ASSESSMENT OF WATER QUALITY FROM SECTIONS OF RIVER CHANIA ADJACENT TO LEATHER INDUSTRIES OF KENYA LIMITED, KIAMBU COUNTY- KENYA

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I56/CE/28298/2013

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE (ANALYTICAL CHEMISTRY) IN THE SCHOOL OF PURE AND APPLIED SCIENCES OF KENYATTA UNIVERSITY

NOVEMBER, 2025

DECLARATION

This thesis is my original work and has not been presented for a degree or any award in any other University

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DEDICATION

I dedicate this work to my husband Francis, my children; Waveney, Lesley, Elvis and Britney for being a source of encouragement throughout the study.

ACKNOWLEDGEMENTS

I am deeply grateful to God for the journey that has brought me to this point. I extend my heartfelt appreciation to my supervisors, Prof. Mildred Nawiri and Prof. Alphones Wanyonyi from the Department of Chemistry at Kenyatta University, for their invaluable guidance and encouragement. I am grateful to Miss Jane, the chief lab technician in the Chemistry Department, along with the entire technical staff from the chemistry, environmental science, agriculture, science and technology as well as food, nutrition and dietetics departments, for their assistance with laboratory procedures and instrumentation. Additionally, I am thankful for the support and insights provided by my peers during my research. Finally, I sincerely appreciate my family for financial, moral, and spiritual support throughout the research period.

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ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectrophotometer
APHA	American public Health association
ANOVA	Analysis of variance
AWWA	American Water Works Association
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DNA	Deoxyribonucleic Acid
DO	Dissolved Oxygen
EC	Electrical Conductivity
EPA	Environmental Protection Authority
FAS	Ferrous Ammonium Sulfate
IARC	International Agency for Research on Cancer
LIK	Leather Industries of Kenya Limited
NEMA	National Environmental Management Authority
pH	Potential of Hydrogen
PVC	Polyvinyl Chloride
SPSS	Statistical package for Social Sciences
TDS	Total Dissolved Solids
TS	Total solids
TSS	Total Suspended Solids
UNEP	United Nations environmental program
USEPA	United States Environmental Protection Agency
UV-Vis	Ultraviolet-Visible Spectroscopy
WEF	Water Environmental Federation
WHO	World Health Organizations
WRA	Water Resource Authority

ABSTRACT

River Chania in Kiambu County, Kenya serves as one of the vital water sources for domestic, industrial and agricultural use, and supports aquatic life. A section of the river flows adjacent to the Leather Industries of Kenya Limited (LIK), which is involved in leather tanning processes, hence this river is prone to pollution from LIK. Water pollution from industrial effluents, agrichemicals, and residential waste remains a global challenge to safe and clean water. According to WHO, various physico-chemical parameters such as pH, Electrical Conductivity (EC), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Total Suspended Solids (TSS), total phenols and heavy metals are used to assess water quality? The study aimed to assess the water quality of river Chania in proximity of LIK. Water samples were collected during the long rains and short rains seasons from the upstream, midstream and downstream sections of the river. The physico-chemical parameters were analyzed using methods developed by the American Public Health Association (APHA), heavy metals were analysed by Atomic Absorption Spectroscopy (AAS), while total phenols were analysed via UV-Vis Spectroscopy. Data was analyzed using R software with One-way ANOVA applied to determine significant differences in parameters across the sampling points in long rains and short rains seasons. Results showed that levels of PH (6.98-7.11), EC (133-250 µS/cm) and COD (20.7-43.7 mg/l) in short rains and pH (6.68-6.76), EC (109-195 µS/cm) and COD (16.8-32.4 mg/L) in long rains seasons, were within WHO acceptable limits, while TSS levels (170-1841 mg/L) and BOD levels (10.50-15.40 mg/L) midstream exceeded the WHO limits in both seasons. Additionally, the concentration of Cr (0.119-0.191 mg/L), Pb (0.016- 0.025 mg/L) and total phenols (0.038-0.143 mg/L) during the long rains season and Cr (0.103- 0.160 mg/L), Pb (0.013-0.02 mg/L) and total phenols (0.007-0.116 mg/L) in short rains season exceeded the WHO limits except Cd (0.003-0.004 mg/L) in long rains and Cd (0.002-0.003 mg/L) in short rains season. Significant variations in the water quality parameters were observed across the river sections, with the highest levels at midstream during both seasons ($p<0.05$). These findings suggest contamination of the river by industrial effluents, agricultural run offs, domestic and sewage wastes, highlighting the need for strict regulatory waste discharge measures, community engagement, and the adoption of technological solutions to mitigate pollution and safeguard water quality.

CHAPTER ONE: INTRODUCTION

1.1 Background of the study

Water is a vital life resource extensively used in home, industrial, and agricultural settings (Tzanakakis *et al*., 2020). Furthermore, all living things, including plants and higher-order animals like humans, need water to survive (Towfiqul *et al*., 2020). Humans can survive for a long duration without food but not water (Igwe *et al*. (2015). Besides, it is essential for humans because it helps the body replace lost fluids occasioned by different physiological processes (Ajloon *et al*., 2022). Additionally, it helps the body's systems eliminate pollutants (Adjovu *et al*., 2023). Given that water is a basic human necessity, obtaining a high quality of life depends on the water's quality (Zhou *et al*., 2017).

Rivers are the most essential water resources globally, with vital role in transportation, serving as a primary water source for various uses (Hasan *et al*., 2020). Additionally, they support the ecosystem, which are integral to the natural water cycle (Ustaoğlu *et al*., 2020). According to Chebet *et al*. (2020), in many regions worldwide, water sources including rivers are crucial for communities. In Kenya rivers are vital for sustaining livelihoods, supporting the economy and maintaining ecosystem. Also, they contribute to biodiversity, facilitate agricultural activities and generate hydroelectric power (Bhuyan and Bakar, 2017). One such river is Chania river which originates from slopes of Kinangop and Aberdare range (Robert *et al*., 2021). Besides, it is a key water source for irrigation and domestic use for nearby communities. However, despite its importance, the river faces significant pollution challenges due to waste discharge from urban areas, agricultural runoff and industrial activities, including those from nearby Leather Industries of Kenya Limited.

Natural water sources are often exposed to various contaminants including organic, inorganic and biological contaminants (Ustaoğlu and Tepe, 2019). According to Zhou *et al*. (2017), Phenols for instance have a vital role in assessing water quality and can pose health risks when present in concentration exceeding the safe limit. Among the most prevalent pollutants in natural water are heavy metals which raise serious concerns due to their accumulation in the human body even in low levels (Othman *et al*., 2018). Some heavy metals, such as hexavalent chromium (Cr^{6+}), are classified as carcinogenic, while trivalent chromium (Cr^{3+}) is relatively non-toxic. Cadmium (Cd^{2+}) is both genotoxic and cytotoxic while prolonged exposure to Pb^{2+} can lead to neurological damage, renal impairment, and developmental disorders, especially in children (Nyantakyi *et al*., 2019). Besides some such as Zinc may not be highly toxic but can still compromise water quality when present in drinking water (Custodio *et al*., 2020). In addition to heavy metal concentration, several water physio-chemical parameters are also key in evaluating water quality (Hoess and Geist, 2022).

The increasing human population and expanding urban activities have contributed to deterioration of water sources occasioning growing water shortage (Zhao *et al*., 2018). A study by Zhou *et al.* (2017) established that in Yinma river basin in China, phenol level in water and sediments varied by season, measuring 10.68mg/L in short rain season and rising to 127.76mg/L in long rains season. Industrial activities in cities such as Chanchun, Jutai and Dehui were identified as major contributors to this contamination. Similarly, rivers are highly vulnerable to pollution from industrial effluents, including those from the leather industries (Ojekunle *et al*., 2023). In their study, Ojekunle *et al*. (2023) indicated that heavy metals serve as key indicators of water quality, with Pb, Cr, Fe, Ni, Cd and Cu concentrations exceeding WHO recommended limits, in some locations such as in Ota and Agbara locations.

According to Jung *et al*. (2016), the release of tannery effluents into the river significantly degrades water quality, posing serious risk to both human health and aquatic ecosystems. Additionally, agricultural activities especially widespread use of commercial fertilizers, organo-pesticides, insecticides and herbicides lead to chemical contamination (Nyantakyi *et al*., 2019; Hoque *et al*., 2023). Many of these agricultural chemicals persists in the environment due to their resistance to natural degradation, further exacerbating water pollution (Hoess and Geist, 2022; Ojekunle *et al*., 2023).

The leather industry is a significant contributor to water pollution due to its use of various chemicals in processing of raw hides and skins into leather (Brêda *et al*., 2020). These chemicals include acids, alkalis, lime, caustic soda and sodium and chromium salts, all have diverse environmental effects (Masum and Islam, 2020). Tanneries in particular are major contamination sources in rivers. River Ganda in Northern India sediments contained Cr (15.29 mg/L), Cd (0.22-0.38 mg/L) and Pb (0.54-0.71 mg/L) exceeding WHO limits (Singh *et al*., 2017). One of the heavy metals with significantly higher concentration is Cr primarily originating from industrial sources. This study identified key industrial contributors of Cr including cement production, leather processing among others (Valesntín- Reyes *et al*., 2019). Similarly, industrial activities have been linked to Cr contamination in water sources (Viczek *et al*., 2020). The most commonly detected form of Cr, hexavalent Cr is a potent oxidizing agent, particularly in acidic conditions (Liang *et al*., 2021).

In Ethiopia, a study by Amanial, (2016) revealed that River Modjo which receives tannery effluents exhibited heavy metal levels and physicochemical parameters which were beyond the WHO standards. The WHO has established permissible limits for various water quality parameters including pH (6.5-8.5), EC (700 µS/cm), BOD (10 mg/L) COD (50 mg/L) and TSS (30 mg/L) (WHO, 2022). However, water samples from river Modjo showed values beyond these limits: pH (8.33-9.33), EC (14496 µS/cm), TSS (2,647–4,979 mg/L), BOD (5,555–6,111 mg/L), and COD (842–960 mg/L), making the water unsuitable for irrigation, domestic use, or recreational activities.

In Kenya, research has shown that a medium-sized tannery can release more than 300 million cm^3 of waste from not only liquor production but also tanning sludge, with chromium reaching up to 5,200 mg/L (Oruko *et al*., 2021). A separate study on wastewater from Asili Tanneries reported chromium and total phenol concentrations of 33,000 mg/L and 3.97 mg/L, exceeding the National Environment Management Authority (NEMA) discharge limits of 2.0 mg/L for chromium and 0.001 mg/L for total phenols as revealed by Oruko *et al*. (2014). When such wastewater is released into nearby water bodies like Nairobi River, it contributes significantly to water pollution. Similarly, river Chania whose sections flow near the Leather Industry of Kenya (LIK), is vulnerable to contamination from tannery effluent discharge.

Previous research on River Chania found that pH and EC levels were within WHO-recommended limits at 8.44 and 316 µS/cm, respectively (Kimani *et al*., 2016). However, several other water quality parameters exceeded WHO thresholds, including total dissolved solids (TDS) (149 mg/L), alkalinity (154 mg/L), ammonia (41.00 mg/L), phosphate (3.50 mg/L), total hardness (156.87 mg/L), sodium (17.44 mg/L), potassium (8.51 mg/L), copper (0.29 mg/L), and lead (2.5 mg/L). Another study on River Chania found that during long rain season, pH levels ranged from 5.88 to 6.83, slightly below WHO standard of 6.5–8.5, while in short rain season, pH remained within acceptable limits Robert *et al*. (2021).

However, key parameters such as total phenols, chromium (Cr), cadmium (Cd), BOD, COD, and TSS have not been adequately assessed in river Chania, especially in areas around LIK. The present study aims to evaluate these physicochemical parameters, selected heavy metals and total phenols in water samples from sections of River Chania near LIK. This information is essential for developing wastewater treatment strategies to mitigate pollution before effluent discharge into rivers. Ensuring proper wastewater treatment not only safeguards water quality but also promotes agricultural productivity, protects human health, and preserves aquatic ecosystems.

1.2 Problem Statement

Water is a fundamental resource essential for sustaining life, supporting ecological balance, and driving economic and social development (Tzanakakis *et al*., 2020). However, global water resources are increasingly threatened by scarcity and pollution. Approximately 3.6 billion people experience water shortages for at least one month annually, primarily due to climate change, population growth, and pollution (Tzanakakis *et al*., 2020). According to López *et al*. (2022), regions historically dependent on consistent rainfall or seasonal snowmelt now face irregular water supply. This is due to climate change, which disrupts rainfall patterns, alters precipitation, and increases evaporation, reducing freshwater availability (Dalezios *et al*., 2018; Ojekunle *et al*., 2023).

At the same time, pollution from human activities further exacerbates this crisis by degrading water quality, hence reduce the availability of safe water, posing serious health risks (Singh *et al*., 2017; Wang *et al*., 2021; Jeong *et al*., 2020). In developing countries like Kenya, the problem is intensified by inadequate wastewater treatment infrastructure (Uddin *et al*., 2018). Among various industrial pollutants, tannery effluents are ranked the most hazardous due to its complex mixture of organic and inorganic compounds, including heavy metals such as chromium, cadmium, and lead, as well as phenols, acids, and alkalis (Masum & Islam, 2020; Brêda *et al*., 2020). These pollutants not only alter the physicochemical characteristics of water but also bio accumulate in aquatic organisms, posing severe health risks such as dermatitis, organ damage, and cancer in humans (Hasan *et al*., 2020; Olusegun & Martincigh, 2021 Vandana *et al*., 2022).

River Chania, a crucial source of water for irrigation, domestic use, and economic activities is under pollution threat emanating from human activities, notably from the Leather Industries of Kenya Limited (LIK), a major tannery located along its course. Reports suggest that LIK releases partially treated effluents containing heavy metals and organic pollutants into the river, potentially exceeding WHO and NEMA standards. Previous studies focused mainly on pH, EC, Cr, and Pb (Kimani *et al*., 2016; Robert *et al*., 2021) leaving critical parameters such as Cd, BOD, COD, TSS, and total phenols underexplored, especially in areas near LIK. Therefore, this study aims to evaluate selected heavy metals (Cr, Cd, Pb), total phenols, and key physicochemical parameters (pH, EC, BOD, COD, TSS) in water from sections of River Chania adjacent to LIK. This leaves a gap in knowledge of the extent of pollution, hence hindering implementation of effective strategies for wastewater management, ultimately protecting public health, promoting agricultural sustainability, and conserving aquatic ecosystems.

1.3 Justification of the Study

Heavy metal contamination poses a significant threat to both environmental and public health due to its persistence, bioaccumulation, and toxicity (Othman *et al*., 2018; Mitra *et al*., 2022). Although the global and national impacts of heavy metals are well recognized, there remains limited local data on the extent of contamination in key water sources such as River Chania. This river is a vital source of water for domestic, industrial, and agricultural use in Thika and surrounding areas, yet it is highly susceptible to pollution from nearby industrial activities, particularly the Leather Industries of Kenya Limited, which reportedly discharges partially treated effluents into this river.

According to Chebet *et al*. (2020), anthropogenic pollution by heavy metals primarily originates from human activities including agriculture, power industries, leather industries, transport sector and municipal waste management facilities. These pollutants accumulate in water bodies, posing serious environmental and health risks, and necessitating urgent measures to monitor and mitigate contamination levels. Tannery effluents are known to contain high concentrations of hazardous metals such as chromium, lead, cadmium, and copper, which can persist in aquatic environments and pose serious health risks to humans and aquatic organisms (Othman *et al*., 2018; Hoque *et al*., 2023). Given these risks, it is critical to assess the current contamination status of River Chania with reference to WHO recommended limits. This study will provide essential evidence to inform policymakers, environmental agencies, and local authorities in formulating effective monitoring, regulation, and mitigation strategies aimed at protecting public health and maintaining ecological integrity.

1.4 Hypothesis

There are no significant differences in physiochemical parameters, total phenol and heavy metals across the sections of river Chania adjacent to Leather Industries of Kenya Limited during long rains and short rains seasons, and the levels do not exceed the WHO permissible limits.

1.5 Objectives

1.5.1 General Objectives

To assess the quality of water from sections of River Chania adjacent to Leather Industries of Kenya Limited, in Kiambu County, during long rains and short rains seasons.

1.5.2 Specific Objectives

i. To determine levels of pH, EC, TSS, BOD and COD in water from upstream, midstream and downstream sections of River Chania adjacent to Leather Industries of Kenya Limited, in long rains and short rains seasons.

ii. To determine levels of total phenols and selected heavy metals (Cd, Cr and Pb) in water from upstream, midstream and downstream sections of River Chania adjacent to Leather Industries of Kenya Limited, in long rains and short rains seasons.

1.6 Significance of the study

This study is crucial in environmental conservation and maintaining ecosystem health. Examining the water quality in sections of river Chania near leather industries provides valuable insights into how pollutants from these industries influence aquatic systems. The leather production process involves hazardous chemicals including Cr and phenols which can harm aquatic organisms and plant life leading to reduced biodiversity and disrupting natural balance of river ecosystem. This study findings will be instrumental in guiding environmental agencies to implement measures that protect the biodiversity of River Chania.

Water from river Chania is used directly or indirectly by the local community not only for domestic purposes but also for agriculture and recreation. Contaminants in the water sources pose severe impacts including diseases such as cancer, organ damage and development challenges. Therefore, understanding the contamination levels and identifying of the pollutants is essential in safeguarding public health ad preventing waterborne diseases. Clean water is critical for agriculture and fishing activities along the river. When polluted, it negatively impacts agricultural yield, contaminate the crops and affect the local livelihood which depends on river Chania for irrigation water. Therefore, quantifying and highlighting the pollution issues, supports the economic interest of the communities relying on the river as a resource.

Additionally, this study promotes accountability among industries near the river. The findings will encourage industries to implement proper effluent treatment methods before discharging waste into River Chania. Furthermore, the study provides scientific data necessary for developing water quality regulations and industry wastewater policies. Based on the findings, regulatory bodies such as Water Resource Authority (WRA) and United Nations Environmental Programs (UNEP) can establish stricter waste disposal guidelines, enforce discharge limits and mandate clear production methods. Moreover, this research serves as baseline data for future studies on water quality trends in the region, particularly long-term changes due to industrialization.

1.7 Scope and limitation of the study

This study focused on assessing the physicochemical quality of water, total phenols and selected heavy metals (Cr, Pb, and Cd) from selected sections of River Chania adjacent to the Leather Industries of Kenya Limited. Water samples were collected from upstream, midstream, and downstream sections relative to the tannery discharge area to determine variations in contamination levels and possible influence of industrial effluents. The study period covers both the wet and dry seasons to capture seasonal variations in pollutant concentrations. The results are expected to provide insights into the extent of industrial impact on water quality and contribute to environmental monitoring and sustainable management of the River Chania ecosystem.

This study was limited to a small section of River Chania adjacent to the Leather Industries of Kenya Limited; therefore, the findings may not represent the overall water quality of the entire river. Although sampling was conducted during both wet and dry seasons, the study did not cover multiple years, which could better reveal long-term trends. Resource and time constraints limited the number of sampling points and laboratory analyses to selected parameters only. Furthermore, access to detailed industrial effluent data, discharge volumes, and upstream pollution sources was limited, making it difficult to quantify the exact contribution of the tannery to observed contamination levels. Nevertheless, the study provides valuable baseline information and highlights critical areas for future research and monitoring.

CHAPTER TWO: LITERATURE REVIEW

2.1 Water Supply and Scarcity

Water is essential for humans, animals, and plants, yet its supply is declining due to population growth, urbanization, industrialization, and climate change (Oruko *et al*., 2014). Despite global efforts to increase water supply through improved infrastructure, updated water management strategies, and technological innovations, many regions still face severe water scarcity (Tzanakakis *et al*., 2020). Over two billion people live in areas with high water stress, and more than one billion lack access to clean and safe drinking water, resulting in approximately 1.4 million deaths annually from water-related diseases (Tzanakakis *et al.,* 2020).

Water scarcity poses a major challenge to agriculture, domestic use, and economic stability, with agriculture consuming about 80% of available water (Dalezios *et al*., 2018). Population growth, higher living standards, and climate change have increased water demand and disrupted the natural cycle (Paranychianakis *et al*., 2015). Because water resources are unevenly distributed, protecting and managing existing sources is vital to meet future water demands and sustain ecological balance (Tzanakakis *et al*., 2020).

2.2 Water Quality and Pollution

Surface water and ground water quality s been deteriorating over time despite being an important environmental component (Uddin *et al*., 2018). According to Mitra *et al*. (2022), human activities mainly contributes to water pollution. Naturally, the water quality is influenced by hydrological, atmospheric, climatic and topographical factors. Moreover, anthropogenic activities such as mining, livestock farming waste from industrial, municipal and agricultural activities have been reported to adversely affect water quality as indicated by Lobato *et al*. (2015).

Recently, developing countries Kenya included have had enormous challenges in water quality protection despite efforts for improved water availability and sanitation. In contrast, the developed countries have been putting effort not only in maintaining their water quality but also improve the water quality amid challenges such as nutrient enrichment of soils in the catchment areas and eutrophication of water resources.

Human population has been increasing over time occasioning an increase in water demand hence an increased pressure to the existing natural water sources (Tzanakakis *et al*., 2020). In addition, urbanization has increased development of industries which contributes to high water contamination. According to Mumo *et al*. (2021), climate change has occasioned increased food insecurity. Therefore, innovative strategies in agricultural production such as synthetic fertilizers are advocated for use. Despite its role in improving crop production, synthetic fertilizers and agricultural chemicals such as pesticides, acaricides and herbicides contribute to water pollution especially when farming is done along the water sources such as rivers. Urbanization has increased the need for transportation. The different means of transportation significantly contribute to increased water pollution thus deteriorating quality of water (Dalezios *et al*., 2018).

Owing to pollution of water sources, it is essential to determine the water quality of water sources so as to manage them correctly. According to Uddin *et al*. (2018), water quality is determined using physical, chemical and biochemical parameters. Information on these properties is vital in formulation of guidelines aimed at protecting and management of water sources.

2.3 Pollutants found in tannery effluents

Various reports indicate that leather processing utilize a large amount of freshwater and chemicals such as sulfides, chlorides, synthetic dyes and salts of chromium, which produce toxic waste, raising questions regarding their environmental sensitivity and eco-friendly nature. For instance, Oruko *et al*. (2014) reported that tannery wastewater is highly polluted, containing toxic substances such as Cr^{3+} up to 5,200 mg/L, Pb up to 2.5 mg/L, Cd up to 0.38 mg/L and phenols up to 3.97 mg/L, which exceed WHO and NEMA limits. Another study by Amanial (2016) revealed that tannery effluents contain elevated levels of BOD up to 6,111 mg/L), COD up to 960 mg/L, TSS up to 4,979 mg/L and total dissolved solids TDS. According to Saxena *et al*. (2017), tannery effluent contains both organic and inorganic contaminants that are cytotoxic, genotoxic, and carcinogenic, posing serious risks to aquatic ecosystems and human health.

2.4 Physio-chemical Properties of Water

2.4.1 Potential of hydrogen

Potential of hydrogen (pH) refers to concentration of hydrogen ions in a solution. It indicates the acidity and alkalinity of water. According to WHO and EPA guidelines, a pH between 6.5 and 8.5 is suitable for drinking water. Water is often slightly basic due to the carbonates and bicarbonates from earth metals. According to Tzanakakis *et al*. (2020), alkaline water have limited buffering effect and acid neutralizing capacity. However, extremely alkaline water has a buffering effect and results in negative health implications electrolyte abnormalities and metabolic acidosis resulting in low potassium levels in the blood. Besides, it results in excessive absorption of nutrients. In contrast, the acidic pH affects the gastrointestinal tract resulting in hyperacidity, stomach and stomach ulcers. In the water flow, acid water corrodes the natural rocks within the aquifers hence occasioning increased chemicals which increase the water contamination. Besides, acidic pH compromises with the water taste.

2.4.2 Electrical Conductivity

Electrical conductivity (EC) measures total concentration of ionized substances in water and serve as an indicator of total dissolved solids (Zaslavsky *et al*., 2022). This is because an increase in EC in drinking water indicates potential contamination of water. The contaminants sources include agricultural runoff, industrial effluents or sewage intrusions. Ability of an electrolyte to conduct current depends on concentration of ionic components. Water with high electrical conductivity has detrimental health effects to human health. According to WHO, EC of drinking water ought to be below 700 μS cm^{-1} (Rice and Baird, 2017). Water with elevated EC levels is unsuitable for household use as it contributes to soil salinity in agricultural areas.

According to Zaslavsky *et al*. (2022) water with high EC corrodes the water pipes and plumbing systems. This leads to leaching of metals, which further contaminating the water as it flows. In addition, agricultural practices such as fertilizers and irrigation increase the level of ions contributing to high conductivity in water sources. High levels of evaporation and natural deposits elevates the EC in water sources.

2.4.3 Biochemical Oxygen Demand

BOD quantifies oxygen amount consumed by aerobic microorganism as they break down organic matter in water sample over a set period and temperature. Typically measured in milligrams of oxygen per liter, BOD is commonly assessed after incubation at 20°C hence an organic pollution indicator in water. Oxygen content in moving water rises due to disturbances from rocks, fallen trees and waterfalls. Consequently, DO levels vary significantly along the course of a stream or river. Oxygen is vital for the survival of aquatic organisms and its unavailability results to hypoxic conditions where oxygen is too low to support life forms. This results to fish and other organism suffocation and death.

Similarly, high BOD indirectly stresses or kill aquatic life and reduces the natural ability to support diverse organism (Gamvroula and Alexakis, 2022). Other studies show that DO deficiency results in bad odor of water occasioned by anaerobic decomposition of organic waste which leads to high oxygen demand by aquatic animals. In Kenya, NEMA recommends a maximum BOD of 30 mg/l for effluent discharge into water bodies. Based on Ngoc *et al*. (2020), low BOD in river indicates that there is minimal organic pollution, adequate oxygen level and healthy ecosystem, to supports diverse aquatic species. Also, it shows that the water has natural capacity for self-purification hence essential to small pollution events and natural environmental fluctuations.

2.4.4 Chemical Oxygen Demand

According to (APHA, AWWA, & WEF, 2023), COD represents mass concentration of oxygen equivalent to the dichromate consume by dissolved and suspended substances when a water sample undergoes oxidation under specified conditions. The presence of organic reducing agents can elevate COD values while organic compounds that do not fully oxidize may lead to lower COD results. COD is a key indicator used to assess the organic load in water, providing insights into water quality. Besides, it is determined by the near complete oxidation of organic matter in wastewater into CO_2 and H_2O using strong oxidizing agents such as potassium dichromate ($K_2Cr_2O_7$) (Jeong *et al*., 2020).

2.4.5 Total suspended solids

Water is a vital resource and understanding the levels of suspended and dissolved solids is essential. Total suspended solids (TSS) consist of larger particles that do not pass through a filter. TSS is measured by determining differences between total solids and TSS (mg/L). Factors such as soil erosion, urban runoff and septic system waste contribute to increased TSS level in water (Jeong *et al*., 2020). According to WHO, TSS in water should be 50 mg/l (WHO, 2022). Elevated total dissolved solids results in runoff containing substances such as chlorides, nitrates and bicarbonates (Jeong *et al*., 2020).

2.5 Heavy metals, phenols and environmental pollution

Heavy metals are metallic elements with a density exceeding 5 g/cm^3 in their pure form (Jagaba *et al*., 2024). Besides, they are leading environmental pollutants resulting to long-term presence and inability to break down naturally, affecting human health and biological ecosystems (Jagaba *et al*., 2024). According to a study by Naja and Volesky, (2009), dissolved heavy metals in water pose a threat to life. When used for irrigation, these metals can enter the food chain, creating potential health risks.

2.5.1 Chromium characteristics and its Impact to human

Chromium is one of the most abundant heavy metals in Earth's crust and occurs in multiple oxidative state. The most common and stable forms are Cr^{3+} and Cr^{6+}, each with distinct chemical properties (Jagaba *et al*., 2024). Hexavalent chromium compounds are highly soluble in water, while trivalent have lower solubility. In acidic conditions, hexavalent chromium acts as a strong oxidizing agent while its effectiveness decreases in basic environments (Liang *et al*., 2021). Hexavalent form is significantly more toxic than trivalent form, being approximately 500 times more hazardous. As a persistent pollutant, chromium can accumulate in ecosystems and enter the food chain, making its detection and monitoring essential in environmental studies (Ukhurebor *et al*., 2021).

Chromium enters environment from both natural and human-related sources. Naturally, it is found in rocks, soil, plants, animals and volcanic emissions (Liang *et al*., 2021). Human activities also contribute significantly, particularly through the improper disposal of industrial waste containing chromium (Valentín-Reyes *et al*., 2019). Effluents from these industries introduce heavy metals into environment and water bodies. Additional sources of chromium include rock erosion, emission from power plants, combustion of liquid fuels, coal burning, municipal and industrial waste, automotive brake lining and chromium-based pigments (Viczek *et al*., 2020). Runoff from manufacturing facilities further elevates concentrations of heavy metals in water sources. In some cases, chromium levels in surface waste and drinking water exceeds the WHO recommendation limit of 0.05 mg/L.

Humans are exposed to chromium primarily in its trivalent form (Cr III) via food, drinking water, air particle inhalation and skin contact. Direct exposure occurs when using chromium-treated products such as leather processed with chromium sulfate or wood preserved with copper dichromate. Occupational exposure is common in industries such as chromate manufacturing, stainless steel production, chrome plating and leather tanning (Jagaba *et al*., 2024). Individuals living near chromium processing plants or waste disposal sites face a higher risk of exposure than general population due to elevated environmental levels of this metal.

Chromium (III) and chromium (VI) are widely used across various industries including metallurgy, mining, leather and wood preservation, cooling tower water treatment, chrome plating and manufacture of dyes and pigments (Liang *et al*., 2021). Besides, smaller quantities re used in textiles, copier toner and during muds. The primary source of Cr is steel and alloys production. Hexavalent chromium compounds as the chromates of calcium, zinc, strontium and lead are highly water soluble-soluble, toxic and known carcinogens. The WHO has established a permissible limit of 0.005mg/L for Cr (VI) in wastewater. Exposure to Cr (VI) can lead to various health complications including the skin conditions such as chronic ulcers and dermatitis, kidney and liver damage. Also, it can cause internal bleeding, dental challenges and respiratory diseases such as asthma, and pneumonia. A significant percentage of individuals exposed to chromium compounds exhibit skin discoloration and other dermatological effect (Liang *et al*., 2021).

Exposure to chromium compounds has been associated with nasal ulceration and perforation. The International Agency for research on cancer identifies Cr as a contributing factor to sinonasal carcinoma. Workers exposed to hexavalent Cr have reported respiratory issues including pneumonia, rhinitis and bronchospasms. Inhalation of chromium compounds has been linked to an increased risk of lung cancer while ingestion of Cr compounds may lead to kidney and liver damage. Additionally, research suggest that Cr (VI) can cause genetic mutations and alter DNA structure.

2.5.2 Lead characteristics and applications

Lead is a heavy metal with low reactivity and exhibits weak metallic properties in its amphoteric behavior in reacting with both acids and bases. Also, it has the ability to form covalent bonds. Pb compounds are predominant found in the +2-oxidation state, unlike the +4-oxidation state that is more common in lighter elements of the carbon group. However, organo-lead compounds are notable exceptions. Similar to other elements in its group, lead has a tendency to bond with itself, forming structures such as chain, rings and polyhedral arrangements.

Lead (II) compounds are the most compounds are the most common in lead's inorganic chemistry. Even strong oxidizers like fluorine and chlorine react with lead to form PbF_2 and $PbCl_2$. The lead (II) ion undergoes hydrolysis and condensation reactions that depend on pH, producing species such as $Pb(OH)_4^{2-}$. A pH increase in solutions containing lead (II) salts triggers these reactions (Viczek *et al*., 2020). As a result, very few lead (IV) compounds exist as can only form in highly oxidizing environments and are generally unstable under normal conditions.

Lead contaminations in the environment primarily results from industrial automotive emissions, the use of leaded gasoline and dust from deteriorating lead-based paints in older buildings. Tap water can be source of lead due to soldered plumbing. Additionally, exposure occurs indoors through household chemicals and tobacco smoke. Other sources of low-level lead contamination include pipes, ammunition, insecticides, and pigments in paints, discarded electric materials, dyes and ceramic glazes. Lead is introduced into the environment through applications such as use of storage batteries, soldering ammunition, radiation shielding and tank lining. Inorganic lead salts are commonly found in insecticides, pigments, and among (Viczek *et al*., 2020).

Lead exposure in human occurs through inhalation, ingestion or skin contact (Grant, 2020). Nearly all inhaled lead enters the body, while Pb absorption rate ranges from 20% to 70% with children reporting significantly higher absorption than adults. Lead poisoning is most commonly caused by consuming contaminated food or water through it can also result from accidental ingestion soil, led-based paint and dust contaminated with Pb.

Lead usefulness stems from its high density, low melting point, ductility and resistance to oxidations. Also, they are highly abundant and affordable hence it is widely utilized in various applications including construction, plumbing, ammunitions, weights, soldering, and fusible alloys. In early 21st century, led-acid batteries were used and contributed to elevated lead levels. These batteries generate stable voltage through chemical reactions involving lead, lead oxide and sulfuric acid. Additionally, lead is used as a proactive sheathing material in high-voltage power cables to prevent moisture from penetrating the insulation.

Lead is considered one of the most hazardous metal due to its severe health impacts. The harmful effects of lead poisoning are well-documented. According to WHO, approximately 26 million people are at risk from lead pollution and an estimated 540,000 deaths occurring annually especially in developing countries. Lead toxicity can harm the kidneys, joints, reproductive systems and cardiovascular system while causing significant damages to both central and peripheral nervous system (Pandey *et al*., 2016). In severe cases, Pb exposure can result in brain and kidney damage.

2.5.3 Cadmium characteristics and applications

Cadmium. A heavy metal s primarily obtained as a byproduct of Zinc ore refining. It is highly mobile within biological systems. While solid Cd is not flammable, its powdered form can ignite, releasing toxic corrosive fumes. Certain Cd salts including $CdCl_2$, $CdSO_4$ and $Cd(NO_3)_2$ are water-soluble with their solubility increasing when exposed to acids, light or oxygen (Naja and Volesky, 2009). This means that lower pH levels enhance Cd solubility in water. Typically, Cd exists in the +2-oxidation state though some compounds have been identified in the +1 state. Cadmium is primarily released into the environment from sources such as fossil fuel combustion, iron and steel manufacturing, cement production, nonferrous metal processing, waste incineration and cigarette smoking. Additionally, natural processes like the volcanic eruptions, mining and application of phosphate fertilizers contribute to indirect Cd exposure as mental originates from the Earth crust (Nyantakyi *et al*., 2019).

Exposure to Cd can occur via airborne particles or dust inhalation, mainly in occupational settings such as battery manufacturing, metal processing, welding and soldering. Cigarette smoke is also significant source of inhaled Cd. Additionally, people come into contact with Cd through contaminated drinking water and food. Cd is used for industrial purposes especially in production of batteries where it is combined with nickel. Also, it is used in pigments, coatings, PVC stabilizers and metal alloys. Furthermore, Cd plays a role in nuclear reactors where it is used in control rods to regulate atomic fission. Other applications include electroplating to prevent corrosion and the production of fungicides, phosphorus and ceramics.

The international agency of Research on Cancer (IARC) classifies Cd as a hazardous metal due to its detrimental effects on human health. Acute exposure to Cd can lead to inflammation, which may cause symptoms such as coughing, short rainsness and irritation of the nose and throat. Additionally, exposure can result in headaches, dizziness, chest pain, pneumonia and pulmonary edema (Bhuyan and Bakar, 2017).

2.5.4 Phenols characteristics and applications

Figure 2.5.1 presents the chemical structure of phenol are compounds.

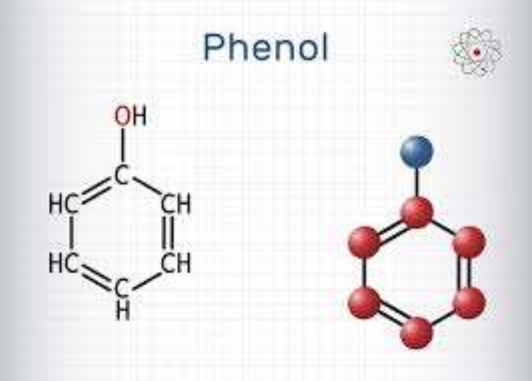

Figure 2.5.1 The chemical structure of phenol

Source: Freepik. (2023)

The compound has limited solubility in water, approximately 6.7g per 100 ml but dissolves readily most organic solvents. The melting point is this metal is 43 °C though adding water significantly lowers it. Besides, 90% phenol water-mixture remains liquid form even at room temperatures. Chemically, it behaves as weak acid, with aqueous solution with pH of 6 and reacts easily with oxidizing agents. Phenol compounds in water are from natural and human related activities. Natural sources include breakdown of organic matter from dead plants and animals. Also, synthesis by microorganisms and aquatic plants contributes to phenolic water. Human activities contributing to phenolic water pollution include industrial processes, household waste, agricultural runoff and municipal waste discharge.

Phenol exposure occurs through various ways including its production and use in industrial applications, smoking and breakdown of benzene under light exposure. Liquid manure also contributes to phenol presence in the environment. Elevated phenol levels have been detected in sediments and ground water due to industrial pollution. In addition to air exposure, cigarette smoking are potential sources of contact with phenol.

Phenol is primarily utilized in the production of phenolic resins, biphenyl A and caprolactam. Other derivatives include alkylphenols, xylenol, cresol and adipic acid. Also, small-scale applications in manufacturing germicidal paints, pharmaceutical dynes and chemical indicators as well as serving as laboratory reagents and general disinfectants. Ingesting phenol results to gastrointestinal irritation. Skin exposure may result in painless blanching, erythema or in severe cases, corrosion and deep tissue necrosis. Additionally, systemic effects of phenol poisoning can include cardiac arrhythmias, respiratory distress, metabolic acidosis, kidney failure and darkened urine. The odour threshold for phenol ranges from 0.021 to 20 mg/m^3 in air, while the threshold for odour in water is 7.9 mg/L (Wachowski and Pietrzak, 2020). The permissible limit for phenol in drinking water is 0.3 mg/L. Higher phenol levels is toxic for higher freshwater organisms.

2.6 Studies done on seasonal variations of water quality of rivers

Water quality is influenced by physical and chemical properties which vary depending on their concentration levels (Jagaba *et al*., 2024). An example is a study done in Buriganga River in Bangladesh which assessed water quality in long rains and short rain seasons. The study established that DO dropped to zero during the short rain season, rendering the water uninhabitable for aquatic life up to 500 meters downstream of the sluice gate (Pasha *et al*., 2023). Similarly, an investigation into the pollution level of Osumi river across different seasons revealed fluctuations in various parameters the COD ranged from 7.97 to 51.63 mg/L during the short rain seasons and increased from 13.4-171.37 mg/L in the long rain season (Paparisto *et al*., 2017).. Additionally, pH level reached a high as 9.04 in both seasons. Moreover, TSS exceeded the USEPA freshwater quality limit of 50 mg/L (Paparisto *et al*., 2017).

According to Katiyar, (2011) from India found that water quality parameters fluctuated between long rains and short rain season. The BOD varied between 18.77 and 31.14 mg/L in short rain season while in long rain season, it ranged from 30-89 to 32.38mg/L. Similarly, the COD ranged from 138-156 mg/l in long rain season and 118.12-119.44 mg in short rain season. The pH remained alkaline and together with other parameters, it exceeded the Bureau of Indian standards. The differences was attributed to discharge from tannery effluents (Katiyar, 2011).

A study by Basweti *et al*. (2018) on levels of physicochemical parameters and polycyclic aromatic hydrocarbons in waters from River Nzoia revealed that levels of pH, temperature, EC and TDS varied in long rains and short rain seasons. Similarly, a study by Nyambaka *et al*. (2016) on Ngong and Nairobi Rivers showed that the levels of physico-chemical parameters like pH and temperature for both rivers varied seasonally but remained within the limits set by WHO and USEPA. However, the levels of turbidity, dissolved oxygen and conductivity exceeded the levels recommended by WHO. This could be due to high organic and inorganic pollution in these rivers.

A study by Kimani *et al*. (2016) on Spatial and Seasonal Variation of Selected Water Quality Parameters in Chania River Catchment, Kenya revealed that; Seasonal variations for both conductivity and TDS were statistically insignificant with the slight increase during the short rain season being related to the fact that volume of the river is low and a high evaporation ratio over rainfall. pH on the other hand was slightly higher in long rain season than in short rain season in agricultural and town area. pH was strongly correlated to nitrate concentration (*r=0.82)* for the long rain season and hence higher pH can be associated to surface run offs carrying nitrogenous fertilizer (Kimani *et al*., 2016).

2.7 Pollution studies on River Chania catchment

Agriculture, mining and industrial waste discharges into rivers during long rains season, significantly alter the physical and biochemical properties of water (Hoque *et al*., 2023). These activities contribute to increased alkalinity, higher levels of suspended solids and elevated sulphide concentration, which can be harmful to both human and aquatic lives (Vivien *et al*., 2012). Similarly, Kimani *et al*. (2016) reported that water from River Chania contained Mn, Cu, Zn, Ni and Pb at concentrations ranging from 53.5-605 mg/L, 10-303mg/L, 22-325 mg/L, 15-77 mg/L and 10-84 mg/L respectively. The contamination was linked to dust from nearby mining activities and chemical fertilisers used in pineapple farms and effluents from Leather industries of Kenya Limited.

Research conducted by Robert *et al*. (2021) indicated that the mean concentration of certain heavy metals in river Chania catchment exceeded WHO permissible limits. An example is Pb which recorded at 0.04 mg/L, surpassing WHO standard of 0.01 mg/L. Conversely, Cr levels remained below 0.02 mg/L both in long rains and short rain season except Thika sampling point, where a mean concentration of 0.045 mg/L was recorded in the long rains season and was within NEMA limit (53.10 ± 2.65 μS/cm) and 16.64 ± 0.40 μS/cm in short rains season. This variation was attributed to effluent discharge into water, which becomes more diluted in long rains season, hence low conductivity than short rain season.

2.8 Literature gaps identified

River Chania in Kenya is experiencing increasing pressure and pollution due to human activities, including industrial effluent discharge. Studies such as those conducted by Robert *et al*. (2021) have assessed the river's physico-chemical characteristics, reporting pH levels ranging from 5.9 to 6.8, which fall slightly below the WHO-recommended range of 6.5 to 8.5. Additionally, research by Kimani *et al*. (2016) identified contamination by heavy metals, with lead (Pb) concentrations recorded at 2.5 mg/L, exceeding recommended limit of 0.001 mg/L. However, these studies did not analyze parameters such as COD, BOD, TSS, total phenols, or certain heavy metals like Chromium (Cr), cadmium (Cd), highlighting a gap in research. Furthermore, they did not specifically examine the impact of the Leather Industries of Kenya Limited, despite its close proximity to the river, as a potential pollution source. Therefore, this study assessed levels of these pollutants in River Chania, considering Leather Industries of Kenya Limited influence and seasonal variations, to address the existing research gap in the Chania River basin.

2.9 Methods commonly used for water quality analysis

Several techniques are available for assessing water quality. These includes titration, gravimetric analysis, ion chromatography, atomic Absorption Spectrophotometry, calorimetry, potentiometric and UV-VIS spectrophotometry. Titration is widely used due to its simplicity, efficiency and time-saving nature. For detecting specific contaminants, AAS is preferred especially Cd while UV-VIS spectrophotometry are used in analysis of phenols. These methods are highly precise, making it ideal for detecting trace amounts of these metals (Sinha *et al*., 2023).

2.9.1 Principles of Atomic Absorption Spectroscopy

An absorption spectrum is generated when electrons move from ground-state to a higher energy state. During this process, atoms absorb ultraviolet or visible light, causing transitions to higher electronic energy level. When light from an element emission spectrum passes through a sample, it is absorbed if it encounters atom of the same element. The extent of absorption provides an indication of the concentration of atoms present in the sample. Absorption spectroscopy measures how ground-state atoms in the gaseous phase absorb light. The analyte's concentration is determined based on the level of absorption, typically using a calibration curve created by comparing results to standards with known concentrations.

The absorption follows Beer-Lambert's law as shown in equation 1.

$$A=\varepsilon.l.c \qquad (1)$$

Where ε is the molar absorptivity in Mcm^{-1}, l is the path length in centimeters and c is the concentration of atoms in moles per liter (Sinha *et al.*, 2023).

2.9.2 Components of AAS

An Atomic Absorption Spectrometer (AAS) consists of several key components that work together to determine the concentration of metals in a sample. The light source, usually a hollow cathode lamp, emits light at a wavelength specific to the element being analyzed. This light passes through the atomizer, which converts the liquid sample into free atoms by heating it either in a flame or a graphite furnace. The monochromator then isolates the characteristic wavelength absorbed by the target atoms, ensuring that only the desired spectral line reaches the detector. The detector measures the amount of light absorbed by the atoms, and this absorption is directly proportional to the concentration of the element in the sample. Finally, the readout system processes the signal from the detector and displays the results, typically in absorbance or concentration units. Together, these components enable accurate quantitative analysis of metals in environmental, industrial, and biological samples. The components are illustrated in figure 2.9.1 below.

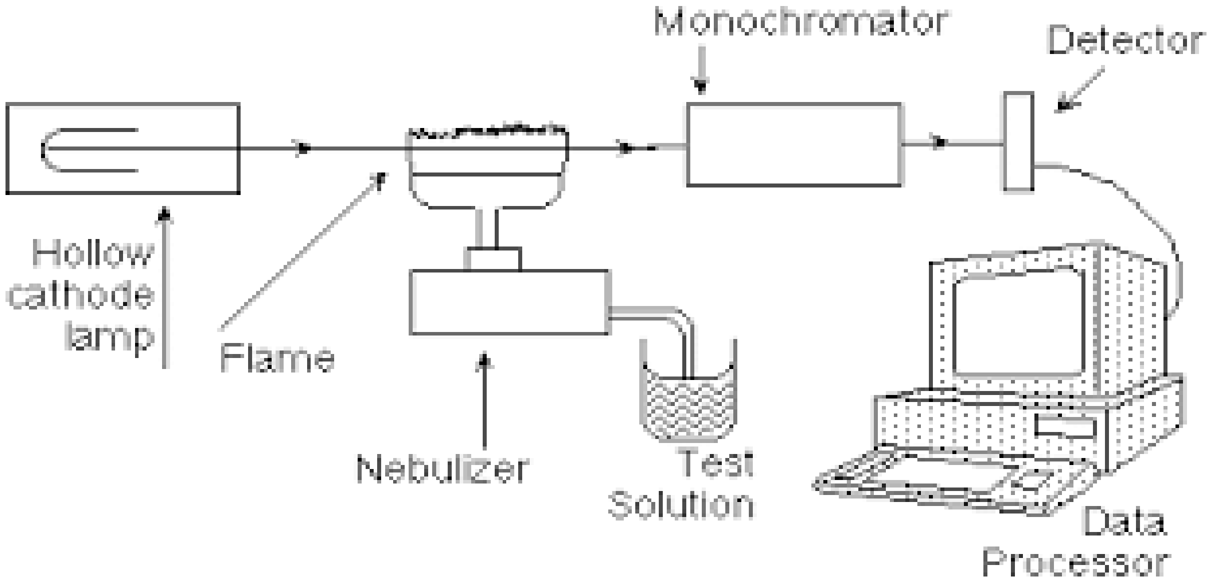

Figure 2.9.1 Schematic diagram of atomic absorption spectrometer
Source: Visita. (2015)

2.9.3 Principles of UV Vis

The UV-Vis spectroscopy relies on the absorption of light in ultraviolet ranging between 200 to 400 and visible regions (Vis) ranging from 400-700 regions of the electromagnetic spectrum. When a sample absorbs light at a particular wavelength, the electrons in the sample molecules or atoms are excited from the lower energy level to the higher energy level. The amount of light absorbed depending on the wavelength is measured to produce the absorption spectrum.

2.9.4 Components of UV Vis

A spectrophotometer consists of several key components, including a light source that emits the light**,** a sample holder, a monochromator with a diffraction grating or prism to separate light into different wavelengths, and a detector that displays the absorbed light in terms of absorbance. These instruments can be classified as either single-beam or double-beam. In a single-beam spectrophotometer, light travels directly through the sample. In contrast, a double-beam spectrophotometer splits the light into two paths—one serving as a reference and the other passing through the sample. The reference beam is considered to have 100% transmission (or zero absorbance). The components of a UV-Vis spectrophotometer is illustrated in figure 2.9.2 below.

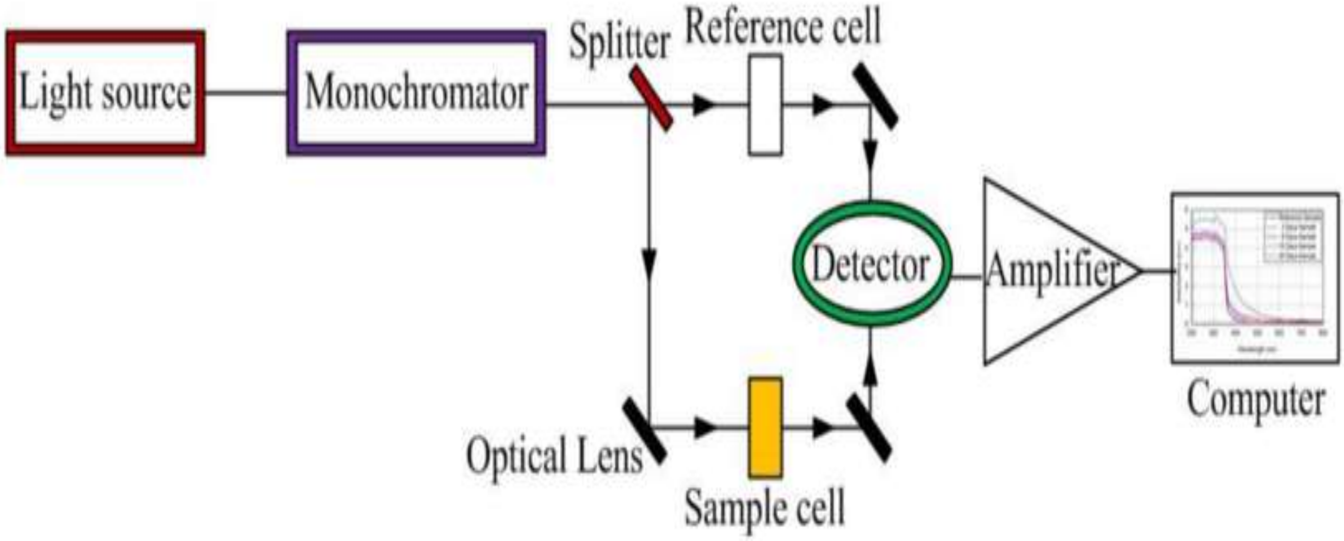

Figure 2.9.2 Schematic diagram of UV-VIS Spectrophotometer

Source: Alshehawy *et al*. (2021)

CHAPTER THREE: MATERIALS AND METHODS

3.1 Study area

River Chania originates from slopes of Kinangop mountain and Aberdare Range and flows through three counties: Kiambu, Murang'a and Nyandarua. River Chania supplies water to large agricultural area, Thika Town and its sorroundings (Robert *et al*., 2021). This study focuses on the section of River Chania located near the Leather Industries of Kenya Limited (LIK) in Thika, Kiambu County.The selected section lies approximately between latitude 1.050° S and 1.059° S and longitude 37.122° E and 37.131° E. This stretch of the river is situated within the midstream section of River Chania, where industrial, urban, and agricultural activities are highly concentrated. The region experiences a bimodal rainfall pattern with the long rains season starting from mid-March to May while the short rains season starts from mid-October to December (Kenya Meterological Department, 2023). The mean annual temperature in this area is approximately 26 °C, while the average annual rainfall ranges between 900 mm and 1200 mm, reflecting the moderate altitude typical of the Thika region (Njuguna *et al.*, 2019). This section was therefore selected for assessing the influence of industrial activities on the water quality and ecological health of River Chania.

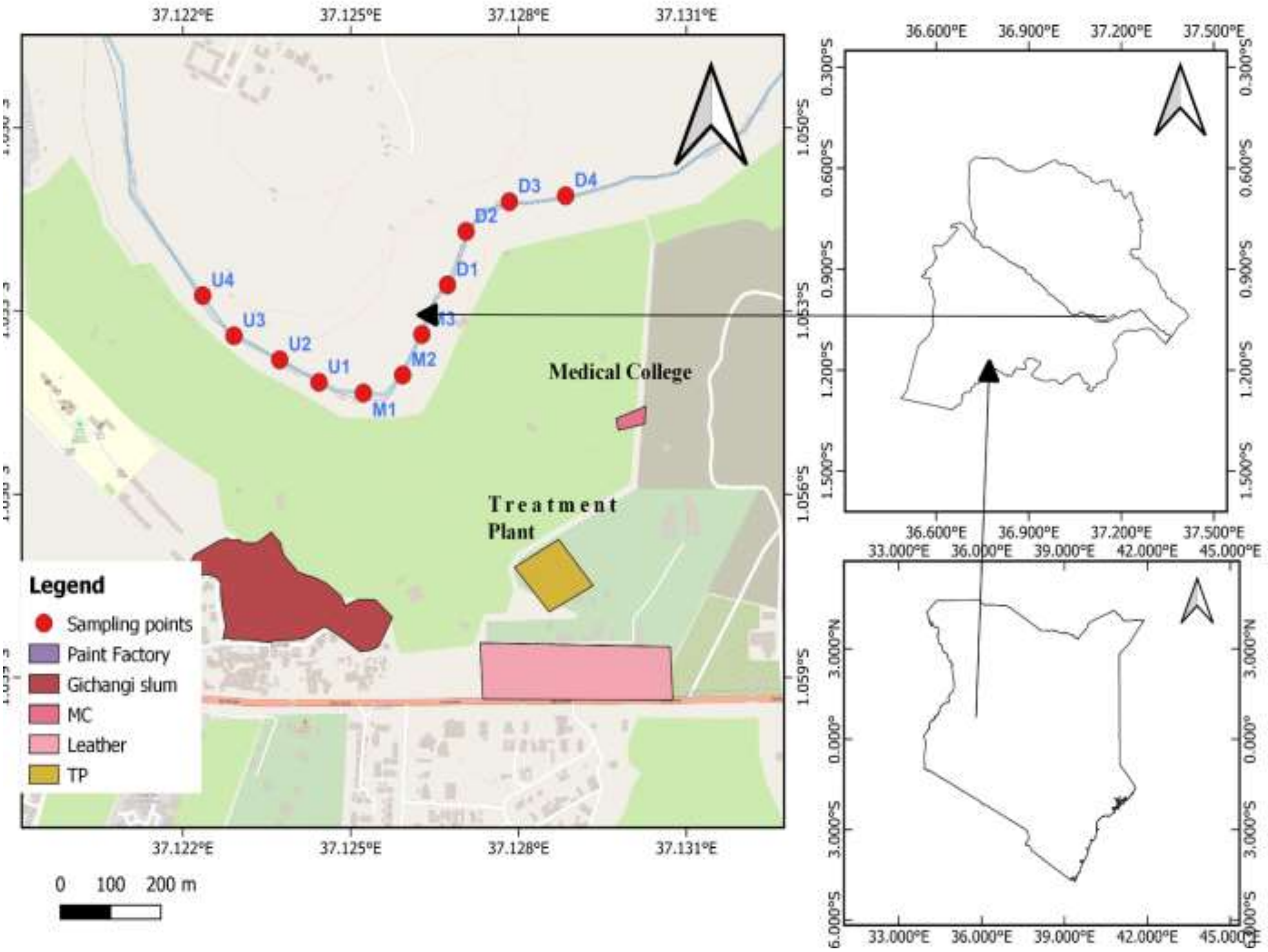

Figure 3.1 Sampling locations along River Chania.

The study area is divided into Upstream (U1–U4, 100 m intervals), Midstream (M1–M3, 50 m intervals), and Downstream (D1–D4, 100 m intervals) sections for data collection.

3.2 Description of the sampling points along river Chania

Eleven sampling points were selected from three sections (upstream, midstream and downstream) of River Chania which is adjacent to Leather Industries of Kenya Limited (LIK). The selection of the sampling points was done with respect to the distance from LIK and ease of access. In the upstream section, four points were selected around Gichangi slum. Here, the river receives domestic effluents from the residential area and agrichemicals from the subsistence farming done along the riverbank. At the middle section, three points were sampled around Makongeni area where LIK is located, and its industrial effluents are released into the river Chania. Moreover, the river receives sewage from urban area, solid wastes from the surrounding communities and run offs from farming. At downstream section, four points were selected in the residential area where residents rely on River Chania water for irrigation and domestic purpose.

3.3 Equipment and chemicals

The equipment that was used during the study included Portable pH and Conductivity meters were used to measure pH and EC respectively. 30 ml glass stoppered BOD bottles, and an Incubator set at 20 ^{o}C was used to measure BOD. Refluxing and titration apparatus were used to measure COD. The oven set at 103 to 105 ^{o} C and a desiccator was used to measure TSS. For heavy metal analysis, a heating block and AA Spectrometer (AA-1275 series model) was used. For total phenol analysis, distillation apparatus and black tube with reagent was used. Besides, the samples were subjected to UV-Vis spectrophotometer analysis.

The chemicals used were: Soap and dilute nitric acid were used for general washing of plastics and glassware while deionized water was used to rinse all the equipment used and also to dilute the samples up to the desired volume. Dilution water enriched with 5 ml of $CaCl_2$, $MgSO_4$, $FeCl_3$ and phosphate buffer for BOD analysis, as recommended by standard methods of examination of water and waste water (APHA). $K_2Cr_2O_7$, H_2SO_4, $HgSO_4$, Ag_2SO_4, $(NH_4)_2.FeSO_4\cdot 6H_2O$ and $[Fe(phen)_3]^{2+}$ (indicator) were used for measuring COD. The same protocol was used in selecting the chemicals and equipment for heavy metals and total phenols analysis: 2.835 g of potassium dichromate (VI), 1.59 g of analytical grade lead (ii) nitrate, 0.275 g of Cd nitrate and 1 g of analytical grade phenol for preparing Cr, Pb, Cd and phenol stock solutions, which gives exactly

1000mg/L., aqua-regia in ratio 3:1 of HCL to HNO_3, hydrogen peroxide for sample digestion, 10 mL of the ammonium buffer, 2 mL of 4-amino antipyrine and 2 ml of ferricyanide solution for colour development and UV-Vis spectrophotometer for phenol analysis.

3.4 Water sampling at river Chania

Water was sampled in triplicate from the selected eleven points during short rains season (October to December 2023) and long rains season (March to May 2023). During each month, a total of 11 samples were collected. This was done for three months, giving a total of 33 samples per season. The periodic sampling was done to determine the consistency of physicochemical parameters in each season. Prior to sample collection, the containers were washed thoroughly with soap and tap water followed by 6% HNO_3 to remove any trace metal contaminants and rinsed with distilled water to remove all the acids. In the sampling section, sample containers were rinsed three times with river water to remove any residual acid or distilled water, which could interfere with the sample chemistry. During sampling, a one-litre plastic container was used to collect water samples, about 10 cm below the surface to avoid surface contamination and sediment interference, as well as avoiding gas exchange which could interfere with DO and BOD. Sampling was done randomly at different points and mixed thoroughly to make a 500 ml composite sample at each sampling point. pH and EC were determined in the river by use of portable pH meter and a conductivity meter as described by the American Public Health Association (APHA) (Rice and Baird, 2017). Samples for analysis of BOD, COD, TSS, and total phenols were preserved and kept in a cooler box at 4 ^{0}C Cd, Cr and Pb, were pretreated using nitric acid of analytical grade, put in an ice-cool box at 4 ^{0}C before being transported to Kenyatta University for laboratory analysis within 24 hours.

3.5 Quality control

Quality control was evaluated by analyzing triplicate water samples collected from the study area to ensure accuracy, precision, and reproducibility of the analytical results. A blank sample was included to check for possible contamination or other interferences that could compromise the quantification of total phenols and heavy metals. Recovery tests were conducted by spiking water samples with known concentrations of standard solutions. The blank water samples were subjected to the same analytical treatment as the environmental samples to ensure consistency and reliability of the measurements (APHA, 2017; USEPA, 2020).

3.5.1 Spike Recovery of Water Sample

The spike recovery method was employed as a quality control procedure to evaluate the accuracy and reliability of heavy metal determinations in river water samples and to identify potential matrix interferences. After collection, river water samples were filtered to isolate the dissolved fraction and subsequently acidified with nitric acid (HNO_3) to preserve the analytes (WHO, 2022). The sample was then divided into at least two equal portions: the Native Aliquot, which is analyzed directly to ascertain the original metal concentration (C original), and the Spiked Aliquot, which was augmented with a known concentration (5 mg/L) of the target heavy metal standard (Cd, Pb, and Cr) (C spike). Both aliquots were analyzed using Atomic Absorption Spectroscopy under identical conditions to determine their respective metal concentrations. The Percent Recovery (%R) was calculated using equation 2.

$$\text{Percent Recovery (\%R)}=\frac{C_{\text{spike}}\text{-}C_{\text{measured}}}{C_{\text{measured}}}\times 100 \qquad (2)$$

The recovery results were evaluated against the acceptable range of **75%–125%**, as recommended by standard analytical protocols (APHA, 2017; USEPA, 2020). Values outside this range indicate significant matrix effects—such as signal suppression or enhancement—caused by the composition of the river water, which can compromise analytical accuracy (Kazi *et al.*, 2018). Adhering to this procedure ensures the validity, precision, and reliability of the reported heavy metal concentrations in the study.

3.6 Determination of Biochemical oxygen demand

The procedure according to Rice and Baird (2017) was followed. To prepare the dilution water 5 liters of double-iodized water were aerated for 24 hours after supplementing with $CaCl_2$, MgSO4, $FeCl_3$ and phosphate buffer solution. This helps in creating a stable, oxygen-rich and nutrients-balanced environment for microorganisms. Thereafter, 10 mL of water sample was added to a 30 ml BOD bottles and topped with 20 ml of dilution water. Samples were poured into BOD bottles in two sets (one blank and sample). The blank was used to account for oxygen consumption or gain due to the water, nutrients or microorganisms themselves, not the sample. This ensured that the measured oxygen depletion was only due to organic matter in the sample. Oxygen concentration of the diluted sample was measured and recorded as DO, then put in the incubator for five days at 20 ^{o}C, after which the final concentration of oxygen was measured and recorded as D5. BOD was measured by calculating the difference in oxygen concentration in the diluted sample before and after a 5-day incubation period. Calculation of BOD_5 was done according to equation 3.

$$\mathrm{BOD}=\frac{\mathrm{D_5\text{-}D_0}}{\mathrm{P}} \tag{3}$$

Where P= Dilution factor $= \frac{\text{volume of BOD bottle in mL/g}}{sample\ volume\ in\ ml}$

3.7 Determination of COD

This analysis was conducted using the standard reflux method in accordance with standard procedures for water and waste water (APHA, AWWA, & WEF, 2023) To ensure that all oxidizable organic compounds are broken down fully, the samples were refluxed for two hours with $K_2Cr_2O_7$ as the oxidizing agent and sulfuric acid in the presence of mercuric sulfate**,** which served to counteract chloride interference. Silver sulfate functioned as a catalyst. The remaining $K_2Cr_2O_7$ after the reaction was considered the analyte, while ferrous ammonium sulfate (FAS) was used as the titrant, with ferroin serving as the indicator. The amount of $K_2Cr_2O_7$ reduced corresponded directly to the oxidizable organic and inorganic matter in the sample, thus determining the COD. COD was calculated by equation (ii)

$$\text{COD (mg/L)}=\frac{(\text{A-B})\times \text{N}\times 8000}{\text{V}} \tag{4}$$

Where; A= volume of FAS used for the blank (mL), B=Volume of FAS used for the sample (mL), N=Normality of FAS solution (M × n-factor), V=Volume of water sample (mL) and 8000=Milliequivalent factor for oxygen.

3.8 Determination of Total Suspended Solids

An empty crucible was weighed, and initial weight recorded followed by addition of 50 ml of unfiltered sample. The crucible with the sample was dried using an oven for 1 hour at 105 ^{o}C. Thereafter, the crucible was removed from an oven, cooled in desiccators and final weight recorded. Heating, cooling and weighing of the crucible was repeated until variations in weight became insignificant. Total solids were calculated by getting the difference between initial weight and the crucible final weight. Similarly, the total dissolved solids were determined by weighing the crucible and the initial weight recorded. Thereafter, 50 ml of the filtered sample was added to the crucible. The crucible with the sample was kept in an oven for 1 hour at 105 ^{o}C. The crucible was then removed from an oven and cooled in desiccators and final weight recorded. Heating, cooling and weighing of the crucible was done repeatedly until variations in weight could not be detected. Total dissolved solids were obtained by subtracting the final weight of the crucible from the initial crucible weight. Moreover, TSS were determined by obtaining the difference between TS and (mg/L) TDS according to equation 5.

$$TSS = TS - TDS \tag{5}$$

3.9 Heavy metals Analysis

3.9.1 Preparation of standard for calibration

Stock solutions (1000 ppm) of Chromium, Lead and Cadmium were prepared by diluting 2.835 g of potassium dichromate (VI), 1.59 g of analytical grade lead (ii) nitrate and 0.275g of $Cd(NO_3)_2$. in 500 mL of deionized water and topped to 1 L respectively. Working solution was prepared by diluting 10 mL of the stock solution with distilled water in a 100 mL volumetric flask to achieve a concentration of 100 ppm. Standard solutions with concentrations of 10 ppm, 8 ppm, 6 ppm, 4 ppm, and 2 ppm were then prepared by diluting 10 mL, 8 mL, 6 mL, 4 mL, and 2 mL of the working solution respectively with 100 mL of distilled water.

3.9.2 Preparation of water samples for FAAS analysis

The analysis of heavy metals, including chromium, cadmium, and lead, was conducted following standard procedures. A 50 mL water sample was digested with 10 mL of aqua regia, prepared in a 3:1 ratio of HCl to HNO_3**,** in a beaker using a heating block digestion method. During digestion, 2 mL of hydrogen peroxide was added gradually until the volume was reduced to 10 mL. The resulting solution was then transferred into a 50 mL volumetric flask and diluted to the mark with deionized water before being aspirated into the FAAS.

The samples were then tested for presence of the heavy metals using a spectrometer (AAS), AA-1275 series model which works on the principle that each metal has its own characteristic absorption wavelength. The standard wavelength for the metals, Lead, Chromium and Cadmium are 405.8 nm, 425.4 nm and 326.1 nm respectively.

3.10 Total phenols

3.10.1 Preparation of standards for calibration

A 1000 ppm phenol stock solution was prepared by dissolving 1 g of analytical-grade phenol in 1 liter of deionized water. A ten (10) ppm working solution was then obtained by diluting 1 mL of the stock solution in 100 mL of deionized water. To prepare standard solutions**,** 10 mL, 20 mL, 40 mL, 60 mL, and 80 mL of the working solution were each diluted with 100 mL of deionized water, resulting in final concentrations of 1 ppm, 2 ppm, 4 ppm, 6 ppm, and 8 ppm**,** respectively.

3.10.2 Preparation of the water samples for UV-Vis spectroscopic analysis

A 300 mL sample was placed in a round-bottom flask equipped with a side condenser and heated until 275 mL of distillate was collected. To complete the distillation process and achieve a total 300 mL distillate volume**,** 50 mL of distilled water was added. This procedure ensured the efficient distillation of volatile phenols, including chlorine-substituted variants.

The collected distillate was transferred to a beaker, where 10 mL of ammonium buffer was added, followed by 2 mL of 4-aminoantipyrine and 2 mL of ferricyanide solution. The reaction was left to develop for 10 minutes, forming a colored complex proportional to the phenol concentration. Both the prepared samples and standard solutions were then placed in clean cuvettes**,** and absorbance was measured at 510 nm using a 4-cm cell, with a Varian DMS 100S double-beam UV-Vis spectrophotometer, against a reagent blank.

3.11 Data analysis

Data analysis for pH, EC, BOD, COD, TSS, phenols, Cr, Cd, and Pb was conducted using R software version 4.3.1. A one-way ANOVA was performed to assess significant differences in physicochemical parameters and heavy metal concentrations between the two seasons at $p < 0.05$. Additionally, Tukey’s post-hoc test was applied to separate differences between the means.

3.11.1 Assumptions in data analysis

In this study, it was assumed that all data collected from river Chania were accurate, reliable and true representative of the actual environmental conditions at the selected sampling sites. The sampling procedures and preservation methods were assumed to have prevented any contamination or loss of the analyte before analysis. The instruments used were presumed to be properly calibrated and functioning within the acceptable limits of precision and accuracy. The instruments were also assumed to be sufficiently selective and sensitive to measure only the intended analyte. It was further assumed that the Interferences –whether chemical, physical, or matrix-related were either absent or negligible, or minimized during analytical procedures and so the data represents the analyte of interest.

For statistical analysis, it was assumed that the data was followed a normal distribution, allowing for application of parametric tests to compare mean concentration across the sampling sites and seasons. All these formed the foundation for analyzing, interpreting the data and drawing meaningful conclusions on the levels of physico-chemical parameters, total phenols and heavy metals in River Chania.

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1 Spike Recovery of Water Sample

Table 4.1 shows the results of the spiked and unspiked water samples with corresponding % recovery. The unspiked results had significantly lower levels of Pb, Cd and Cr (0.125, 0.005, and 0.012) than the spiked samples (4.957, 4.7123, and 4.635). The concentration for all the spiked samples was 5. The recovery percentage varied with the highest being Pb (96.64%) followed by Cd (94.146%) and Cr (92.46%). This method is valid because the recovery % falls within the acceptable range recommended by WHO for drinking water analysis (80-120%).

Table 4.1 Level of the spiked and unspiked water samples with corresponding % recovery

Samples	**Heavy metals spiked**		
	Cd	**Pb**	**Cr**
Unspiked sample (mg/L)	0.005	0.125	0.012
Spiked sample(mg/L)	4.7123	4.957	4.635
Conc spiked (mg/L)	5	5	5
% recovery	94.146	96.64	92.46

4.2 Physicochemical Parameters of the Water from River Chania

The pH, EC, BOD and COD level water from river Chania during long rains and short rains seasons are presented in Table 4.2.

Table 4.2 Level of physico-chemical parameters in water from river Chania in long and short rains seasons

	Long rains-River sections (n=3)				**Short rains-River sections (n=3)**				
Parameters	**Upstream**	**Midstream**	**Downstream**	**P Value**	**Upstream**	**Midstream**	**Downstream**	**P value**	**WHO limit**
pH	6.68 ± 0.04^{c}	6.88 ± 0.03^{a}	6.76 ± 0.03^{b}	<0.05	7.11 ± 0.03^{a}	6.98 ± 0.03^{c}	7.04 ± 0.01^{b}	<0.05	6.5-8.5
EC (S/cm)	109.00 ± 23.10^{c}	195.00 ± 1.41^{a}	164.00 ± 24.5^{b}	<0.05	133.00 ± 1.56^{c}	250.00 ± 80.6^{a}	192.00 ± 1.23^{b}	<0.05	700
BOD (mg/L)	4.92 ± 0.79^{c}	15.40 ± 2.88^{a}	8.42 ± 0.52^{b}	<0.05	3.25 ± 0.75^{c}	10.40 ± 0.53^{a}	7.49 ± 0.46^{b}	<0.05	10
COD (mg/L)	16.80 ± 1.64^{c}	32.40 ± 1.94^{a}	23.90 ± 0.79^{b}	<0.05	20.70 ± 1.07^{c}	43.70 ± 7.98^{a}	26.90 ± 1.56^{b}	<0.05	50
TSS (mg/L)	307.00 ± 14.00^{c}	1841.00 ± 275.00^{a}	569.00 ± 78.40^{a}	<0.05	170.00 ± 72.90^{c}	884.00 ± 86.90^{a}	407.00 ± 27.10^{b}	<0.05	30

Note: Mean±SE values followed by same small letter within the same row do not differ significantly from one another (One-Way ANOVA, means separated using Turkey Post hoc test, $p<0.05$)

The pH ranged between 6.7 and 6.9 (midstream) in long rain season and 7.0 (midstream) -7.1 (upstream) in short rain season. The pH level differed significantly between the sampling points in long rains and short rain season ($p<0.05$) (Table 4.2).

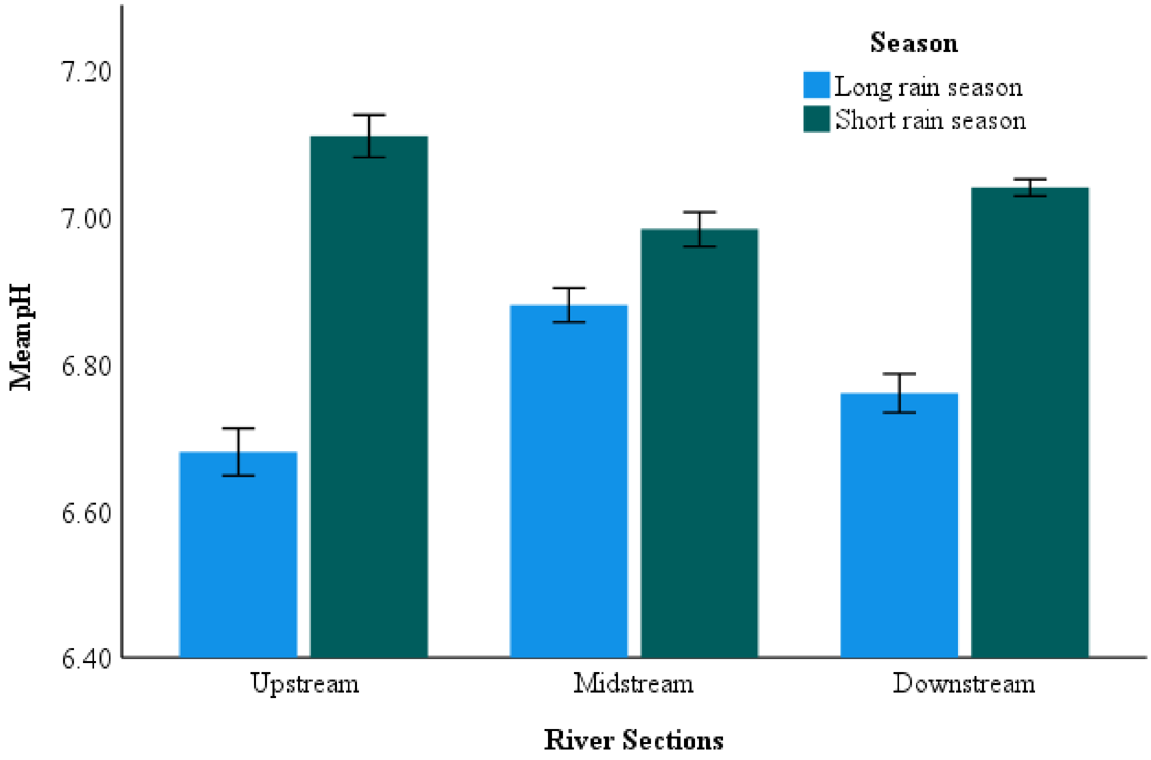

Figure 4.2.1 Seasonal variation in levels of pH in water from Chania. Key: Wet-long rains, Dry-short rains

During the short rains season, pH values (6.98-7.11) were slightly higher than those recorded in the long rains season (6.68-6.88) although in both seasons, the values were within the WHO recommended range (6.5–8.5) (Figure 4.2.1). The lower pH during the long rains season may be attributed to runoffs from the agricultural activities and industrial waste, which introduces minerals and acidic compounds into the river. Additionally, higher rainfall increases water volumes, which enhances dilution of dissolved minerals and organic compounds, reducing the river's buffering capacity and consequently lowering pH. Rainwater itself typically has a slightly acidic pH (approximately 5.6–5.8), and its contribution further decreases pH during periods of heavy rainfall.

In contrast, during the short rains season, reduced rainfall results in limited dilution and minimal introduction of acidic inputs from surrounding farms and industries along River Chania, leading to slightly higher pH values. The findings align with those of Kimani *et al*. (2016), who also reported pH levels within WHO limits in both seasons, with higher pH in the short rains season. They attributed this pattern to increased evaporation and reduced water volume during the short rains, which concentrates organic matter and mineral constituents, thereby elevating pH levels.

The study results showed the EC ranged from 109-195 µS/cm in long rains season and 133-250 µS/cm in short rains season. In long rain season, a higher EC was recorded in midstream section (195 µS/cm) followed by downstream (164 µS/cm) while the upstream section registered the lowest value (109 µS/cm). A similar pattern was observed during the short rains season, with the midstream section recording the highest EC value (250 µS/cm), followed by the downstream section (192 µS/cm). The elevated EC values at the midstream section in both seasons may be attributed to runoff carrying dissolved ions from surrounding agricultural farms, domestic sewage from nearby settlements, and effluents from LIK and other industries located near this stretch of the river. As the river flows downstream, dilution from underground inflows reduces ion concentration, resulting in lower EC levels compared to the midstream section. EC values at all sampling points remained within WHO recommended limits. Furthermore, EC levels differed significantly across the sampling points in both seasons ($p < 0.05$).

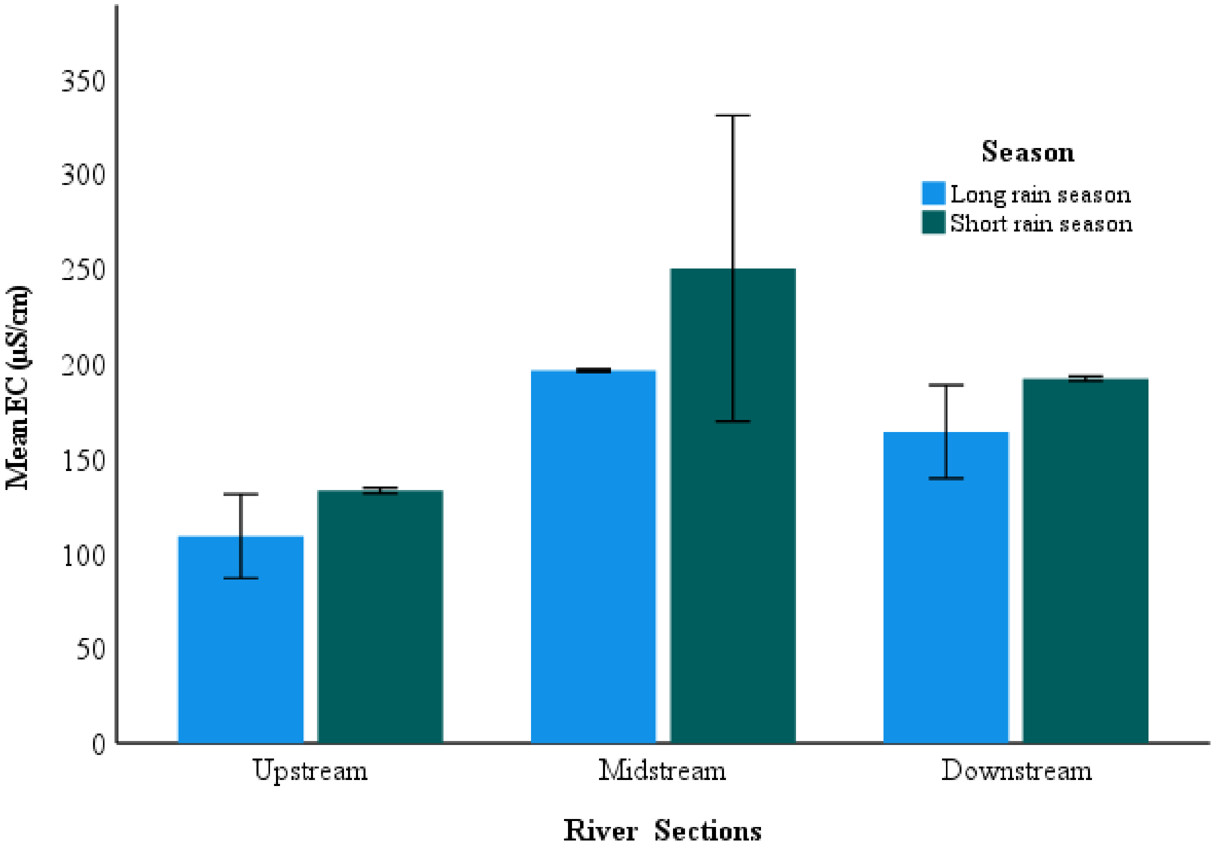

Figure 4.2.2 Seasonal variation in levels of EC in water from river Chania. Key-Wet-long rains, Dry-short rains

Seasonally, EC levels were higher during the short rains season than in the long rains season (Figure 4.2.2). The elevated EC during the short rains season may be attributed to increased evaporation, which concentrates dissolved ions in the river due to reduced water volume. Limited runoff during this season also contributes to more stable EC levels across sampling points, as fewer external inputs alter ion concentrations. Additionally, the short rains season is characterized by minimal rainfall, resulting in reduced dilution and consequently higher EC values.

In contrast, the long rains season exhibited lower EC values. The substantial rainfall during this period increases water volume and dilutes dissolved ions, leading to reduced conductivity. The significant variation in EC among sampling points during the long rains season may be influenced by local geography, where differences in land use and runoff inputs introduce varying concentrations of dissolved substances into specific sections of the river. The observed seasonal EC patterns correspond with findings by Kimani *et al*. (2016), who reported EC levels within WHO limits and consistently higher during the short rains season. They attributed the elevated EC in the short rains season to higher temperatures and lower water volume, which increase the concentration of dissolved ions.

In long rains season, BOD ranged from 4.92-15.40mg/L and 3.25-10.40mg/L in the short rains season. The BOD differed significantly between the sampling points and seasons ($p<0.05$) (Table 4.2). In the long rains season a significantly high BOD was recorded in the midstream (15.0mg/L) which was above the WHO standard (10 mg/L). However, downstream and upstream had BOD (8.42mg/L and 4.92mg/L) which was within the WHO standard. This similar trend was noted in short rains season with midstream recording BOD more than WHO standard and significantly higher (40 mg/L) than downstream (7.49 mg/L) and upstream (3.25mg/L). This may be attributed to higher organic waste from sewage waste, agricultural runoff including fertilizers and industrial effluents from various industries including LIK. This organic matter provides conducive environment and substrates for microbial growth and multiplication which is associated with high oxygen consumption hence high BOD. At the midstream, the velocity of runoff is low than in upstream hence there is stagnation which gives time for the organic matter to settle and be used by water microbes hence high BOD (Zhao *et al*., 2020). Upstream has faster-flowing-cleaner water and less organic pollution. Also, it receives limited pollutants because its location is farther from human activities which generate organic waste. This is contrary to the downstream where there is high dilution from water inflows thus reduced concentration of organic pollutants leading to lower BOD than the upstream and midstream and the BOD ranged from 0.84-1.69 mg/L (Ustaoğlu *et al.*, 2020).

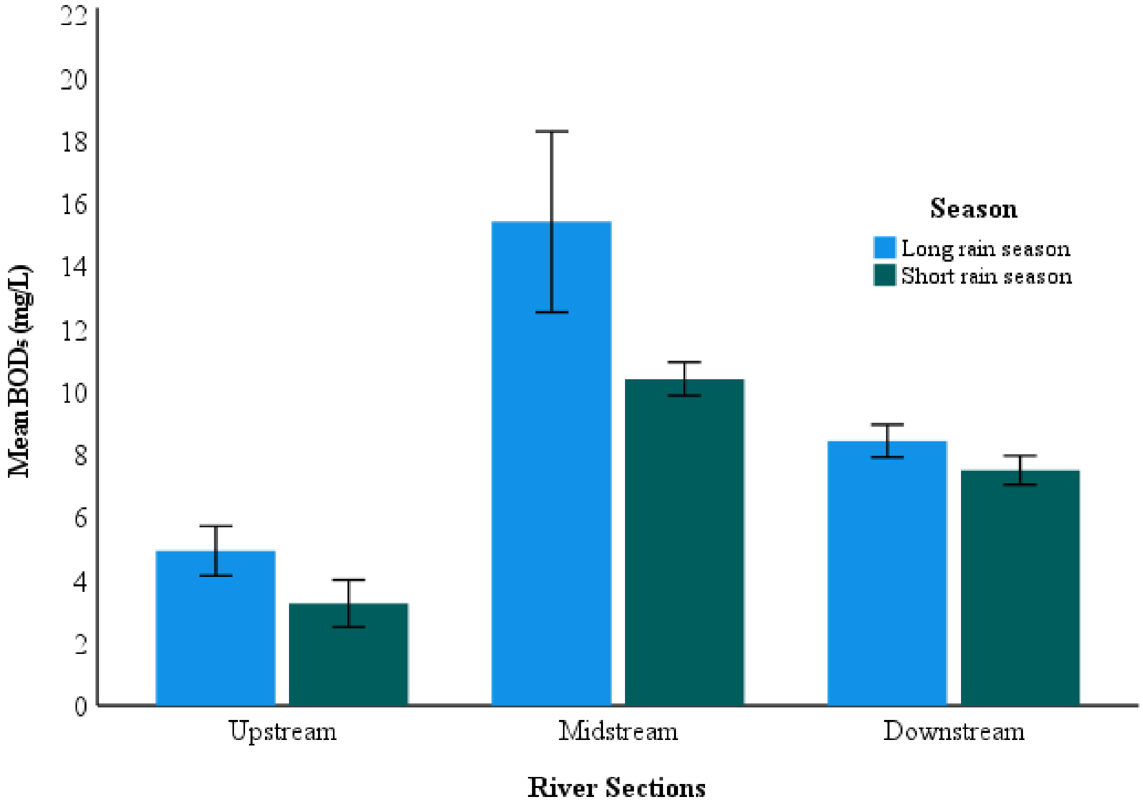

Figure 4.2.3 Seasonal variation in levels of BOD in water from river Chania. Key-Wet-long rains, Dry-short rains

Short rains season had lower BOD than long rains season (Figure 4.2.3), being attributed to the difference in water level. Long rains season has high water runoff hence collect high organic matter and nutrients which cause spike in BOD level. In short rains season the water level is low hence low organic matter in the water flowing in the river thus low BOD (Ustaoğlu and Tepe, 2019).

The COD ranged from 16.80-32.40mg/L in long rain season and 20.70-43.70mg/L in short rain season. The COD varied significantly between sampling points in long and short rain seasons ($p<0.05$) (Table 4.2.1). In long rain season, midstream had significantly high COD (32.40mg/L) than the downstream (23.90mg/L) and upstream (16.80mg/L). In the short rain season, the COD was high in midstream (43.70mg/L) than downstream (26.90mg/L) and upstream (20.70mg/L). This is due to run off from agricultural activities, effluents from domestic and industrial activities including LIK. In the two seasons, none of the sampling points had COD higher than WHO limit for COD. These findings corroborates with Wang *et al*. (2021) where the COD was high in midstream due to high pollution levels from domestic sewage, industrial effluents and agricultural substances utilizing oxygen. The pollution level is significantly high short rain season than long rain season hence high COD levels in short rains than in long rain season (Figure 4.2.4). This may be due to dilution of organic and inorganic substances by rainwater in long rain season.

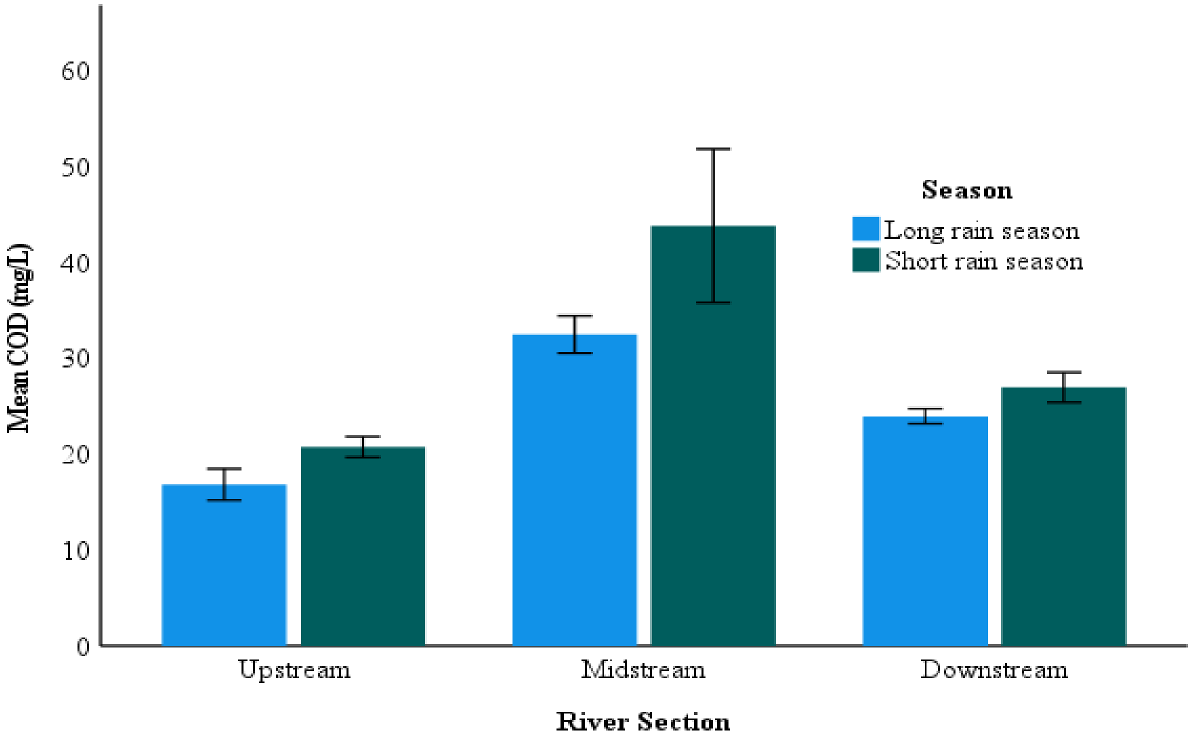

Figure 4.2.4 Seasonal variation in levels of BOD in water from river Chania. Key-Wet-long rains, Dry-short rains

TSS ranged from 307-1841mg/L in long rain season and 170-844 in short-rain season. Besides, it varied significantly between sampling points in both seasons ($p<0.05$) (Table 4.2). In the long rain season the TSS was significantly high in midstream **(**1841 mg/L) than upstream (307.00mg/L) and downstream (569.00mg/L). Similarly, in short rain season, midstream had significantly higher TSS (884 mg/L) followed by the upstream (407 mg/L) while downstream recorded the lowest TSS (170mg/L). This is because the midstream is located in an area with various industries compared to the upstream and downstream. The TSS in the three sampling points and in the two seasons exceeded the WHO threshold for TSS in drinking water. This corroborates with Adjovu *et al*. (2023) where TSS reduced as result of many reservoirs of Colorado river which help in settling out of sediments as it flowed from headwaters to terminus. The TSS ranged from 2-38200 mg/L in the eight sampling stations. The finding is also supported by a study done by Njuguna *et al*.

(2019) where in the midstream, there was high waste level from industries, sewage and agrichemicals ,which find their way to Chania river through its tributaries hence higher in midstream than upstream and downstream.

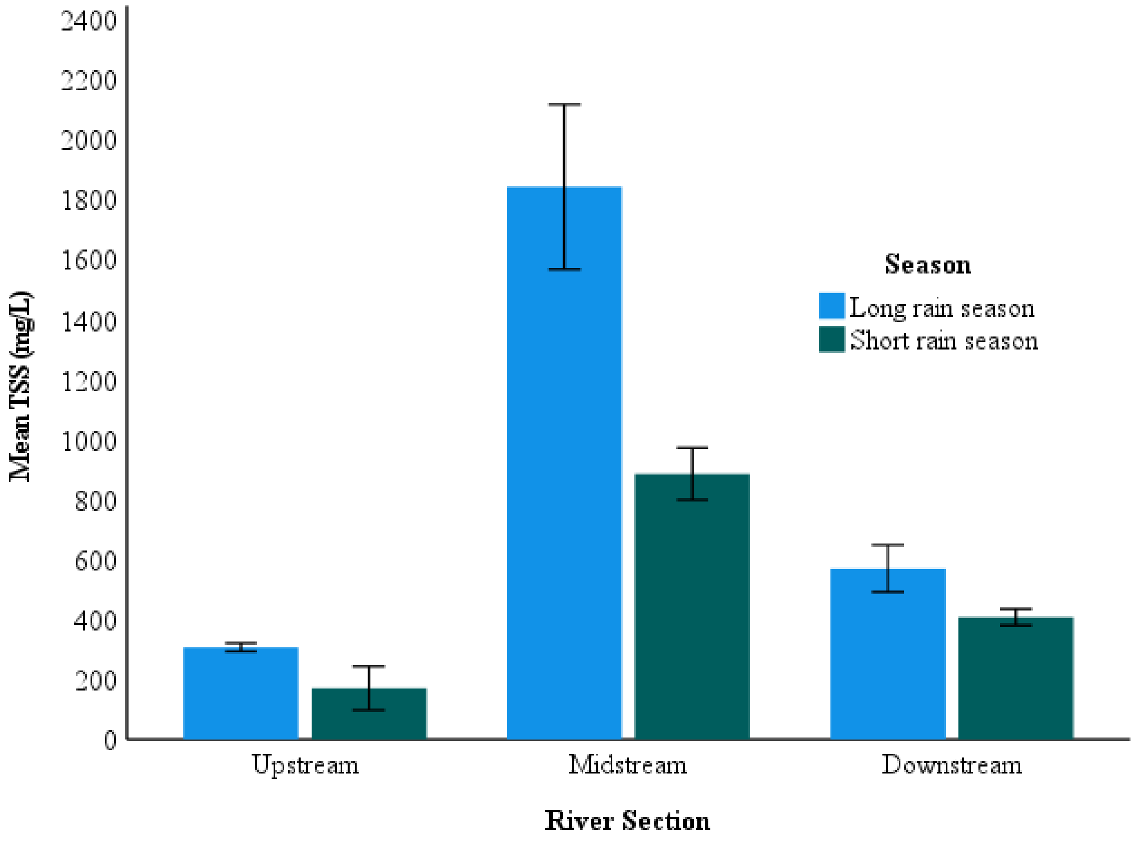

Figure 4.2.5 Seasonal variation in levels of TSS in water from river Chania. Wet-long rains, Dry-short rains

The TSS was higher in long rain season than short rain season (Figure 4.2.5). This is because of erodible soil that is carried by rainwater which in turn results to higher sediment and TSS during the long rain season (Towfiqul *et al*., 2020). Additionally, rainfall washes agricultural and industry by products during the long rain season hence a spike in TSS than in the short rain season, while in the short rain season, there is limited rainfall hence less runoff carrying the suspended solids (Hoess and Geist, 2022).

4.3 Selected heavy Metals and Total Phenols in Water Obtained from River Chania

The Cr, Cd, Pb and total phenol levels in water obtained from river Chania are presented in Table

4.3

Table 4.3 Levels of selected heavy metals and total phenols (mg/l) (mean±SE) in long rains and short rains seasons

Parameters	**Long rains-River sections (n=3)**				**Short rains-River sections (n=3)**				**WHO limit**
	Upstream	**Midstream**	**Downstream**	**P value**	**Upstream**	**Midstream**	**Downstream**	**P value**	
Total Phenol	0.042 ± 0.032^{b}	0.143 ± 0.020^{a}	0.038 ± 0.029^{b}	<0.001	0.011 ± 0.003^{b}	0.116 ± 0.008^{a}	0.007 ± 0.000^{b}	0.049	0.001
Cr	0.119 ± 0.005^{b}	0.191 ± 0.016^{a}	0.145 ± 0.005^{b}	0.002	0.103 ± 0.006^{b}	0.160 ± 0.004^{a}	0.134 ± 0.003^{b}	<0.001	0.05
Cd	0.003 ± 0.000^{b}	0.004 ± 0.000^{a}	0.003 ± 0.000^{b}	0.01	0.002 ± 0.000^{b}	0.003 ± 0.000^{a}	0.002 ± 0.000^{b}	<0.001	0.003
Pb	0.016 ± 0.002^{b}	0.025 ± 0.004^{a}	0.016 ± 0.002^{b}	<.001	0.014 ± 0.002^{b}	0.020 ± 0.002^{a}	0.013 ± 0.002^{b}	<0.001	0.01

Note: Mean±SE values followed by same small letter within the same row do not differ significantly from one another (One-Way ANOVA, means separated using Turkey Post hoc test, p<0.05.

The total phenol levels ranged from 0.038-0.143mg/L in the long rains season and 0.007-0.116mg/L in the short rains season. In long rains season the total phenol level differed significantly across the sampling points ($p<0.001$). The highest total phenol level was recorded in midstream (0.143 mg/L) followed by the upstream (0.042 mg/L) while downstream had the lowest phenol levels (0.038). In the short rains season, total phenol level differed between the sampling points ($p=0.049$). The midstream section had the highest total phenol (0.116 mg/L) than upstream (0.103 mg/L) and downstream (0.007 mg/L). Besides, level of phenol in both seasons was significantly higher than WHO limit (0.001 mg/L).

The highest phenol level in the midstream may be due to accumulation of runoff containing the industrial, agricultural or urban wastes which often collects at the midsection of rivers due to the water pattern. The midstream could be exposed to higher pollutant levels mainly from human activities such as factories and settlements, reinforcing the likelihood of a local, consistent source of phenol pollution in that area. The finding is in line with Chebet *et al*. (2020) where the level of water contaminants varied between the various sampling points with S4 and S5 recording pollutants exceeding WHO permissible limits

Although the level of phenol in the upstream was lower, it was still significant, and this shows potential pollution upstream. However, the pollution could be lower in upstream than midstream because there are fewer human activities in upstream. In contrast, the downstream had the lowest phenol level due to the dilution effect which expands downstream, potentially reducing the pollutant concentration. The finding corroborates with Zhou *et al*. (2017) where the phenol levels differed between the sampling sections of Yinma River basin in China due to differences in pollutant levels across the river. Some sections had elevated phenol levels because it receives pollution from runoffs, agriculture and fish farming. River section near farmland areas had high phenol levels because farming involves the use of pesticides, and fertilizers which are washed off during the rainy season into the river and this contributes to the high phenol levels.

The phenol levels varied between the seasons, with long rains season recording higher levels than short rains season, (Figure 4.3.1). This may be as a result of water level difference. Short rains season has reduced water flows and less runoff and contamination sources hence reducing the likelihood of new contaminants entering the river from agricultural, industrial and urban sources. Consequently, the phenol may remain relatively constant along the river length. A higher phenol reported in long rains season was due to increased input of pollutants into aquatic environment along with water runoff. Also, there is a higher sorption of sediments from different concentrations in long rains season than in short rains season.

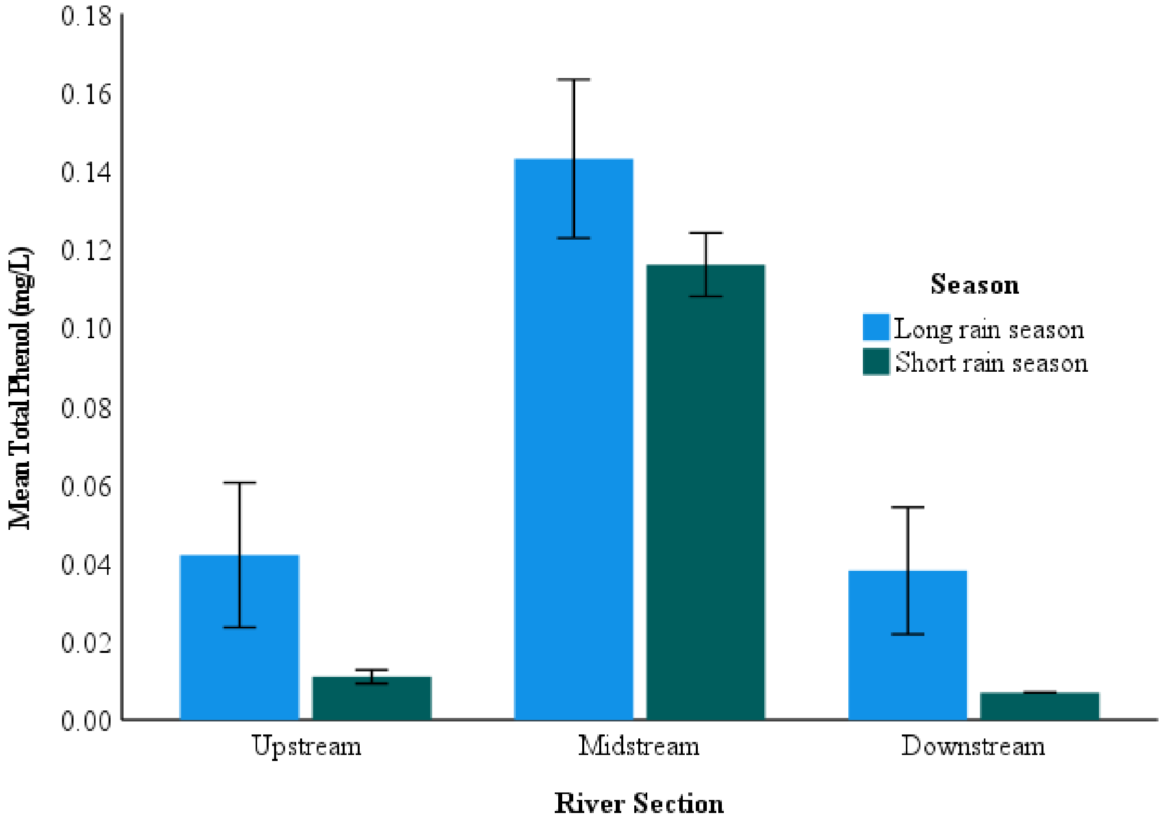

Figure 4.3.1 Seasonal variation in levels of total phenols in water from river Chania. Key-Wet-long rains, Dry-short rains

Although the levels of total phenols differed in long rains and short rains seasons, phenol levels remained high in the midstream in both long rains and short rains seasons suggesting that the contamination in this section is persistent and not in the upstream and downstream. The Cr levels ranged from 0.145-0.191 mg/L in long rains season and 0.103-0.160 mg/L in short rains season. In long rains season, Cr level in water sampled from river Chania differed significantly between the sampling points (p=0.002). Midstream section had significantly high Cr (0.191 mg/L) than downstream (0.145 mg/L) and upstream (0.119 mg/L). Similar trend was observed in short rains season with midstream recording higher Cr (0.160 mg/L) than downstream (0.134 mg/L) and upstream (0.103 mg/L). In both seasons Cr level was higher than (0.05 mg/L) WHO recommended limit.

Cr differences between sampling points in the two seasons may be attributed to differences in activities such as industrial discharge and agrichemicals along river Chania. In long rains season, the discharge is high due to runoff occasioned by rain. In short rains season, runoff is low hence low levels of Cr. This is in line with Nyantakyi *et al*. (2019) where the Cr level differed significantly across the different Tano river plain sections due to differences in industrial and agricultural effluents discharged to the river at different sections. Besides, sediments from the agricultural farms released into rivers undergo changes including pH and redox potential when environmental conditions change hence serve as source of heavy metal pollutants such as Cr in water sources including rivers (Singh *et al*., 2017).

According to Singh *et al*. (2017), Cr emissions in surface water is mainly from municipal effluents. Chania River especially midstream section is adjacent to industries including LIK and near towns such as Thika town. Besides, the section has high human settlements with intense human activities hence high road activities which involve use of vehicles. The waste from vehicles such as radiators, tyre wears are washed off to the river during the rainy seasons hence contributes to the high Cr levels in midstream and in long rains season than the short rains season. Industrial processes such as LIK and textile industries are among the main source of effluents containing Cr compounds (Valentín-Reyes *et al*., 2019). According to Liang *et al*. (2021) Cr(III) is commonly found in soil because it is stable and during rainy season, it is washed off as runoff hence significantly higher levels in water during long rain season than short rain season.

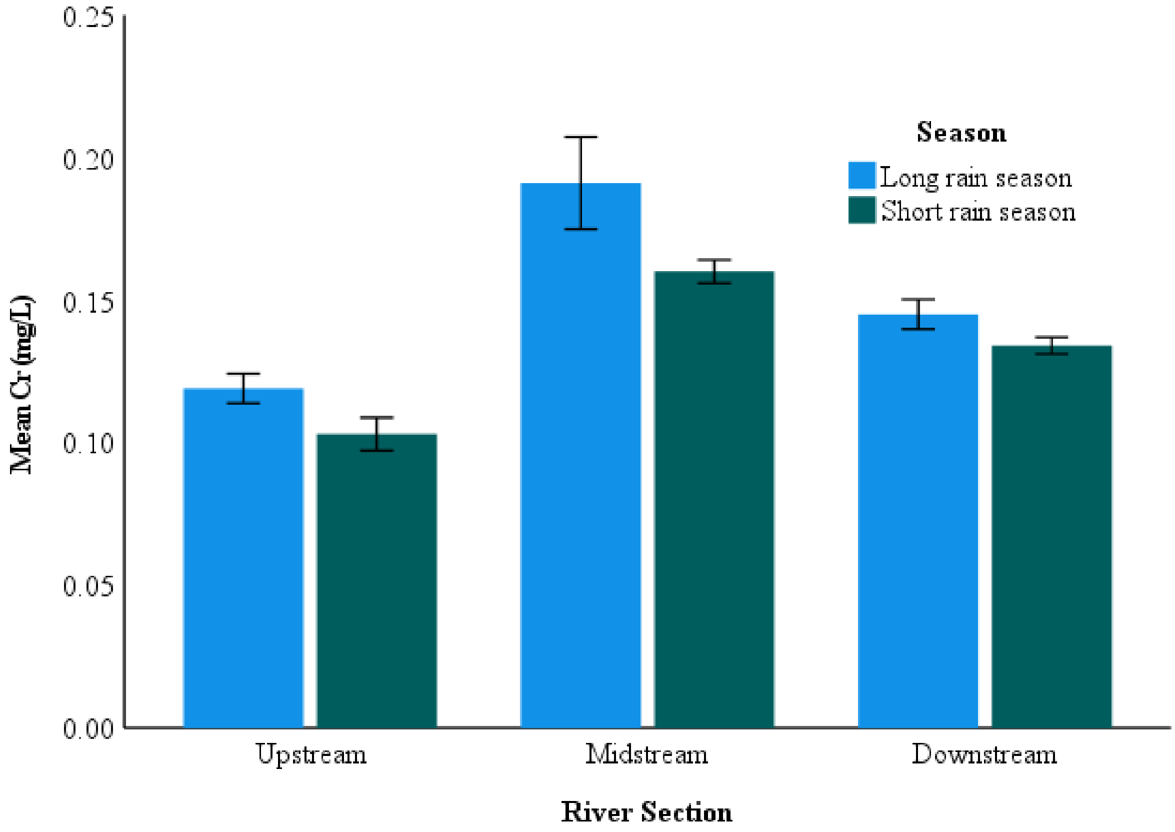

Figure 4.3.2 Seasonal variation in levels of Cr in water from river Chania. Wet-long rains, Dry-short rains

The Cr level was significantly high in the midstream in both seasons. However, Cr was high in long rains season than in short rains season (Figure 4.3.2). Elevated level in midstream might have been occasioned by persistent flow of chromium from other sources which accumulates in the midstream. In addition, long rains season had higher levels of Cr which could be linked to increased water flow in long rains season. High flow of water is inclusive of contaminants and enhanced leaching of chromium from soils and rocks into the water hence high in long rains season than in the short rains season. This finding corroborates with Oruko *et al*. (2014) where Cr (33000mg/L) was reported and it was attributed to effluents from Asili tanneries. The mean Cr and Cr (VI) concentrations (204.9 and 943) was above WHO permissible limits.

Cd levels ranged from 0.002-0.004mg/L in long rain season and 0.002-0.003mg/L in short rains season (Table 4.3). The Cd level differed significantly between the sampling points in long rains season (p=0.01). The midstream section recorded significantly high Cd level (0.004 mg/L) than upstream and midstream with Cd level of 0.03 mg/L each. Upstream and downstream had Cd level which was within WHO recommended limit (0.003 mg/L) while midstream Cd exceeded the limit. This is contrary to short rains season where all sampling points had Cd level within WHO limit (0.003 mg/L). However, midstream had higher Cd level (0.003 mg/L) than upstream and downstream with 0.002 mg/L each. Cd level was significantly high in long rains season than in short rain season (Figure 4.3.2). This may be attributed to high speed and excessive runoff during the long rain season compared to short rain season which has no or limited runoff. As a result, a lot of pollutants containing Cd are carried into the river. The finding is in line with Nyantakyi *et al*. (2019), where the heavy metal concentrations including Cd was high in the long rain season than short rain season. Oruko *et al*. (2014) reported Cd of 1.21 mg/L from final effluents discharged by Asili tanneries.

Similarly, Bhuyan and Bakar, (2017) reported that, agricultural waste, urban runoff and discharge of untreated industrial waste results to high Cd concentrations discharged to rivers in long rains seasons than in short rains season. Cd was significantly higher in water (0.03-0.05 mg/L) than sediments (0.01-0.13 mg/L). Besides, it was significantly higher than WHO permissible limits. In areas where environmental regulation is limited, and technologies on wastewater treatment is not enforced, heavy metal such as Cd, are significantly high in the water sources.

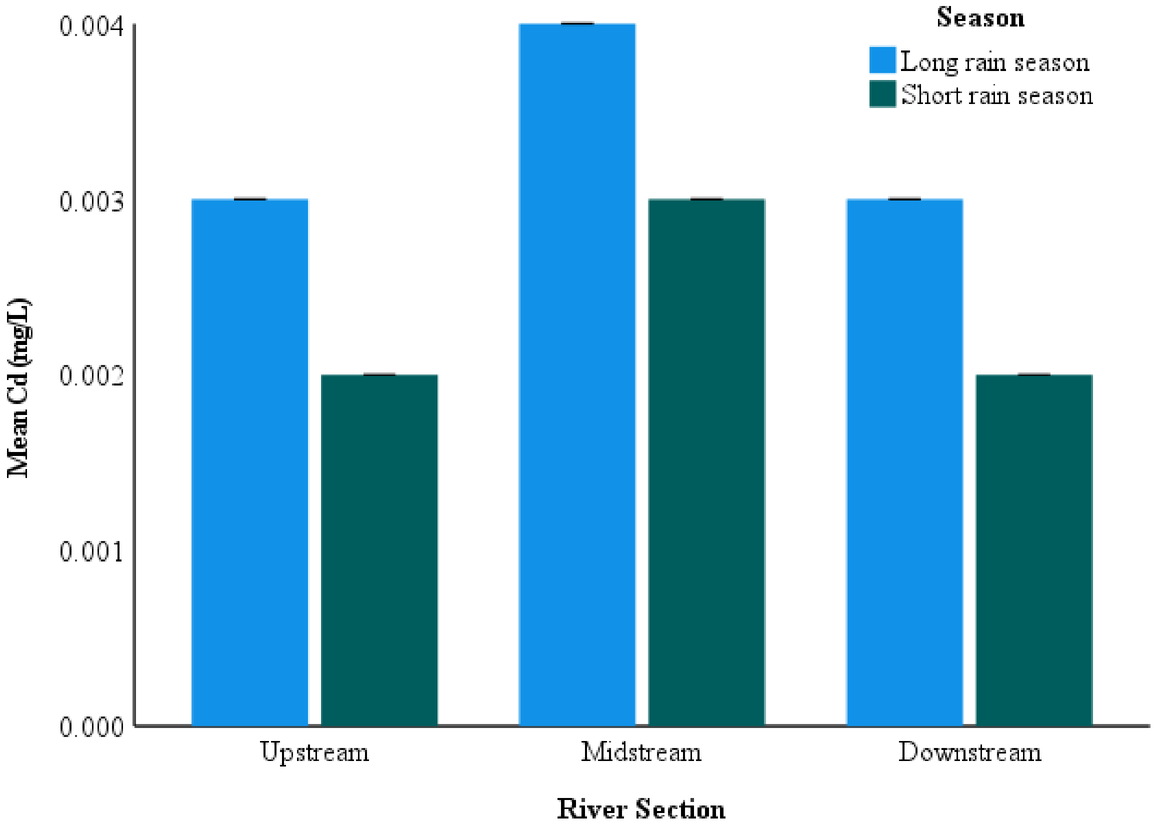

Figure 4.3.3 Seasonal variation in levels of Cd in water from river Chania. Key-Wet-long rains, Dry-short rains

Moreover, in long rain season, there is increased desorption and heavy metals solubility properties hence present in high concentrations than in short rains season. According to Nyantakyi *et al*. (2019), Cd above permissible level poses serious health risks to population including brain damage, skin diseases, kidney failure and nervous system destruction. Therefore, dependents of fresh water from Chania River are at risk to serious health complications should if the heavy metal contaminations menace is not dealt with.

The Cd level differed significantly between the sampling points ($p<0.05$) in long rains and short rains season. Midstream sampling points had significantly higher Cd level in the short rains and long rain season. This shows that the Cd contamination is not uniform across the area and could be influenced by specific local sources and environmental characteristics which are unique to each sampling point. Besides, it suggests that the source of Cd is localized in midstream mainly the industrial discharge, urban runoff or some agricultural activities which introduces Cd. The high Cd level in sampling points in the long rains season than in short rains season may have been occasioned by increased runoff from surrounding land, washing more of the Cd from soils and sediments. This corroborates with who established that Cd discharged from industries producing iron and steel, cement, nonferrous metals, and fertilizers.

Apart from the LIK, Thika town has various industries including the iron and metal plants whose effluents are washed off to the rivers during rainy season. Considering that Chania rivers flows a rich-agricultural area when phosphate fertilizers are used, it contributes to the Cd levels in the water during the long rains season as described by Nyantakyi *et al*. (2019). Similarly, there is enhanced leaching during long rain season resulting to high Cd in long rains season than short rains season. This is in line with Ojekunle *et al*. (2023) who established that the Cd level on water obtained from Agbara ranged from 0.01-0.03mg/L which was above WHO permissible limit of 0.001 mg/L.

Pb levels ranged from 0.016 to 0.020 mg/L during the long rains season and 0.013 to 0.020 mg/L during the short rains season (Table 4.3). In both seasons, Pb levels differed significantly across the sampling points ($p = 0.001$), with the midstream section recording the highest concentrations (0.025 mg/L during the long rains and 0.020 mg/L during the short rains) (Table 4.3). At all sampling points and in both seasons, the observed Pb levels slightly exceeded the WHO guideline value of 0.01 mg/L.

The spatial variation in Pb levels is likely attributed to effluent inputs from local industries and sewage discharge. This finding is consistent with Custodio *et al.* (2020), who reported that elevated Pb levels in rivers predominantly originate from industrial activities (48%), followed by agricultural activities (27.3%) and mixed sources (24.7%). These activities are more concentrated in the midstream section, where human and industrial activities are highest, and less pronounced in the upstream and downstream sections. This pattern explains the significant differences in Pb concentrations observed across the sampling points. The Pb level differed significantly between the sampling points in long rains and short rains seasons. The highest Pb was recorded at the midstream. The high Pb in the midstream in the short rains and long rains season shows that there is a localized source of lead contamination in this area. The Pb in the Chania River was 23 mg/L while in Montario River the Pb level was 21.10 mg/L. The potential source of this contamination includes industrial discharge, urban runoff or their specific activities within the river section which elevates Pb level. Similarly, Pb in long rains season may be attributed to increased runoff which increases the Pb levels in the water in long rain season than short rain season. This finding is in line with a study by Ojekunle *et al*. (2023) where the level of Pb was ranged between 0.09-0.28mg/L hence above WHO permissible limit (0.001mg/L).

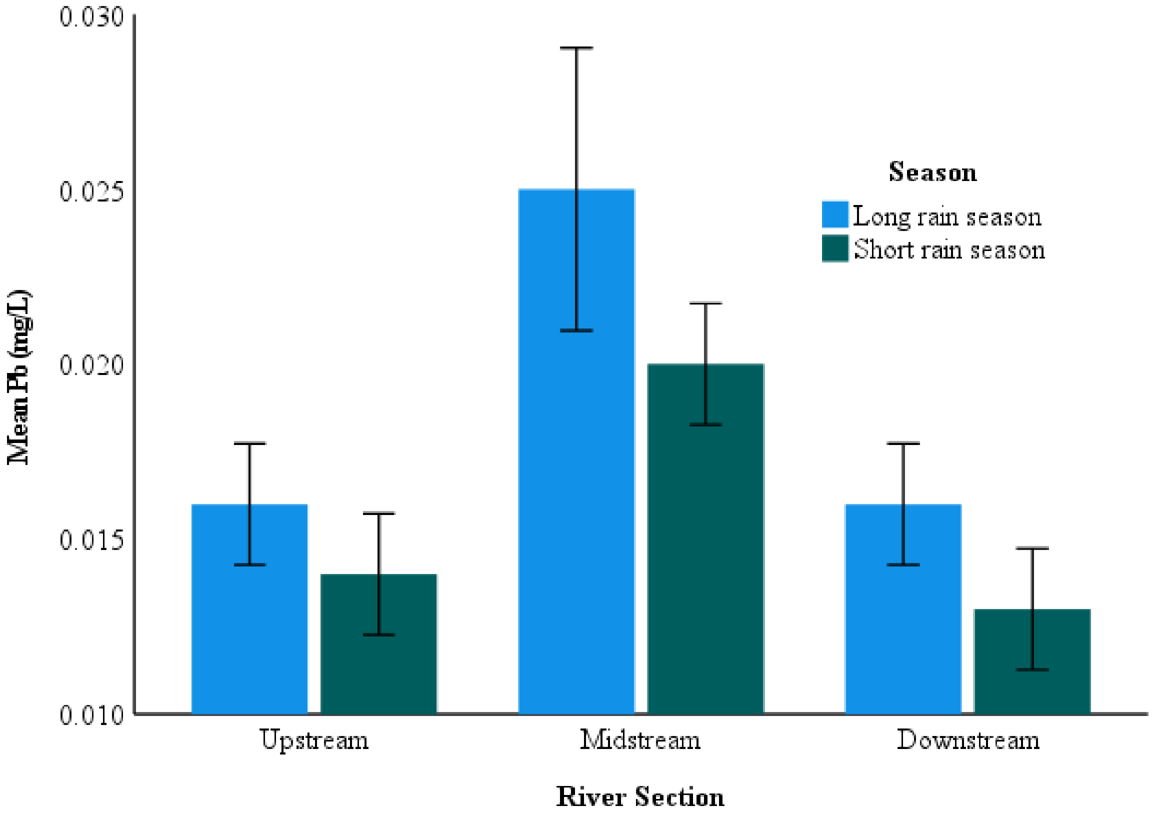

Figure 4.3.4 Seasonal variations in levels of Pb in water from river Chania. Key-Wet-long rains, Dry-short rains

Seasonally, Pb level was significantly high in long rains season than short rains season. The variation is explained by increased runoff which carries heavy metal laden debris to the river hence high levels of heavy metals such as Pb. According to Nyantakyi *et al*. (2019), high water level during the long rains season results to increased wash off of pollutants into the surface water sources such as rivers. In addition, soil erosion, leaching and atmospheric deposition results to increased heavy metals in rivers, lakes and oceans (Custodio *et al*., 2020).

Additionally, Pb is used in the production of various industrial products including insecticides and pigments paints (Viczek *et al*., 2020). River Chania flows through agricultural areas utilizing insecticides, pesticides in control of insects and pesticides. Residues from these products are washed off during rainy season to the soil and to water sources thus contributing to increased levels of Pb in the long rains season than short rains season. Besides, areas around Thika town have various industries utilizing paints, glass and plastics which are known to have Pb. Waste from these industries is disposed-off and finds its way to water sources including Chania River.

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The assessment of physico-chemical parameters (pH, EC, TSS, BOD, and COD) were successfully examined in water samples. The results showed clear spatial variation along the river, with the midstream showing highest values for EC, TSS, BOD, and COD. This confirms the influence of anthropogenic activities such as effluent disposal from nearby industries and runoffs from agrichemicals. Upstream recorded comparatively lower concentrations, reflecting minimal industrial interference. Besides, most physico-chemical parameters were within the WHO-recommended limits, except TSS, which exceeded the limits in both seasons. BOD values exceeded the WHO-recommended limits at the midstream section only, indicating a significant organic pollution at this section. Seasonally, most contaminant concentrations were significantly higher during the long rains season than in the short rains season, except for pH, electrical conductivity (EC) and COD which were higher in short rains season.

Total phenols and selected heavy metals (Cd, Cr, and Pb) varied significantly across the sampling sections with midstream recoding the highest. This confirms the effect of tannery effluent which commonly uses chromium and colour pigments in tanning processes. These contaminants exceeded the WHO recommended limits, except for cadmium (Cd), which indicates potential ecological and health risks. These contaminants exhibited higher concentrations during the long rains season compared to the short rains season, indicating increased runoff and leaching during heavy rainfall periods thus contribute to elevated pollution levels.

5.2 Recommendations

i. The findings of this study indicate that the main sources of contaminants in River Chania are likely to be agricultural activities conducted along the riverbanks and industrial effluent discharge from nearby manufacturing industries, including Leather Industries of Kenya Limited. It is therefore recommended that farmers and local communities be sensitized on the environmental, ecological, and public-health risks associated with improper handling of agrochemicals, fertilizers, pesticides and poor effluent disposal. Awareness programs led by county authorities, environmental officers, and local leaders should be developed to promote best agricultural practices, including controlled use of fertilizers, proper storage and disposal of farm inputs. Such interventions would significantly reduce nutrient loading, chemical runoff, and sedimentation in the river.

ii. Environmental management agencies, including the National Environment Management Authority (NEMA), county water authorities, and relevant governmental bodies, should intensify efforts to implement sustainable water resource management strategies within the River Chania catchment. These measures should include strict control of agricultural runoff, enforcement of regulations governing industrial, municipal, and sewage effluent discharge, and regular inspection of wastewater treatment facilities. Additionally, periodic environmental monitoring and compliance audits should be conducted to ensure industries adhere to established standards. Strengthening policy frameworks, enhancing community participation in water governance, and promoting integrated watershed management are essential steps toward safeguarding the river’s ecological integrity.

iii. Although this study provides valuable insights into the contamination status of River Chania, further scientific investigation is necessary to gain a more comprehensive understanding of the pollution:

a) Determination of individual phenolic compounds in River Chania, as phenols exist in various forms that may differ significantly in toxicity, environmental persistence, and health impacts. Advanced analytical techniques such as GC-MS or HPLC should be employed to quantify and characterize specific phenolic species.

b) A broader assessment of heavy metals in the river ecosystem, encompassing additional metals not covered in the current study and examining their spatial and temporal variations. Such studies should also evaluate bioaccumulation in aquatic organisms, sediment–water interactions, and potential human exposure pathways. This information would provide a scientific basis for long-term monitoring, risk assessment, and formulation of targeted mitigation strategies.

c) Future research should be expanded to cover a larger geographical area within the River Chania catchment and adjacent sub-catchments. This will help capture spatial variations in water quality and provide a more comprehensive understanding of pollution sources and trends across the wider watershed.

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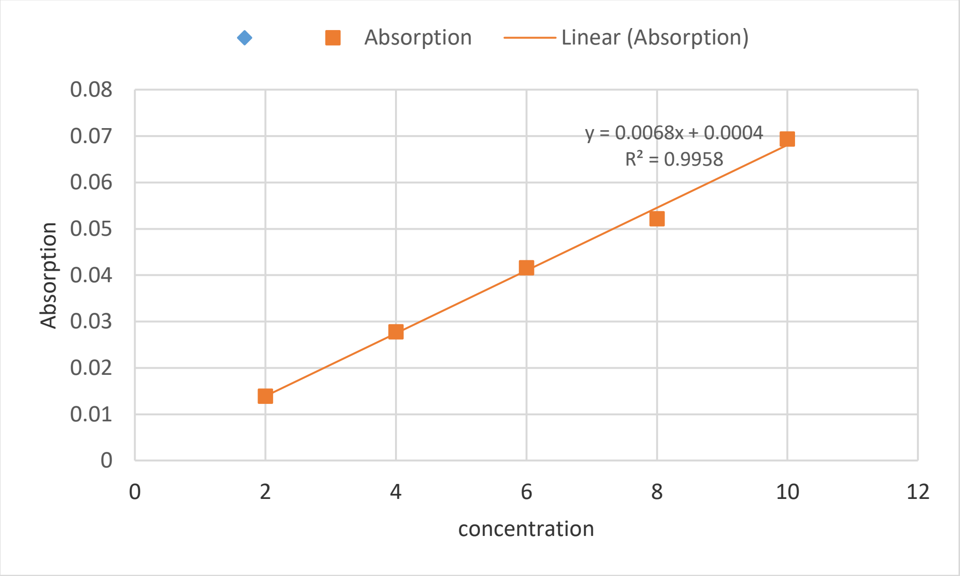
APPENDICES

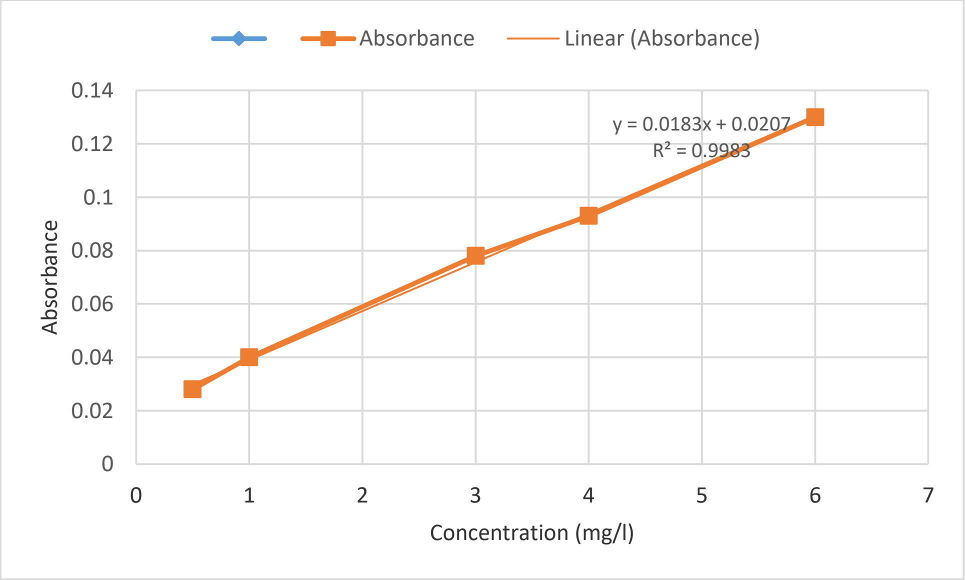
Appendix 1: Calibration Curve of Cr: Absorbance against Concentration

Concentration	2	4	6	8	10
Absorbance	0.0139	0.0278	0.0416	0.0522	0.0694



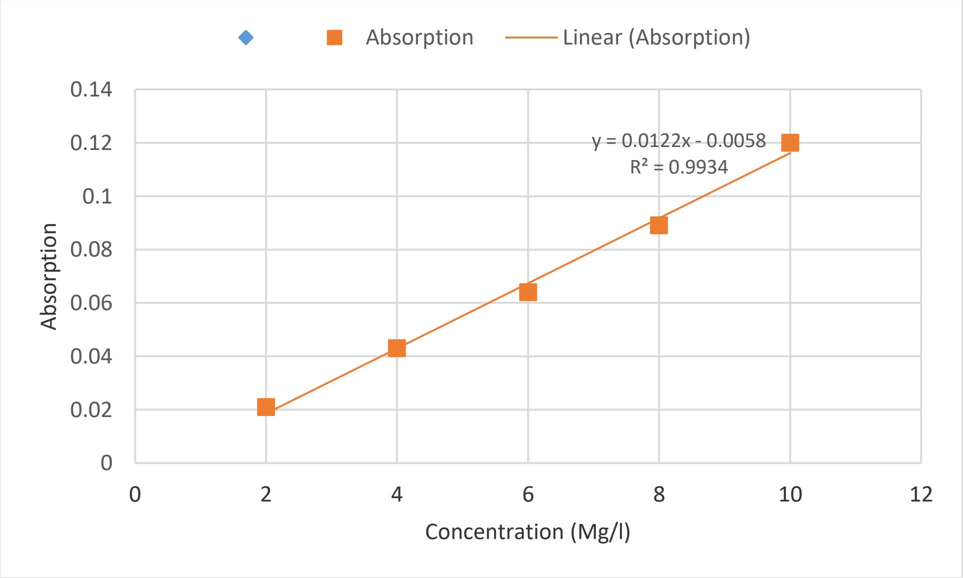
Appendix 2: Calibration curve of Cd: Absorbance against Concentration

concentration	0.5	1	3	4	6
Absorbance	0.028	0.04	0.078	0.093	0.13



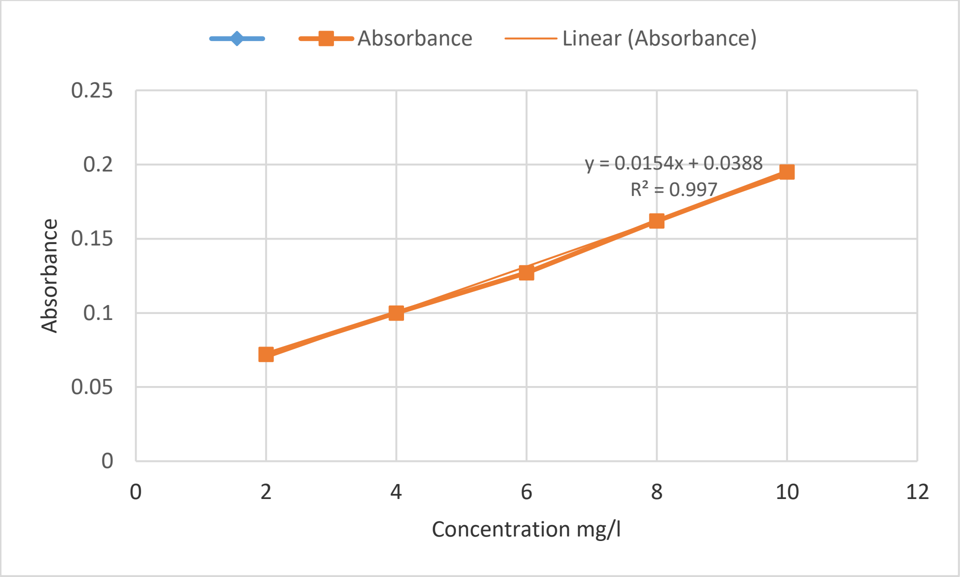
Appendix 3: Calibration curve of Pb: Absorption against Concentration

concentration	**2**	**4**	**6**	**8**	**10**
Absorbance	**0.021**	**0.043**	**0.064**	**0.089**	**0.12**



Appendix 4: Calibration curve for total phenols: Absorption against Concentration

concentration	**2**	**4**	**6**	**8**	**10**
Absorbance	**0.072**	**0.1**	**0.127**	**0.162**	**0.195**



Appendix 5: Analysis of heavy metals Using AA spectrometer