Assessment of Industrial Waste Load of River Borkena and Its Effects on Kombolcha Town and the Surrounding Communities

by

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Abstract

Water pollution is a major threat to human population and dumping of pollutants into water body result in rapid deterioration of water quality and affect the ecological balance in the long run. The present study was undertaken to assess pollution load from river Borkena. In urban and suburban parts of Kombolcha, the use of industrial wastewater for irrigation purpose is a common practice. Local farmers in Borkena watershed use the wastewater to irrigate their agricultural fields for cultivation of vegetables. But they suffered from loss of productivity of leafy vegetables and skin injury because of their exposure to the wastewater during irrigation practices. That is why this study focused on assessing the amount of industrial waste load on river Borkena and its effects on communities in the watershed. The main aim of this study was: to assess the physico-chemical characteristics of River Borkena before and after industrial waste discharges mixed to it by the waste carrier small streams; and its environmental impact on the surrounding communities and vegetable farms. The methodology consisted: 1) Basic survey in order to assess the physical and chemical characteristics of the river water, and 2) a case study performed by focus group discussions with the community authorities and farmers in the study area who used the river water mainly for irrigation purposes. Sampling was conducted at 6 sites in the study area during low and high flow periods with an interval of three months for a period of one year in order to account for the seasonal hydrological cycle of the river water. Laboratory measurements of river water and leafy vegetables for metal concentration were also determined to investigate the effect of the use of the river water for growing vegetables and other personal cases. The findings of this dissertation showed metal concentrations in leafy vegetables and irrigation water are within the permissible limits of FAO/WHO standards and not significant for the time being, but is expected to be a challenge in the near future if not well addressed. The concentrations of metals in leafy vegetables will provide baseline data and it shows that, in the current situation consumption of leafy vegetables grown in the study area may not have health risks in the context of metal concentrations. To avoid the entrance of metals into the food chain, municipal or industrial wastes should not be drained into the river and farmlands without prior treatment. The continuous monitoring of the soil, vegetable plant and irrigation water quality are prerequisites for the prevention of potential health hazards to human beings. Finally this study fills the gaps in information for concerned regional and federal governmental offices and may use it as an input to design regulations and policies which benefits the communities in the watershed.

Key Words: Water quality, Leafy vegetables, Industrial waste, Trace elements

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List of Abbreviations

ATSDR	Agency for Toxic Substances and Disease Registry
CCME	Canadian Council of Ministers for Environment
CRGE	Climate Resilient Green Economy
DL	Detection Limit
EC	European Community
EPA	Environmental Protection Agency
EPE	Environmental Policy of Ethiopia
FAAS	Flame Atomic Absorption Spectrometry
FAO	Food and Agriculture Organization
FDA	Food and Drug Administration
GDP	Gross Domestic Product
GEMS	Global Environment Monitoring System
ICMR	Indian Council of Medical Research
ISO	International Organization for Standardization
IPCS	International Programme on Chemical Safety
IWA	International Water Association
JECFA	Joint FAO/WHO Expert Committee on Food Additives
MCL	Maximum Contaminant Limit
MEDaC	Ministry of Economic Development and Cooperation
NTU	Nephlometric Turbidity Unit
OSHA	Occupational Safety and Health Administration, (an agency of the US government)

UNDP	United Nations Development Program
UNESCO	United Nations Educational, Scientific and Cultural Organization
UNICEF	United Nations International Children's Emergency Fund
US NRC	United States National Research Councel
WHO	World Health Organization

Chapter 1 Introduction

1.1 Background of the study

1.1.1 Water quality assessment

Rapid urban growth induces global environmental change, particularly when it comes to production, consumption, and the generation of waste. Rampant urbanization, the construction of new settlements, and rapid industrialization not only polluted water resources but also led to water shortages in different regions (Singh et al., 2020). The wide array of pollutants discharged into aquatic environment may have physico-chemical, biological, toxic and pathogenic effects (Goel, 2000). Freshwater bodies (e.g., rivers) are the major source of water to fulfil the daily water demand for household, agriculture and industrial activities (Eliku T. and Leta S., 2018). Urbanization and industrial advancement deteriorate water quality of freshwater bodies in the current world and provoked serious research concerns to safeguard natural resources and promote sustainable environmental management (Kumar *et al*., 2017a; Lone *et al*., 2020). In the developing world, rivers flowing through urban areas face the threat of extinction due to endpoint discharges of partially treated or untreated effluents (Mishra and Kumar 2020). Rivers are primary natural resources with many uses particularly as utility water by sectors such as industry, agriculture, livestock, transportation and recreation. For all these activities, rivers must have a healthy and constant water quality (Ustao-glu *et al*., 2020). It is evident that water pollution is a major threat to human population, so that dumping of pollutants into water body deteriorates its quality and affects the ecological balance in the long run. The quantity and quality of fresh water resources are decreasing due to global warming, climate change, urbanization, industrialization and agricultural activities (Tepe and Cebi, 2019). The ever-increasing world population faces serious challenges in accessing safe water resources for both urban and rural environments especially in areas of water shortage (Xiao *et al.*, 2019).

It is one of the greatest challenges of Agenda 2030 for Sustainable Development to provide clean and potable water for human and agricultural purposes in order to prevent environmental and human health risks. This includes aspects of water quality, accessibility and availability to further address the normative criteria of the human right to water (WHO/UNICEF, 2017; UN-Water, 2018). According to the United Nations, most of the world's population will be living in cities by the year 2030. In developing countries, urban agglomerations are growing at twice the rate of overall population growth. One of the consequences of this urban explosion is the generation of an enormous amount of waste. Despite the many social, environmental, and economic differences between large cities, there are some obvious similarities in terms of environmental quality (UNDP, 1998). Industrialization is considered vital to the nation's socioeconomic development as well as its standing in the international community. Most of the environmental pollution problems arise from anthropogenic sources mainly from domestic and industrial activities. Though water pollution is an old phenomenon, the rate of industrialization and consequently urbanization has exacerbated its effect on the environment (Asonye *et al.*, 2007). Wastewater could be any water that has been adversely affected in quality by anthropogenic influence. It comprises liquid waste discharged by domestic residences, commercial properties, industry, and agriculture and can encompass a wide range of potential contaminants and concentrations (Goel, 1997).

Direct discharge of industrial wastewater to soil surface or water bodies severely contaminates the environment. Therefore, it is necessary to give treatment to disposed water before letting it off as effluent, to avoid contamination of natural system. Soil and water quality are issues, which affect the quality of our food, health and environment in general. Regina and

Nabi (2003), reported that, increased demand of water because of population growth, agriculture and industrial development has tremendously deteriorated the chemical, biological and physical characteristics of the natural water resources. Water quality monitoring has one of the highest priorities in environmental protection policy (Simeonov *et al.*, 2002). The main objective is to control and minimise the incidence of pollutant-oriented problems, and to provide water of appropriate quality to serve various purposes such as drinking water supply, irrigation water, etc. The quality of water is identified in terms of its physical, chemical and biological parameters (Sargaonkar and Deshpande, 2003). The particular problem in the case of water quality assessment is the complexity associated with analysing the large number of measured variables (Saffran, 2001).

The present study was undertaken to assess pollution load from river Borkena. Attempts were made to assess the extent of pollution by measuring the physical and chemical parameters of water quality such as pH, total dissolved solids, electrical conductivity, total hardness, alkalinity, turbidity, and others with in the industrial effluent. The complete assessment of the industrial waste stream at river Borkena was made using basic survey. Samples were collected from the waste receiver river four times within a year in order to account for the seasonal hydrological cycle of the river water. Water quality assessment was conducted at 6 sites in the study area during low and high flow periods. The criteria for choice of sampling sites was made first; at the upstream before industrial effluents mix to the main river, second; tributary streams before and after mixing to river Borkena, and finally; downstream points for comparative studies.

1.1.2 Assessment of metals concentration in wastewaters

Water scarcity has been increasing all over the world and in many countries may become absolute by the year 2025 (Seckler *et al.*, 1999). This problem becomes more apprehensive when recognizing that the severity of surface water pollution is a worldwide problem (Yan, 1998). To tackle the problem, several measures for sustainable water resource utilization have been developed, of which wastewater reclamation and reuse is currently one of the top priorities (Anderson *et al*., 2001).

As pointed out by Sharma N. *et al.,* (2021) metals are significant environmental pollutants as their increasing toxicity is becoming a concern for our ecosystem. Hence, a minute quantity is highly toxic for the flora, fauna, and other forms of life found on the earth (Abed-el-Aziz *et al*., 2017). Contamination caused by metals has posed serious threats to the ecosystem and physical health i.e. diseases related to liver, heart damages, cancer, neurological, cardiovascular, and central nervous system damage with sensational disturbances (Sumiahadi and Acar, 2018). Mining and manufacturing industries are the topmost sources that pollute the soil, air, and water bodies (Rezania *et al*., 2016; Yadu *et al*., 2020). High concentrations of metals (such as Pb, Zn and Cr) in aquatic environments are harmful for ecological systems (Geng *et al*., 2015; Xu *et al*., 2018a). Metals are usually hard-degradable and can cumulate in food chains by converting into more toxic metallo-organic compounds and eventually do harm to human health (Salah *et al*., 2015; Geng *et al*., 2015; Vareda *et al*., 2016; Vareda *et al*., 2019; Kumar *et al*., 2019). However, metals will be toxic to humans, if the metals are exposed or ingested in larger amounts (Rajan *et al*., 2012; Ouyang *et al*., 2002; Pirsaheb *et al*., 2013).

The metal pollution of aquatic ecosystems is increasing due to the effects from urbanization and industrialization (Sekabira *et al*., 2010; Zhang *et al*., 2011; Bai *et al*., 2011; Grigoratos *et al*., 2014; Martin *et al*., 2015). The main anthropogenic sources are disposal of untreated and partially treated industrial effluents and sewage containing toxic metals. Both natural and anthropogenic activities are responsible for the abundance of heavy metals in the environment

(Wilson and Pyatt, 2007; Khan *et al*., 2008). The presence of heavy metals in water is toxic even at very low concentrations (Tiwari *et al*., 2007).

In many parts of Ethiopia, specially in River Borkena the main source of metal pollution is originated from the leather tanning and metal finishing sectors. According to Sayo S. *et al*., (2020), due to the noxious effects of metals, and in order to guarantee food safety, it is imperative to periodically monitor sewage effluents for metal contamination levels to determine the quality of wastewater being discharged to the environment.

1.1.3 Assessment of metals concentration in vegetables

World's urban communities are increasing faster than global population as the urbanization progresses in the least-developed regions (UN-HABITAT, 2004). Urban development caused momentous alteration to the environment by increasing the waste material accumulation through anthropogenic activities (Chen, 2007). Land spreading of untreated sewage effluents is practiced all over the world because of the economic advantage it offers over effluent treatment. In several studies, minerals such as Fe, Mn, Ni, Zn, Cu, Co, Cr, Cd, As, and Pb are important environmental contaminants, mainly in areas irrigated with wastewater (Khan *et al*., 2008; Li *et al*., 2012; Qureshi *et al*., 2016; Sultana *et al*., 2019). Urban expansion is promoting a concern for farmers to use contaminated land for food crop's production (Nabulo, 2009). In urban and sub-urban areas, land contamination with toxic metals is common as a result of industrial and municipal activity. Wastewater irrigation to increase the yield of food crops or vegetables is the principal source of contamination in urban agricultural lands (Qadir e*t al*., 2000). These effluents are rich in toxic metals and are a chief contributor to metals loading in waste irrigated and amended soils (Singh *et al*., 2004; Mapanda *et al*., 2005).

Presence of elements in food sources is essential for maintaining good health. At the same time, these elements may have adverse effects if consumed at concentrations higher than certain defined tolerable limits (Koubov´a *et al*., 2018; Zoroddu *et al*., 2019). For toxic metals such as Pb, the side effects occur even when consumed in trace amounts (Aschale *et al*., 2019). WHO and FAO have provided acceptable guideline values for essential and toxic elements in food sources (FAO/WHO, 2011). As Naangmenyele Z. *et al*., (2021) noted, the list of elements in the guidelines is not exhaustive and research is still ongoing to discover possible health risk effects of some of the elements in the periodic table. Vegetables have been an important part of everyday healthy foods and are regularly consumed by humans on a daily basis (Marles, 2017; Koubov´a *et al*., 2018; Manzoor *et al*., 2018). Some soils and vegetables from irrigation systems have been reported to be polluted with metals around the African continent including Ethiopia (Weldegebriel *et al*., 2012; Woldetsadik *et al*., 2017; Aschale *et al*., 2019), Zimbabwe (Mapanda *et al*., 2007), South Africa (Malan *et al*., 2015) and Ghana (Ackah *et al*., 2014; Boamponsem *et al*., 2012; Lente *et al*., 2014).

Vegetables constitute an important part of the human diet since they contain carbohydrates, proteins, as well as vitamins, minerals, and trace elements. It is known that serious systemic health problems can develop as a result of excessive accumulation of dietary metals such as zinc (Zn), chromium (Cr), and lead (Pb) in the human body (Oliver, 1997). One important dietary uptake pathway of metals could be through vegetables irrigated with contaminated wastewater.

In Ethiopia very few published data on metal contamination of vegetables in Borkena watershed is available. Environmental abetment practice is almost missing due to the lack of environmental management and un-operational environmental pollution laws. In urban and suburban parts of Kombolcha, the use of industrial wastewater for irrigation purpose is a common practice. Cultivation of vegetables with the industrial and sewage effluents of the drains is a common practice in the coinciding agricultural land along the watershed of river Borkena. Local farmers across the river basin use the wastewater to irrigate their agricultural fields for cultivation of vegetables.A large quantity of various vegetables is sold in the supply market of the town of Kombolcha & others. This study was conducted to assess the metal concentration in the vegetables and eminent transfer to the food chain which assist in evaluating the related health hazards linked with it.

1.1.4 Effects of contamination of Borkena river on vegetables grown in the watershed. (A case study in Kombolcha town and the surrounding communities)

Water contamination is one of the main causes of health problems in human beings. About 2.3 billion peoples are suffering from water related diseases worldwide (UNESCO, 2003). In developing countries more than 2.2 million people die every year due to drinking of unclean water and inadequate sanitation (WHO and UNICEF, 2000). Water related infectious and parasitic diseases account for approximately 60% of infant mortality in the world (Ullah *et al.*, 2009). A critical problem of developing countries is improper management of the vast amount of waste generated by various anthropogenic activities and the unsafe disposal of these wastes into the ambient environment. This has rendered these natural resources or water bodies unsuitable for both primary and secondary usage (Fakayode, 2005).

Waste and wastewater management are highly regulated within the municipal infrastructure under a wide range of existing regulatory goals to protect human health and the environment; promote waste minimization and recycling; and reduce impacts to residents, surface water, groundwater and soils. Over the last two decades, the Ethiopian government has put in place a number of policies, strategies and laws that are designed to support sustainable development.

The country has developed and implemented a wide range of legal policy and institutional frameworks on environment, water, forests, climate change, and biodiversity.

The Environmental Policy of Ethiopia was approved in 1997 and is the first key document that captured environmental sustainable development principles. Ethiopia also has an overarching framework and a national strategy towards a green economy, the “Climate Resilient Green Economy” (EPA in Collaboration with MEDaC, 1997).

According to Regulation No. 159/2001 E.C. of the Federal Laws and Regulations of Ethiopia concerning prevention of industrial pollution, industries should:

- prevent or, if that is not possible, shall minimize the generation of every pollutant to an amount not exceeding the limit set by the relevant environmental standard.
- dispose of it in an environmentally sound manner.
- handle equipment, inputs and products in a manner that prevents damage to the environment and to human and animal health.

The basis for the Environmental Policy of Ethiopia (EPE) are articles 92.1 and 92.2 of the constitution of the Federal Democratic Republic of Ethiopia. These articles enshrine the following rights:

Article 92.1:- “Government shall endeavour to ensure that all Ethiopians live in a clean and healthy environment” and

Article 92.2:- “Government and citizens shall have the duty to protect the environment. Some of the articles of the EPE directly or indirectly address waste management issues. These include:

- Article 3.7 addresses issues related to Human Settlement, Urban Environment and Environmental Health,

- Article 3.8 addresses issues related to the Control of Hazardous Materials and Pollution from industrial Waste

But according to Tadesse (2004), the management of waste in the urban centres of Ethiopia is the responsibility of the Municipal Division of Health. All municipalities, except the chartered cities of Addis Ababa and Dire Dawa who have cabinet representation, exercise some autonomy in managing their own affairs; the other chartered cities and the certified smaller urban centres are mandated “to provide, maintain and supervise environmental health services along with other activities in their own areas”. However worthy these objectives sound, most of the municipalities and urban centres do not seem to have efficiently run environmental planning and management institutions let alone sufficient resources for discharging their responsibilities effectively. According to Alebachew *et al*. (2004), deficiencies of sanitary services, low capacity for urban waste management and the absence of regulations and scientific criteria for enforcement pose increasing environmental and public health hazards in the major towns of Ethiopia.

This case study made an attempt to assess industrial waste pollution with a focus on the environmental impact of water pollution of River Borkena in general and on agricultural production, human health, and livelihood in particular in the semi-urban and rural communities around Kombolcha town. These issues were studied with the help of primary data collected from selected representative samples (farmers and agricultural office experts) from the communities and additionally laboratory assessment of heavy metal concentration was made on river water and the vegetables grown downstream within Borkena watershed especially from farm lands which used this waste water for irrigation purposes.

1.2 Statement of the problem

Water is an essential component of life and over the years man has depended on it for survival (Eja, 2002). It is a vital resource for agriculture, transport, industry, recreation and many other human activities. Despite its importance, water is the most poorly managed resource in the world (Fakayode, 2005). Fresh water resources are becoming scarce in many countries, as a result of population growth, increasing pollution, poor water management practices, and climatic variations. According to some recent projections, in 2025 two thirds of the world's population will be suffering moderate to high water stress and about half of the population will face real constraints in their water supply (Lazarova *et al.*, 2001).

Rivers worldwide serve as the recipients of great quantities of waste discharged by agricultural, industrial and domestic activities. Increasing water pollution causes not only the deterioration of water quality but also threatens human health and the balance of aquatic ecosystems, economic development and social prosperity. Metals have been excessively released into the environment due to rapid industrialization and have created a major global concern. Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries, etc., (Kadirvelu *et al.*, 2001a; Williams *et al.*, 1998). Discharge of industrial wastes in to a body of water may affect the physical and chemical properties of the receiving water.

Interaction of wastes discharged from a variety of industrial processes may cause serious damage. When tannery and sulphite wastes are mixed with wastes containing iron salts, a dense inky coloration is produced and the receiving water is extensively denuded of dissolved oxygen. When wastes containing sulphides come in to contact with acidic wastes they give off hydrogen sulphide, which gives rise to toxicity and causes serious depiction of oxygen in the receiving water (Sierp, 1959). Inappropriately managed waste can attract rodents and insects, which can harbour gastrointestinal parasites, yellow fever, worms, the plague and other conditions for humans; and exposure to hazardous wastes, particularly when they are burned, can cause various other diseases including cancers. Toxic waste materials can contaminate surface water, groundwater, soil, and air which cause more problems for humans, other species, and ecosystems (Diaz *et al*, 2006)

In general rivers have been cradles of many civilizations and are responsible for supporting and maintaining various forms of life. However, rapid urbanization with associated economical and industrial development has exerted tremendous pressure on these vital resources leading to the impairment of water quality and various ecosystem services. River Borkena, one of the major rivers in north eastern Ethiopia, is facing serious challenges for its very survival mainly because of various anthropogenic activities. This river has a catchment area that is widely utilized for domestic, agricultural, and industrial activities. In addition to this, the river also acts as a sink for sewage, industrial effluents and agricultural runoff. As it has been seen from photograph 1.2 and 1.3, it receives large quantity of wastewater from the surrounding industries, domestic wastes and sewage of Kombolcha town. The quality of the river water is deteriorating from time to time due to the indirect discharge of wastes by the tributary rivers.

Since Kombolcha is one of the most important industrial areas in Ethiopia and is situated on the bank of river Borkena, industries of diverse fields such as tannery, textile, meat processing, steel products, brewery, flour mills, dairy and a huge industrial park are located in the town. The rapid urbanization and population growth in the town because of industrialization poses a major threat of metal pollution for river Borkena. Monitoring of metal contamination is important because increased concentration of metals in fresh water bodies increases the threat to human health and the environment due to biological magnification. Specially as it is observed from the site visits of the study area, the use of river Borken for irrigation purposes, caused loss of productivity of vegetables, such as lettuce, as can be seen in photograph 1.4. As it has been observed from photograph 1.1, significant proportion of the Kombolcha and surrounding population still rely on river Borkena for irrigation, washing and animals drinking, but they have suffered from serious loss of productivity of vegetables grown using the wastewater discharges for irrigation purpose. Additionally the farmers in the watershed suffered serious skin injury because of their exposure to the wastewater during irrigation practices. That is why this study focused on assessing the amount of industrial waste load on river Borkena and its effects on the communities who are settled with in the watershed.

Photograph1.1 River Borkena before the tributary streams mixed with the industrial waste discharges. The surrounding people used the river water for washing clothes and children stay in water to protect them-selves from the hot weather.

Photograph 1.2 River Loyale, containing industrial waste load from tannery, meat processing industry and textile industry, before mixed with river Borkena.

Photograph 1.3 River Worka containing industrial waste discharges from Brewery before mixed with River Borkena.

Photograph 1.4 Lettuce grown using the industrial waste discharges for irrigation purpose suffered from foliar drying and loss of productivity.

1.3 Significance of the study

In the recent years, attempts have been made to estimate the various impacts of industrial pollution and sewage on soils that has been used for agricultural purposes specifically in the town of Kombolcha and the surrounding areas. However, these studies have not taken into account the impacts on crops and vegetables that were produced by the farmers who used the effluent polluted water for irrigation practices and the health effects on humans and animals. Additionally the pollution status of river Borkena has not been studied well so far. Therefore this study will fill the gaps in information for concerned regional and federal governmental offices and may use it as an input to design regulations and policies which benefits the communities within the watershed.

1.4 Research aim and Objectives

To proceed with the investigation of, the ways in which industrial waste water pollution, as perceived by the people living in Borkena watershed affects the communities day to day life, the following aim and a more specific list of objectives were formulated.

The main aim of this study is: to assess the physico-chemical characteristics of River Borkena before and after industrial waste discharges mixed to it by the waste carrier small streams; and its environmental impact on the surrounding communities and ecosystem.

This aim was achieved by addressing the following objectives:

1. To measure water quality parameters, such as pH, electrical conductivity, alkalinity, hardness, turbidity, dissolved solids, etc. and metal concentrations for the river water before and after the industrial effluents has been mixed to the river at different seasons in order to account for the seasonal hydrological cycle of the river water.
2. To determine metal concentrations of vegetables grown in the watershed that used the river water which receives discharged industrial effluents for irrigation purpose and compare the results with international standards from the point of view of health hazards whether or not they are in the safe side.
3. To investigate the environmental and ecological impacts of waste water discharged by industries from Komnolcha town on human and animals health, agriculture, and water quality by performing a case study using interview/questionnaire on the surrounding communities and professionals from the district office of agricultural department.
4. To compare the results of water quality measurements with drinking and irrigation water standards set by international regulatory standards.
5. To recommend a course of action for improving industrial waste management of industries found in Kombolcha town.

1.5 Research questions

The research seek to address the following important questions

1. Is really Borkena River polluted by the discharges of industrial waste from industries in Kombolcha town?
2. How much are the effects of waste water load from River Borkena on vegetables grown around the river basin which uses this water for irrigation purpose?
3. What are the impacts of this industrial waste load on the surrounding communities and ecosystem?
4. How much is the pollution of Borkena River compared to international water quality standards for drinking and irrigation?
5. Is there any action taken to aware the communities and the industries about the amount of waste load discharged to the river and its effect on the environment?

1.6 Thesis overview

The main body of this thesis included five chapters. Chapter 1 includes the background for water quality assessment in terms of water quality parameters and assessment of heavy metal concentrations of wastewater. Following is statement of the problem that emphasized the problems in the Borkena watershed and how it worsen with time and then significance of the study comes next. Research aim and objectives with research questions are also stated clearly as it has been given in the previous pages. Chapter 2 describes the literature reviews on physico-chemical parameters, some major ions and selected heavy metals and their toxicity for humans, animals and plants.

In chapter 3 description of the study area and research methodology are stated. Generally the thesis included basic survey which assesses water quality of river Borkena by water quality parameters, and a case study to describe the effects of water quality in the watershed.

Chapter 4 describes results from the determination of water quality based on water quality parameters and heavy metal concentrations in river water using descriptive statistical methods and compared with WHO standards.

Chapter 5 reviews the case study based on laboratory determination of metals in wastewater and vegetables grown on farm lands within the watershed and focus group discussions with farmers. Additionally the results from the previous water quality measurements were used so that they are compared with WHO/FAO irrigation water standards and all are combined and triangulated to deduce for the effects of wastewater on humans, animals and vegetables farming.

The thesis also contains an appendix. Appendix A which include interview questions for focus group discussions and agricultural experts.

Chapter 2 Literature Review

2.1 Assessment of industrial waste load of River Borkena

Access to clean water is essential for health, economic and social well-being of any human population (Chakravarty I. and Bhattacharya A.S.K., 2017). However, in many developing countries, water quality is the main concern for it has been compromised due to wide range of natural and human influences (Bhaja and Kundu, 2012). Water quality monitoring has one of the highest priorities in environmental protection policy (Simeonov *et al*., 2002). The quality of water is identified in terms of its physical, chemical and biological parameters (Sargaonkar and Deshpande, 2003).

2.1.1 Physico-chemical parameters of water quality measurements

There are a number of physico-chemical parameters that are measured to define the quality of water bodies. Among which some are Total Dissolved Solid (TDS), Biochemical Oxygen Demand (BOD), Electrical Conductivity (EC), pH, Temperature, Alkalinity, Hardness, Turbidity, Nitrate, Fluoride and Chloride ion cocentrations in water. Safran (2001), states that the particular problem in the case of water quality monitoring is the complexity associated with analysing the large number of measured variables.

2.1.1.1 pH

pH is known as a measure of the hydrogen ion concentration. It is an important indication of its quality and provides information about various geochemical equilibriums or solubility calculation (Shyamala *et al*., 2008). Water generally becomes more corrosive with decreasing pH; however, excessively alkaline water also may be corrosive. The pH of river water depends on many factors such as carbonate system i.e. the concentration of carbonates and carbon dioxide and on the nature of discharged pollutants (wastewaters, atmospheric deposits).

Higher value of pH is normally associated with high photosynthetic activity in water (Hujare, 2008) and natural waters are alkaline due to presence of sufficient quantities of carbonates (Trivedy and Goel, 1984). The large variation in pH of water found indicator of a high productivity of natural water (Sreenivasan, 1976). (Krishna Ram *et al*., 2007) documented that the pH range of 6.7 to 8.4 is considered to be safe for aquatic life to maintain productivity. However, pH below 4.0 and above 9.6 found hazardous to life.

The level of pH of water has an important influence on living organisms and on many uses of the water. Excessive acidification of surface water accelerates the leaching of heavy metals and radionuclides from the bottom sediments. The pH of water also has a great influence on the biochemical processes occurring in surface waters. The most adequate pH intervals on irrigation waters are 6.0-8.5, (Ayers *et.al.*, 1985, 1994)

The pH of water along with alkalinity affects the solubility and availability of nutrients and other chemical characteristics of irrigation water. Higher water pH levels can be tolerated if the water alkalinity is not excessive. High pH (>7.0) may reduce the availability of various metals and micronutrients causing deficiency symptoms. High pH is often accompanied by high alkalinity. Less commonly, low pH (< 5.0) may result in toxic high levels of metals like iron and manganese; this is usually found in combination with low alkalinity.

2.1.1.2 Total Hardness

Hardness is the property of water which prevents the lather formation with soap and increases the boiling points of water (Trivedy *et al*., 1986). The total hardness is an important parameter of water quality whether it is to be used for domestic, industrial or agricultural purposes. It is due to the presence of excess of calcium (Ca), magnesium (Mg) and iron (Fe) salts. Meshram (2005), has noticed, hardness is essential for normal growth of aquatic ecosystem and Krishnaram *et al.* (2008b), noted that calcium as cation causes water hardness in natural water and favours to zooplankton production, alkalinity and phosphate content of water body. The carbonate and bicarbonate concentrations are useful to determine the temporary hardness and alkalinity. Hardness in water is also derived from carbon dioxide (CO_2) released in bacterial action from soil through in percolating water. The water hardness is primarily due to the result of interaction between water and geological fragmentation. High value of hardness in summer season was mainly attributed due to rising temperature, increasing solubility of Ca^{2+} and Mg^{2+} salts (Garg, 2003).

According to (WHO, 2003) no health-based guideline value is proposed for hardness. However, the degree of hardness in water may affect its acceptability to the consumer in terms of taste and scale deposition. A guideline value of 500 mg/L (as calcium carbonate) was established for hardness, based on taste and household use considerations, and no health-based guideline value for hardness was proposed in the 1993 Guidelines, although hardness above approximately 200 mg/L may cause scale deposition in the distribution system. The degree of hardness of drinking-water is important for aesthetic acceptability by consumers and for economic and operational considerations.

2.1.1.3 Alkalinity

Alkalinity of natural water is generally the result of content of bicarbonates and is usually expressed in terms of presence of calcium carbonate. Alkalinity favours to zooplankton population (Singh *et al*., 2002; Kiran *et al*., 2007). The higher value of alkalinity indicated the presence of bicarbonate, carbonate and hydroxide in the water bodies (Jain *et al*., 2000). The pH has direct relationship with total alkalinity, reported by (Bharadwaj and Sharma, 1999). The total alkalinity of water is mainly caused by Ca^{2+}, Mg^{2+}, Na^{+}, NH_4^{+} combined either as carbonates or bicarbonates or occasionally as hydroxides.

The permissible limit stipulated by ICMR (1975), for alkalinity is120 mg/L. One of the most important water quality parameter to affect irrigation waters is alkalinity. It is a measure of the dissolved materials in water that can buffer or neutralize acids. Alkalinity is typically reported as milligram per litre (mg/L) of calcium carbonate. While the separate carbonate and bicarbonate alkalinity test results are helpful in understanding the source of alkalinity and the potential for other contaminants in the water, from an irrigation perspective the total alkalinity is the most important water test result, because high alkalinity, not pH, exerts the most significant effects on growing medium fertility and plant nutrition. Higher pH levels are typically not a problem unless the alkalinity exceeds the acceptable range.

2.1.1.4 Turbidity

Turbidity is a measurement of the cloudiness of water, and is measured by passing a beam of light through the water photometrically. It is a measure of water clarity and is inversely proportional to penetration of light. Cloudiness is caused by materials suspended in water that obstructs light transmission through the water. Clay, silt, organic matter, plankton and other microscopic organisms (bacteria, viruses and protozoa) are typically attached to particulates, cause turbidity in natural water (Bhanja *et al*., 2000). It has been recognized as a valuable limiting factor in the biological productivity of the water bodies.

Data are emerging that show an increasing risk of gastro-intestinal infections that correlates with high turbidity. This may be because turbidity is acting as an indicator of possible sources of microbial contamination. According to Kelley C.D. *et al.* (2015), some pathogens like *V. cholerae*, *Giardia lambdia* and *Cryptosporidia*, exploit the high water turbidity to hide from the effect of water treatment agents and cause waterborne diseases. Consequently, high water turbidity can promotes the development of harmful algal blooms (Epstein P.R., 1993; Sagir Ahmed M. *et al*., 2007).

Turbidity is measured by nephelometric turbidity units (NTU) and can be initially noticed by the naked eye above approximately 4.0 NTU, but according to Gorchev H.G. and Ozolins G. (2011), the WHO recommended value for turbidity in raw water is less than 5 NTU.

2.1.1.5 Total dissolved solids

In freshwater ecosystem dissolved solids originate from natural sources and found depend upon location, geological basin of the water body, drainage, rainfall, and inflowing water. The animal pollution and human interference such as sewage, urban runoff and industrial wastewater also contribute to enrichment of dissolved solids (Krishna Ram *et al*., 2007). The amount of TDS in a water body found to be useful parameter in describing the chemical density as a fitness factor and as a general measure of edaphic relationship and productivity of the water (Jhingran, 1982). High content of TDS elevated the density of water so that it influences osmoregulation and reducing gas solubility, utility of water for drinking, irrigation and industries (Edmondson, 1959; Manivasakam, 2003). Additionally water with high TDS indicates more ionic concentration which is of inferior palatability and can induce unfavourable physicochemical reactions in the consumers. Kataria *et al*. (1996), reported that increase in value of TDS indicate pollution by extraneous sources and adversely affects the quality of running water. High TDS concentration of water may cause laxative or constipation effects (Kumarasamy, 1989) beside the taste.

According to (WHO, 2003) in the first edition of the *Guidelines for Drinking-water Quality*, published in 1984, a guideline value of 1000 mg/L was established for TDS based on taste considerations. No health-based guideline value for TDS was proposed in the 1993 Guidelines, as reliable data on possible health effects associated with the ingestion of TDS in drinking-water were not available. However, the presence of high levels of TDS in drinking-water (greater than 1200 mg/L) may be objectionable to consumers. Water with extremely low concentrations of total dissolved solids may also be unacceptable because of its flat, insipid taste. The TDS permissible limits of WHO is 500 mg/L (WHO, 2003). High levels of TDS may aesthetically be unsatisfactory for bathing and washing.

2.1.1.6 Electrical conductivity

The importance of electrical conductivity is its measure of salinity which greatly affects the taste and thus has a significant impact on the user acceptance of the water as potable (Pradeep J., 1998; Goel, 2000). EC talks about the conducting capacity of water which in turn is determined by the presence of dissolved ions and solids and their total concentration, mobility, valence and temperature. Water conductivity increases with raising temperature (Queensland G., 2018).

The higher the ionisable solids, the greater will be the electrical conductivity. The WHO permissible limit for electrical conductivity, in water is 600 mhos cm^{-1} (WHO, 2003). When this exceeds 3000 mhos cm^{-1}, the germination of almost all the crops would be affected and it may result in much reduced yield (Srinivas *et al*., 2000; Goldman and Horne, 1983). It is known that the salinity tolerance of plants is related to the salinity of the soil, described as electrical conductivity. That is why it is directly related to the concentration of ions dissolved in the water, which implies electrical conductivity of water is a direct function of its TDS (Harilal *et al*., 2004). Elevated conductivity levels in water can damage growth media and rooting function resulting in nutrient imbalances and water uptake issues.

2.1.1.7 Chlorides

Chlorides occurs naturally in all types of water. Chloride in river water results from agricultural activities, industries and chloride rich rocks. The most important source of chloride in natural water is discharge of sewage. Sources of chloride in natural water may be from soil, municipal or industrial sewage and wastes of animal origin (Girija et al. 2017), and often serve as a chemical pollution indicator for sewage contamination. Chlorides are usually present in low concentrations in natural waters and play vital role in photophosphorylation reactions in autotrophs. Large contents of chloride in freshwater is usually taken as an indicator of pollution (Venkatasubramani and Meenambal, 2007). The sewage water and industrial effluent are rich in high chloride and hence the discharge of these wastes result in high chloride level in fresh water (Haslan, 1991).

Secondary Maximum Contaminant Limit (SMCL) of 250 mg/L for chloride is the level above which the taste of the water may become objectionable to the consumer. In addition to the adverse taste effects, high chloride concentration levels in the water contribute to deterioration of domestic plumbing, water heaters and municipal water works equipment. High chloride concentrations in the water may also be associated with the presence of sodium in drinking water. The excess sodium and chloride in drinking water may induce heart failure and hypertension (Husain and Ekbal, 2003). Chloride can damage plants from excessive foliar absorption (sprinkler systems) or excessive root uptake (drip irrigation).

According to WHO (2003), in the first edition of the *Guidelines for Drinking-water Quality*, published in 1984, a guideline value of 250 mg/L was established for chloride, based on taste considerations. No health-based guideline value for chloride in drinking-water was proposed in the 1993 Guidelines, although it was confirmed that chloride concentrations in excess of about 250 mg/L can give rise to detectable taste in water. Since chloride is difficult to remove from water, advanced treatment using membranes (reverse osmosis) or distillation is required. Dilution with low chloride water can also be used.

2.1.1.8 Fluorides

Fluorides occurs as fluorspar (fluorite), rock phosphate, triphite, phosphorite crystals etc. in nature. The source of fluoride in river waters can be phosphatic fertilizers from agricultural runoff and discharge of domestic wastes or wastes from the surrounding industries (Bhosle *et al*., 2001). The fluoride permissible limit of WHO is 1.0 – 1.5 mg/L. Values over 1.5 mg/L may cause dental fluorosis or mottling of permanent teeth in children between the ages of birth to 13 years, and that progressively higher concentrations lead to increasing risks of skeletal fluorosis; therefore steps have to be taken to reduce the risk of dental fluorosis (WHO, 2003).

There is evidence of fluoride being a beneficial element with regard to the prevention of dental caries. The protective effects of fluoride increase with concentration up to about 2 mg of fluoride per litre of drinking-water; where the minimum concentration of fluoride in drinking-water required to produce this protective effect is approximately 0.5 mg/L. Elevated fluoride intakes can have more serious effects on skeletal tissues. Skeletal fluorosis (with adverse changes in bone structure) may be observed when drinking water contains 3 – 6 mg of fluoride per litre, particularly with high water consumption (Fawell *et al*., 2006; IPCS, 2002; US NRC, 2006).

2.1.1.9 Nitrates

Nitrates are formed in water due to oxidation of ammonia by bacterial action and their presence indicates that nitrogenous organic matter is under nitrification. The presence of higher value than the standard recommended by WHO for drinking water is an indication of pollution in the river and will cause eutrophication as a nutrient, hence reducing water quality. Algal bloom and aquatic plant growth will reduce oxygen, pH, alkalinity, increases TSS, reduce penetration of light so less rate of photosynthesis but de-nitrification needs addition of biodegradable organic carbon in fertilizer industry (Makhijani and Manoharan, 1999; PAKEPA, 2005b).

High levels of methaemoglobin formation can give rise to cyanosis, referred to as blue-baby syndrome. Although clinically significant methaemoglobinaemia can occur as a result of extremely high nitrate intake in adults and children, the most familiar situation is its occurrence in bottle-fed infants (Gupta *et al*., 2000; Weyer *et al*., 2001). Nitrates in water are also linked with high probability for bladder and ovarian cancer, insulin dependent diabetes mellitus and geno-toxic effects at the chromosomal level (Ward *et al*., 1996).

According to WHO (2007), nitrate can reach both surface water and groundwater as a consequence of agricultural activity, from wastewater disposal and from oxidation of nitrogenous waste products in human and animal excreta, including septic tanks. Surface water nitrate concentrations can change rapidly owing to surface runoff of fertilizer, uptake by phytoplankton and de-nitrification by bacteria. In general, the most important source of human exposure to nitrate is through vegetables. In some circumstances, however, drinking- water can make a significant contribution to nitrate intake.

The Guideline value for nitrate in drinking water is 50 mg/L to protect against methaemoglobinaemia in bottle-fed infants which results from short-term exposure (WHO, 2007). Methaemoglobinaemia in infants appears to be associated with simultaneous exposure to microbial contaminants. According to the WHO (GEMS, 1988), the maximum concentration of nitrate ion for public water supplies is 45 mg/L. The guidelines for drinking water quality of the European Community (EC, 1980) provide a reference value of 25 mg/L and a maximum admissible limit of 50 mg/L for nitrate.

2.1.2 Trace Elements

Trace element refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration. To a small extent, it enters the body system through food, air, and water, bio-accumulated over a period of time (Athalye *et al.*, 2001).These metals include Pb, Cd, Zn, Hg, As, Ag, Cr, Cu, Fe and the platinum group elements (Upadhyay *et al.*, 2007). If the concentration of a metal exceeds its limit in drinking water, it can affect the human health. Metal contamination in aquatic environments has become a significant concern due to its toxicity, abundance and persistence in the environment, and its subsequent accumulation in aquatic habitats (Fu et al., 2014; Islam et al., 2017; Wu et al., 2017).

2.1.2.1 Chromium

Chromium (Mn) is a naturally occurring element found in rocks, animals, plants, soils, volcanic dusts and gases (ATSDR, 2000). The main source of chromium is chromite ore (Levey and Greenhall, 1983). Chromium occurs in oxidation states from Cr^{+2} to Cr^{+6}, with Cr^{+3} as the most common form and Cr^{+6} being used in industrial purposes. Only Cr^{+3} and Cr^{+6} forms are of biological significance, with Cr^{+6} being more toxic. Total chromium, Cr, is expressed as Cr^{+3} and Cr^{+6} combined. The trivalent Cr is an essential nutrient that serves as a component of the "glucose tolerance factor", and is thought to be a cofactor for insulin action, and helps the body use protein and fat (Casarett *et al*., 2001; ATSDR, 2000). Biological systems transform Cr^{+6} into Cr^{+3} (Casarett *et al*., 2001; Harte *et al*., 1991). The metal chromium is used for making steel, tri- and hexavalent forms are used for chrome plating, dyes and pigments, mordant dying, leather tanning, wood preservatives, and as anti-corrosives in cooling systems, boilers, and oil drilling mud (Casarett *et al*., 2001; ATSDR, 2000). Chromium enters the air mostly as fine dust particles that settle over water, where it strongly binds to soil particles (ATSDR, 2000). A controllable source of chromium into aquatic environments is the wastewater from chrome-plating and metal-finishing industries, textile plants, and tanneries (Casarett *et al*., 2001).

The average chromium concentration in human blood, without excessive exposure, ranges from 20 to 30 μg/L and is evenly distributed between erythrocytes and plasma (Casarett *et al*., 2001). Respiratory exposure of high levels of chromium can cause nose irritation, nose bleeds, ulcers and holes in the nasal septum, and dietary exposure of high levels of chromium can cause upset stomach and ulcers, convulsions, kidney and liver damage, and death. Hexavalent chromium had been determined to be a human carcinogen (Casarett *et al*., 2001; ATSDR, 2000).

The U.S. EPA (2003), has set the MCL for total chromium in drinking water at 100 μg/L, but the U.S. EPA (1986), indicated that acute toxicity of Cr^{+6} decreases with increasing water hardness and pH. In the first edition of the *Guidelines for Drinking-water Quality*, published in 1984, the guideline value of 0.05 mg/L for total chromium was retained; total chromium was specified because of difficulties in analysing for the hexavalent form only. The 1993 Guidelines questioned the guideline value of 0.05 mg/L (50 μg/L), because of the carcinogenicity of hexavalent chromium by the inhalation route and its geno-toxicity, although the available toxicological data did not support the derivation of a new value. As a practical measure, 0.05 mg/L, which is considered to be unlikely to give rise to significant health risks, was retained as the provisional guideline value until additional information becomes available and chromium can be re-evaluated (WHO, 2003).

2.1.2.2 Manganese

Manganese (Mn), is an essential element for humans and other animals. It occurs naturally in many food sources, surface water and groundwater sources, particularly in anaerobic or low oxidation conditions, and this is the most important source for drinking-water. The most important oxidative states for the environment and biology are Mn^{2+}, Mn^{4+} and Mn^{7+}. The greatest exposure to manganese is usually from food.

The Guideline value of manganese in drinking water is 0.4 mg/L. The presence of manganese in drinking-water will be objectionable to consumers if it is deposited in water mains and causes water discoloration. Concentrations below 0.05 – 0.10 mg/L are usually acceptble to consumers. At levels exceeding 0.1 mg/L, manganese in water supplies causes an undesirable taste in beverages and stains sanitary ware and laundry (WHO, 2003).

Adverse effects can result from both deficiency and overexposure. Manganese is known to cause neurological effects following inhalation exposure, particularly in occupational settings.
Manganese does not appear to have any toxicological significance in drinking water at the quantities generally occur in raw waters. In some cases, chronic poisoning by manganese can result by extended exposure to very high levels in drinking water, manifested by progressive

deterioration of central nervous system, lethargy and symptoms stimulating Parkinson’s syndrome (Goel, 1997; WHO, 2004). According to IPCS (1999), the higher metal levels in soil may cause negative impact on crops, inhibiting the growth in one or other way. However, one of the most important factors is the pH of the soils. Alkaline pH of the soil would usually restrict the mobilization of the metal in soil matrix and consequently, the metal uptake by crop plant would be controlled, obviously reducing the risk of metal toxicity.

2.1.2.3 Lead

Lead (Pb) is the most toxic metal which has destroyed human health and the environment (Küpper, 2017). Pb is a naturally occurring toxic metal that can be found in all parts of the environment (ATSDR, 2005). The principal source of lead exposure in humans is food, however, other sources include: lead-based indoor paint in old houses; dust from environmental sources; contaminated drinking water; burning of fossil fuels; and mining and manufacturing activities (Levey and Greenhall, 1983; ATSDR, 2005). Children are especially at risk, with a major problem being the ingestion of flaking lead-based indoor paints. Atmospheric lead concentrations have decreased due to restrictions and the phasing out of leaded gasoline. (Harte *et al*., 1991) indicated that, since 1976, vehicular lead releases have declined more than 97%.

Lead mainly affects the nervous system, but can affect about every organ and system in the body (ATSDR, 2005). The symptoms of lead poisoning, often vague and mimicking other conditions, include: pallor, vomiting, abdominal pain, constipation, listlessness, stupor, loss of appetite, irritability, and loss of motor coordination (Casarett *et al.*, 2001). Lead exposure can alter growth and development in children, cause cancer, skin problems, respiratory, gastrointestinal, nervous, and renal system complications and others (Rai P.K. et al., 2019).The International Agency for Research on Cancer classified lead as a 2B carcinogen, the

Department of Health and Human Services classified lead as anticipated to be a human carcinogen, while the U.S. EPA determined that lead is a probable carcinogen (ATSDR, 2005). As with cadmium, lead is also an endocrine disruptor that can adversely affect male mammalian reproductive systems (Telisman *et al*., 2000). In addition, deleterious effects of lead may be mediated in part by gene function alterations (Hanas *et al*., 1999). Placental transfer of lead occurs in humans as early as the 12^{th} week of gestation and continues throughout development. Young children absorb 4-5 times as much lead as adults, and the biological half-life may be considerably longer in children than in adults. Lead is a general toxicant that accumulates in the skeleton. Infants, children up to 6 years of age and pregnant women are most susceptible to its adverse health effects. Lead also interferes with calcium metabolism, both directly and by interfering with vitamin D metabolism. There is evidence from studies in humans that adverse neurotoxic effects other than cancer may occur at very low concentrations of lead and that a guideline value derived on this basis would also be protective for carcinogenic effects (FAO/WHO, 2011).

Drinking water is an important source of lead. The daily intake of lead for drinking water is approximately 10 µg (Casarett *et al*., 2001). The U.S. EPA (2007), estimates that 10 to 20% of human exposure to lead may come from drinking water and those formula-fed infants can receive 40 to 60% of their exposure to lead from drinking water used in the making of the formula. The action limit for lead in drinking water is 15 µg/L. The U.S. EPA acute water quality criteria value for lead is 65 µg/L and the chronic water quality criteria is 2.5 µg/L (ATSDR, 2004). According to WHO (2003), the provisional guideline value for lead in drinking water is 0.01 mg/L (10 µg/L). The guideline value is provisional on the basis of treatment performance and analytical achievability.

2.1.2.4 Zinc

Zinc (Zn) is one of the most common elements in the earth's crust and can be found in air, soil, water, and foods (Casarett *et al*., 2001; ATSDR, 2005). Zinc is a nutritionally essential metal, with severe health consequences arising due to zinc deficiency (Casarett *et al*., 2001; Harte *et al*., 1991). Zinc is combined with copper to form brass and with both copper and tin to form bronze (Levey and Greenhall, 1983; Harte *et al*., 1991; ATSDR, 2005). Zinc can be found in rust preventatives, batteries, coins, paints, dyes, rubber, wood preservatives, photocopying paper and smoke bombs used for riot control (Harte *et al*., 1991; ATSDR, 2005). Zinc enters the environment due to natural processes and human activities such as mining, steel production, coal burning and waste incineration (ATSDR, 2005). The diet is normally the principal source of zinc. Human exposure can be from ingestion of contaminated food, water and beverages, dietary zinc supplements and industrial exposure (Harte *et al*., 1991; ATSDR, 2005).

Excessive or lower Zn concentrations from food are of great concern to different consumers (Qureshi et al., 2016; Kacholi and Sahu, 2018). For example, a lack of Zn can cause anorexia, diarrhea, dermatitis and depression, immune dysfunction and poor wound healing (Amin et al., 2013; Kacholi and Sahu, 2018). Acute exposure to large levels of zinc can cause stomach cramps, nausea, vomiting, anaemia and diarrhoea. Workplace exposure to zinc oxide fumes can result in metal fume fever, with symptoms that include rapid breathing, shivering, fexver, sweating, chest and leg pains and weakness. But zinc has not been found to be carcinogenic (Casarett *et al*., 2001; Harte *et al*., 1991; ATSDR, 2005).

There is no National Primary Drinking Water Standard for zinc and the National Secondary Drinking Water Standard has been set at 5 mg/L, a non-enforceable standard based on taste and odour (U.S. EPA, 2003; ATSDR, 2005). Zinc will bio-accumulate in fish and other organisms, but not in plants (ATSDR, 2005). Water containing zinc at concentrations in excess of 3 – 5 mg/L may appear opalescent and develop a greasy film on boiling. However, drinking-water containing zinc at levels above 3 mg/L may not be acceptable to consumers, because it imparts an undesirable astringent taste to water. When zinc is found in irrigation water, corrosion from galvanized pipes in the irrigation plumbing should be investigated as a possible source. Levels above 0.3 mg/L can be toxic to some plants especially in low pH growth media (WHO, 2003).

2.1.3 Wastewater Treatment

Progressively developmental achievements are being accomplished in order to develop new strategies for wastewater treatment and fulfil the requirements of clean water (Ahmed and Haider, 2018). However, it has been challenging to treat discharged water containing pollutants thoroughly with available methods (Nguyen and Juang, 2019). Treatment can be used to reduce volume, mobility, and/or toxicity of hazardous waste where expertise and facilities are available. Several techniques have been reported for wastewater treatment in the literature. They typically include physical, chemical, and biological processes that are considered effective enough for water treatment in many ways.

a. Physical method

Mass transfer strategy is the base of the physical pollutant removal methods (Samsami *et al.*, 2020). It is more likely to be used due to its simplicity, flexibility, high efficiency, and pollutant recyclability (Foroutan *et al.*, 2019; Wong *et al.*, 2019). The fewer chemical requirement is another advantage of this approach. Physical treatment seems highly reliable than the other treatments because it does not depend on living organisms (Samsami *et al.*, 2020).

b. Chemical method

Several chemical oxidation processes are reported for a range of catalysis applications (Shafiq *et al*., 2020, 2021). However, the advanced oxidation process is considered an essential technique for wastewater treatment. Oxidation may involve electrochemical oxidation, photo-electrochemical oxidation and UV assisted Fenton's oxidation and ozonation. Generally, catalysts and pH play an essential role in the oxidation process (Ahmad *et al*., 2015).

c. Biological treatment

Microorganisms decompose or degrade organic wastes in biological treatment via aerobic or anaerobic cycle (Saxena and Bharagava, 2017). Microbes use organics as an energy source by degrading them. Biofilms are developed for the removal of contaminants from sewage water.

Chapter 3 Research Design and Methodology

3.1 Study Area

The town of Kombolcha is located on the north eastern part of Ethiopia immediately south east of Dessie in the Amahara region at $11^{0}06'$ north latitude and $39^{0}45'$ east longitudes which is shown by Figure 3.1 and 3.2. River Borkena crosses the town emerging from the west and running to the south east direction. In its way all through the town, it receives industrial effluents indirectly through its tributary streams named Worka and Leyole as can be seen from Figure 3.3. Most of the factories are found closely together in the middle of the town nearby the tributary streams of river Borkena. The study area includes the Borkena river basin starting from Kombolcha town up to 20 kilometres downstream.

The biophysical appearance of the land is mostly flat plain in the study area and mountainous and gorgeous nearby. The socioeconomic status of the people is dependent on farming crops and vegetables for marketing. There are about 450 farmers in the study area who are using river Borkena for irrigation to grow crops and vegetables.

Figure 3.1 Location of Ethiopia in Africa
Taken from (http//worldatlas.com)

Figure 3.2 Loction of Kombolcha town in Ethiopia
Taken from (Zinabu *et al.*, 2011).

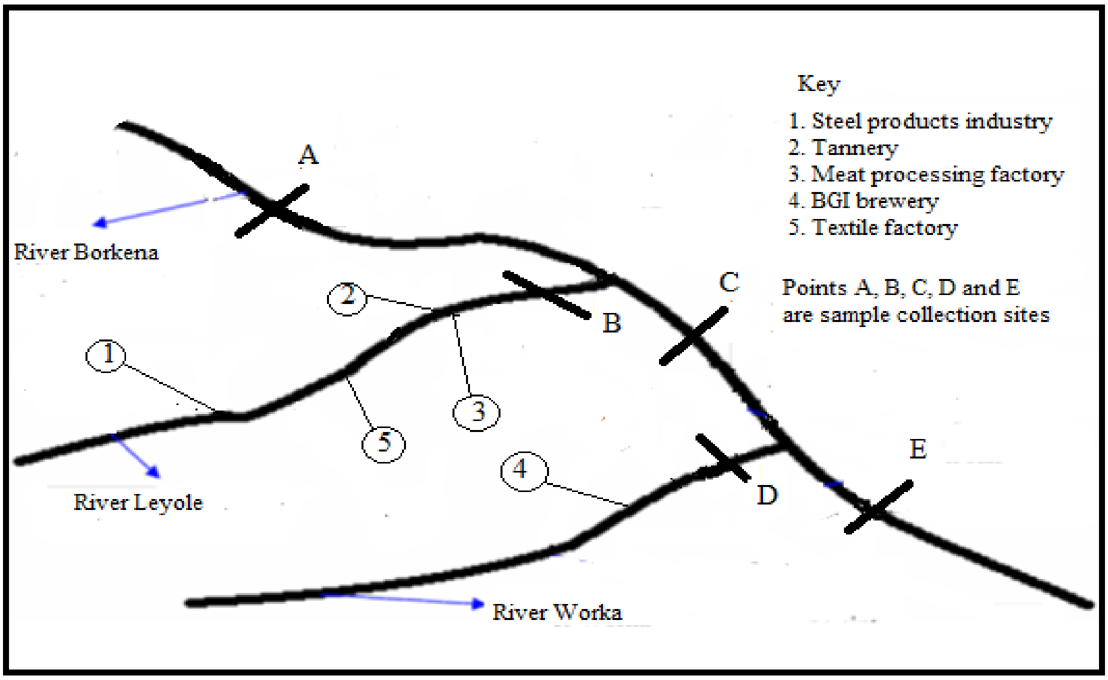

Figure 3.3 Sketch of locations of factories, river Borkena and its tributary streams with respect to the industrial effluent points and sample collection sites.

3.2 Methods and Materials

3.2.1 Methodology/Research design

The methodology consisted:

I. The use of basic survey (laboratory analysis of river water) in order to assess the physical, and chemical characteristics of the river water.

II. A case study using focus group discussions with the community authorities and other community members living with in the study area who are involved in using the river water for different purposes (like; for animals drinking, irrigation and cleaning) and laboratory analysis of river water and vegetables grown within the watershed for their metal concentration was done to investigate the effect of the use of the river water for growing vegetables and other personal cases.

The research employed a case study method that examines the critical impacts of the waste carrier water when it used for personal and agricultural consumptions by the communities with in the watershed. The researcher have chosen this approach, because it allows to uncover the long existing problems of the communities in their contexts.

The problem of industrial waste pollution at Borkena watershed continues to evolve at a rapid rate and in ways that are difficult to predict. The case study have traced these complex problems better than other methods. The researcher have done intensively continuous field observations and conducted focus group discussions with those community members who have involved in irrigation practices using the waste water and with experts from the district/woreda agriculture office.

3.2.2 Collection of samples

I. The sampling strategy was designed in such a way to cover a wide range of determinants at key sites that accurately represent the water quality of the river systems and account for tributary inputs that can have important impacts upon downstream water quality.

Sample collection for laboratory analysis of the river water were conducted starting from the town Kombolcha located across Borkena river basin from upper, mid and downstream sites. Samples were collected from the river water (including tributaries, i.e. small streams carrying industrial effluents) quarterly of a year to monitor changes caused by the seasonal hydrological cycle during site visits from Sep 1st 2017 up to August 30th 2018. Samples collected and preserved were brought to Dessie city water and sewage service laboratory, Dessie, Ethiopia; and being analysed for their water quality parameters.

II. In order to study the effects of the industrial waste on communities around the river, data were collected using interviews from representative samples that were selected randomly from the community members. The community leaders and experts from district office were also part of the sample interviewed.

Water samples that were used for irrigation practices were collected from each site using pre cleaned polyethylene bottles that were soaked in 10% HNO_3 overnight and washed thoroughly with deionized water as according to (Chary *et al*., 2008). The collected samples were acidified by adding 2 mL of conc. HNO_3 per litre of the sample to avoid precipitation of metals. Samples were brought to the chemistry laboratory of Addis Ababa University, Ethiopia; and making the waste water sample digests and being analysed for their metal concentration.

Sample collection for vegetables that are grown along the river basin which used the river water for irrigation purpose were done from the town Kombolcha up to 20 kilometres downstream; during site visits from March 1, 2018 to May30, 2018.

A diversity of vegetables are grown in the study area; among which leafy vegetables such as lettuce and cabbage were collected from different sites of the sampling zone in 3-5 replicates and stored in labelled polyethylene sampling bags. They were harvested in edible and non-edible parts and washed with tap water to remove any kind of deposition like soil particles. Edible parts of vegetables were dried and ground into powdered form for making the plant digests and analyzed for their metal concentration.

3.2.3 Physico-chemical parameters and major ions

The collected samples were analyzed for various physiochemical parameters to ascertain the characteristics of the Borkena river water and compared with drinking and irrigation water standards as prescribed by WHO and FAO. The measurements included the parameters pH, turbidity (Tur), electrical conductivity (EC), total dissolved solids (TDS), calcium hardness, magnesium hardness, total hardness, nitrate (NO_3^-); choride (Cl^-), fluoride (F^-) and Alkalinity.

The measurements were conducted for all samples from the river water during Sep, 2017 up to Aug, 2018 using standard methods in Dessie city water and sewage service laboratory, Dessie, Ethiopia; except for the pH values which were measured at the spot using a pH meter.

3.2.4 Metals concentration in vegetables and water samples

Metals concentrations of Cr, Mn, Pb, and Zn for the vegetables and waste water samples were determined. The measurements were performed in June, 2018 in the chemistry laboratory of Addis Ababa University, Ethiopia. To determine the concentration of metals for vegetable and wastewater samples, atomic absorption spectroscopy (AAS) was used.

Chapter 4 Results and Discusions

4.1 Water quality parameters

4.1.1 pH

The pH balance of a water supply describes how acidic or alkaline it is. The acidity or alkalinity of a water supply can affect plant growth, irrigation equipment, pesticide efficiency and drinking water quality.

It is evident that the pH of water is an important indication of its quality and provides valuable information about various geochemical equilibrium. Higher value of pH is normally associated with high photosynthetic activity in water (Hujare, 2008), and natural waters are alkaline due to presence of sufficient quantities of carbonates (Trivedy and Goel, 1984). Higher value of pH (8.25- 8.63) was observed at site A throughout investigations. This may be due to the presence of large quantity of domestic waste flow from the city of Kombolcha and dissolution of carbonate rocks from the river bank, since site A is located in the near distance below the point of mix of a small stream called Berbere river which carries most of the town’s waste and above the mixing points of industrial wastes to the main river. Relatively lower values of pH 6.8 in quarter 4, i.e. a dry and hotter season and 6.9 in quarter 2, i.e. a dry and cold season has been observed at site D, due to inflow of a small stream (Worka river) containing mainly waste discharges from brewery before mixed with Borkena river. As it can be seen from the graph of pH variation in different seasons (Figure 4.1), it did not show a a similar trend.

In general the pH values ranged from 6.80 at site D in quarter 4, to 8.63 at site A in quarter 2. (Table 4.1). These pH levels were within the WHO optimum limits for drinking and potable water, which is 6.5 - 8.5 (WHO, 2006), except at site A in quarter 2. The higher pH in quarter 2 at site A, may be due to lower volume of the river water during this season, so that dilution of domestic waste is expected to be low which contain wastes from cottage industries that produce liquid detergents. But this does not mean the water is suitable for drinking; because other factors have to be considered. Most of the values of pH obtained for all the samples fell within the WHO range, but were slightly above the natural background level of 7.0 as can be seen from Table 4.1. This increase in pH of water samples above the natural background levels may be due to the presence of dissolved carbonates and/or bicarbonates present in the water, and domestic waste discharges drained into the river system as it traverses the study areas.

Table 4.1 pH distribution at sampling sites within a year (quarterly reported)

Quarter	Sampling Sites					
	A	B	C	D	E	F
1	8.48	7	8.20	8.256	8.28	8.213
2	8.63	7.5	8.05	6.9	7.7	8.51
3	8.25	8.25	8.1	8.1	8.05	8.05
4	8.35	7.65	7.65	6.8	7.45	8.4

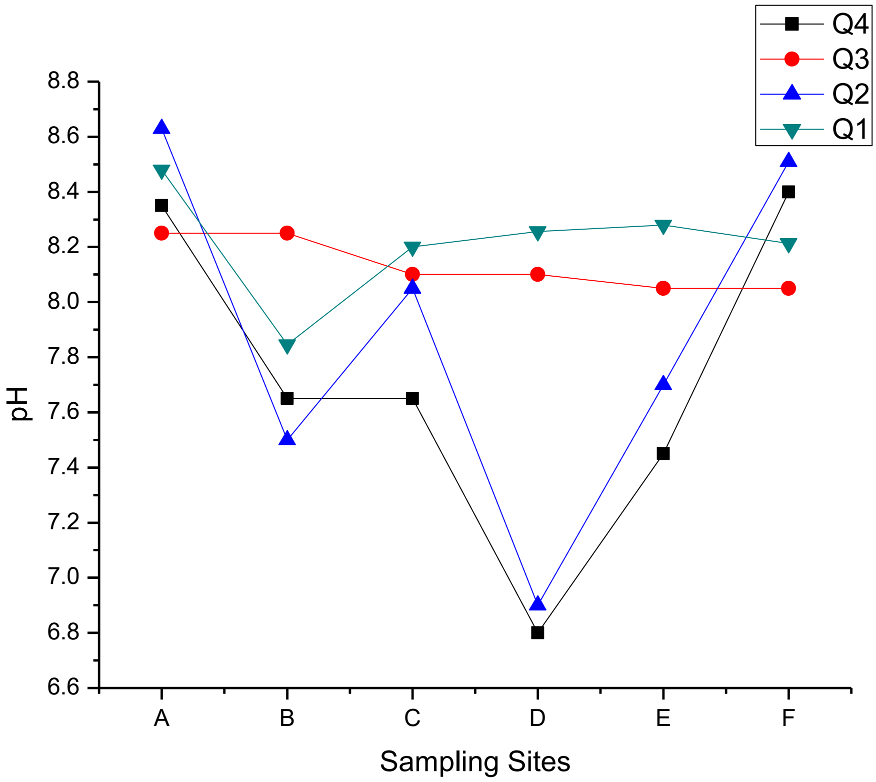

Figure 4.1 pH distribution of river Borkena at different sampling points in quarter 1 (Q1), quarter 2 (Q2), quarter 3 (Q3) and quarter 4 (Q4).

4.1.2 Electrical Conductivity

Electrical conductivity refers to the specific electrical conductance of water i.e. the ability of water to pass electric current. The conductivity of water in micro siemens per centimetre (μScm^{-1}) is roughly proportional to the concentration of dissolved solids (mostly inorganic salts) it contains. Thus conductivity is important in ecology and environmental management as an indicator of the total dissolved inorganic salts and other solids in water. The electrical conductivity value for the water samples during all investigation periods were ranged from 546 $\mu S\ cm^{-1}$ - 1287 μScm^{-1}, as given in Table 4.2. The recommended value (GEMS, 1988) and (WHO, 2006) of electrical conductivity for potable water is below 2500 μScm^{-1}.

The lowest electrical conductivity values for Borkena river water were observed at Site A in quarter 1, (i.e. September 2017, during a cold rainy season), because low values of electrical conductivity may be attributed to the freshwater nature of the water body. The value reported at site A in quarter 1, may be due to the presence of dilution effect of the water body since it is recorded in the rainy season and before any industrial wastes have been discharged to the river. The highest electrical conductivity values during the investigation periods were observed at Site D in quarter 4, (i.e. May 2018, a hot dry season). This may be due to the presence of industrial waste effluent mainly in the water body from the brewery and the evaporation effect which reduces dilution by decreasing the water volume as expected.

As it can be seen from the graph shown in Figure 4.2, variations in EC in all seasons show similar trend, i.e. the maximum values are recorded at sites B and D which are direct industrial effluent carriers, whereas the minimum values are recorded at site A which is a place found before industrial effluents mixed to the main river. This fact realizes that, the main contribution of EC in River Borkena originated from the industrial waste discharges. On the basis of the data measured during the study periods, the level of EC reflected the worsening effect of water quality due to discharges from industrial plants before and after it mixed to the main river, but within the permissible limit of WHO, i.e. 2500 µS/cm. EC values obtained in this study were lower than the EC values (864 –1778.5 µS/cm) recorded for urban streams in Machakos municipality, Kenya (Tomno R.M. *et al.*, 2020).

Generally, electrical conductivity values investigated were more degraded for water bodies which carry direct discharge of industrial wastes owing to enrichment in electrolytes, possibly due to discharge of industrial and domestic wastes. That is why water quality of sites B and D were strongly degraded resulting in high conductivity values, but the discharge of waste loads may not depend on seasons.

Table 4.2 EC (µS/cm) distribution at sampling sites within a year (quarterly reported)

Quarter	Sampling Sites					
	A	B	C	D	E	F
1	497	829	582.3	713.3	599.66	566
2	546	1136.3	812	1133.6	809	800.66
3	590	912	667	826	729	759
4	547	800.3	642	1287.3	732	712

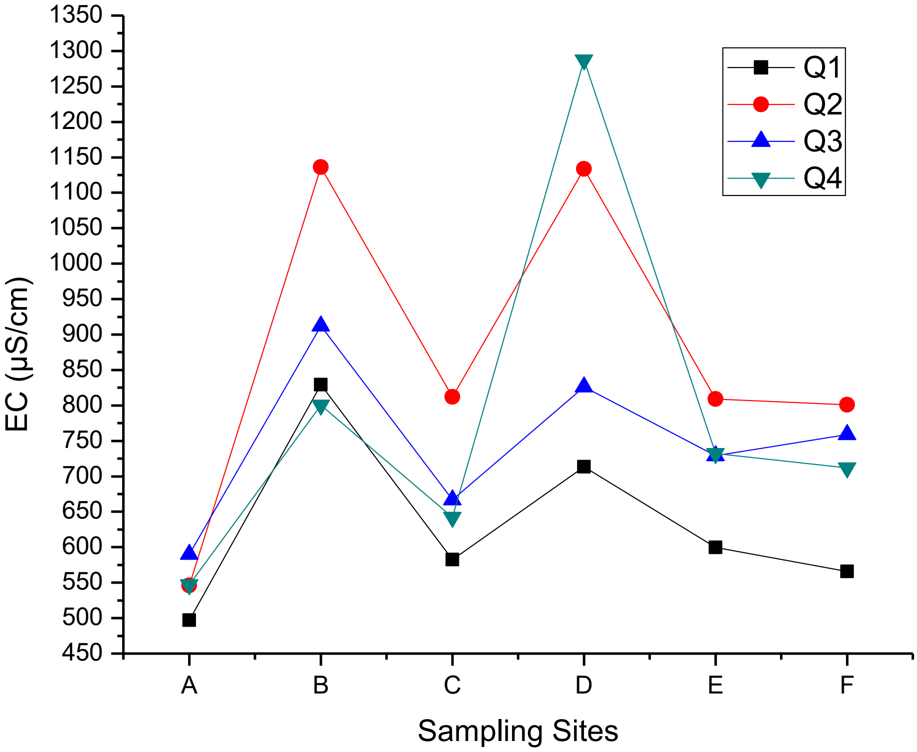

Figure 4.2 EC (µS/cm) distribution of river Borkena at different sampling points in quarter 1 (Q1), quarter 2 (Q2), quarter 3 (Q3) and quarter 4 (Q4).

4.1.3 Total dissolved solids

Water with high TDS indicates more ionic concentration which is of inferior palatability and can induce unfavourable physicochemical reactions in the consumers. As Kataria e*t al.*, (1996) reported, increase in values of TDS indicate pollution by extraneous sources and adversely affects the quality of running water. In the present study the concentration of TDS was given in Table 4.3 and found to be high at site D (645 mg/L) in quarter 4 (i.e. May 2018, a hot dry season) which has decreased potability and reduced utility of water for drinking, irrigation and industrial purposes. This may be due to lower volume of the river water because of evaporation which contributed to higher concentration of dissolved solids since it is a hot dry season. Minimum value of TDS was seen at site A (248.66 mg/L) in quarter 1 (i.e. September 2017, a cold rainy season) and it may be due to dilution effects which decreased the concentration of dissolved solids that came from inflow of higher volume of rain water before any of the industrial effluents have been mixed with the main river since it is a cold rainy season.

In general throughout investigation, the minimum values of TDS were recorded in quarter 1, for all sampling sites as expected, because it is a cold and rainy season where the rate of evaporation is low and dilution effects are high. Whereas slightly higher values of TDS were reported at sites B and D in all seasons, and this may be due to the presence of large amounts of industrial effluents carried by tributary streams Loyale and Worka respectively before they mixed with the main river. As can be observed from the graph (Figure 4.3), variations in TDS in all seasons show similar trend, i.e. the maximum values are recorded at sites B and D which are direct industrial effluent carriers, whereas the minimum values are recorded at site A which is a place found before the mix of industrial effluents to the main river. Therefore variations in

TDS of river Borkena can probably be related to pollution through the discharge of domestic and industrial wastes into the river. TDS values obtained in this study were lower than the TDS values (577.5 –865.83 mg/L) recorded for urban streams in Machakos municipality, Kenya (Tomno R.M. *et al*., 2020).

Most of the values of TDS fell within the tolerable limits for drinking water of WHO, since it did not exceed 500 mg/L. The TDS values followed the same trend as electrical conductivity, as it is pointed out by Singh and Chandel, (2006). It has been observed that a linear relationship existed between TDS and EC throughout the study, i.e. EC increased with increase in TDS.

Table 4.3 TDS (mg/L) distribution at sampling sites within a year (quarterly reported)

Quarter	Sampling Sites					
	A	B	C	D	E	F
1	248.66	414	291	356	300	283
2	273	568.66	405.66	566	404	400
3	296	456	335	414	364	380
4	273	400.3	321.3	645	366	356

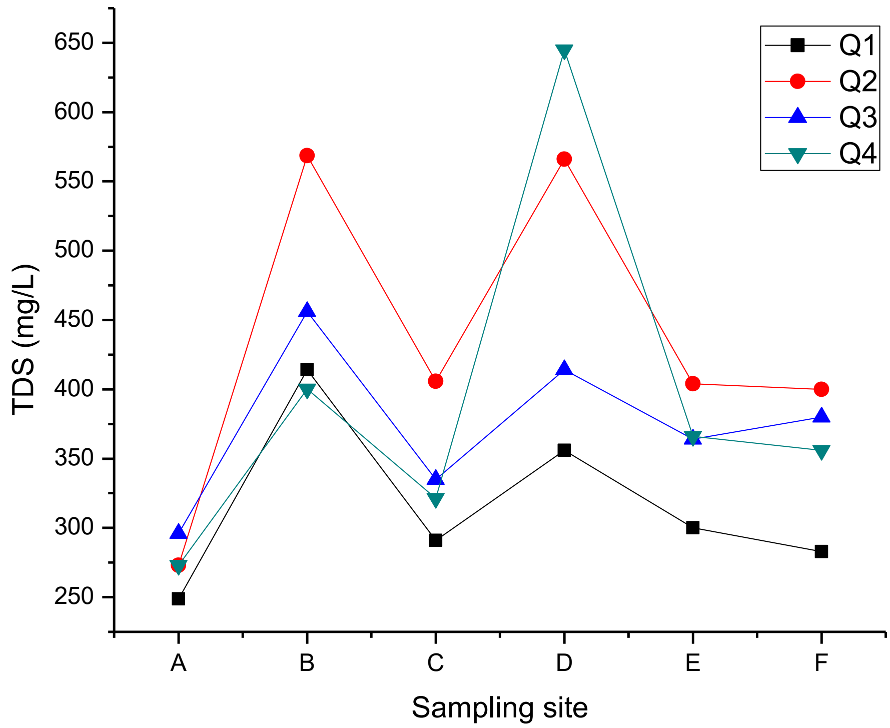

Figure 4.3 TDS (mg/L) distribution of river Borkena at different sampling points in quarter 1(Q1), quarter 2 (Q2), quarter 3 (Q3) and quarter 4 (Q4).

4.1.4 Turbidity

Turbidity is an optical property relating to light absorption and scattering in water. It is an important parameter because it affects the penetration of sunlight into the water body and its measurement is a key test of water quality. Turbidity results from the scattering and absorption of incident light by the particles and the transparency is the limit of visibility in the water. Both can vary seasonally according to biological activity in the water column and surface run-off carrying soil particles.

Turbidity as a measure of water clarity is inversely proportional to penetration of light in water and was ranged (6.00 - 8.74 NTU) at site A, (19.66 -150.30 NTU) at site B, (3.15 - 22.56 NTU) at site C, (19.26 - 81.56 NTU) at site D, (6.00 - 20.33 NTU) at site E and at site F it was (0.79 - 22.53 NTU) as it can be seen from Table 4.4. Site B was found significantly turbid throughout investigation due to the industrial waste discharges from the tannery, textile, and meat processing industries to a small tributary stream called Leyole. Jain (2000), reported that disposal of sewage and industrial effluents contribute suspended matter to the rivers. The minimum value of turbidity was reported to be 0.79 NTU at site F, in quarter 4 (i.e. June 2019, a dry and hotter season) as it can be observed from a graph, shown in Figure 4.4, This may be due to the slower flow rate and lower volume of the river water, so that suspended matters got more time to settle at a relatively longer distance in downstream from the point of mix of the industrial effluents.

variations in turbidity in all seasons shows more or less similar trend, i.e. the maximum values are recorded at sites B and D which are direct industrial effluent carriers, whereas the minimum values are recorded at site A & F which are places found before industrial effluents mixed to the main river and a far down stream site from the point of mix of industrial effluents where gradual settlement of suspended matters are likely respectively.

The turbidity of the river water across all sampling points ranged between 0.79 and 150.3 NTU by which most results are above the regulatory limits of 5 mg/L that is pointed out by WHO.

Table 4.4 Turbidity (NTU) distribution at sampling sites within a year (quarterly reported)

Quarter	Sampling Sites					
	A	B	C	D	E	F
1	8.473	118.66	10.23	19.26	13.56	10.07
2	6.53	120.66	22.56	19.46	20.33	2.038
3	6.00	150.3	6.68	81.56	6.00	22.53
4	6.41	19.66	3.15	50.83	12.66	0.79

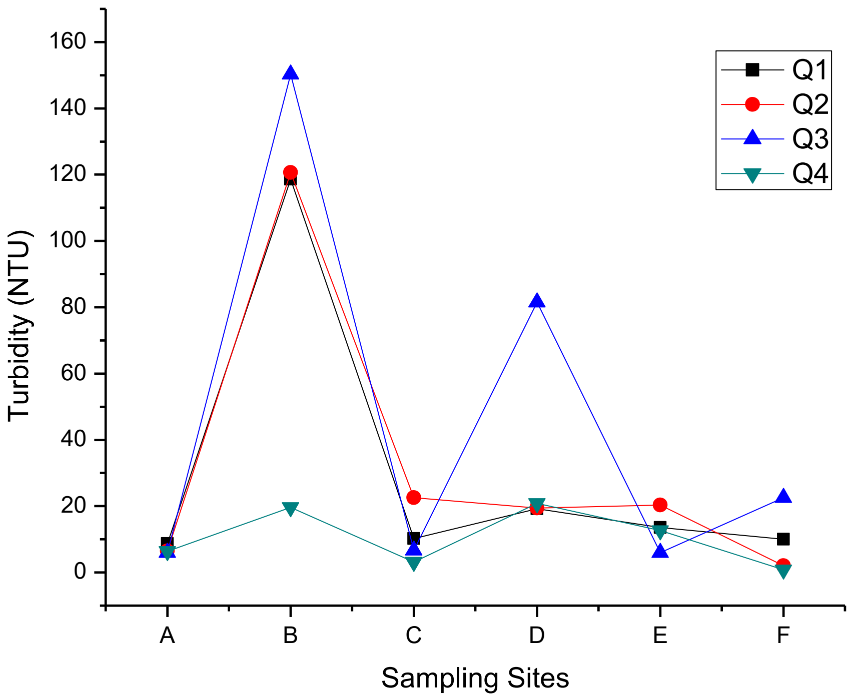

Figure 4.4 Turbidity (NTU) distribution of river Borkena at different sampling sites in quarter 1 (Q1), quarter 2 (Q2), quarter 3 (Q3) and quarter 4 (Q4).

4.1.5 Total Hardness

Total hardness indicates that magnesium and calcium salts are present in the water sources. The higher hardness value in summer season was mainly attributed to rising temperature, thereby increasing the solubility of Ca^{+2} and Mg^{+2} salts (Garg, 2003). Sometimes low values in the wet season are probably due to dilution from rain water. Total hardness varied from 248.8 mg/L at site A in quarter 3 (March 2018, a wet season) to 585 mg/L at site E in quarter 2 (December 2017, a dry season). The concentration of total hardness of water samples in river Borkena were found within the maximum permissible limit outlined by EPA, i.e. 500 mg/L except few values that are slightly higher as can be seen from Table 4.5.

Hardness in water also caused by the dissolved metallic ions. (Krishna Ram *et al.*, 2008b) noted that, calcium as a main cation or factor causes water hardness in natural water. Hardness of water depends mainly upon the amounts of calcium and magnesium salts or both. The limits of calcium and magnesium ions in potable water range from 75 to 200 mg/L and 50 to 100 mg/L respectively, (ICMR, 1975) as pointed out by Abegaz (2005). In the present study, the Ca^{2+} and Mg^{2+} ions content of the Borkena river water samples ranged from 8.0 mg/L at site B in quarter 3 to 460 mg/L at site E in quarter 2 and 45 mg/L at site B in quarter 2 to 420 mg/L at site F in quarter 4, respectively. The calcium ion concentration was found below the limit given by the CCME, i.e. 1000 mg/L for livestock use as pointed out by Abegaz (2005). Water samples from different sites were found to be hard (150 - 300 mg/L) and very hard (>300 mg/L), according to hardness description used in the UK (Reeve, 2002). Therefore, in the present study most measured values for total hardness fall in the range of very hard, according to this hardness description. As it can be observed from the graph shown in Figure 4.5, variation of total hardness in most seasons did not show similar trend.

Hard water can affect soil, stock and domestic water use, pipes and equipment. High hardness of aquatic ecosystem points out towards eutrophication (Pandey, 2008). It is evident that, hardness levels have a bearing on the toxicity of some metals. In general, these toxic effects are markedly less in waters with a significant degree of hardness. Increasing water hardness generally decreases metal toxicity, possibly due to calcium competition for the cell surface (Guèguen *et al.*, 2004). Hardness is an indication of the amount of calcium and magnesium in the water. Calcium and magnesium are essential elements for plant growth. Calcium in the range of 40 - 100 mg/L, and magnesium in the range of 30 - 50 mg/L are considered desirable for irrigation water.

Table 4.5 Total Hardness (mg/L) distribution at sampling sites within a year (quarterly reported)

Quarter	Sample code					
	A	B	C	D	E	F
1	302.13	302.3	274	281	295.3	326
2	358.66	262	511.66	256.33	585	302.66
3	408	248.8	325.8	363	515.3	311.66
4	446.3	381.3	456	447	500	490

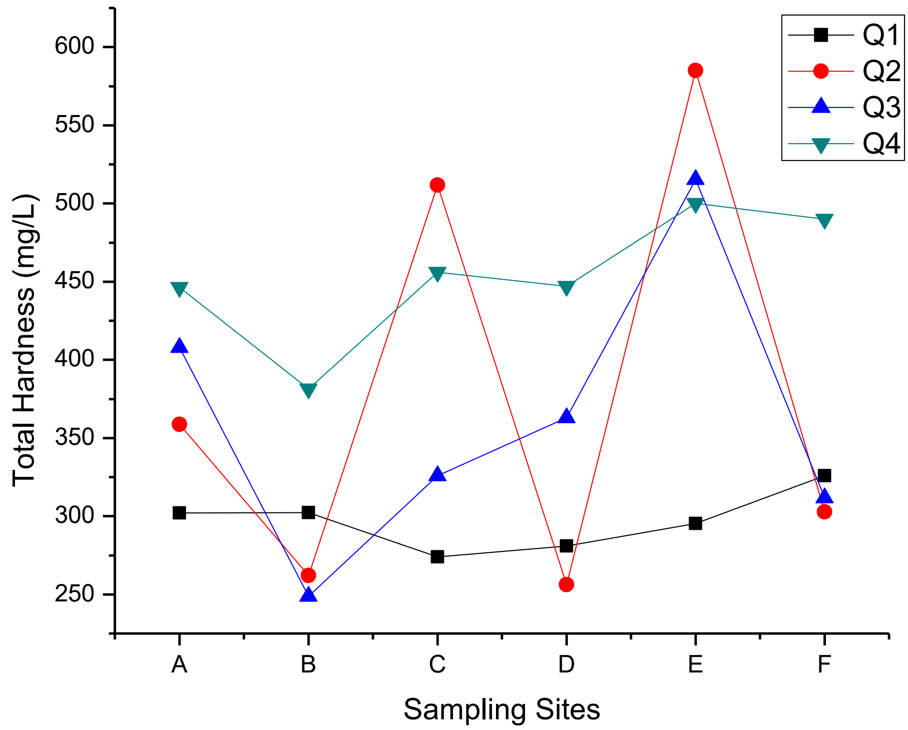

Figure 4.5 Total Hardness (mg/L) distribution of river Borkena at different sampling sites in quarter 1(Q1), quarter 2 (Q2), quarter 3 (Q3) and quarter 4 (Q4).

4.1.6 Chloride

Excess of chloride in inland water is usually taken as an index of pollution. The salts of sodium, potassium and calcium contribute to chlorides in water. High chloride concentration in the water may also be associated with the presence of sodium in drinking water. Chloride can be directly toxic to plants, and may contribute to raising the soluble salts or electrical conductivity (EC) level of the growing medium, or may inhibit water uptake by plants.

In the present study, the chloride ion content in Borkena river water samples ranged from 36 mg/L at site A in quarter 4 (i.e. June 2018, dry season) to 240 mg/L at site B in quarter 3 (i.e. March 2018, wet season) as can be seen from Table 4.6. The concentration of chloride in the Borkena river water samples were found within the limits of the CCME for use as irrigation water and the limits for domestic purpose fixed by EPA (1989), i.e., 250 mg/L as pointed out by Abegaz (2005).

The minimum value of chloride ion concentration is recorded at site A, in quarter 4 and it may be due to the decreased amount of domestic waste flow to the main river, because it is a dry hot season and the small stream that carried domestic wastes from the town gets very small in size. As it can be seen from the graph shown in Figure 4.6, variation of chloride ion concentration in all seasons show similar trend, i.e. the maximum values are recorded at sites B and D which are direct industrial effluent carriers, whereas the minimum values are recorded at site A which is a place found before the mix of industrial effluents and site F, a place far downstream from the point of mix of industrial discharges to the main river. Therefore variations in chloride concentration in river Borkena may probably be related to pollution through the discharge of industrial wastes into the river. It can be seen observed that a linear relationship existed between chloride concentration and EC throughout the study, i.e. chloride concentration increased with increase in EC.

Table 4.6 Chloride (mg/L) distribution at sampling sites within a year (quarterly reported)

Quarter	Sampling Sites					
	A	B	C	D	E	F
1	56	140	80	86.3	73.6	79.66
2	73.33	120	90	183.33	70.33	84
3	105	240	130	210	105	46.66
4	36	120	82	110	105	46.66

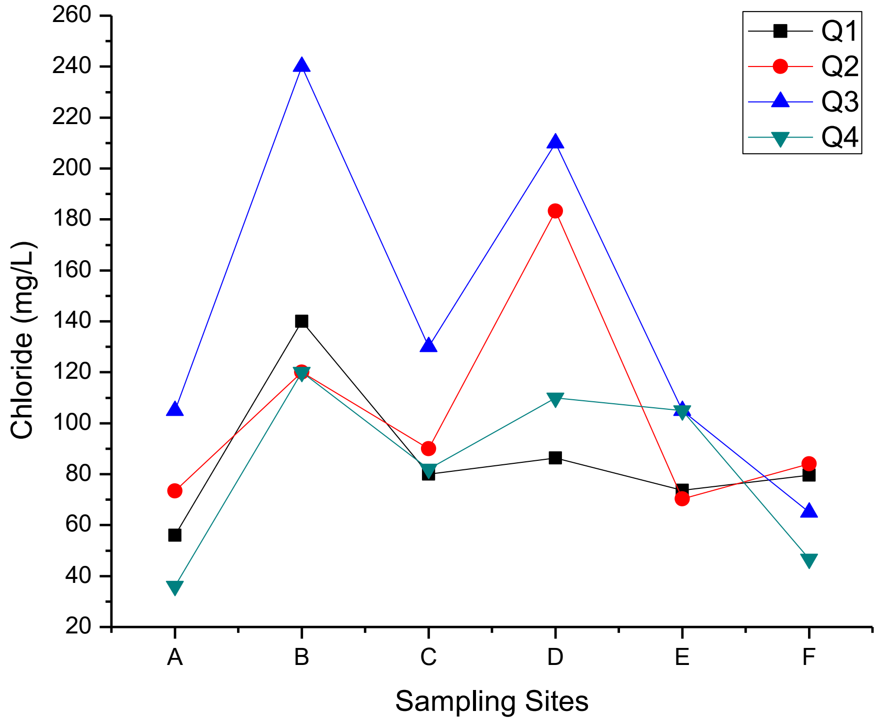

Figure 4.6 Chloride (mg/L) distribution of river Borkena at different sampling sites in quarter 1 (Q1), quarter 2 (Q2), quarter 3 (Q3) and quarter 4 (Q4).

4.1.7 Fluoride

One of the important anions in drinking water is fluoride. It is an essential element for human health and both its deficiency and over-exposure lead to adverse effects in teeth and bones. In relation to its effect on human health the optimum range of fluoride concentration in drinking water is very narrow. In a range of 0.7–1.2 mg/L, it is necessary for the prevention of dental caries but above 1.5 mg/L it causes dental and skeletal fluorosis (Center for Disease Control and Prevention (CDCP, 1999). According to the WHO guideline the maximum limits of fluoride in drinking water must not exceed 1.5 mg/L (WHO, 1994) and the same limit is recommended by Pakistan Environmental Protection Agency (PAK-EPA, 2008).

Large variation in fluoride concentration is not documented in all samples of water from river Borkena during the whole investigation periods as it can be seen from Table 4.7. The high concentrations of fluoride are attributed mainly due to leaching from fluoride-bearing minerals, industrial wastes, agricultural fertilizers and domestic wastes (Naseem *et al.*, 2010; Shah and Danishwar, 2003; Siddique *et al.*, 2006).

The maximum values of fluoride concentrations are recorded at site B and D throughout investigation period, where they are mainly containing industrial waste discharges from the surrounding industries but within the WHO limits. It is recorded 1.5 mg/L at site D in quarter 2 (December 2017, a dry season) and 1.3 mg/L at site B in quarter 4 (June 2018, a hot dry season). This may be due to low volume of river water that results from higher rate of evaporation which increases the concentration of fluoride in the water sample. The minimum values of fluoride are recorded at site A, upstream from the mixing point of industrial waste discharges to the main river throughout investigation periods in general, and it is 0.193 mg/L in quarter 4, which is below the WHO permissible limit. Variation of fluoride concentration throughout all seasons may not show similar trend as it can be observed from Figure 4.7, but it was present in levels high enough to damage foliage plants, it is because concentratio in irrigation water is expected to be less than 0.75 mg/L.

In general 66.6 % of the river water samples contain fluoride concentration within the WHO permissible limits for drinking water, and the rest 33.3% are below but not much far from the permissible limit.

Table 4.7 Fluoride (mg/L) distribution at sampling sites within a year (quarterly reported)

Quarter	Sampling Sites					
	A	B	C	D	E	F
1	0.51	0.903	0.713	0.9	0.75	0.66
2	ND	0.6	0.7	1.5	1.456	0.733
3	ND	0.44	0.93	0.95	0.963	0.713
4	0.193	1.3	1.00	0.67	0.38	0.35

ND: Not Detected

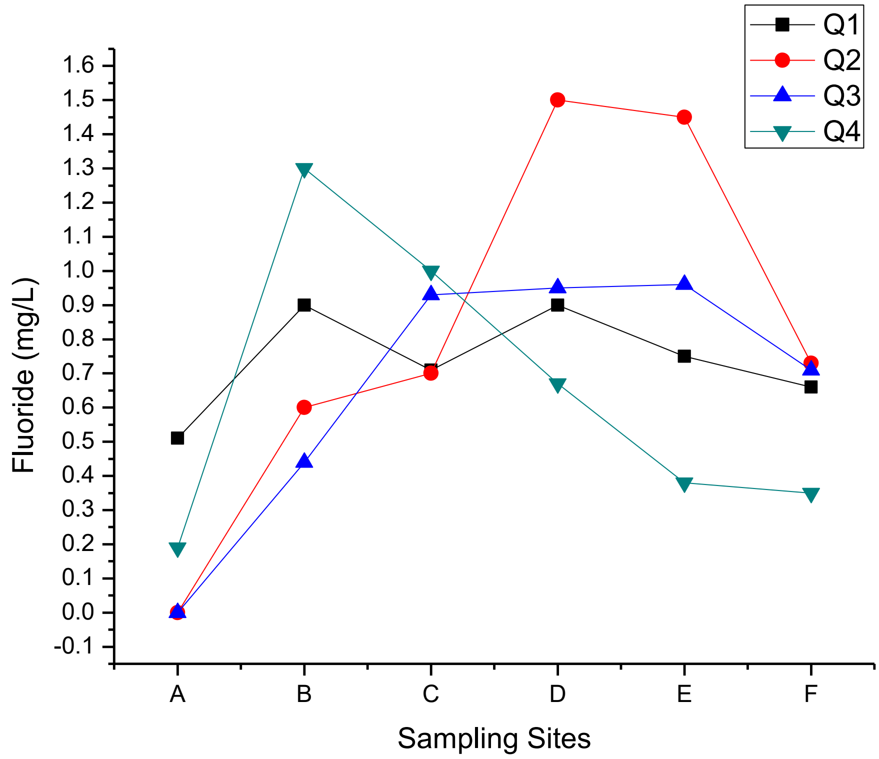

Figure 4.7 Fluoride (mg/L) distribution of river Borkena at different sampling points in quarter 1(Q1), quarter 2 (Q2), quarter 3 (Q3) and quarter 4 (Q4).

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4.1.8 Nitrates

Among the anions of nitrogenous compounds nitrates are important from the health point of view. These are usually measured during monitoring water pollution throughout the world. Exposure to nitrates from various environmental sources is possible; however drinking water is considered the main source. Normally surface water contain low concentrations of nitrates but can reach high values due to run off or leaching from agricultural lands (PAK- EPA, 2005b). The presence of higher value in water is an indication of pollution in the river and will cause eutrophication as a nutrient, hence reducing water quality.

Water samples from Borkena river contains nitrate concentration ranged from 0.14 mg/L at sampling site B in quarter 2 to 79 mg/L at sampling site F in quarter 1 as can be seen from Table 4.8. A relatively higher values of nitrate concentration in quarter 1, may be due to leaching of nitrogenous fertilizers from the agricultural farm lands near the river bank, since it is a wet rainy season. Most of the values recorded for nitrate were below the WHO permissible limits of 50 mg/L, except for few values recorded in quarter 1, but in general variation of nitrate concentration in all seasons may not show similar trend as it is observed from Figure 4.8.

According to WHO (GEMS, 1988), the maximum concentration of nitrate ion for public water supplies is 45 mg/L. The guidelines for drinking water quality of the European Community (EC, 1980) provide a reference value of 25 mg/L and a maximum admissible limit of 50 mg/L for nitrate.

The nitrates found in the water samples could have come from leaching and run-off from human activities such as agriculture where nitrogenous fertilizers are used in the farmlands along the river. Other sources such as domestic effluents and raw waste effluents from factories usually have relatively high levels of ammonia and nitrogenous wastes which can lead to rapid multiplication of bacterial population. These can elevate the levels of nitrates in the adjacent water bodies through aerobic and anaerobic bacterial activities (Nolan and Hitt, 2006).

Table 4.8 Nitrate (mg/L) distribution at sampling sites within a year (quarterly reported)

Quarte	Sampling Sites					
	A	B	C	D	E	F
1	19.3	70.4	17.86	14.9	66	79
2	2.56	0.14	15	3.36	4.46	3.7
3	ND	ND	ND	4.16	ND	2.40
4	3.23	2.56	ND	4.16	ND	2.40

ND: Not Detected

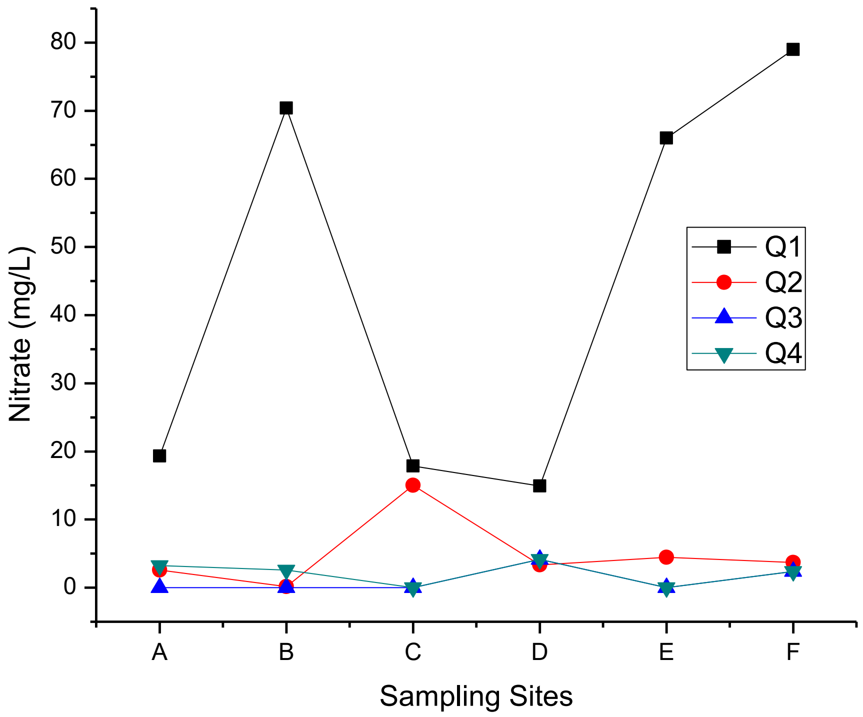

Figure 4.8 Nitrate (mg/L) distribution of river Borkena at different sampling sites in quarter 1 (Q1), quarter 2 (Q2), quarter 3 (Q3) and quarter 4 (Q4).

4.1.9 Alkalinity

Alkalinity of natural water is generally the result of content of bicarbonates and is usually expressed in terms of calcium carbonate. Its presence favours zooplankton populations (Singh et al., 2002; Kiran *et al.*, 2007). As it can be seen from Table 4.9, the maximum value of alkalinity was 320 mg/L at site D in quarter 4 (June 2018, dry hot season), while the minimum among measured values is 5 mg/L at site A and C in quarter 1 (September 2017, wet season).

Some values recorded in present investigations were above the permissible limit stipulated by ICMR, i.e. 120 mg/L (ICMR, 1975) especially in quarter 4. But as it is observed from Figure 4.9, variation of alkalinity in all seasons may show similar trend in such a way that it is increased at site F, a place which is far downward from the point of mix of industrial efluents. This mat be due to leaching of caronate rocks from the river banks as it go far downstream from the point of mix of industrial waste discharge points.

Table 4.9 Alkalinity (mg/L) distribution at sampling sites within a year (quarterly reported)

Quarter	Sample Sites					
	A	B	C	D	E	F
1	5	26.66	5	38.33	11.6	46.66
2	ND	ND	ND	ND	ND	134.13
3	246.6	26.6	ND	35	ND	ND
4	235	ND	ND	320	ND	255

ND: Not Detected

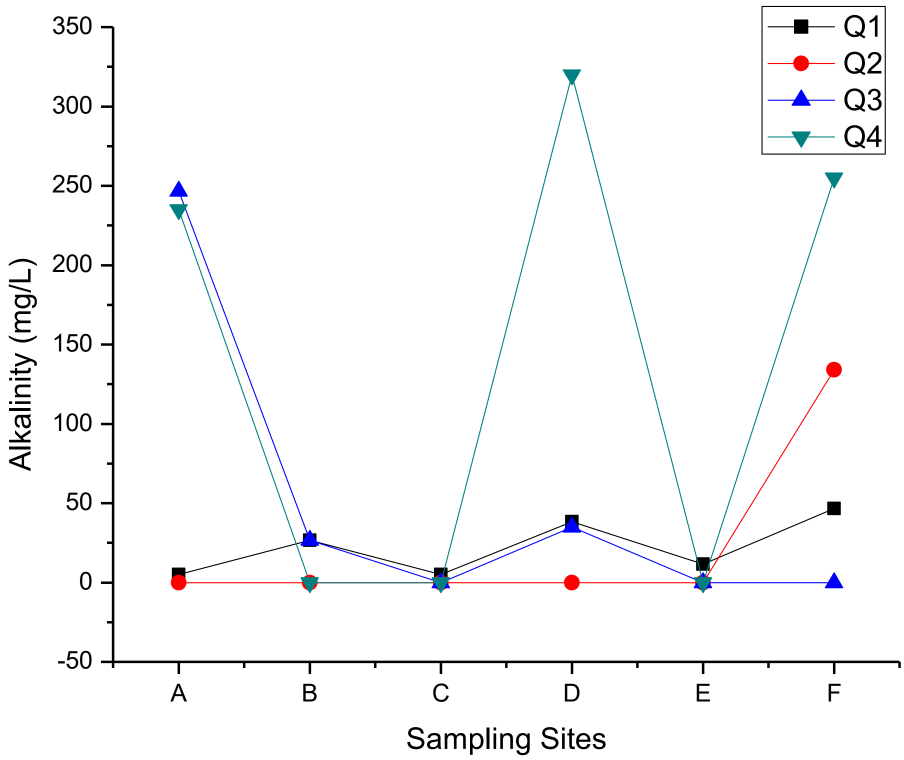

Figure 4.9 Alkalinity (mg/L) distribution of river Borkena at different sampling sites in quarter 1 (Q1), quarter 2 (Q2), quarter 3 (Q3) and quarter 4 (Q4).

Chapter 5 Effects of Contamination of Borkena River on Vegetables Grown in the Watershed. (A case study in Kombolcha town and the surrounding communities)

5.1 Introduction

There is high demand for water in developing countries due to population increase, urbanization, industrialization and agriculture (Chatanga *et al.,* 2019). This has resulted to water pollution especially in major towns and cities. River water quality is highly dependent on physical, chemical and biological quality of the hydrological system, because it is linked to human interactions (Udayakumar et al. 2014; Mukate et al. 2019). Water quality plays an important role in all aspects of human and ecosystem survival. Water quality degradation resulting from point and nonpoint source pollution has become a serious issue worldwide due to natural processes (e.g., weathering, precipitation, soil erosion, etc.), anthropogenic activities (e.g., agricultural, urban and industrial activities) and the increased utilization of water resources (Fulazzaky et al. 2010; Sharma and Bhattacharya 2017). The hydro-geochemical properties of water are important factors determining their use for domestic, industrial, and irrigation purposes; however, they are easily polluted due to their critical roles in transporting municipal and industrial pollution and runoff from agricultural land (Singh et al. 2004; Rahman and Hossain 2019). Thus, it is important to identify and understand the sources, their interactions, and effects of water pollutants.

Wastewater can contain different types of pollutants including metals, organics, pharmaceuticals and pathogenic organisms which can pollute the agricultural land and crop plants with potential environmental and human health risks (Khan et al., 2014; Lü et al., 2014; Bhatia et al., 2015; Meng et al., 2016; Zhang et al., 2019; He et al., 2020). Previous studies indicated that due to the scarcity of fresh water around the world, wastewater (treated and untreated) is extensively used to grow vegetables in municipal areas (Pedrero et al., 2010; Angelakis et al., 2018). According to Guadie A. (2020), in Ethiopia, almost in all parts of the country, wastewater is directly dumped into the surrounding environment without treatment. In some parts of the country, farmers used wastewater for irrigating their land to grow vegetables and other crops. Several studies have shown that, metals such as Fe, Mn, Ni, Zn, Cr, and Pb are among the few environmental contaminants mainly in areas irrigated with wastewater (Khan et al., 2008; Li et al., 2012; Qureshi et al., 2016; Sharma et al., 2008; Sultana et al., 2019). As a result of public and environmental health problems WHO and FAO have established the maximum permissible limits for metals content in water and vegetables.

One of the increasing major problems faced with the cultivation and consumption of ready-to-eat fresh produce has been the escalating rates of disease outbreaks (Uyttendaele *et al.*, 2015). Leafy green vegetables such as cabbage and lettuce have been classified by the World Health Organization (WHO, 2008) as a priority focus area relating to the safety of fresh produce from a global perspective. This is mainly due to the increased consumption of these raw vegetables and the frequency of disease outbreaks associated with leafy green vegetables. One common challenge of primary production across farming systems is the contamination of fresh produce with metals, arising from contaminated source of water for irrigation. It is therefore important to note that water is a significant source of contamination of food produce; for this reason, much attention has been given to the role of irrigation water in fresh produce supply chains. Vegetables have been an important part of everyday healthy foods and are regularly consumed by humans on a daily basis (Koubov´a et al., 2018; Manzoor et al., 2018;

Marles, 2017). Therefore the potential accumulation of toxins harboured in vegetables is very high (FAO/WHO, 2003, 2004b; Boeing et al., 2012; Azi et al., 2018).

The present study was carried out around the industrial areas of Kombolcha, Amhara regional state, Ethiopia, where irrigation of vegetables with wastewater is a very common practice. Knowledge on the contamination of vegetables with metals from industrial areas of Kombolcha is not well established yet. Therefore the aims of the current study were therefore to investigate and compare the extent of metals (Cr, Mn, Pb, and Zn) contamination of irrigation water, and leafy vegetables (Cabbage and Lettuce) grown in the Borkena watershed which is a major supplier of fresh produce around Kombolcha town and other areas with WHO and EU standards.

5.2 Methodology

This research employs a case study that examines the critical impacts of the waste carrier water when used for personal and agricultural consumptions by the communities within the watershed. The research consists two parts, where section a, deals with a qualitative research method and section b, deals with a quantitative methods to determine the concentration of metals in water and vegetable samples.

The researcher have done continuous field observations and conducted focus group discussions with selected farmers who have involved in irrigation practices using the wastewater and with experts from Kalu district agriculture office for collecting information, opinions and recommendations.

The researcher has selected three villages (Kedida, Chorisa and Tulu babogna) within the study area that are found downstream from the point of mix of industrial effluents. Three focus group discussions each of them containing 15 members have been conducted with farmers. The villages are selected for the study on the basis of their nearness to the point of mix of industrial effluents to the main river where higher concentration of contaminants are discharged through. The research also studied the extent of metal contamination of Borkena river water and its effects on vegetables grown on farmlands along the river bank.

5.3 Tools Used in the Study

The tools used in this research were focus group discussions with selected farmers and interviews with experts from the woreda (district) agriculture office that are included in section a, and laboratory determination of metal concentrations for water and vegetable samples which are included in section b. The desirable semi-structured open ended questions for focus group discussions with farmers and semi-structured open ended interview questions for experts were created and collected information directly from the participants. The questions for focus group discussion and experts were included in appendix B.

5.4 Sample collection, preservation and measurement

5.4.1 Irrigation water sampling

Water samples that have been used for irrigation practices were collected from each site in pre-cleaned polyethylene bottles. These bottles were soaked in 10% HNO_3 overnight and washed thoroughly with deionized water. The collected unfiltered samples were acidified by adding 2 mL of conc. HNO_3 per litre of the sample to avoid precipitation of metals. Samples were brought to the chemistry laboratory, Addis Ababa University, Addis Ababa, Ethiopia. The bottles were capped tightly and stored at 4 ^{0}C to prevent evaporation (Singh *et al.*, 2005; Sehgal *et al.*, 2012), until it prepared for making water digests.

5.4.1.1 Preparation of samples and measurement

The wastewater sample was shaken well and a 100 mL measured volume was treated with 10 mL of conc. HNO_3 in a conical flask. The flask was heated on a hot plate and digestion continued until the volume reaches 10 mL. After cooling, the solution was filtered and transferred quantitatively in to a 50 mL volumetric flask and adding distilled water up to the mark. Finally measurements for individual samples were made using ZEEnit 700 P FAAS (analytikjena).

5.4.2 Plant sampling

A diversity of vegetables are grown in the study area; among which cabbage and lettuce were collected from the sampling zone in 3 replicates and stored in labelled polyethylene bags and brought to the chemistry laboratory, Wollo university, Dessie, Ethiopia, where they were harvested in edible and non-edible parts, and finally washed with tap water to remove any kind of deposition like soil particles. Edible parts of vegetables were oven dried and ground into powdered form and stored in polyethylene bags until it used for acid digestion (Jamali *et al.*, 2009).

5.4.2.1 Preparation of samples and measurement

Wet digestion of duplicate samples of 0.5g of leaves of each vegetable were weighed in digestion flasks and treated with 5 mL of concentrated HNO_3. A blank sample was prepared applying 5 mL of HNO_3 into empty digestion flask (Sahito *et al.*, 2002). The flasks were heated for 3 hours at 80-90 ^{o}C and then the temperature was raised to 150 ^{o}C at which the samples were made to boil. Concentrated HNO_3 and 30% H_2O_2 were further added to the sample (3-5 mL of each was added occasionally) and digestion continued until a clean solution was obtained. After cooling, the solution was filtered with Whatman No. 42 filter paper. It was then transferred quantitatively to a 25 mL volumetric flask by adding distilled water. Finally measurements for individual samples were made using ZEEnit 700 P FAAS (analytikjena).

5.5 Data analysis

The information gathered were used for evaluation and analysis of data collected in different methods. The qualitative data for section a, from focus group discussions and experts interview were analysed and triangulated with quantitative descriptive statistics data for section b, which were tabulated and compared with international standards in order to explain the effects of metal contamination of Borkena river on the communities within the watershed. The results for quantitative determination of metals in wastewater and vegetable samples with some international standards are given in Table 5.1, below.

Table 5.1 Metal concentrations for irrigation water and vegetable samples

Sample code	Metal Concentrations (ppm)			
	Manganese (Mn)	Chromium (Cr)	Lead (Pb)	Zinc (Zn)
A/(Water)	0.0236	BDL	BDL	0.0988
B/(Water)	0.3323	BDL	BDL	0.0695
C/(Water)	0.0080	BDL	BDL	0.0860
D/(Water)	0.0040	BDL	BDL	0.0725
E/(Water)	0.0020	BDL	BDL	0.0878
F/(Water)	0.0022	BDL	BDL	0.0636
Lettuce /(Vegetable)	0.2323	BDL	BDL	0.2783
Cabbage /(Vegetable)	0.2199	BDL	BDL	BDL
Detection limit	-	0.012	0.007	0.024
FAO standard for irrigation water	0.2	0.1	5.0	2.0
Indian standard for irrigation water	0.1	0.05	0.1	5.0
WHO/FAO standard for leafy vegetables	2.3	-	0.3	100
EU standard for leafy vegetables	-	-	0.3	-
Indian standard for leafy vegetables	20	-	2.5	50

Note: BDL= Below Detection Limit

EU standards for leafy vegetables, (EU, 2002, 2006)
Indian standard for leafy vegetables, irrigation water, (Awashthi S.K., 2000)
WHO/FAO standard for leafy vegetables, (WHO/FAO, 2001, 2003, 2007)
FAO standard for irrigation water, (FAO, 1985)

Table 5.2 FAO water quality standards for irrigation water

Water quality parameters	pH	EC (µS/cm)	TDS (ppm)	Turbidity (NTU)	Chloride (mg/L)
FAO standard for irrigation water	6.5 – 8.4	700 - 3000	450 - 2000	-	< 350

Water quality parameters	Fluoride (mg/L)	Nitrate (mg/L)	Tot. Hardness (mg/L)	Alkalinity (mg/L)
FAO standard for irrigation water	< 1.0	< 50 but no concern for plants	< 150	< 150

FAO standard for irrigation water, (FAO, 1985)

5.6 Results and discussions

5.6.1 pH

From the point of view of water quality suitability for irrigation purposes, the pH of the river water is in the safe limit of WHO/FAO standards throughout investigation in all sites as it can be seen in Table 5.2. pH values obtained in this study were slightly acidic than the pH values (7.5 –8.45) recorded for urban streams in Machakos municipality, Kenya (Tomto R.M. *et al*., 2020)

5.6.2 Electrical Conductivity (EC)

In general electrical conductivity (EC), is one factor which contributes for salinity problems in water bodies. It ranges from (500 – 1287) µS/cm in which it is moderately polluted to be used for irrigation purposes. Even if it is within the safe limits from the basis of WHO/FAO irrigation water standards, as can be seen from Table 5.2, frequent uses of this water for growing vegetables may bring about foliar drying and reduced productivity of leafy vegetables such like lettuce. This fact is also supported by the focus group discussion results, According to the responses for question No 11 and 16 of the focus group discussion (Appendix A), farmers in the study area have suggested that drying of leafy vegetables could be the consequence of the river water pollution. In addition to this, the researcher has also observed, farm lands grown with lettuce were burned their leaves that was irrigated by waste effluent water of Worka stream as it can be seen in photograph 1.4.

5.6.3 Total Dissolved Solids (TDS)

Total dissolved solids (TDS), contribute to the salinity of the water body in a similar way to electrical conductivity (EC). Its value ranges from (248 - 645) mg/L throughout study. Even if these values are below the WHO/FAO maximum allowable concentration (MAC), for irrigation water as it can be observed from Table 5.2, frequent use of this water may have additive effect to cause foliar drying and reduced productivity of leafy vegetables grown in the watershed. This result is also supported by the responses obtained from the focus group discussions and experts interview of question No 11, 12 and 16 (Appendix A), in such a way that, changes in colour, reduced productivity and drying of leafy vegetables are suggested by farmers and experts as the main problems in the watershed.

5.6.4 Chloride

The chloride concentration ranges in this study from (36–240) mg/L in all investigations, which is of course below the WHO/FAO standards for irrigation water Table 5.2). Maximum values are reported from sites B & D which are industrial effluents carried by Loyale and Worka streams respectively. Since chloride concentration is one factor that contribute to salinity problems, it may result in foliar drying of leafy vegetables and reduced productivity observed in the watershed. This result is also supported by the focus group discussion of question No 11, 12 and 16 (Appendix A), in which respondents suggested that, reduced productivity of vegetables grown in the watershed is one of their problems and mainly its sources could be the industrial wastewater. As can be seen from Table 5.3, according to Ayers and Westcot (1985), except for sites B and D, the Borkena river water shows very slight restriction for agricultural use. But sampling sites B and D, are Loyale and Worka rivers respectively which are direct industrial effluent carriers, so that they show slight to moderate restriction for agricalural use.

Table 5.3 Water quality standards for agricultural use (Ayers and Westcot, 1985).

Potential Irrigation Problems	Units	Degree of Restriction		
		None	Slight to moderate	Severe
Salinity				
EC	(µS/cm)	< 700	700 – 3000	> 3000
TDS	(mg/L)	< 450	450 – 2000	> 2000
Specific Ion Toxicity				
Chloride	(mg/L)	< 140	140 – 350	>350

5.6.5 Trace Elements

In the present study, the concentrations of metals are generally in the safe limit of the WHO/FAO standards for both irrigation water and leafy vegetables. Among leafy vegetables which undergo analysis, lettuce stored metals more than cabbages. Only manganese (Mn) and zinc (Zn) are observed with significant amounts which are essential elements for plant growth and they are below the maximum permissible limit of the WHO/FAO standard. Chromium (Cr) and the toxic element Lead (Pb) are found with a very small amount and below detection limit in both irrigation water and leafy vegetables. A maximum lead (Pb) limit for human health has been established for edible parts of crops by World Health Organization (WHO) to be 0.3 mg/kg (FAO/WHO, 2001), but this limit in China is 0.2 mg/kg (Chinese Department of Preventive Medicine, 1995). According to Singh *et al*. (2010), lead (Pb) is a non-essential element, is toxic, and not required by organisms at any level.

The average metal concentrations of Borkena river are given to be: 0.0620 mg/L for Mn, 0.797 mg/L for Zn, whereas Pb and Cr are below detection limits. But according to Abegeaz S.M. (2005), the average metal concentrations of Tinishu Akaki River (TAR) are given to be: 0.854 mg/L and 0.951 mg/L for Mn, and 0.0373 mg/L and 0.0178 mg/L for Zn in seasons I and II respectively. TAR is a river in the capital Addis Ababa, Ethiopia, which carries many kinds of wastes from different, sources (domestic, industrial, agricultural) and expected to be highly polluted. As it can be observed from the data, the average concentration of Mn in Borkena river is much smaller than TAR but the average Zn concentration in Borkena river is larger than TAR. In general the metal concentrations in vegetables produced in Borkena watershed are within the permissible limits of FAO/WHO standards. Therefore the problems suggested by farmers participated in the focus group discussions may not be related with metal contamination of the river water.

5.7 Conclusions

In this study, most of the water quality measurements fall within the WHO permissible limits for drinking water. But some of the values for turbidity and alkalinity were beyond the permissible limits, which indicate pollution of river Borkena by extraneous substances, especially from industrial effluents. In general water quality parameters for Borkena river shows significant spatial variations than seasonal variations. From the basis of irrigation water quality, even if most parameters fall within the safe limits of WHO/FAO irrigation water standards, frequent uses of this water for growing vegetables may bring about foliar drying and reduced productivity of leafy vegetables such like lettuce. On the other hand the results for metals reveal that Mn showed relatively high concentration in irrigation water sample, i.e. a little bit more than the WHO/FAO standard, but in the safe limit for vegetables. The other metals found below the permissible limits of WHO/FAO standards for irrigation water and vegetables. This study provides a brief insight into the current scenario of vegetable contamination and possible future health risk overview. A need exists to monitor the wastewater and vegetables of the study area and to develop different strategies to prevent the accumulation of metals in vegetables that may ultimately minimize the chronic health risk to the exposed population.

5.8 Recommendations

The use of sewage water for irrigation has gained importance throughout the world due to limited water sources and wastewater treatment costs for discharge. The availability of land with suitable topography, soil characteristics and drainage enables the sewage effluent to be applied as a source of both irrigation water and plant nutrients. Sewage water contains a high amount of organic matter, nutrients and certain metals that are toxic to plants when present above a certain limit.

It was observed that different vegetables accumulate and translocate variable amounts of metals from the soil into their tissues. To avoid the absorption of these metals, most of the vegetable species growing in metal-polluted areas cannot be consumed. But in this study the accumulation of toxic metals in vegetable samples due to the sewage water irrigation is very small and not significant for the time being.

The study presents findings from assessment on metal contamination in irrigated urban vegetable farming around Kombolcha and the surrounding communities. The assessment was done to determine whether metal contamination should be a present concern to public health, and also to encourage future studies as metal contamination is expected to be a challenge in Borkena watershed in the near future if not well addressed.

Continuous irrigation of agricultural lands by wastewater for several years increased metals in soils and plants. The concentrations of metals in vegetables will provide baseline data and it shows that, in the current situation consumption of vegetables grown in the study area may not have health risks in the context of metal concentrations. To avoid the entrance of metals into the food chain, municipal or industrial wastes should not be drained into river and farmlands without prior treatment. The continuous monitoring of the soil, vegetable plant and irrigation water quality are prerequisites for the prevention of potential health hazards to human beings.

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Appendix A: Interview questions for focus group discussion

Research Title: Assessment of industrial waste load of River Borkena and its effect on Kombolcha town and the surrounding communities.

Interview questions

1. What attitudes and opinions do people have about the present quality of Borkena River and about the effects this water could have on:

   i) People?

   ii) Animals?

   iii) Plants?

2. Do people use this river water for bathing? Yes ☐ No ☐
3. If the answer to (2) is yes, what changes have you noticed on their health?
4. If the answer to (2) is no, explain why not people used the river water for bathing.
5. Have people ever used this river water for drinking purposes?

   Yes ☐ No ☐

6. If the answer to (5) is yes, what changes have you noticed in their health?
7. If the answer to (5) is no, explain why not people used the river water for drinking purposes.
8. Have animals ever used this river water for drinking purposes?

   Yes ☐ No ☐

9. If the answer to (8) is yes, what changes have you noticed in their health?
10. If the answer to (8) is no, explain why not animals used the river water for drinking purposes.

11. If there is any difference in productivity of the land that has been used for growing plants by using this river water for irrigation purposes, what kind of differences have you observed in recent years?
12. Do people think Borkena River is polluted? (If yes, explain your opinion of the level of pollution in Borkena River. i.e. high, medium, or lowpollution level)
13. Why do people think the Borkena River is polluted? (Opinion of how serious the following potential issues are in the watershed: overpopulation, industrial pollution, agricultural pollution, sewage discharge, poor water quality or any other issue/s.
14. How do people think water quality in the Borkena River can be improved? (Opinion of management strategies for improving water quality. eg. reduction in industrial discharges, reduction in sewage discharges, improving or enforcing laws, or any other issue/s)
15. Is there a difference in the level of impact how the industrial waste load influenced the life of the people in the watershed? (i.e. in urban, suburban and rural area) For professional district officers.

    Yes ☐ No ☐
16. If the answer to (15) is yes, explain the difference how the industrial waste loads influenced people’s life in the watershed. (i.e. in urban, suburban and rural area) For professional district officers.