Signature Date

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Name of department head Signature Date

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Abbreviation

AAS	Atomic Absorption Spectrophotometer
ANOVA	Analysis of variance
BOD	Biochemical oxygen demand
COD	Chemical Oxygen Demand
DO	Dissolved oxygen
EC	Electrical Conductivity
EDWQ	Ethiopian drinking water quality
EEPA	Ethiopian Environmental Protection Authority
EPA	Environmental Protection of America
EWTC	Ethiopian Water Technology Center
FAAS	Flame Atomic Absorption Spectrophotometer
GFAAS	Graphite furnace Atomic Absorption Spectrophotometer
GPS	Global Positioning System
ICP-AES	Inductive coupled plasma atomic emission spectroscopy
ICP-MS	Inductive coupled plasma mass spectroscopy
MCL	Maximum Contaminant Level
MCLG	Maximum contaminant Level Goal
pH	Power of hydrogen
SNNPR	South nation nationalities people's region
TA	Total Alkalinity
TDS	Total Dissolved Solids
TH	Total hardness
UNEP	United Nations Environment Program
USDA	United States Department of Agriculture
USEPA	United state environmental protection agency
WHO	World Health Organization
WT	Water temperature

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Abstract

Water is one of the most important natural resources required for the life of animals and plants. In this study, physico-chemical properties and some selected metal contents of Dal River,at Gachit District, West Omo Zone, Ethiopia was investigated. Water samples were collected from three sites, at proximity to Wangech, administrative town of Gachit District, along the River course based on their accessibility and conveniences. The physico-chemical parameters and metal contents were determined using portable multi-meter and the Palintest water quality testing apparatus. Accordingly, the average phyico-chemical properties obtained from the studied samples were: temperature (16.97±0.38°C), pH (6.47±0.15), DO (5.51±0.57mg/L), TA (50.57±2.23mg/L), TDS (108.17±2.48mg/L), EC (169.13±3.78µS/cm), NO_3^- (3.4±0.26mg/L),Cl^-(20.03±4.2mg/L) and TH (36.57±1.03mg/L). The level of selected heavy metals such as Cu, Fe, Cr, and Ni in the water samples were ranging from 0.01 ± 0.00 - 0.02 ± 0.00 mg/L, 0.14±0.01- 0.29 ±0.03 mg/L, 0.04± 0.00 - 0.46± 0.03 mg/L and 0.04 ±0.00 mg/L, respectively. Nitrite and phosphate ions, Zinc metal were not detected in all water samples. Except, nickel, the studied parameters were found to be below the permissible limits set in the national and WHO guidelines for river water. Finally, although the obtained results indicated the water satisfy the recommended river water guideline, regular monitoring of the quality of such the river water has paramount importance to safe the health of surrounding community and downstream users.

***Keywords*:** *Physico-chemical properties, Selected Heavy metals,Dal River,Portable multi-meter, Palintest,*

1. Introduction

1.1. Background of the study

Water is one of the most important natural resources required to balance the ecosystem, particularly for the life of animals and plants. It is still a vital product for humans, used for drinking, cooking, farming, transportation and recreation, among other purposes [1]. For the survival of humans, water is necessary as it regulates body temperature for proper functioning, waste transport and the balance of human physiology [2]. For a country's sustainable development adequate amounts and good quality of fresh water are needed [3].In Ethiopia, the major sources of drinking water for large urban and rural communities are spring, well and river waters. While there is no systematic and comprehensive water quality monitoring programs in the country, there is growing evidence of water contamination issues in some areas of the country.The main causes of contamination could be soil erosion, household waste from urban and rural areas, and industrial waste or effluent [4].

River waters are the most available sources of water used for household or other purposes. They are also susceptible to numerous pollutants of natural or human origin. For example, they can be contaminated with human feces, agricultural runoff, various industrial discharges and household waste. These contaminants contain chemicals that are harmful to human health and the survival of aquatic life and wildlife [5].

The seasonal variations in both of the anthropogenic and natural processes such as temperature and precipitations also affect the quality of river water and lead to different attributes. Thus, it is important to perform river quality assessment to detect the alterations of the water quality and evaluate pollution sources. Effective monitoring of physicochemical and microbiological parameters can prevent river water pollution and this type of initiative has a special significance to protect human health from water pollution. Concentrations of heavy metals and physico-chemical parameters can be a threat together with decreasing water quality that can cause disease [6]. However, this metals and parameters study in Dal River is not done and thus a detailed empirical study is needed to assess the present water quality and physico-chemical parameters and heavy metals of this river. For this purpose, this study was aimed at analyzing some selected physico-chemical parameters and selected heavy metals of surface water of Dal River.

As in many rural areas of Ethiopia, in the West Omo zone, river waters are used for drinking, irrigation, recreation and for other household purposes. However, with the increase and uncontrolled use of agricultural chemicals, rapid growth of population urbanization and technologies thereon, the quality of river water in the region is deteriorating. As a result, this study has been examined certain physico-chemical characteristics and some heavy metal content of the Dal River in the Gachit District in the west Omo zone of Ethiopia.

1.2. Statement of the Problem

Water is essential for all living things. It is difficult to imagine that clean and safe water are available naturally as it contains contaminants from humans and animals as well as other biological activities [7, 8]. However, as noted in the literature, good water quality is crucial for the future health of human and aquatic ecosystems [9].In many parts of rural Ethiopians, river waters are used for drinking and other demotic purposes without doing any treatment. However, these waters may be polluted by natural and anthropogenic activities, urban housing, agricultural runoff, industrial effluents, human settlements, etc. In rural areas of the West Omo zone, the supply of clean, potable drinking water (tap water) is not yet provided to communities. As a result, communities in the region use river water for drinking and other purposes without any treatment. Additionally, so far, no scientific studies have been done on the quality of the river waters of the area. Therefore, the purpose of this study was assessed the physico-chemical characteristics and concentrations of selected heavy metals in the Dal River, Gachit District, West Omo zone, South Nations, Nationalities and Peoples Region (SNNPR), Ethiopia in terms of water quality parameters.

1.3. Objective of the study

1.3.1. General Objective

The general objective of this study is to assess physico-chemical parameters and some selected heavy metals contents of Dal river water from Gachit District, West Omo Zone, Ethiopia.

1.3.2. Specific Objectives

The specific objectives of this study were:

- ✓ To determine physico-chemical parameters such as temperature, pH, DO, total hardness, total alkalinity, TDS, EC, Nitrite, Nitrate, Phosphate and Chloride of the river water.
- ✓ To determine the level of selected metals (Cu, Fe Cr, Ni and Zn*)* of the river water.
- ✓ To compare the results with the national and international standards of water quality for drinking.

1.4. Significance of the Study

The significances of this study are to provide adequate information on the status of physico-chemical parameters and selected metal contents of Dal river water which is used for different domestic purposes in the study area. The findings of the research work may also help concerned government or non-governmental officials regarding the quality of the studied river water. It could also be used as base line information about the quality status of the Dal river water for other researcher.

2. Literature Review

2.1. River water

A river is a reflection of society. Many ancient civilizations flourished on the river shore [10]. It is a system that includes both the main stream and tributaries, transporting a significant load of material in the dissolved and particulate phases from natural and anthropogenic sources. These issues can shift downstream into intensive chemical and biological transformations. The stability of the river ecosystem is largely dependent on external factors such as municipal and industrial waste, agricultural fertilizers and pesticides. The irrational use of agrochemicals, the release of wastewater from livestock operations, and soil erosion can greatly affect water quality [11].

Water quality is defined by the chemical, physical and biological content of the water. The Water Quality Guidelines provide baseline information on water quality parameters and toxicologically relevant values for the protection of specific water uses. River water is a system that includes both the main stream and tributaries, which may be contaminated by natural and man-made sources. For these reasons, most rivers require some treatment before they can be used for other domestic purposes [12, 13].

2.2. Physico-chemical Parameters of river water

The study of physical and chemical properties serves as indicators of water quality for expected purposes. This study does not include identification of specific chemical species. These studies involve evaluation of temperature, total alkalinity (TA), total hardness (TH), hydrogen ion concentration (measured as pH), electrical conductivity (EC), total dissolved solids (TDS), dissolved oxygen (DO), Nitrite ion (NO_2^-), Nitrate ion (NO_3^-), Phosphate ion (PO_4^{3-}) and chloride ion (Cl^-) [14,15].

2.2.1. Temperature

Water temperature is an important factor that plays an important part in the body's metabolic activities. Fresh water is usually better than hot water. Temperature affects the acceptability of a number of other inorganic components and chemical contaminants which can affect the taste of the water. A high-water temperature increases the growth of microorganisms and can increase problems associated with taste, odor, color and corrosion [16, 17].

2.2.2. pH

Measuring pH is one of the most important and commonly used tests in water chemistry. pH is a significant factor in determining the chemical and biological properties of water. It affects the chemical forms and environmental impacts of many chemical substances in water. For example, many metals dissolve as ions at lower pH, precipitate as hydroxides and oxides at a higher pH, and then dissolve again at a very high pH. The pH value is an indicator of the chemical state in which these compounds will be found and must be taken into consideration when setting water quality standards. The pH of pure water at 25°c is 7.0, but the pH of environmental waters is affected by dissolved oxygen and exposure to minerals [14, 16, 18].

2.2.3. Electrical Conductivity

Electric conductivity (EC) is the measure of the capacity of water to produce electric current. It is a function of how many ions or particles are charged to the water.EC determinations in aquatic studies provide information on the amount of ionic content dissolved in water. Low values are characteristic of high-quality, low-nutrient waters. High values indicate salinity problems and/or eutrophic waterways in which plant nutrients (fertilizers) are more abundant. High values are a good indicator for potentially polluted sites. A sudden change in EC can indicate a direct release or another source of pollution to water. However, EC readings do not provide information on specific ion composition and levels in water. Ions like sodium, potassium and chloride give water its capacity at EC. It is often used to estimate the amount of TDS instead of measuring each dissolved component individually [3, 19, and 20].

2.2.4. Total Dissolved Solid

Total dissolved solids mean solids that are totally dissolved in water. These solids are filterable in nature. It is defined as residue upon evaporation of filterable sample. Total suspended solids (TSS) are substances which are not dissolved in water and are not recyclable. They can be obtained in the form of residues when a non-recyclable sample evaporates onto filter paper [3, 16].

Determination of the "solids" content is important for aesthetic and practical reasons. Water with high solids content can have no palatability. Palatability of water with a TDS level below around 600 mg/L is generally considered good. Drinking water becomes significantly and more disagreeable at TDS levels above about 1000 mg/L. The presence of high levels of TDS may also be unacceptable to consumers, due to excessive scaling in water pipes, heaters, boilers and domestic appliances. Solids dissolved in natural waters can include carbonates, bicarbonates, chlorides, sulfates, phosphates, nitrates, magnesium, sodium, iron, manganese and other substances. Poor taste in water often results from high levels of TDS with some metals present, including iron, copper, manganese and zinc. Water with TDS $<$ 1000 mg/L generally has an acceptable taste. Higher TDS can negatively affect drinking water taste and may have a laxative effect [14, 16, and 18].

Subsequently, four classes of water are proposed based on the procedures adopted from [18] and are given in table 1 below.

Table 1: Water quality classification based on TDS content

TDS in mg/L	**Water quality**
0 – 1000	Fresh water
1000 – 10, 000	Brackish water
10, 000 – 100, 000	Salty water
> 100, 000	Brine

2.2.5. Total Alkalinity

The alkalinity of water corresponds to its ability to neutralize acids. The alkalinity of many waters is mainly related to the carbonate, bicarbonate and hydroxide content. Waters with high alkalinity may not be suitable for some applications because of the high cost of acid neutralization of large amounts of water, but the advantage is resistance to acid precipitation. A change in alkalinity may be an indication of pollution problems. Alkalinity is important to fish and other aquatic life because it buffers both natural and human-induced pH changes [3,14,21].

Alkalinity can be divided into two types according to its titration procedure – the phenolphthalein alkalinity and total alkalinity (TA) (methyl orange alkalinity). The phenolphthalein alkalinity is the acid-neutralizing power of hydroxide (OH^-) and carbonate ions (CO_3^{2-}) present in the water sample, whereas total alkalinity represents all the bases in it (OH^-, CO_3^{2-}, and HCO_3^-). The amount of acid used to reach the end point of phenolphthalein (pH = 8.3) is taken as the phenolphthalein alkalinity; whereas the total amount of acid consumed to reach the end point of methyl orange (pH 4.4) is the total alkalinity. The results of alkalinity are usually reported as mg $CaCO_3$ per liter of water [14, 21].

2.2.6. Total hardness

Hardness is often referred to as the soap consuming property of water. Hardness may be divided into two types, carbonate and non-carbonate. Carbonate hardness includes portions of calcium and magnesium, and certain number of bicarbonates. Hardness caused by calcium and magnesium is usually indicated by precipitation of soap scum and the need for excess use of soap to achieve cleaning. Public acceptability of the degree of hardness of water may vary considerably from one community to another. The taste limit for the calcium ion is in the order of 100-300 mg/L, depending on the associated anion, and the gustatory limit for magnesium is probably lower than for calcium. In some cases, consumers allow water hardness to exceed 500 mg/L [3, 16, and 18]. Classification of water based on hardness is given in Table 2.

Table 2: Water classes based on hardness [14,18]

Hardness [$CaCO_3$ (mg/L)]	Water Class
0 – 75	Soft
75 – 100	Moderately hard
150 – 3000	Hard
> 3000	Very hard

Hardness has some similarities to alkalinity. Like alkalinity, hardness is a property of water that is not attributable to a single component and, consequently, certain ions need to be adopted to express hardness quantitatively as a concentration. Similar to alkalinity, hardness is typically expressed in an equivalent concentration of $CaCO_3$. However, hardness is a property of cations (Ca^{2+} and Mg^{2+}) while alkalinity is a property of anions (HCO_3^- and CO_3^{2-}) [14].

2.3. Chemical Parameters

2.3.1. Major Chemical Parameters

The major chemical parameters are those most frequently present in natural waters at concentrations above 1.0 mg/L. These are the cations calcium, magnesium, potassium, and sodium and the anions bicarbonate, carbonate, chloride, fluoride, nitrate, and sulfate. Several additional chemical parameters are sometimes included with the major constituents because of their importance in the determination of water quality and some of them sometimes reach concentrations comparable to the above parameters. These are aluminum, boron, iron, manganese, nitrogen in forms other than nitrate (such as ammonia and nitrite), organic carbon, phosphate, and the dissolved gases oxygen, carbon dioxide, and hydrogen sulfide [14,15].

2.3.1.1. Chloride

Chloride is widely distributed in nature, usually in the form of sodium, potassium, and calcium salts (NaCl, KCl and $CaCl_2$). Chloride in natural waters comes from the alteration of chlorinated minerals, the salting of roads for the control of snow and ice, the intrusion of seawater into coastal regions, drainage by irrigation, old underground brine, geothermic water and industrial wastewater. Concentrations in unpolluted surface waters and non-geothermal ground waters are generally low, usually below 100 mg/L. Thus, chloride concentrations in the absence of pollution are normally less than those of sulfate or bicarbonate. Chlorides in water are more of a taste than a health concern, although high concentrations may be harmful to people with heart or kidney problems. There are no primary drinking water standards for chloride. The EPA secondary standard for chloride is 250 mg/L, based on adverse effect on taste [14].

Chlorides may impart a salty taste to drinking water in concentrations between 100 – 700 mg/L. The limit for domestic purposes is fixed at 250 mg/L. Concentrations above 250 mg/L are increasingly likely to be detected by taste, but some consumers may get used to low chlorine-induced taste levels. High levels of chloride in water used for industrial processes and supply can significantly increase the corrosion rate of steel and aluminum. High chloride concentrations can be toxic to plant life. Irrigation with water containing 140 – 350 mg/L of chloride may cause slight to moderate plant injury [16,18].

2.3.1.2. Dissolved Oxygen

Dissolved oxygen (DO) is the measure of how much oxygen is dissolved or conveyed in water. In drinking water, a small amount of DO is desirable because it adds to the taste of water. However, high levels of dissolved oxygen can contribute to corrosion problems in pipes [22].The DO content of water is affected by the source, temperature, treatment, and chemical or biological processes that occur in the distribution system. Depletion of DO in water supplies can encourage the microbial reduction of nitrate to nitrite and sulfate to sulfide. It can also cause an increase in the concentration of ferrous iron in water. Very high levels of DO may exacerbate corrosion of metal pipes. The concentration of DO is controlled by other parameters such as water temperature, degree of agitation and the extent of organic pollution [14, 16, 21].

2.3.1.3. Nitrates

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. The nitrate is taken up by plants during their growth and used in the synthesis of organic nitrogenous compounds. Surplus nitrate readily moves to the groundwater. High concentrations of nitrate in surface or groundwater generally indicate agricultural contamination from fertilizers and manure seepage [16, 23].

Drinking water standards for nitrate are strict because the nitrates can be reduced to nitrites in human saliva and in the intestinal tracts of infants during the first six months of life. Nitrite oxidizes iron in blood hemoglobin from ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}). The resulting compound, called methemoglobin cannot carry oxygen and thus, resulting oxygen deficiency called methemoglobinemia. It is especially dangerous in infants (blue baby syndrome) because of their small total blood volume. A health-based guideline value for nitrate of 50 mg/L (expressed as nitrate ion) was recommended in the WHO Guidelines for drinking-water quality to prevent methemoglobinemia [14, 21, 24].

2.3.1.4. Nitrite

Nitrates and nitrites are naturally occurring ions that belong to the nitrogen cycle. Nitrite ion (NO_2^-) contains nitrogen at a relatively unstable oxidation stage. Nitrites come from fertilizers through runoff, wastewater and mineral deposition. Unfortunately, it can also stimulate the growth of bacteria when introduced to elevated levels in a body of water. Concentrations of nitrite in drinking water are typically lower than 0.1 mg/L. The recommendation for nitrite in the form of nitrite is based on human evidence that nitrite doses that cause methemoglobinemia in infants range from 0.4 to over 200 mg/kg body weight [16].

2.3.1.5. Phosphate

Phosphorus is an essential nutrient for aquatic plants and animals. Phosphate (PO_4^{3-}) at high concentration in water bodies accelerate the growth of microscopic (algae) to macroscopic (macrophytes) and excessive growth of these aquatic plants can cause eutrophication and this results in deficiency of DO which kills fishes and other aquatic fauna. Toxicity of PO_4^{3-} in humans includes impaired renal function and tumorolysis Syndrome. Sewage, detergent use and fertilizer runoff are common sources of phosphates. Phosphorus is also a constituent of animal wastes [14, 25].

Compounds containing phosphorus that are of interest to water quality include orthophosphates (all contain PO_4^{3-}), trisodium phosphate (Na_3PO_4), disodium phosphate (Na_2HPO_4), monosodium phosphate (NaH_2PO_4), and diammonium phosphate ($(NH_4)_2HPO_4$). Orthophosphates are soluble and are considered the only biologically available form. In the environment, hydrolysis slowly converts polyphosphates to orthophosphates. To measure total phosphate, all forms of phosphate are chemically converted to orthophosphates or hydrated forms [14].Table 3 presents national and international guideline values for physico-chemical of river water quality.

Table3. National and international standards of physico-chemical parameters of river water

Parameters	EDWQ [2]	WHO [24]
Temp	-	15-25°C
pH	6.5-8.5	6.5-8.5
EC	1000µS/cm	500µS/cm
TDS	1000mg/L	1000mg/L
DO	-	>5mg/L
TA	-	400mg/L
TH	-	400mg/L
NO_2^-	3mg/L	3mg/L
NO_3^-	50mg/L	50mg/L
PO_4^{3-}	5mg/L	5mg/L
Cl^-	250mg/L	250mg/L

2.3.2. Minor Chemical Parameters

Minor chemical parameters are those present in natural waters in concentrations less than 1.0 mg/L. These include trace elements and naturally occurring radioisotopes: antimony, arsenic, barium, beryllium, bromide, cadmium, cesium, chromium, cobalt, copper, iodine, lead, lithium, mercury, molybdenum, nickel, radium, radon, rubidium, selenium, silver, strontium, thorium, titanium, uranium, vanadium, and zinc [14, 15].

2.3.2.1. Heavy Metals

Heavy metals are elements with a high atomic weight and are typically toxic to plant and animal life at low concentrations. Heavy metals tend to accumulate in the food chain. They are intrinsic, natural constituents of our environment and generally present in small amounts in natural aquatic environments. The presence of these metals in aquatic systems originates from natural interactions between water, sediments and atmosphere with which water is in contact. The levels fluctuate as a result of natural hydrodynamic chemical and biological forces [26,27].

Heavy metals in waters can be from natural or anthropogenic sources. Currently, anthropogenic inputs of metals exceed natural inputs. 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 [14].

2.3.2.2. Biological roles of heavy metals

Trace elements have four roles in living organisms. These are 1) in close association with enzymes, some of the trace elements are an integral part of the catalytic centers at which the reactions of biological chemistry occur. Working in concert with a protein, and frequently with other organic coenzymes, the trace elements attract substrate molecules and facilitate their conversion to a specific end product. 2) Some trace elements donate or accept electrons in reduction or oxidation reaction. These redox reactions are of primary importance in the generation and utilization of metabolic energy through the ‘burning’ of foods in cells. 3) Some trace elements, especially iron, bind, transport and release oxygen in the body. 4) Some trace elements have structural roles, imparting stability and three-dimensional structures to important biological molecules [28,29].

2.3.2.3. Health concerns of some heavy metals

Heavy metals such as Cu, Cr and Fe have great health concern, because of their toxicities. Copper (Cu) is an essential nutrient, but at high doses it has been shown to cause stomach and intestinal distress, liver and kidney damage, and anemia. Persons with Wilson's disease may be at a higher risk of health effects due to copper than the general public. There is inadequate evidence to state whether or not copper has the potential to cause cancer from a lifetime exposure in drinking water. Because plumbing in homes and commercial buildings is the main source of copper in drinking water supplies, EPA has established a tap water action level >1.3 mg/L in 10% or more of tap water samples rather than an MCL and MCLG of 1.3 mg/L [14,15,27].

Trivalent chromium (Cr^{3+}) is an essential trace nutrient, and plays a role in prevention of diabetes and atherosclerosis. It is essentially nontoxic; the harmful effects of chromium to human health are caused by hexavalent chromium (Cr^{6+}). Since oxidants such as chlorine or ozone readily oxidize Cr^{3+} to the toxic hexavalent form, water quality limits are usually written for total Cr concentrations. EPA has found Cr to potentially cause the following health effects from acute exposures at levels above the MCL: skin irritation or ulceration. Long term exposures to Cr at levels above the MCL have the potential to cause dermatitis and damage to liver, kidney, circulatory and nerve tissues. There is no evidence that Cr in drinking water has the potential to cause cancer from lifetime exposures. A MCL of 0.1 mg/L (total Cr) and MCLG of 0.1 mg/L (total Cr) are recommended for drinking water. These standards are based on the total concentration of Cr^{3+} and Cr^{6+} forms of dissolved chromium [14, 15, 28].

Iron (Fe) is an essential nutrient in animal and plant metabolism. It is not normally considered a toxic substance. It is not regulated in drinking water except as a secondary standard for aesthetic reasons. Adults require between 10 and 20 mg of iron per day. Excessive iron ingestion may result in hemochromatosis, a condition of tissue damage from iron accumulation. This condition rarely occurs from dietary intake alone, but has resulted from prolonged consumption of acidic foods cooked in iron utensils and from the ingestion of large quantities of iron tablets. Iron can be toxic to freshwater aquatic life above 1 mg/L and may interfere with fish uptake of oxygen through their gills above 0.3 mg/L. EPA has no primary drinking water standard for iron. The EPA secondary drinking water standard (non-enforceable) is 0.3 mg/L as total iron [14, 15].

Table 4 presents national and international standards for some selected heavy metals of river water quality.

Table 4. National and international standards of river water quality of heavy metals

Metals	EDWQ (mg/L) [2]	WHO (mg/L) [24]
Cu	2	2
Fe	0.3	0.3
Ni	-	0.07
Cr	0.05	0.05
Zn	5	3

2.3.2.4. Analytical methods for heavy metal analysis

The levels of heavy metal ions in water are generally at mg/L. For precise and accurate analysis of heavy metal water analytical techniques such as neutron activation analysis (NAA), inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), x-ray fluorescence spectrometry, and graphite furnace or flame atomic absorption spectrometry (GFAAS). However, some of these techniques are expensive and difficult to use, i.e., they need skilled person to operate [29].However, Palintest supports a comprehensive range of advanced water and environmental analysis equipment technologies with a wide range of multiparameter platforms and associated chemical tests. Among them, photometer 7500 is the most popular due its versatility simplicity and Reliable of use, and it has been designed to simplify the process of testing and managing water quality data. Palintest photometric methods require a reaction time to develop optimize sensitivity, the recommended time period being documented in the Palintest Phot Book and included as part of the method parameters programmed into the Photometer 7500 [31,32,33].The photometer works by measuring the amount of light passing through the sample and filtered at the selected wave length too the detector.

3. Materials and Methods

3.1. Sampling area, sampling site and sample collection

The study was performed on the Dal River, which was available in the West Omo Zone, Southern Nations, Nationalities, and Peoples' Region (SNNPR), Ethiopia. The West Omo area is located 730 km from Addis Ababa, Ethiopia, at latitude 7°41.055 N and longitude 36°51.063 E. Dal River is located at about 12 km from Jemu, administrative center of West Omo Zone, 1.5 km from Wangech, the administrative center of Gachit District. The elevation of the area is nearly 4167 masl. Dal River has about 148 km length, approximate average size of 4 m and a 0.8 m average depth. It flows from East of the Gachit District and join River OmoinWest Omo Zone.

Prior selecting the sampling sites, the area, accessibility and use of the River water was visited. Then, the specific sampling sites were selected based on the accessibility, convenience for sampling, water characteristics, and land useand human activities along the River basin. Accordingly, three sampling sites were selected, namely, K'ulinestation (Site 1) which located approximately 0.6 km from site 2, Kerenba station (Site 2) which located 0. 6 km from site 1 and 0.8 km from site 3, and Ereydach station (Site 3) which located approximately 0.7 km from site 2. Table 5 shows the specific the coordinates, altitude and observed information of sampling sites. Coordinate and altitude were obtained using global positioning system (GPS).

Table 5. Sampling sites, sampling code and observation

Sample code	Coordinate	Altitude	Observation
Site 1 K'uline	Latitude: N-7^{0}41'05.32'' Longitude: E-36^{0}51'06.48"	4177 m	The land around the river is a farmland and partly covered with vegetation.
Site 2 Kerenba	Latitude: N-7^{0}41'25.35'' Longitude: E-36^{0}51'06.53''	4176 m	Agricultural activities, car washing, human activities.
Site 3 Ereydach	Latitude: N-7^{0}41'14.24'' Longitude: E-36^{0}51'36.18''	4174 m	The land around the river has covered with grasses, eucalyptus trees,farmland and recreational site.

From the three selected sampling sites, totally 9 water samples were collected in September, 2020, during the morning time following the WHO guideline for water sampling [24]. Prior to sampling, sample bottles, were rinsed three times with the water to be sampled. Then, from each site, three samples, (each 1 L) were collected from the right bank, left bank and center (mid) of the River. The collected samples leveled and stored in the ice box for transportation to Jimma University Analytical Chemistry laboratory. In the laboratory, samples collected from the same site were composited by combining equal volume of each sample.

3.2. Chemical and reagents

During the experimental work, Analytical grade chemicals were used. HNO_3 was obtained from (LOBA, Chem.India), $AgNO_3$ (Indian Platinum, India) and K_2CrO_4 (LABMERK Chemicals, India). Alkaphot tablet, Hardicol No 1,Hardicol No 2 tablets, NitraVer3 tablet, nitrite reagent powder, nitrate reagent powder, Coppercol No 1tablet, Coppercol No 2 tablet, Chromicol No 1 tablet, Chromicol No 2 tablet, iron tablet, Nickeltest No 1 tablet,Nickeltest No 2 tablet and zinc tablets obtained from (Hali. A Halma, UK). Double distilled water was used throughout the work.

3.3. Apparatus and equipment

Polyethylene bottles were used for sample collection. Ice box was used for storing the samples during transportation to the laboratory from the sampling sites. A portable multimeter (900P Bante instrument, UK) used to measure DO, temperature, pH, TDS and EC at the sampling sites. Palintest spectrophotometer (photometer 7500, Halma, UK) was used analysis of other parameters of the samples. Other classical glassware wasalso used during the study.

3.5. Sample analysis procedure

3.5.1. In-situ measurement

A portable multimeter (900P Bante) analytical method was used to determine the concentration of temperature, pH, DO, TDS and EC were measured at site of sampling. Each individual procedure for in-situ measurement of physico-chemical parameters were following the methods as described in the instrument's manual [30]. The procedures are described in sections as follows;

Temperature: After putting on the instrument, the temperature probe was inserted in to the water at the sampling site. Then, the temperature value was recorded when the reading was stable.

pH: The instrument was first calibrated for the pH by using buffer solutions with pH4, pH7 and pH10 at the laboratory. After the calibration, the instrument was taken to the filed for the analysis. At the sampling sites, to measure pH the water samples were taken into the beaker and the pH probe was immersed and pH value was recorded when the reading was stable.

DO, EC and TDS: Prior to their analysis the instrument was calibrated according to manufacturers' recommendations. Then, 500 mL of water sample was taken in to [30]. Then, DO, EC and TDS were measured by dipping in water samples until the stable measurements value were observed.

3.5.2. Laboratory analysis procedures of physico-chemical and selected heavy metals

Palintest photometer 7500 was used to determine the concentration of total alkalinity, total hardness, nitrite, nitrate, phosphate and some selected heavy metals (Cu, Fe, Ni, Cr and Zn) in the river water samples. Each parameter was measured following the manufacturer operation guideline of the photometer [34]. Chloride was determined using the argentometric titration [35]. The method used for the analysis, the reagents, the essentiality and toxicity profiles are factors used to select the mentioned heavy metals. The procedures are briefly described in sections as follows;

3.5.2.1. Physico-chemical analysis procedures

Total alkalinity (TA): To investigate TA of the sample, 10 mL water sample was added to three sample cells. Then, an Alkaphot tablet was added to each cell and mixed until it was completely dissolved. After standing for a minute, a yellowish colored solution was formed. A blank sample, i.e., 10 mL untreated sample water, was taken in another sample cell. The Alkaphot tablet used to calibrate thePalintest instrument to 0.0 - 500 mg/L $CaCO_3$ as has been mentioned in the manual [34]. So, during the analysis, the blank sample was first inserted and to blank the instrument. Then, the prepared samples were inserted to determine TA of the sample, which a displayed in mg/Lof $CaCO_3$.

Hardness (TH): To determine to TH, 10 mLwater sample was taken sample cell.Similarly, 10 mLuntreated samplewater sample was taken in another sample cell, as a blank sample. Then,one Hardihood No-1 and Hardicol No-2 tablet, which calibrate the instrument for 0-500 mg/L $CaCO_3$ were sequentially added and mixed until they were fully dissolved. The resulting solution was allowed to stand for about 2 min,to obtain a purple-colored solution. Then, TH of the sample was measured following the procedure earlier used for TA measurement.

Nitrate (NO_3^-): To measure the nitrate content of the samples, 10 mL water was taken into sample cell. Then a NitraVer5 nitrate reagent, which calibrate the instrument for 0 – 20 mg/L,was added and shaken vigorously for a min. The content was allowed to stand for 5min to develop amber coloredsolution. 10mL of untreated sample water was used as blank solution. Finally, the nitrate content was measured in mg/L following similar procedure for another parameter.

Nitrite (NO_2^-): To determine the nitrite content, 10 mL of water sample was taken into sample cell. Then, a NitraVer3, nitrite reagent: which calibrate the instrument for 0 - 0.5 mg/L NO_2^- was added and swirled to completely dissolve it. Then, the resulting solution was allowed to stand for 20 minuntil it developsa pink colored solution. 10mL untreated samplewater was used as a blank sample. Finally, the nitrite content of water samples was measured directlyin mg/L, NO_2^-.

Phosphate (PO_4^{3-}): Similar to other parameters, 10mL sample water was taken and mixed with reactive high range phosphorus regent, which calibrate the instrument for 0-4 mg/L PO_4^{3-}. The mixture was allowed to react for 7 min. 10 mL water was used as a blank reagent. Finally, phosphate content of the samples was recorded in mg/L PO_4^{3-}

Chloride (Cl^-): Chloride content of the samples was determined by titration method [35]. Accordingly, 100 mLwater sample was taken in to 1000 mL conical flask. Then 1.0mL of 0.5% $K_2CrO_4$was added as indicator. Then, the resulting sample solution was titrated with 0.05 M

$AgNO_3$ solution until pink-yellow color was observed, indicating the end point of titration.Finally, Cl^- content of the samples was calculated as:

$$\text{Chloride (mg/L)} = \frac{(V_1 - V_2) \times N \times 35.45 \times 1000}{V_3}$$

Where; V_1 = Volume of $AgNO_3$ used by the sample, V_2 = volume of $AgNO_3$used in the blank titration, V_3 = Volume of the sample taken for titration and N = normality of $AgNO_3$solution, 35.45= molar mass of chlorine, 1000 mL= 1 L.

3.5.2.2. Some selected heavy metal analysis procedures

Iron (Fe): To determine the Fe content of the sample, 10mL sample water was taken to the sample cell and then iron LR tablet which works in (0 – 1 mg/L Fe)was added and mixed until it was completelydissolved. The content was allowed to stand for a minute until pink colored solution was developed. 10 mL untreated sample water was used as a blank sample to calibrate the instrument (blank the instrument). Finally, the iron content was recorded as mg/L of Fe.

Copper (Cu): To measure the Cu content of the water samples, two reagents including Coppercol No-1 and Coppercol No-2 tablets, which serve to measure 0 – 5 mg/L Cu concentration range, were dissolved in 10 mL water sample. Similar, to another parameter 10mL untreated sample water served as a blank. Finally, the Cu content was recorded as mg/L.

Nickel (Ni): To 10mL sample water, Nickeltest No-1 and Nickeltest No-2 tablets were added and mixed to complete dissolution. Up on standing the content for about 2 min,fully pink colored was developed. The instrument was made blank using 10 mL untreated sample water.Then, the Ni content of the water samples was recoded in mg/L.

Chromium (Cr): To measure the Cr content of the River water samples, two different reagents namely, Chromicol No-1 and Chromicol No-2 tablets, which works in the range of 0 – 1.0 mg/L Cr,were dissolved in a sample cell contain 10 mL sample. Afterstanding the resulting content for 10 min full colored solution was developed. As a blank sample 10mL untreated sample water was used. Eventually, the Cr was recordedin mg/L.

Zinc (Zn): Similar to other metal analysis, to 10mL sample water, Zn tablet which works in the range of 0 – 4 mg/L Znwas added and mixed to complete disillusion. To ensure complete dissolution of the tablet, the content was allowed to stand for 5 minuntilclear blue coloredsolution was developed. 10 mL untreated sample water was used as blank sample to measure Zn content of water inmg/L.

3.6. Data analysis

Data were analyzed using Minitab 16 setup and Microsoft Excel 2016. Descriptive data were generated for all variables and presented as means ± standard deviation (mean±SD) of replicate analysis. The data obtained from the three sites have analyzed using One-way ANOVA at $p > 0.05$. Pearson's correlation analysis ($p > 0.05$) was also used to study the correlation of the studied parameters.

4. Result and Discussion

4.1. Physico-chemical parameters of Dal River

The assessment of ecological conditions in the sampling sites provided a better knowledge of the physical and chemical characteristics of the area. The obtained physico-chemical parameters of the Dal River water are summarized in Table 7.

Table 6. Comparison for concentration of physico-chemical parameters with related reports

Parameters	Dal river report	Other related works report	Guideline [24]
Temp ^{0}C	16.7-17.4	17.5-22.5 [37] and 18.25-19.75 [38]	15-25 °C
pH	6.3-6.6	6.51±0.02 [40] and 6.19±0.06 [41]	6.5-8.5
EC µS/cm	165-172.4	109.5-121 [4]	500 µS/cm
TDS mg/L	105.5-110.4	133-179 [42]	1000 mg/L
DO mg/L	4.9-6.03	5.03-5.59 [41]	> 5 mg/L
TA mg/L	49-53	43.13-43.33 [13]	400 mg/L
TH mg/L	35.7-37.7	31-47 [43]	400 mg/L
NO_2^- mg/L	ND	ND [37]	3 mg/L
NO_3^- mg/L	3.1-3.6	5.23-7.55 [42]	50 mg/L
PO_4^{3-} mg/L	ND	ND [40]	5 mg/L
Cl^- mg/L	15.8-24.2	12.4-31.45 [40]	250 mg/L

Table 7. Physico-chemical parameters of Dal River (mean ± SD, n = 3)and Statistical P-values

Parameter	Site 1, mg/L	Site 2, mg/L	Site3, mg/L	Statistical p-value	
				P-value	**Significance (p=0.05)**
Temp	17.4±0.57	16.8±0.06	16.7±0.06	0.082	Not Significant
pH	6.5±0.12	6.6±0.15	6.3±0.06	0.048	Significant
EC	165.0 ±1.04	170.0 ±2.31	172.4±2.00	0.007	Significant
TDS	105.5±0.64	108.6±1.33	110.4±1.25	0.005	Significant
DO	4.9±0.67	5.6±0.12	6.03 ±0.12	0.043	Significant
TA	49.0 ±3.46	49.3±1.53	53.0 ±3.46	0.263	Not Significant
TH	37.7±2.89	35.7±2.89	36.3±4.04	0.763	Not Significant
NO_2^-	ND	ND	ND	-	-
NO_3^-	3.6±0.29	3.5±0.6	3.1±0.91	0.695	Not Significant
PO_4^{3-}	ND	ND	ND	-	-
Cl^-	15.8±1.76	20.1±4.1	24.2±2.61	0.039	Significant

ND= Not detection.

Temperature: Temperature is one of the important factors that control the dynamics of aquatic environments:it affects body metabolism, reproduction, rate of reactions and rate of degradation of organic material [36].The obtained temperature of the River wasvaried from 16.7±0.06 °C(Site 3) to 17.4±0.57 °C(Site 1), which were almost similar. The obtained values were also within the permissible limit set in WHO guideline [24]. Compared to other reported values such as 17.5-22.5°C [37], 18.25-19.75°C [38] and 18.72-23.84°C [39], Dal River has lower temperature, indicating its suitability for aquatic life.

pH: The pH values of the River were varying 6.3±0.06 (site 3) to 6.6±0.15 (site 2). Site 2 and site 3 exhibited almost similar pH values and which arewithin WHOpermissible limit for river water [24].Statistical analysis showed that there was significant difference among the pH of sampling sites, indicating may be the availability of varioussources of impurities. The obtained resultsagree with some reported studies, i.e., 6.51±0.02 [40] and 6.19±0.067 [41]. pH of River water changes due to photosynthesis, respiration, air temperature exposure, geology and mineral content of a catchment area, and agricultural runoff that affect pH [41].

Electrical conductivity (EC): EC of the River water was ranging from 165±1.04µS/cm (site 1) to a maximum of 172.4±2.0 µS/cm (site 3). The observed highECmay be probably associated to the availability of nutrients, waste from residents and chemicals applied to agricultural farmland. One way ANOVA analysis showed that the EC of the three sampling sites were significantly different. EC of the water is a function of a number of ions loaded into the solution another measure (dissolved materials). Compared to other studies reported in the literature from Ethiopia such as conductivity of Maichewand Edagahamus Rivers, which were varied from 105.7 to 108.2µS/cm and 109.5 to 121µS/cm, respectively [4], Dal River demonstrated higher conductivity, indicating the possibility of a greater number of ins in the sampling sites.

Total dissolved solid (TDS): TDS is an important parameter in the evaluation of water suitability for irrigation or other use as solid can clog pores and components of the water distribution system. The obtained concentration of TDS in the studied water samples were ranged from 105.5±0.64mg/L (Site 1) to 110.4±1.25mg/L (Site 3), which are below the permissible limit set in EDWQ [2] and WHO [24]. The statistical analysis also showed the presence of significant variation in terms of TDS among the sampling sites.

Dissolved Oxygen (DO):DO is the lifeblood of aquatic life. In water concentration of DO decreases due to decay of agricultural runoff. DO concentrations lower than 5.0 mg/L are detrimental to aquatic life [39]. In this study, DO values were ranging from 4.9±0.67 to 6.03±0.12 mg/L, with an overall average of 5.51 mg/L, indicating the suitabilityof Dal River for aquatic ecosystem life. However, the three sampling sites exhibited significant difference in terms of DO concentrations, as $p > 0.05$. Variation in DO from one site to another for the same set of samples may be due to differences in location and more significantly due to differences in the time of sampling as it is known that the DO levels naturally fluctuate throughout a day.Generally, the obtained DO values of the sampling sites were within the permitted limits set by WHO [24].

Total Alkalinity (TA): TA is used to measure the capacity of the water to neutralizeacids, buffer capacity. Alkalinity of water is primarily due to the presence of bicarbonates and carbonates formed by reactions in the water and ground through which the water percolates. It canalso be obtained as a result of rock alteration, waste disposal and microbial breakdown of organic matter in the water body [39]. In the current study, the measured TA values were varied from 49±3.46 (Site 1) to 53±3.46 mg/L (Site 3), which are within the limit prescribed in WHO guideline [24], indicating the number of hydroxides and carbonates in recommended limits [39].But the statistical test showed as there were significant variations among the sampling sites in terms of TA at $p < 0.05$.

Total Hardness (TH): Water hardness is typically caused by the presence of two multivalent cations: calcium and magnesium. The observed results showed that THof the samples were varied 35.7±2.89 and 37.7±2.89mg/L. According to these findings the Dal River water is categorized under fresh water, which has TH ranging from 0-75 mg/L. The obtained TH values for all sites were also below the WHO limit [24], similar to other reported THvalues from other river [42, 43].

Nitrite: Nitrite (NO_2^-) is not usually expected to present in significant concentrations except in a reducing environment. In the current study, nitrite was not detected, indicating the presence of less pollutant in the water [37].

Nitrate: Nitrate (NO_3^-) is found naturally in the environment and is an important plant nutrient. The nitrate concentrations in surface water are normally low, but can rich high level as a result of agricultural and industrial activities.In this study, the nitrate concentrations of the water were varied from 3.1±0.91mg/L (site 3) to 3.6±0.29mg/L (site 1), which are below EDWQ [2] andWHO [24], confirming the absence of contamination.

Phosphate (PO_4^{3-}): The level of phosphate is useful for measuring water quality, as it is an important plant nutrient and can play a limiting role among all other essential plant nutrients. In this study phosphatewas not detected in all water samples, this could be related to its less solubilityin water. Many authors have also reported that phosphate is rarely detected in water samples [40].

Chloride (Cl^-): Natural waterusually contain some salinity from contact with soils, rocks, and other natural materials. High chloride content in river waters may indicate pollution by wastewater, industrial waste or the intrusion of seawater into freshwater bodies [41, 42]. The chloride content ofthe studied Dal River samples wasranged from 15.8±1.76 to 24.2±2.61 mg/L. Its level at the three sampling sites is significantly different ($p < 0.05$). But they are all within EDWQ [2] and WHO [24] permissible limits.

4.2. Concentration of the measured metals of river water sample

Concentrations of heavy metals in surface water are influenced by source imputation, sediment characteristics, organic materials, temperature and sometimes subsoil mineral composition underlying in the area where surface water is located. Thus, one can expect a spatial and temporal variation in the concentration of heavy metals in sediment and water [37]. In this study the concentration levels of five metals including Cu, Fe, Ni, Cr and Zn were investigated and their results are presented in Table 8.

Table 8.Concertation of heavy metals in Dal River (mean ± SD, n = 3) and Statistical P-values

Metals	Site-1 in mg/L	Site-2 in mg/L	Site-3 in mg/L	Statistical p-value	
				P-value	Significance (p=0.05)
Cu	0.01± 0.00	0.02 ± 0.00	0.01±0.00	0.296	Not Significant
Fe	0.29±0.03	0.26±0.01	0.14±0.01	0.000	Significant
Ni	0.04± 0.00	0.46± 0.03	0.33±0.05	0.210	Not Significant
Cr	0.04± 0.00	0.04±0.00	0.04± 0.00	0.885	Not Significant
Zn	ND	ND	ND	-	

Copper: The obtained concentrations of Cuwere ranging from 0.01± 0.00 mg/L (site 1) to a maximum of 0.02±0.00 mg/L (site 2), which are below the maximum permissible limit set inEDWQ [2] and WHO [24] guidelines. The river samples contained lower concentrations of Cu, may be due to the minimal exposure of the River to Cu-containing contaminants.

Chromium: Cr is an essential micronutrient for animals and plants and is considered a major biological and polluting component. In general, the natural chromium content of drinking water is very low, which is almost similar to the value obtained in this study (0.04±0.01 mg/L). Excess chromium may be toxic, in particular in hexavalent form. The obtained concentration of Cr was almost similar to other studies0.005 ± 0.00mg/L [38] and 0.03 ± 0.00mg/L [40].

Iron: In water, iron occurs primarily in ferrous or ferric form. In surface water it is usually found in the ferric state. In this study, the obtained iron contents varied from 0.14±0.01 mg/L (site 3) to 0.29±0.03 mg/L (site 1), which are all within permissible limit (0.3 mg/L) WHO [24] for drinking water. Its concentrations were also significantly different among the sampling sites ($P< 0.05$).

Nickel: In this study, nickel was detected in the range of0.04±0.00 mg/L (site 1) and 0.46±0.03 mg/L (site 2). The obtained Ni concentrations at Site 2 and Site 3 were higher than its permissible limit set (0.07 mg/L) in WHO guideline in drinking water [24]. The observed unusual high concentrations of Ni at the two sampling sites may be to be due to the leakage Ni contains materials from the surrounding.

Zinc: Zn is one of the major micronutrients that play a vital role in the physiological and metabolic processes of many organisms. However, higher levels of zinc can be toxic to the organism [4]. In this study Zn was not detected in all water samples.

The comparison of mean concentrations of metals in Dal River with other reported literatures are tabulated in table 9. The maximum and minimum levels of concentration are related to Ni in downstream and upstream and Fe in upstream areas, respectively (Table 9).

Table 9. Comparison for concentration of heavy metals with reports of other works

Metals	Dal river report	Other related works report	Guideline [24]
Cu mg/L	0.01 - 0.02	0.05 - 0.08 [37] and 0.003-0.014 [40]	2
Fe mg/L	0.14 - 0.29	0.08 - 0.217 [44] and 0.091-0.21 [40]	0.3
Ni mg/L	0.04 - 0.46	0.034 - 0.459 [4]	0.07
Cr mg/L	0.04	0.03 – 0.05[37]	0.05
Zn mg/L	ND	ND [4]	3

4.2.1. Correlation study of the physico-chemical parameters

Table 8 shows the Person correlation studies of the physico-chemical parameters of Dal River. As can be seen temperature of the River water has strongly positively correlated with TH (r = 0.89)and NO_3^- (r = 0.72), slightly correlated with pH (r = 0.32) and Cr (r=0.38), strongly negatively correlated with EC (r = -0.98), TDS (r = -0.97), DO (r = -0.97), TA (r=-0.99), chloride (r = -0.93) and Ni (r = -0.91).

Table 10. Correlation between physico-chemical parameters among the selected sites of Dal River

Parameter	Temp	pH	EC	TDS	DO	TA	TH	NO_3^-	Cl^-
Temp	1								
pH	0.32	1							
EC	-0.98	-0.49	1						
TDS	-0.97	-0.52	0.99	1					
DO	-0.97	-0.54	0.99	0.99	1				
TA	-0.99	-0.41	0.99	0.99	0.99	1			
TH	0.89	-0.14	-0.79	-0.77	-0.76	-0.85	1		
NO_3^-	0.72	0.89	-0.84	-0.86	-0.87	-0.79	0.34	1	
Cl^-	-0.93	-0.65	0.98	0.99	0.99	0.96	-0.66	-0.93	1

Correlation is significant at the p-value is 0.05 level (1-tailed).

The pH of the studied samples was highly correlated with NO_3^- (r = 0.89)and slightly correlatedtemperature (r = 0.32). EC of the sample also showed high positive correlation with TDS (r = 0.99), TA (r= 0.99), Cl^-(r= 0.98), and DO (r= 0.99) as well as high negative correlation withTH (r = -0.99) and NO_3^-(r = - 0.84). TDS was strongly correlated with chloride, EC, DO and TA (r = 0.99). EC have highly correlation with TDS and TA because of their correlation was depend on the ions and precipitation of solid materials.

Dal River DO was highly correlated with EC, TDS, TA and chloride (r > 0.99). The alkalinity of the Dal River was strongly correlated with EC, TDS, DO (r=0.99) and chloride (r= 0.96). Nitrate was highly correlated with pH (r = 0.89), and temperature (r = 0.72)as well as negatively strongly correlated with EC, TDS, DO and TA. Finally, chloridewas highly correlated with EC, TDS, DO, and TA and negatively strongly correlated with pH and NO_3^- content of the water.

4.2.2. Correlation study of the metals

The obtained data from the metals Pearson correlation study are given in Table8. It was observed that the Cu and Cr content of the river were strong correlated withNi. Fe has shown weak correlation with Cu, Cr and Ni.

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

Metal	Cu	Fe	Ni	Cr
Cu	1			
Fe	0.33	1		
Ni	0.74	-0.39	1	
Cr	-1	-0.33	-0.74	1

5. Conclusion and Recommendation

5.1. Conclusion

The study results showed that the physico-chemical parameters such as temperature, pH, EC, TDS, TA, TH, DO, NO_2^-, NO_3^-, PO_4^{3-} and chloride of Dal River were within the national and international standards.The finding demonstrated that the river water is categorized under fresh water, which is suitable for drinking and other domestic activities based on the studied parameters. Based on the values recorded, samples which were collected from site3>2>1, in terms of the values of some physico-chemical parameters. In terms of metal content site2 > 1 > 3, this could be due to dilution of the pollutants, precipitation of some ions, and absorptionby aquatic plants and animals. Generally, except Ni, the contents of all the studied physico-chemical parameters and heavy metals are safe level for animals and other purpose.

5.2. Recommendation

Based on the findings the researcher would like to forward the following recommendation:

- Although, the findings showed that the studied river water is safe, further study is required on seasonal base to come up with more convincing results.
- Microbial parameters of the river water should be carried out to supplement the generated data.
- Government, communities of the area and other responsible authorities should support further study

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