

**ANALYSIS OF SELECTED TOXIC METALS AND POLYCYCLIC AROMATIC
HYDROCARBONS IN THE MOLO RIVER WATER BASIN, KENYA**

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Requirements for the Award of Master of Science Degree in Chemistry of Egerton
University**

EGERTON UNIVERSITY

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DECLARATION AND RECOMMENDATION

Declaration

This thesis is my original work and has not been submitted or presented for examination in any institution.

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DEDICATION

This thesis is dedicated to my mother Esther Sote Kiptaiwa, father Joshua Chepsergon; it is because of you that I am soldiering on. To my beloved wife, your unwavering support and patience has been a firm anchor throughout this journey. To my children Kibet, Jepkorir and Miningwo your curiosity, joy and dedication to learning inspired me for more. This work is for you.

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ABSTRACT

Water quality is affected by the concentration of heavy metals, cations, anions, microbes, and organic compounds, which when present outside concentrations recommended by guideline values provided by regulatory bodies like world health organization (WHO) and European commission (EC), the water is deemed polluted. These pollutants in water bodies are associated with several health impacts on humans and aquatic organisms, such as effects on reproductive health, respiratory system, cardiovascular system and cancers. Using simple random sampling technique based on altitude and excluding the biological parameters and pays attention to the physical and chemical parameters by determining the concentration of some selected anions, cations, heavy metals, and polycyclic aromatic hydrocarbons (PAHs) in the Molo River water basin in Nakuru County. The water basin serves the people of Nakuru and Baringo Counties residing along Molo river water basin. The Nakuru – Eldoret highway passes through the basin with several vehicle accidents reported around Salgaa and the Sachangwan areas along the highway which has led to monumental oil spills, considered precursors for olefins and polycyclic aromatic hydrocarbons (PAHs) in the water basin. Agricultural activities including thriving flower farms, weathering and timber treatment in the basin are exposing the basin to pollution impacts resulting from organic contaminants and heavy metals. PAHs were extracted and analysed using Gas chromatograph (GC-MS), heavy metals analysed using atomic absorption (AAS), whereas sediment morphology was determined using a scanning electron microscope (SEM). The data generated for physical and heavy metals were used to calculate WQI and WPI which gave a single dimensionless numbers for overall water quality and pollution status. The average WQI obtained was 57.47 indicating that the water is slightly polluted. Also the average WPI obtained was 0.77 indicating that the water from the water basin is not of good quality. Sediment morphology and composition showed the presence of heavy metal pollutants of concern which include lead, manganese and copper. With respect to PAHs, cumulative unsubstituted PAHs $\sum_{18} = 216.51 \pm 0.51$ ppm, Substituted PAHs $\sum_{21} = 138.34 \pm 0.88$ ppm, Hetero-atomic $\sum_{14} = 23.86 \pm 0.35$ ppm, and a total PAH load of 378.71 ± 1.08 ppm. The detected PAHs had calculated total BaP-TEQ of 5.14 ppm. These PAHs reported included six (6) PAHs listed in the 16 priority pollutants which include acenaphthene, fluorine, fluoranthene, pyrene, chrysene and bezo[a]pyrene. This indicates the need for formulating policies to mitigate contamination in the basin frequent monitoring to provide timely status of contamination.

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LIST OF ABBREVIATIONS AND ACRONYMS

| | |
|----------------|--|
| AAS | Atomic Absorption Spectrophotometer |
| ADD | Average Daily Dose |
| ANFIS | Adaptive Neuro-Fuzzy Inference System |
| ANN | Artificial Neural Network |
| BaP | Benzo (a) Pyrene (Bap) |
| BaP-TEQ | Benzo(a)Pyrene Toxic Equivalent |
| BOD | Biochemical Oxygen Demand |
| CCMEWQI | Canadian Council Of Ministers Of Environment Water Quality Index |
| COD | Chemical Oxygen Demand |
| CYP1A1 | Cytochrome P450 1A1 |
| DDT | Dichlorodiphenyltrichloroethane |
| DNA | Deoxyribonucleic Acid |
| DO | Dissolved Oxygen |
| EC | European Commission |
| EDX | Energy Dispersive X-Ray Spectroscopy |
| EWQS | Egyptian Drinking Water Quality Standards |
| FAO | Food And Agriculture Organization |
| FIS | Fuzzy Inference System |
| GC-MS | Gas Chromatography-Mass Spectrometry |
| GPS | Geographical Positioning System |
| HI | Hazard Index |
| HQ | Hazard Quotient |
| IARC | International Agency For Research On Cancer |
| ISQGs | Interim Sediment Quality Guidelines |
| NEMA | National Environmental Management Authority |
| NSFWQI | National Sanitation Foundation Water Quality Index |
| OCPs | Organochlorine Pesticides |
| OWQI | Oregon Water Quality Index Indices |
| PAHs | Polycyclic Aromatic Hydrocarbons |

| | |
|---------------|---|
| PCBs | Polychlorinated Biphenyls |
| POPs | Persistent Organic Contaminants |
| RfD | Reference Dose |
| SDGs | Sustainable Development Goals |
| SEM | Scanning Electron Microscope |
| SPE | Solid Phase Extraction |
| TDS | Total Dissolved Solids |
| TIC | Total Ion Current Mode |
| US.EPA | United States Environmental Protection Agency |
| WAWQI | Weighted Arithmetic Water Quality Index |
| WHO | World Health Organization. |
| WPI | Water Pollution Index |
| WQI | Water Quality Index |

CHAPTER ONE

INTRODUCTION

1.1 Background information

Water is one of the most essential requirements for life but lots of its deposit is in the oceans, seas, and ice caps. To nurture a healthy nation, water supply must be adequate, safe and accessible to all. Climate change and the ever increasing demand from the rising human and animal population are continuously increasing pressure on water resources. In September 2015, the United Nations general assembly adopted a set of 17 sustainable development goals (SDGs) to end poverty, protect the planet and ensure prosperity for all while protecting the planet (Alcamo, 2019; Allen *et al.*, 2018). Of these 17 SDGs, goal 6 aims at increasing access to clean drinking water and sanitation for all. Besides drinking, water finds its use in industry, domestic systems, and agriculture. For these uses water can be sourced from rivers, lakes, oceans, wells, boreholes and, or harvested rainwater.

Quality of water varies significantly depending on the source, time, and geographical location with the different uses having differing quality requirements. International bodies like world health organization (WHO), United States environmental protection (USEPA) and locally bodies like National environment management authority (NEMA) and Kenya bureau of standards have set standards or guidelines that define acceptable levels of various physical, chemical, biological, and radiological characteristics in water. Assessment of water quality uses several indices which include water quality index (WQI) and water pollution index (WPI) which takes into account different physical, chemical and biological quality parameters (Dunca, 2018). Water quality is termed polluted when its composition changes failing to meet the quality requirements of the intended use. Water pollutants which include heavy metals and organic contaminants can be introduced to water sources through anthropogenic sources such as agricultural, industrial, and domestic effluent or through natural sources such as volcanic eruptions and weathering of rocks (Talabi & Kayode, 2019).

Different forms of a metal do not have an equal impact on the environment or organisms. Their bio-availability is influenced by physical factors such as temperature, phase association, adsorption, thermodynamic equilibrium, complexation kinetics, lipid solubility, octanol/water partition coefficients and sequestration (Adams *et al.*, 2020). Some acute and chronic toxic effects of heavy metals varies with the metal oxidation state for instance the toxicity of different

forms of mercury follows the order; $\text{Hg}^0 < \text{Hg}^{2+}$, $\text{Hg}^+ < \text{CH}_3\text{-Hg}$, Mn^{3+} is more toxic than +2, +4, +6, and +7 oxidation states, and organometallic compounds of Pb, Hg, and Sn are more toxic than their corresponding inorganic forms (Okereafor *et al.*, 2020). Studies have shown that the most toxic forms of heavy metals in water are free metal ions, followed by strong metal complexes and metal species associated with colloidal particles least toxic (Sonone *et al.*, 2020). The total concentration of trace metal residues does not provide information regarding metal toxicity, environmental mobility, biogeochemical behaviour, bioavailability, all of which are highly reliant on the chemical species of heavy metal. This necessitates measurement of heavy metals as "totals" as well as the quantification of distinct chemical forms of these heavy metals, a process known as speciation (Uchimiya *et al.*, 2020).

Organic compounds are also considered one of the major contaminants of water and they may originate from human activities and natural sources. In the urban environments they are majorly associated with motor vehicles while agricultural activities are the major source in rural areas (Kurwadkar, 2019). The major categories of organic contaminants may include compounds such as pesticides and their residues, polycyclic aromatic hydrocarbons (PAHs), furans, polychlorinated biphenyls (PCBs), pharmaceuticals and dioxins among others (Brenkus *et al.*, 2024). PAHs are a group of organic compounds that occur naturally in coal, crude oil, fossil fuel and gasoline among others.

Pesticides are substances or mixtures of substances used for the purpose of controlling or eliminating pest and plants. Humans get exposed to these organic pollutants through inhalation, ingestion or through skin contact (Zowada *et al.*, 2020). Over 98% of sprayed pesticides reach non-target species, air, water and soil. They can also undergo biotic or abiotic transformation into forms that are more or less toxic forms and or remain unchanged in some cases remaining in the applied chemical form. All these forms have been found in various compartments of the environment water being at the centre (Syafudin *et al.*, 2021). These organic contaminants have low polarity and are largely insoluble in water enabling them to dissolve and bio-accumulate in fat. These properties, allow them to be adsorbed by sediments, get bio-accumulated in the organisms, and persistent in the environment for long (Ren *et al.*, 2018).

Human exposure to these organic contaminants even at low concentrations is associated with various health effects such as endocrine disruption, reproductive and respiratory system effects, mutagenic and carcinogenic effects, immunologic, neurological effects and

cardiovascular disorders among others which varies with age, habits, health conditions and rate of exposure (Agarwal *et al.*, 2022; Pascale & Laborde, 2020). Human hair, saliva, semen, nails, urine and blood are used as biomonitoring matrices for human exposure to pollutants with their presence in these matrices confirming the extent of exposure (Esteban & Castano, 2009).

This study focuses on the Molo river water basin a component of the Lake Victoria basin which also forms part of the larger Nile water basin. The quality of Nile water basin water is closely linked with the quality of the smaller basins forming it including the Lake Victoria basin and the Molo river water basin. Understanding the water quality status of the Molo Water Basin is thus essential not only for local environmental management but also for sustaining the broader hydrological and socio-economic systems linked through the Lake Victoria and Nile basins.

The major economic activity in the Molo river water basin is agriculture. The Nakuru – Eldoret highway passes through the basin with several vehicle accidents reported around Salgaa and the Sachangwan areas along the highway, which has led to monumental oil spills considered precursors for olefins and PAHs in the water basin. Agricultural activities including thriving flower farms, weathering and timber treatment in the basin are responsible for the pollution impacts resulting from organic contaminants and heavy metals.

1.2 Statement of the problem

Heavy metals and polycyclic aromatic hydrocarbons are among the major pollutants of natural water systems that have attracted a lot of attention because of their toxicity even at low concentrations. Heavy metals are not degradable and tend to bio-accumulate in human and animal biological structures to very toxic levels hence leading to serious health risks. The persistent organic contaminants (POPs) which include PAHs and are known to last for several years in the environment before degrading with ability to bio-accumulate and bio-magnify in tissues of living organism resulting in several health impacts on humans, such as effects on reproductive health, respiratory system, cardiovascular system and cancers. The Molo river water basin whose origin is the Mau Complex has served the residents of Nakuru and Baringo Counties for many years. The water basin is the main source of livelihood for communities living around the basin; however, few studies have been done to document the levels of toxic heavy metals and hazardous organics in the area with a view to sensitizing the community on the potential health risks that may be associated with exposure to these harmful substances. In addition, factors such as climate change, erosion, flash floods and leaching processes in the groundwater systems may

also create periodic disruptions in the levels of toxic heavy metals and harmful organics. Therefore, there is need for periodic monitoring of the Molo river water basin to ensure suitable water quality standards and minimize public health problems.

1.3 Objectives

1.3.1. General objective

To investigate the levels of selected toxic heavy metals and presence of hazardous organics in the larger Molo water basin with the view of evaluating their potential risks to human health and the environment.

1.3.2 Specific objectives

- i. To determine the concentration levels of selected potentially toxic heavy metals (Cr, Pb, and Cd) in the Molo River water basin and compare with the WHO limits.
- ii. To profile the elemental composition and morphology of the Molo River water basin sediments.
- iii. To determine the concentration of PAHs in the Molo River water basin.

1.4 Research questions

- i. Will the concentrations of heavy metals along the Molo River water basin be below the WHO permissible levels?
- ii. What is the elemental composition of sediments in the Molo river water basin?
- iii. What is the concentration of PAHs in the Molo River water basin?

1.5 Justification

The exponential rise in human population and climate change coupled urbanization, modern agricultural practices and increased industrialization has led to increased demand of fresh water and decrease in quality of water. Increase in anthropogenic activities in addition to natural phenomena like weathering of rocks and soil erosion around water resources introduces pollutants to the water. Remediation of heavy metals in water systems requires their determination and subsequent speciation of heavy metals to enable the establishment of the appropriate techniques. Moreover, organic contaminants including PAHs possibly from flower farms around the Molo river water basin, car-washing and oil spillage from Salgaa and Elburgon trading centres are yet to be documented. It is well-established that PAHs are compounds with a high potential of exposure and can cause adverse health risks to natural ecosystems and higher-

order animals such as man because they are carcinogenic as well as mutagenic. Farming activities, oil spillage along the Eldoret – Nakuru highway, and timber treatment in the larger Molo river water basin exposes water bodies to pollution and compromise water quality. Therefore this study is necessary in understanding the pollutants that compromise the quality of water in the Molo river water basin and its environs. This will inform public health policy, contribute to water quality data and literature since little studies on water quality have been done on the area of study. The area of study has experienced a lot of accidents that might pollute the water bodies in the area with PAHs and also the agricultural activities in the area could contribute to heavy metal pollution through application of pesticides and fertilizers.

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CHAPTER TWO

A REVIEW OF THE CURRENT STATUS OF WATER QUALITY IN THE NILE WATER BASIN

Abstract

Water, largely fresh water, is important for sustenance of life and human socio-economic development however 2.5% of the earth's water is fresh. Most of fresh water is locked up in ice and underground water precipitating the need of ensuring its quality is always within the required limits. At least 3 billion people rely on water whose quality is unknown due to lack of monitoring. Found in east and central Africa, the Nile water basin covers 11 countries with the river Nile flowing through it before draining to the Mediterranean Sea. River Nile water was pivotal for the ancient civilization in the ancient Egypt and it is still very important in modern times. This significance of the basin has led to conflict and cooperation over shared water resources. Using traditional review, literature on water quality in the Nile water basin was summarized to point out gaps, compare the water quality of the area of study with other areas and give out recommendations. The water quality of the Nile water basin is on the margin of the USEPA, EU, WHO guidelines of drinking water, the guideline for use in agricultural production and to support aquatic. Cases of contamination outside the recommended limits like cadmium in little Akaki River in Ethiopia, aldrin and dieldrin in Tanzanian side of L. Victoria was reported. These clearly show heavy metal contamination above the WHO limits in Nile water basin. Effect of fish cages, micro-plastics, heavy metals, organic contaminants and Suspended sediment load majorly from human activities such as agriculture, industries and municipal wastes are pushing the water quality limits of the basin towards poor quality. This study recommends intervention like transboundary laws and regulations such as proper waste disposal guidelines and right agricultural practices to mitigate the risks before it gets out of hand.

2.1 Introduction

Water is an important resource for sustaining life and human socio-economic development however fresh water scarcity coupled with climate change and the rapid population growth is limiting access to this resource. Over 70% of the earth's surface is covered by water but 2.5% of this water is fresh water with most of the fresh water locked up as ice and underground water (Mishra, 2023). A majority of plants and animals need this fresh water for hydration, metabolism, nutrient transport, habitat, and temperature regulation. Water quality monitoring helps provide a clear quality status of water being utilized for the various purposes. Over 3 billion people rely on water whose quality is unknown due to lack of monitoring putting them at a significant health risk. the quality of fresh water is lowered by climate through rising temperatures, frequent floods, and droughts (Dixit *et al.*, 2022).

The Nile water basin is found in east and central Africa where it covers 11 countries. These countries include Tanzania, Uganda, Burundi, Rwanda, the Democratic Republic of Congo, Ethiopia, Kenya, Eritrea, South Sudan, Sudan, and Egypt. From Lake Victoria and Lake Tana, the river Nile flows through the Nile water basin before it drains into the Mediterranean Sea (Abtew *et al.*, 2019; Pemunta *et al.*, 2021). The main tributaries of the river Nile are the Blue Nile which originates from L. Tana, White Nile from L. Victoria, and the Atbara from northwest Ethiopia. The Nile water basin is divided into two broad sub-systems of eastern Nile sub-system and the equatorial Nile sub-system. The eastern Nile sub-system comprises of main Nile sub-basin, Blue Nile sub-basin, Baro-Akobo-Sobat sub-basin, and Tekeze-Atbara Sub-basin. The equatorial Nile sub-system comprises of White Nile sub-basin, Bahr El Jebel sub-basin, Bahr El Ghazal sub-basin, Victoria Nile sub-basin, L. Victoria sub-basin, and L. Albert sub-basin (Onencan & Van de Walle, 2018).

Nile water basin has been of significance back from the pre-colonial period where the water of the river Nile was critical in the rise of one of the earliest great civilization in north-eastern Africa. The Nile River water provided the ancient Egyptians with fertile soil, irrigation water, drinking water, fishing resources, livestock sustenance, and a vital transportation route (Halawa, 2023). These benefits have persisted over the years and more recently hydroelectric power generation coming in as a new benefit. This new development has led to conflict and cooperation over shared water resources including the conflict between Ethiopia and Egypt over the construction of the Grand Ethiopian Renaissance dam, and between Kenya and Uganda over L. Victoria maritime resources (Allam & Eltahir, 2019; Mwinyi *et al.*, 2022).

This study aims at summarizing water quality studies in the Nile water basin to bring out the general water quality status of the basin. It will help point out the pollutants affecting water quality in the region, general water quality status, effects of human activities, and provide critical information in choice of infrastructure and formulation of policy.

2.2 Water quality

Optimal quantity and quality of water is essential for life to thrive on earth. rising human population coupled with associated human activities like industrialization and natural factors like climate change has mounted significant pressure on quantity and quality of water (Cosgrove & Loucks, 2015). Water quality expresses suitability of water to sustain various uses or processes. it varies from place to place, season to season and time to time (Ram *et al.*, 2021). The quality of water is defined by physical, chemical, and biological characteristics against the intended use giving the suitability of given water source for the specific use. Physical characteristics of water include factors such as turbidity, temperature, color, odor and electrical conductivity among others. Chemical parameters include pH, chlorides, fluorides, organic contaminants and heavy metals among others while biological parameters include bacteria, algae and virus content of the water (Jasim, 2020).

Slow disintegration of large plastic materials when exposed to photo-oxidative, thermal, chemical, microbial and mechanical forces results in tiny plastic particles of sizes below 5mm commonly referred to micro-plastics (Yang *et al.*, 2021). They have very large surface area enabling them to adsorb pesticides and polycyclic aromatic hydrocarbons on their surface leading to combined toxicity. The rising human population in the Nile water basin exposes the water bodies in the Nile basin to pollution by the micro-plastics.

Pesticides which are chemical compounds applied to control pests and weeds on agricultural lands to boost crop and animal production. They come with enormous negative impacts on the environment and its inhabitants. The soil matrix has a high affinity to pesticides making it serve as a storage compartment. Through surface runoff they find their way to water bodies where they have been reported in low concentration. Once in the human body, they mimic important hormones leading to reduced body immunity, impaired hormone balance, effects on reproductive health, impaired growth, and carcinogenicity among others (Syafudin *et al.*, 2021). Up the food chain bioaccumulation and bio-magnification increases their concentration. Low awareness about risk and safe handling of pesticides among farmers as reported by Abong'o *et al.* (2014) further increases the potential to exposure. Many farmers

miss information on safety and dose recommendation further aggravates the risk of these chemicals finding their way to water bodies and ultimately affecting human health.

Regular monitoring water resources quality is important for a health ecosystem, use in the industry, various agricultural activities, domestic use and in the long run an health nation (Grafton *et al.*, 2013). Each of the various uses or processes of water their own quality requirements which are affected by a wide range of natural and human influences. The most important of the natural influences are geological, hydrological and climatic factors.

2.2.1 Water quality index

Traditionally the quality of water is evaluated through comparison of the experimentally obtained values of a given parameter against the existing guidelines. More often than not, many parameters are tested per sample and in a given study, one samples more than one sample making the data generated huge and hard to evaluate and give a conclusive status of the water quality. Water quality index(WQI) originally developed by Horton in 1965 is the most effective method of measuring water quality based on the selected water parameters (Tyagi *et al.*, 2013). However, over time, it has gone through modifications by different experts so that any minor change in the value of any parameter affects the total value of the water quality index (Chidiac *et al.*, 2023). Water quality indices are generally categorized into four categories based on area of application and mode of determination.

The first category of WQI is the public indices which includes the National Sanitation Foundation Water Quality Index (NSFWQI) used for general water quality evaluation disregarding the intended use in the evaluation process. NSFWQI is based on the analysis of nine variables or parameters, such as, biochemical oxygen demand (BOD), dissolved oxygen(DO), Nitrate, Total Phosphate, Temperature, Turbidity, Total Solids, pH, and Faecal Coliforms (Gradilla-Hernandez *et al.*, 2020). The second category of indices which takes into consideration the intended use of the water in evaluation like drinking or industrial is the specific consumption indices. It includes the British Columbia, Canadian Council of Ministers of Environment Water Quality Index (CCMEWQI) and Oregon Water Quality Index indices (OWQI. CCMEWQI provides a water quality assessment for the suitability of water bodies to support aquatic life in specific monitoring sites in Canada. It also provides information about the water quality for both management and the public. A slight modification enables application of these category in many water agencies in various countries (Alexakis, 2022). OWQI assesses swimming and fishing water quality with the determination of sub-indexes by curve or analytical relations (Chidiac *et al.*, 2023).

The third category of WQI is the planning indices that are used for planning and decision making in water quality management projects. The fourth category of water quality indices is the Weighted Arithmetic Water Quality Index (WAWQI) which uses statistical methods to evaluate the water quality (Akhtar *et al.*, 2021; García-Ávila *et al.*, 2022; Mehreen Ahmed *et al.*, 2021). Public indices, specific consumption indices, and planning indices use expert opinion in allocating weight to the various parameters resulting in same variable allocated different weights by various panels of experts making them subjective. WAWQI uses arithmetic mean method to assign weight to the parameters removing the subjectivity affecting the first three making them more objective.

These WQI simplifies complex water quality data sets into a single dimensionless number that represents overall water quality at a certain location and time allowing for comparisons of water quality between different sources or water of the same source from different seasons or sampling points (Lkr *et al.*, 2020). This number gives the combined impact of the different factors that characterize quality of water telling whether the overall quality of a water body poses a potential threat to the various uses of the water (Akter *et al.*, 2016).

2.3 Methodology

The review methodology adopted is the traditional review to summarize literature on water quality in the Nile water basin, point out gaps, compare the area of study with other areas and give out recommendations based on the findings.

2.4 Gaps in previous studies

Studies on water quality in the Nile water basin looks at individual categories of pollutants like heavy metals or organic contaminants independently in specific parts of the water basin. With this approach, the general water quality status of the water basin will not come out clearly. This review summarizes the studies with an intention of giving a clear water quality status of the water basin.

2.5 The study area

The Nile basin is defined by the river Nile flowing from its source in the equator of eastern African at L. Victoria and Lake Tana through North Africa and draining to the Mediterranean Sea. In its journey from Lake Victoria and Lake Tana to the Mediterranean Sea, the river Nile flows through a length of 6,695 km. The major tributaries of the river Nile are Kagera, Victoria Nile, Bahr el Jebel, Bahrel Ghazal, Baro-Akobo-Sobat, Blue Nile,

Tekeze-Atbara, White Nile, and the Main Nile. The basin also contains natural lakes including Victoria, Kyoga, Albert, Edward, and the Tana and manmade lakes like Lake Nasser.



Figure 2.1: A map of the Nile River basin countries and its primary water resources (Abd Ellah, 2020).

Figure 2.1 was reproduced with permission from Egyptian Journal of Aquatic Research, Elsevier.



Figure 2.2: A map of the Nile water basin – adopted from Madani *et al.* (2011)

2.6 Characteristics of water quality

Water quality is influenced by physical, chemical, and biological parameters. Physical parameters include temperature, turbidity, total dissolved solids, electrical conductivity, colour, and odour. The chemical parameters include pH, DO, BOD, Chemical Oxygen Demand (COD), anions, heavy metals and organic pollutants. Biological parameters refer to living organism in water like total coliforms and faecal coliforms which are crucial indicators

of water health and pollution levels. These parameters are monitored to indicate the quality of water.

2.6.1 Effect of fish cages

The fishing industry has immense significance from beneficial health effects on the human body through the nutritional impact, balance in aquatic ecosystem, and the economic contribution from the fish supply chain. The practice of the cage culture targeting to reduce predation, improved efficiency in feeding, husbandry, health management, and in harvesting fish farming is a common practice in the Nile water basin (Mwamburi *et al.*, 2021; Njiru *et al.*, 2019; Obiero *et al.*, 2022).

On top of the benefits of cage culture, there has been concern on its potential pollution impact through residual food and faecal matter, metabolic by-products, and residues of biocides (Nyakeya *et al.*, 2022). Fish cage farming can lead to increased turbidity, decrease DO, increase BOD, increased eutrophication, and increase in COD. The pollution potential of cage fish farming can be worsened by establishment of cage aquaculture without effective management practices that mitigate negative impacts of cage fish farming and ensure long term health of aquatic ecosystem demonstrated by Baluku *et al.* (2025).

Mawundu *et al.* (2023) determined the influence of net cages on water quality and trophic status of L. Victoria at Kadimu Bay and reported physicochemical factors and eutrophic state for aquatic life processes which were within the standard limits which implied fish cage culture was not a threat to water quality. The findings were in agreement with the research by Ngodhe (2019) on impacts of *Oreochromis Niloticus* cage culture on water quality of Winam gulf of L. Victoria. Musa *et al.* (2022) reported significant effects to nutrients, planktons and macroinvertebrates restricted to a close vicinity of Nile tilapia cage culture on water and bottom sediment quality in Anyanga Beach, Kadimu Bay. These findings points at the possibility of minimal effects of cage culture which if not practiced well can lead to detrimental effects on water quality. In the short run, the water system is able to absorb and balance impact of cage culture however there is a big risk if it is not practiced with strict adherence to best practices for cage fish farming (Ragasa *et al.*, 2022).

2.6.2 Effects of human activities

Human activities sometimes referred to anthropogenic activities has profound effect on water quality through contamination and degradation of aquatic ecosystems. These activities include agricultural activities, industrial discharges, mining, domestic discharges, and modern transport. Fertilizers and pesticides used in agricultural practices find their way

to water bodies through service runoff leading to eutrophication and its associated challenges. Agricultural activities also exacerbate erosion through ploughing and overgrazing. Industrial discharge contains heavy metals and organic wastes that end up increasing biochemical oxygen demand and lowering dissolved oxygen. Urbanization and construction activities can lead to discharge of domestic effluents to water bodies leading to eutrophication. Mining activities leads to long term degradation of water bodies through discharge of acidic mine wastes and heavy metals. Transportation pollutes water through oil and fuel spills, and runoff from roads causes' acid rain, and waste dumping from vehicles and ships.

A study of water quality and trophic status of lake Baringo in Rift valley by Walumona *et al.* (2021) reported monthly WQI values that exceeded 100, the upper limit for drinking water, indicating the lake's water is unsuitable for human consumption. The high WQI was attributed to higher turbidity from rainfall mediated erosion in the anthropogenic influenced catchment. Chebet *et al.* (2020) reported Fluoride, electrical conductivity, phosphates, sodium and potassium above the WHO permissible limit in river Molo water basin which serves as the source of Lake Baringo. These water quality parameters are largely attributed to human activities. A study by Chui *et al.* (2023) reported that degree to which human activity affects water quality varies with the season when they evaluated seasonal variations in surface water quality in River Njoro and Lake Nakuru. Ongom *et al.* (2017) concluded that L. Kyoga was polluted by human activities from the elevated levels of nitrites and phosphates by their study. The influence of human activities on water quality was further confirmed by the impact of wastewater discharge and agriculture on water quality and nutrient retention of Namatala wetland in Eastern Uganda (Namaalwa *et al.*, 2020). The researchers reported sediment and nutrient loads were strongly related to seasonal variation in rainfall, river discharge, and to the corresponding peaks in agricultural practice. However it was noted that the wetland was able to regulate sediment and nutrient but further conversion to agriculture could put this function of the wetland at risk. However, A study by Saturday *et al.* (2021) on spatio-temporal variations in physicochemical water quality parameters of L. Bunyonyiin Southwestern Uganda showed significant seasonal variations of physicochemical parameters but within the WHO limits.

Goher *et al.* (2021) did a comprehensive insight into L. Nasser environment with respect to water quality and biotic communities before operating the renaissance dam. This study showed high variations in spatial, temporal distribution, and physic-chemical parameters within the Egyptian drinking water quality standards (EWQS), the USEPA and the WHO. It also complied with the criteria for irrigation water by Food and Agriculture

Organization (FAO) and for aquatic life by CCME implying L. Nasser water was suitable for different purposes. A study by Korium (2021) on the impact of nutrients and water quality in some khors of L. Nasser reported physiochemical parameters within USEPA and WHO for drinking, FAO for irrigation, and compliance with CCME for aquatic life further confirming suitability of L. Nasser water for different purposes.

2.6.3 Heavy metals

Metal elements either essential or nonessential based on their importance to living organisms. Essential metal elements like Fe, Cu, Zn, Co, and Cr are important for living organisms in low concentrations for physiological and biological functions. Although important at low concentrations, these elements become toxic when taken in excess. Nonessential metal elements have no known physiological or biological role in living organisms (Bibi *et al.*, 2023). Aluminium, cadmium, lead, mercury, beryllium, barium, bismuth, thallium are examples of Nonessential metal elements. These elements are toxic and when organisms are exposed to, they develop toxicities depending on dose and duration of exposure.

Toxicity of heavy metals varies from one element to element and organ to organ. The main threats to human health associated with exposure to lead, cadmium, mercury, chromium and arsenic (Balali-Mood *et al.*, 2021; Z. Rahman & Singh, 2019). The mechanism of heavy metal toxicity can be through metal-induced oxidative stress, disruption of enzyme function, and interference of essential metal ions.

Oxidative stress results from generation reactive oxygen species that affect oxidant-antioxidant balance subsequently damaging biological molecules like proteins and lipids through oxidation (Fu & Xi, 2020). Under oxidative stress, redox sensitive transcription factors get activated giving out signals that may lead to uncontrolled cell proliferation or excessive cell death leading to pathological consequences (Valko *et al.*, 2006). Most heavy metals bind strongly the sulphur atoms in thiol groups in enzymes and proteins weakening sulphur bonds. Cellular regulatory proteins and signalling proteins that control apoptosis, cell cycle regulation, and repair of deoxyribonucleic acid (DNA), methylation of DNA, cell growth and differentiation contain the thiol group. The fact that they have the thiol group predisposes them to binding strongly with heavy metal and consequently causing carcinogenesis (Permyakov, 2021). Heavy metals bind to proteins leading to inhibition of protein folding and protein aggregation (Jacobson *et al.*, 2017).

Ssanyu *et al.* (2023) investigated socio-economic variables that determine community risk perception of heavy metal pollution in the L. Victoria wetlands associated with different land use. The study found age, education and occupation as significant predictors of the community risk perception of the wetlands' heavy pollution. Less than 25% of respondents were able to identify related implications of heavy metal contamination on human health. The researchers attributed this to the low pollution risk awareness among the wetland dwellers. It points out to lack of clear and accurate information to help people understand the risks, how pollution affects their bodies and the environment, and mitigation. This can be overcome by incorporating environmental pollution risk concepts at the different education levels and using proper risk communication strategies to enable local communities to exploit natural resources safely and protect their health.

In surface water, undissolved pollutants are sorbed to suspended particles. When the sorption affinity is high enough the suspended particles with the sorbed pollutants settle as sediments. This process removes the pollutants out of the water phase consequently concentrating the pollutants in the sediments. Under the right conditions of desorption like pH and redox conditions desorption of the pollutants occurs allowing the movement of the pollutants to the water phase making the sediments act as a source of pollutants (Chiaia-Hernandez *et al.*, 2022; Rizk *et al.*, 2022).

Odhiambo *et al.* (2023) in comprehensive analysis of the spatial bacterial distribution and metabolic functions in sediment Kisat and Auji that flows through Kisumu City revealed that sediment samples from the highly urbanized, mid, and lower stream catchment zones of both streams had significantly higher levels of total organic carbon, total nitrogen, total phosphorous than the less urbanized upper catchment zone. The sediments were severely polluted with lead, cadmium, and copper. Baguma *et al.* (2022) also analyzed the sediments from Port Bell, L. Victoria for heavy metal contamination. Pollution load indices from the findings signified contamination levels with no serious concerns; however, ecological risk indices showed considerable pollution with regard to Cd. The researchers associated the considerable ecological risk to anthropogenic sources. The anthropogenic association of heavy metals was further reported by Al-Afify and Abdel-Satar (2022) where they established that the sediments downstream at the Rosetta Branch of the Nile was polluted by heavy metal.

The pollution majorly came from cadmium, nickel, and lead with no seasonal variation posing low to moderate overall ecological risks. Ribbe *et al.* (2021) studied trace element behaviour in sediments of Lake Victoria. The researchers reported no critical trace-

element contamination in the sediments with heavy metal concentration with high levels of Cu, Ti and V in near shore sediments. The urban areas surrounding the site hosts many industrial facilities associated with industrial waste discharge signifying contamination from anthropogenic sources. Mukisa *et al.* (2020) reported above the WHO permissible guideline of 0.01 mg/L levels of lead, high pH and turbidity in rivers Mubuku, Rwimi and Nyamwamba in Western Uganda.

An inlet of L. Victoria contains higher concentrations of pollutants as compared with the main lake site. Winam Gulf was reported by Outa *et al.* (2020) to have significantly higher values for electrical conductivity, organic carbon, bound nitrogen, trace elements Cr, Zn, As, Ag, Cd and Pb in water and surface sediments as compared with the main lake site. This findings further point to increasing pollution from anthropogenic activities in the area surrounding Winam gulf. Winam Gulf hosts various industrial activities whose effluents find their way into the L. Victoria with the potential of contaminating the lake water. The contribution of these activities to heavy metal loads of lake water and fish from the gulf is not fully quantified. the influence Winam Gulf surrounding anthropogenic activities and seasons on the metal levels in water and fish was reported by Kiema *et al.* (2017) they reported above WHO limits of metals in lake water and fish which is attributable to intense anthropogenic activities near the lake.

Flower farms discharging wastewater into rivers without proper treatment exposes the rivers to pollution. Consequently the water users get predisposed to serious health and socioeconomic problems due to direct and frequent exposure to river pollution. The discharge of untreated water into water systems was reported by Dessie *et al.* (2022) all of the factories included in their study violated the regulatory limit for one or more pollutants set by the environmental protection agency of Ethiopia, USEPA and the FAO with respect to release of wastewater high in pollutants.

Table 2.1: Heavy metals in sediments of the River Nile water basin

| Site | | Cu | Cd | Pb | Cr | Zn | Reference |
|-------------------------------------|----|-------|--------|--------|-------|------|-----------------------|
| 1. Port Bell, Victoria(g/kg) | L. | 6.467 | 3.283 | 42.184 | 0.456 | | (Baguma et al., 2022) |
| 2. L. Nasser (mg.kg ⁻¹) | | 17.32 | 0.2546 | 1.99 | - | 31.4 | (Rizk et al., 2022) |

| | | | | | |
|--|------|--------|--------|--------|--------------------------------|
| 3. Little Akaki River - sediment, Ethiopia (mg/kg) | 3.14 | 129.68 | 109.51 | 148.28 | (Mekuria <i>et al.</i> , 2020) |
|--|------|--------|--------|--------|--------------------------------|

Extensive research on river pollution by heavy metals and associated impacts on the adjacent community has been conducted. Holeta and Golli Rivers in Ethiopia was studied by Temesgen and Shewamolto (2022) and reported above WHO and irrigation water levels of Cd, Ni, Cr, Fe, Pb and Mn. There is a regular built up of heavy metal concentration in the River Nile as reported by Abdel-Raheem *et al.* (2024) . Their study in Manzala Lake showed and increasing trend of heavy metal pollution from 1968 to 2020.

Table 2.2: Heavy metals in water compartment of the River Nile water basin

| Site | Cu | Cd | Pb | Cr | Zn | Fe | Ni | Mn | Co | Ref. |
|---|--------------|-------------|------------|-------------|-------------|-----------------|-----------|-------------|-------------|--------------------------------|
| WHO Limits(mg/L) | 2.0 | 0.003 | 0.01 | 0.05 | - | - | 0.07 | 0.08 | - | (W.H.O, 2011) |
| L. Nasser (mg element.L ⁻¹) | 3.26 | 0.039 | 0.028 | - | 8.70 | - | - | - | - | (Rizk et al., 2022) |
| Rosetta Branch | 14–72 | 0.81–2.3 | 9.3–67.9 | 3.9–27.4 | 21.1–133 | 396–1640 | 3.9–25.1 | 40–220 | 5.0–28.1 | (Al-Afify & Abdel-Satar, 2022) |
| Holeta River | 0.1053±0.068 | 0.003±0.003 | 0.05±0.01 | 0.1805±0.13 | 0.6050±0.29 | 204.3200±129.73 | 0.19±0.15 | 3.8535±3.31 | 0.0445±0.04 | (Temesgen & Shewamolt o, 2022) |
| Golli River | 2.4175±2.36 | 0.01±0.002 | 0.02±0.002 | 0.1670±0.15 | 0.9725±0.89 | 60.1525±37.68 | 0.16±0.12 | 2.748±2.63 | 0.03±0.02 | (Temesgen & Shewamolt o, 2022) |

The data in Table 2.2 clearly shows a high heavy metal load way above the limit set by WHO an indication that the water of the Nile water basin has been seriously contaminated with heavy metals. Bioaccumulation and bio-magnification further worsens the pollution effects through pollutants increment up food chains. It points out to the need of regular monitoring of sea food products including fish for the presents of pollutants. Heavy metal analyses in water, sediment and fish indicated that water quality is excellent and that the fish are safe for human consumption. The findings of a study by Mekuria et al. (2020) on sediment enrichment with heavy metals, pollution load and potential ecological risks downstream of the little Akaki River in Central Ethiopia reported sediments highly enriched with Cd and Pb exceeding USEPA and interim sediment quality guidelines (ISQGs) limits as shown in Table 2.1. These findings point to the potential of occasionally posing adverse effects on sediment dwelling aquatic life.

The researchers associated the origin of the heavy metals to industries and agrochemicals. This can be mitigated by treatment of wastewaters from domestic and industrial sources to meet national discharge standards before discharge into the river system. Heavy metal levels in the water compartments are relatively low as compared with the levels in the sediments in River Nile water basin as highlighted in Table 2.1 and Table 2.2 because sediments act as a source and sink of heavy metals.

2.6.4 Organic contaminants

Organic contaminants are hydrophobic, have low biodegradability and are stable chemically enabling them to persist in the environment for long. Application of pesticides and other human activities Nile water basin contributes to detection of organic contaminants in the L. water and sediments. Extensive research has been carried in the basin with many studies reporting lower levels of organic contaminants in the water phase as compared to the sediment.

A Wenaty *et al.* (2019) reported higher concentrations of the organic contaminants in sediments as compared to the water phase in Lake Victoria. Organochlorine in the lake water and sediments were below EU and FAO residue limits. Based on the threshold effect concentration for fresh water ecosystems aldrin and dieldrin levels constituted a threat to aquatic life and people. Aldrin and dieldrin as a threat to aquatic life was further reported by Wasswa *et al.* (2011) where they identified and quantified endosulphan sulphate Aldrin, dieldrin, dichlorodiphenyltrichloroethane (DDT) and its metabolites. The concentrations reported were a threat to the lake quality based on threshold effect concentration for fresh

water ecosystems. Ogola *et al.* (2024) detected many organochlorine pesticides (OCPs) that exceeded typical maximum residue limits in River Kibos–Nyamasaria an inlet river of Lake Victoria. This study reported a downstream increase in OCPs concentrations demonstrating that rivers serve as a source of pollutants in lakes. This raises concern of potential pollution from organic contaminants of the water resources. The need for regular monitoring of water quality to ensure human and environmental health is important. This regular monitoring and implementation of appropriate mitigation measures safeguards water quality.

Dalahmeh *et al.* (2020) reported a number of pharmaceutically-active substances in Kampala demonstrating contamination of water resources by wastewater. The findings were in agreement with Kimosop *et al.* (2016) who reported quantifiable levels of the selected antibiotics in wastewater treatment plants, hospital lagoons, and rivers within L. Victoria. The highest concentration was in sludge, demonstrating the preferential partition of antibiotics onto solid phase. These findings demonstrate the need of proper waste handling and treatment of wastes before discharge. When implemented and enforced these measures will help prevent possible contamination of water resources. The big difference between the amount of pharmaceutical compounds found in water and the amount needed to cause pharmacological effects lowers the risk of this category of compounds to cause harmful effects. (Bruce *et al.*, 2010; Kumari & Kumar, 2020). Unfortunately, bioaccumulation, bio-magnification and antibiotic resistance pose long term environmental and health risks.

Agriculture, which includes sugarcane farming that practices burning sugarcane each harvesting season, chemical manufacturing industries, industrial waste treatment plants, municipal solid waste incinerators, and shipping industry emit PCBs to the environment. A Wenaty *et al.* (2019) reported presence of PCBs and OCPs at higher levels in the sediments than the water in the Tanzanian side of L. Victoria. The mean residue levels of most of these pollutants were below the EU and FAO threshold effect concentration and maximum residue limits for fresh water ecosystems. Aldrin and dieldrin were exceptions whose concentrations constituted a threat to aquatic life and people who depend on the water. Ssebugere *et al.* (2014) reported lower levels of PCBs in Lake Victoria ant Napoleon Gulf. the levels in the two studies was much higher than those reported by Afful *et al.* (2013).

Detection of pollutants in water and sediments even though at allowable limits signals a risk of bioaccumulation and bio-magnification. This puts at risk aquatic organisms and the entire food chain including people who feed on products from such water bodies. PCBs were detected below the maximum recommended limits, low cancer risks, and insignificant non-cancer risks for fish and fishery products by Alex Wenaty *et al.* (2019). This suggests that

consumption of these fish products do not pose a human health risk however risks of bioaccumulation and magnification cannot be assumed.

Levels of organic contaminants in most water body outside the Nile water basin has been reported to be within the allowable limits. Montuori *et al.* (2020) reported that sediments had within acceptable limits of PCBs and OCPs in the Volturno River and its estuary in Italy. These contaminants were not a threat to immediate biological effects on the sedimentary environment. However, a study by Nthunya *et al.* (2019) in the Nandoni dam in Limpopo Province detected several phenolic compounds higher than the south African standard, USEPA and WHO acceptable limits in drinking water with concentrations of PAHs falling within the threshold limits.

2.6.5 Micro-plastics

Micro plastics comprise tiny particles of sizes less than 5 mm resulting from disintegration of larger plastic materials. Their presence in the environment leads to health effects on human and aquatic organisms that include malnutrition from blockages of the gut, inflammation, infertility, and mortality (Guzzetti *et al.*, 2018; Lee *et al.*, 2023). Micro-plastics have been reported in in air, soil and various water bodies (Hale *et al.*, 2020). F. R. Khan *et al.* (2020) reported a high levels Polyethylene, polyethylene terephthalate and polypropylene microplastics ingested by fish sampled from Nile River in Cairo. Polyethylene/polypropylene copolymer, Polyethylene, Polyester, Polyurethane, and Silicone rubber polymers were recovered by Biginagwa *et al.* (2016) from the gastrointestinal tracts of sampled fish from L. Victoria. Similar composition of Polyethylene and Polypropylene micro-plastics were found in surface water of L. Victoria with all the micro-plastics being of secondary sources.

Secondary microplastics are formed from disintegration of larger plastic debris to less than 1mm in size. Dusaucy *et al.* (2021) reported that the common micro-plastic size class studied was 300 mm to 1 mm. T. A. Aragaw (2021) identified polyethylene terephthalate, polyethylene, and high density polyethylene in the shorelines of L. Tana, a similar composition of what was reported in L. Victoria with the addition of high density polyethylene. Hydrophobic pollutants get sorbed onto the surfaces of these small sized plastic particles influencing mobility and bioavailability of these hydrophobic pollutants (Gateuille & Naffrechoux, 2022; Prajapati *et al.*, 2022). Sorption of organic contaminants onto the surface of micro-plastics concentrates the microplastics and also leads to synergistic

effects of pollution from the sorped organic contaminants on aquatic biota (Chang *et al.*, 2022).

Despite the negative effects of micro-plastics in the environment, there is currently no standard method for collecting, analysing, and reporting on micro-plastics (Enfrin *et al.*, 2021). This makes comparison of data from different sources and regions very difficult. The micro-plastic menace calls for regulations that reduce micro-plastic wastes production. Some African countries have adopted these regulations although implementation has been largely unsuccessful. The absence of such regulations in most of the African countries further exacerbates the environmental threat posed by microplastics (Aragaw, 2021). Most fishing nets are made of plastics therefore serving as a source of micro-plastics. Jeevanandam *et al.* (2022) reported microplastics composed of very high polyester (82%), polyethylene (15%) and polystyrene (3%) in Hawassa Lake of Ethiopia. The researchers attributed these microplastics to fishing nets, ropes and plastics bags. Polyethylene, polypropylene, polyethylene terephthalate, polyethylene vinyl acetate, and polytetrafluoroethylene was further reported by Shabaka *et al.* (2022) in the Nile delta estuaries. These findings confirm the presence and extent of microplastic pollution a solely anthropogenic pollutant in the Nile water basin and the need to institute regulations to mitigate the emerging environmental threat.

2.6.6 Suspended sediment load

Suspended sediments comprises fine inorganic particles of clay and silt (below 0.063 mm), fine sand (0.63-0.250 mm), and particulate organic matter. Under the influence of gravity suspended particles settle out of suspension through sedimentation (Huynh *et al.*, 2024). However, sometimes suspended sediments are fine to the extent that turbulent eddy outweigh sedimentation. This causes them to be suspended in the water phase. The suspended matter reduces light penetration in the water column consequently reducing photosynthesis affecting aquatic plant life and the entire food chain. The reduction in penetration of light into the water column leads to a drop in water temperature shifting in ion concentration leading to a drop in water temperature. They damage fish gills leading to respiratory distress, however act as habitat for microbes (Walch *et al.*, 2022).

Suspended sediment load is one of the measures and benchmarks of soil erosion and sometimes sediment transport rates (Bannatyne *et al.*, 2022). Eroded soil from agricultural areas is the biggest contributor to transported sediment in the Simiyu River as reported by James *et al.* (2023) because farming activities often disturb the soil surface. The Nile

sediment load is dictated by the constructed dams upstream before draining into the Mediterranean Sea. As the Nile river flows downstream, Wind-blown particles mix with fluvial and deltaic deposits a process enhanced by man's extensive modifications of the river course in the last century (Garzanti *et al.*, 2015).

2.7 Tools used to monitor and assess water quality

2.7.1 Hazard quotient

hazard quotient (HQ) is the risk factor applied to non-carcinogens and it relates the dose delivered at the point of exposure in form of average daily dose (ADD) to a toxicological result on a given organ represented by the reference dose (Rfd) as shown in equation 2.1 (Rahman *et al.*, 2021).

$$HQ = \frac{ADD}{Rfd} \quad (2.1)$$

HQ assumes existence of a given pollutant in isolation however; pollutants in the environment do not exist singularly in isolation but as a mixture. The cumulative risk to a given organ as a result of simultaneous exposure to several non-carcinogens in the environment is found by adding the HQ values of the individual pollutants in existence to obtain a Hazard Index (HI). HI and HQ <1 (less than 1) are considered acceptable values which means adverse effects are not likely to occur (Billionnet *et al.*, 2012; Genthe *et al.*, 2013).

2.7.2 AquaChem

Aquachem is comprehensive application software for data management, data analysis and reporting by waterloo hydrogeologic. The software has ability to convert units, calculate charge balance errors, plotting, modelling, and statistical data manipulations (C. Kumar, 2012). The software can analyse trends for tens or hundreds of samples and parameters within a short period of time and assess aqueous geochemical interactions during acid mine drainage (Said *et al.*, 2022). Aquachem was used by El Kashouty (2013) to analyse groundwater chemistry and to perform geochemical modelling, including inverse modelling to assess mineral saturation states and ion exchange processes in the limestone aquifer between Beni Suef and El Minia. The limited documented applications of AquaChem in the Nile water basin highlights the fact that it has not been extensively used in the Nile water basin.

2.7.3 Artificial neural network (ANN)

Artificial neural network is an intelligent system inspired by biological neural networks. It has the ability of solving a variety of problems through recognition of pattern, prediction, optimization, associative memory, and (Chen *et al.*, 2020; Thakur & Konde, 2021). Banda and Kumarasamy (2024) employed a neural network-based methodology to construct a novel WQI model suitable for analysing South African rivers which gave index values and water quality evaluations comparable to universal WQI results. Through reduction of water quality monitoring stations and parameters it cuts cost and reveal the pattern of water quality for decision making (Isiyaka *et al.*, 2019).

2.7.4 Adaptive neuro-fuzzy inference system (ANFIS)

Adaptive neuro-fuzzy is a an accurate and interpretable artificial intelligence algorithm that can combine Fuzzy Inference System (FIS) and artificial neural networks (ANN) to approximate highly complex and non-linear systems (Shah *et al.*, 2021). Statistical models in recent times largely embrace the ANN due to its ability to capture complex nonlinearities in a system better than linear regression methods. They work by mimicking how the human brain process information through input layers to achieve a desirable output. It combines the merits of the neural network and theories of fuzzy logic systems in its operation to learn the features of a given data and alter the system parameters to suit the required error criterion of the system. Therefore they translate knowledge of experts in the form of rules and artificial neural networks automate the process reducing the searching time. Masrur Ahmed and Shah (2017) developed ANFIS model which accurately predicted biochemical BOD, Mohadesi and Aghel (2020) predicted inorganic indicators of water quality using ANFIS/Genetic Algorithm and Neural Network, and Yan *et al.* (2010) used an ANFIS model that applied several physical and inorganic chemical indicators including dissolved oxygen, chemical oxygen demand, and ammonia-nitrogen to classify the water quality of major river basins in China where the model predicted 89.59% of the river quality status.

2.8 The benefits of water monitoring and assessment

Water covers 71% of the earth surface, however a small percentage of water is fresh water. The quality of water for drinking, aquatic life, irrigation, and industry are under constant threat from pollutants from human activities and natural factors. As a result, contamination of this scarce and vital resource has become a threat to human health and the environment (Babuji *et al.*, 2023). Monitoring and assessment of water quality is important

for finding specific contaminants and their source. This helps to identify existing and emerging problems from analysis of water quality trends. It also helps identify short- and long-term water quality patterns that are of importance in managing and preventing water contamination. monitoring and assessment is equally important for compliance with water quality standards and determining whether pollution control programs are working ultimately these informs plans and policies that improve water quality to meet designated use water and for managing emergencies (Chapman & Sullivan, 2022; Keiser *et al.*, 2019).

2.9 WHO and European commission limits and their implication on the water basin

Extended exposure to pollutants over many years give rise to health concern leading to adverse health effects. WHO, EU, and USEPA have established internationally accepted guideline values for chemical substances based on possible health concerns (Garnick *et al.*, 2021; WHO, 2011). The limits for selected toxic heavy metals set by the WHO and the European Commission are presented in Table 2.3. A guideline value represents the concentration of a particular contaminant that does not result in any significant risk to health over a lifetime of consumption. Potential effects of chemical contaminants on drinking water on the basis of physical parameters like taste, odour and appearance are minimal. Sometimes when these parameters test levels are high, they make the water unpalatable leading to rejection of water at even very low concentration of the contaminants of health concern although no guideline value has been set (Addisie, 2022). Pesticide metabolites are of relevance to drinking water guidelines if it has pesticide target activity properties comparable to those of the parent substance or either it or its transformation products generate a health risk for consumers (Fenner *et al.*, 2013).

Table 2.3: Selected water quality guidelines.

| Element | WHO limits (mg/L) | EC limits (mg/L) | US EPA limits(mg/L) |
|-----------|-------------------|------------------|---------------------|
| Arsenic | 0.01 | 0.01 | 0.01 |
| Fluoride | 1.5 | 1.5 | 4.0 |
| Chromium | 0.05 | 0.025 | 0.1 |
| Copper | 2.0 | 2.0 | 1.3 |
| Lead | 0.01 | 0.005. | 0.015 |
| Nickel | 0.07 | 0.02 | - |
| Manganese | 0.08 | 0.05 | - |
| Cadmium | 0.003 | 0.005 | 0.005 |
| Mercury | 0.006 | 0.001 | 0.002 |

| | | | |
|--|----------|---------|-------------|
| Nitrate (as NO ₃ ⁻) | 50 | 50 | 10 |
| Nitrite (as NO ₂ ⁻) | 3 | 0.5 | 1 |
| Aldrin and dieldrin | 0.000 03 | - | unregulated |
| 2,4-D | 0.03 | - | 0.07 |
| Eldrin | - | - | 0.002 |
| Chlorpyrifos | 0.03 | - | - |
| Lindane | 0.002 | - | 0.0002 |
| Methoxychlor | 0.02 | - | 0.04 |
| Metolachlor | 0.01 | - | unregulated |
| Benzo[a]pyrene | 0.0007 | 0.00001 | 0.0002 |
| DDT and metabolites | 0.001 | - | - |
| pH | 6.5-8.5 | - | - |
| Dioxin | - | - | 0.00000003 |
| Glyphosate | - | - | 0.7 |

Pesticides Total' is the sum of all individual pesticides detected and quantified in the monitoring procedure (0.50 µg/L). In terms of the number of contaminants covered and on the limits provided in Table 2.3, it is evident that the WHO has established guideline values for most of the selected pollutants followed by USEPA and the European Commission.

2.10 Remediation strategies involved in water supply and infrastructure

Presence of a pollutant substance at a significant concentration can cause adverse effects on public health and or the environment. This calls for actions normally referred as remediation to be taken by the respective authorities to return the water quality from being polluted to the desired levels (Khatri & Tyagi, 2015). The remediation approaches include filtration, evaporation, reverse osmosis, ion-exchange, redox reactions, precipitation, and electrochemical removal. Remediation removes the contaminants and treats the contaminated site in order to change the harmful chemicals into less harmful ones and or contain the pollutants in the state they are in the polluted site. These remedies prevent pollutants from entering into other compartments of the environment in order to avert their spread to the people.

Water remediation approaches are either incident-specific or site-specific taking hours to months or years. They are divided into three phases that include characterization,

Decontamination, and Clearance phases which may overlap or occur simultaneously (Kumar *et al.*, 2019). Characterization phase determines the extent of contamination which includes identifying the contaminants, their concentration, contaminants interaction, and mobility in the water system. Through chemical analysis, the magnitude of contamination is determined and the contaminants located with an objective of determining the extent remediation applied (Sánchez-Castro *et al.*, 2023) . Once the extent of contamination and the risks are defined appropriate water treatment methods are selected, appropriate infrastructure chosen and implementation decontamination. Contaminant properties and extensive system contamination can necessitate the whole infrastructure decontamination (M. T. Khan *et al.*, 2021). Management and disposal of any contaminated wastes including contaminated water, infrastructure unable to be decontaminated, and or by-products generated during decontamination is also part of decontamination.

Decontamination approaches can be biological, chemical or physical. Biological approaches, commonly referred to as bioremediation, involve the use of organisms such as plants, bacteria, and fungi for remediation (Pant *et al.*, 2021). Bioremediation involves the breakdown hazardous substances into less toxic or nontoxic forms. The hazardous substances can be organic substances and in some cases reducing or oxidizing inorganic substances like nitrate. Bacteria species such as *Pseudomonas aeruginosa* can convert mercury (Hg^{2+}) to Hg a nontoxic form (Ma *et al.*, 2019). Prokaryote has been used in bioremediation of oil spills where inorganic nutrients are added to help bacteria already present in the environment to grow. As the bacteria multiply they feed on the hydrocarbons in the oil droplet consequently breaking them into inorganic compounds (Baniasadi & Mousavi, 2018). Some species like *Alcanivorax borkumensis* produce surfactants that break oil into droplets that can be accessed by bacteria that degrade the oil (Panchal *et al.*, 2018). Oil-consuming bacteria are naturally present in water bodies and help in natural bioremediation. Reports of up to 80 percent of the non-volatile components of oil degraded within one year of the spill has been documented (Bacosa *et al.*, 2022).

Bioremediation has attracted significant interest with researchers genetically engineering other bacteria to consume petroleum products. Engineering of catabolic enzymes constructs organisms that perform a number of related or unrelated metabolic activities with enhanced degradative rates and broad substrate specificity enhancing predictability and efficiency of the process (Das *et al.*, 2023). Similarly, use of genes that encode the biosynthetic pathway of bio-surfactant improves the rate of biological degradation by improving pollutant bioavailability in the natural ecosystem. Incorporation of genes that give

the used organism resistance to critical stress factors also enhances survival and performance of the designed catalyst (Imam *et al.*, 2022; Sokal *et al.*, 2022). Phytoremediation is a cost-effective variant of bioremediation that uses plants to absorb the chemicals over time with very large volumes of contaminated compartment of environment treated in-situ without excavation (Garbisu & Alkorta, 2001; Mani & Kumar, 2014).

Chemical remediation introduces chemicals to remove the contaminant or make it less harmful. Chemical remediation can be achieved through chemical precipitation, oxidation, ion exchange, and carbon absorption. Reactive barrier includes a permeable wall in the ground or at a discharge point that chemically reacts with contaminants in the water. Barriers such as those made of limestone can increase the pH of acid mine drainage removing dissolved contaminants by precipitation into a solid form (Budania & Dangayach, 2023). Physical remediation consists of removing the contaminated water and either treating with filtration, extraction, sedimentation, containment and or disposing of it.

Nano-remediation which involves the application of reactive materials of size 1.0–100 nm size has become a major focus of research and development due to its great potential of remediation (Fei *et al.*, 2022). It initiates catalysis and chemical reduction of contaminants resulting in detoxification and transformation of pollutants. The small size and novel surface coatings of the nanoparticles promotes their wider distribution in comparison to larger-sized particles making them best suited for in - situ applications.

2.11 Conclusions

The Nile water basin has greatly influenced human settlement since the prehistoric age. However, the resultant human activities have greatly contributed towards the deterioration of water quality over time. Discharge of municipal wastes has negatively impacted on water quality as shown in presence of pharmaceutically active compounds, high conductivity, and biochemical oxygen demand. Agriculture has also contributed pesticides, OCPs, and PCBs, in the water basin. Heavy metal, one of the major contaminant of the water basin has been largely attributed to industrial activities, mining and municipal with little contribution from the soil. Most of the water quality parameters in the basin remain within the recommended levels however caution is warranted due to the reported high levels of cadmium, aldrin and dieldrin. Sediments in the water basin have effectively acted as sink for pollutants from their relatively high concentration of pollutants as compared to the pollutants in the water column. This is an important process that limits the transport of pollutants downstream through reduction of pollutants in the flowing water reducing the transportation

of risks. Micro-plastics, an emerging pollutant which in entirety comes from anthropogenic activities have also been reported in the water basin. Aquatic animals from the basin have been severely exposed to pollutants to levels that pose risks to their survival or affecting those who feed on them. These finding points at the need of instituting policies, laws and regulations to govern the management of the transboundary water resource. These measures will mitigate the already out of limits pollutants and prevent the within limits pollutants from crossing the limits. There is need also to do public sensitization through mechanisms like education and media on the consequence human activities on water quality.

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CHAPTER THREE
THE USE OF WATER QUALITY INDEX AND WATER POLLUTION INDEX IN
ASSESSING THE WATER QUALITY AND SUITABILITY OF THE RIVER MOLO
WATER BASIN, KENYA

Abstract

Water quality assessment has become a very essential scientific procedure for qualifying water for drinking and general purpose use, and better public health policy on clean water supply. Various tools have been employed to determine the status of water systems for drinking, industrial and general use. For the purpose of this study, WQI and WPI were adopted to evaluate the water of the Molo water basin. The study was carried out in December, 2021 during the dry season. The WHO has defined limits of these parameters beyond which the quality of water is considered unsuitable for a specific use. This study determined concentrations of heavy metals, major cations, major anions, and sediment morphology and sediment elemental composition. Temperature, pH, electrical conductivity, salinity and TDS were determined in situ. Concentration of chlorides, fluorides, phosphates, sulphate, hydrogen carbonate, and total carbonate in water samples were determined by a titroline processor. Shimadzu AA-7000 series Atomic absorption spectrophotometer (AAS) under air-acetylene flame was used to determine concentrations of heavy metals. Biobase FP640 flame photometer was used to determine K, Ca, Na, and Mg concentration. Sediment topology determined using a scanning electron microscope coupled with an energy dispersive X-ray spectrometer (SEMEDX) operated at 25 kV. Of the major cations Na reported the highest concentration at 1800 mg/L whereas in the anion category, the Cl gave the highest concentration at 110 mg/L. The highest pH, TDS and salinity were 8.5, 146.33, and 282.67, respectively. The data obtained were used to determine the WQI and WPI of the Molo water basin based on the WHO standards. The average WQI obtained was 57.47 indicating that the water is slightly polluted. Also the average WPI obtained was 0.77 indicating that the water from the water basin is not of good quality. The findings showed the presence of heavy metal pollutants of concern which include lead, manganese and copper. Therefore, with respect to WQI, WPI and sediment morphology, the water basin is significantly polluted. There is need for government and health authorities to formulate policies aimed at regulating pollution activities which may endanger the Molo water basin.

3.1 Introduction

The inevitable advancement in industrialization, mechanized agriculture, and accidental waste discharge coupled with natural disasters are posing serious threats to safe drinking water. It is against this backdrop that extensive research on water quality has been carried out by various researchers and public health authorities. Water is an important resource for human life essentially because it is used in agriculture, industry, and for domestic purposes. From a domestic standpoint, water is mainly used for cooking, drinking, cleaning, personal hygiene and watering gardens (Kadibadiba *et al.*, 2018; Walker, 2019). Water for domestic use in Africa is primarily sourced from rivers, springs, wells, Lakes, boreholes, dams, rain water, piped water and pans. These sources of water provide essential and non-essential nutrients directly and indirectly (Onyango *et al.*, 2018).

Water quantity and water quality are two key characteristics that provide information on availability, sufficiency and suitability of water. Water quantity is basically defined as the sufficiency to serve the intended purpose whereas water quality is defined as the suitability of water to serve an intended purpose without any negative health impacts over the lifetime of its use (Adimalla & Qian, 2019; Gunda *et al.*, 2019). Fresh water pollutants include pathogens, organic matter, minerals, pesticides, pharmaceuticals and plastics. The sources of pollutants include industrial wastes, agriculture, domestic effluent, soil erosion, rock weathering, volcanic activities and forest fire accidents being the main sources (Akhtar *et al.*, 2021). Climatic, geomorphological and geochemical conditions determine the physical and chemical characteristics of river water system drainage basin with river currents and turbulence being the major factors for water to achieve continuous mixing and flow histories (Anh *et al.*, 2023).

The assessment using WQI and WPI, sometimes combined with hazard quotient and hazard index provides information on suitability of water. Water quality varies depending on the source, location and time (Pacheco *et al.*, 2018; Xu *et al.*, 2019). They summarize information on factors such as the concentration of DO, bacteria levels, the amount of salt (salinity), amount of suspended material (turbidity), the concentration of microscopic algae, concentration of pesticides and heavy metals present in the water system. WQI summarizes the data from these factors into a single dimensionless number that ranges from 0-100. Some WQI systems categorize 0 as poor or very bad water quality, with water quality improving as the values increase toward 100. Conversely, other systems assign 0 as excellent water quality, and water quality decreases as the values increase. The differences are caused by the type of index with dictates the specific methodology employed to calculate the WQI.

In Kenya, water quality index has been applied to assess groundwater resources in Langata sub-county for portability by Ochungo *et al.* (2019) by sampling thirty nine boreholes. The calculated WQI was 53.18 where the groundwater quality was categorized as good quality. Ustaoglu *et al.* (2020) assessed stream quality and health risk in Turnasuyu Stream in Turkey and obtained an average of 18.97 which they categorized as excellent water quality. It is considered good for drinking and does not pose a potential hazard to human health. However Njuguna *et al.* (2020) that that water quality index was not reliable risk assessment tool because it did not correlate well with hazard quotient and hazard index besides portraying all sampling sites bearing suitable water for drinking. in L. Chaohu basin in China Wu *et al.* (2021), rated the basin moderate with mean WQI value of 69.1. Ewaid *et al.* (2020) developed a WQI and used it to evaluate water quality for Iraqi rivers Tigris, the Diyala, Euphrates, and Diwaniyah. it yielded an average annual water quality index of the Tigris river as 73.25 which can be categorized as good, and water quality index values of 69.52 for the Diyala river, 60.9 for Euphrates river, and 66.75 for Diwaniyah river which gave the conclusion that Iraqi waters are generally good for drinking and domestic use.

Dissolved minerals both organic and inorganic affect the taste, odour, and the general acceptability of drinking water and are measured as total dissolved solid (TDS). Devesa and Dietrich (2018) reported that most water consumers and trained professionals are unable to differentiate the taste of tap water at room temperature when the difference in TDS between the waters is $\Delta TDS < \approx 150$ mg/L. it is closely related with electrical conductivity by a conversion factor between 0.5 and 0.9 multiplied with electrical conductivity to give TDS depending on the water. Pure water is a poor conductor of electricity but with the dissolved minerals; its electrical conductivity gets improved indicating a relationship between TDS and conductivity.

On the other hand, different metals and metalloids are present in different water systems but some trace metals like cadmium whose presence even in minute concentrations is a precursor for detrimental health effects on humans and the aquatic life (Shrestha *et al.*, 2021). Because of their non-biodegradability, toxicity, ability to accumulate in the environment heavy metals are hazardous (Zaynab *et al.*, 2022). Some heavy metals known to be toxic to humans include mercury, arsenic, cadmium, chromium, copper, lead, and zinc. Although copper, chromium, and zinc are essential micronutrients, they are toxic at elevated levels (Bjørklund *et al.*, 2020; Michalczyk & Cymbaluk-Płoska, 2020). In the water system there exists an equilibrium distribution of metals between water and sediments. This

equilibrium is disturbed by changes in the physio-chemical parameters such as pH and redox potentials.

Suspended particles in water form complexes with dissolved metal ions accumulate and settle as sediments (Pohl, 2020). At low pH, the metal ions are in their positively charged ionic form and get adsorbed on fine particles like clay in water which grows in size and ultimately settle as sediments (Debnath *et al.*, 2021). Molo water basin is situated in an agriculturally rich area and relatively populated settlements such as Eburgon, Kibunja, Salgaa and Molo. Rivers Molo and Elburgon, and its tributaries are likely to be polluted by domestic effluent discharge, combustion events, oil spills, timber treatment, and accidents around the Salgaa stretch of the Eldoret –Nakuru highway, and agricultural activities.

3.2 Materials and methods

This research focused on the Molo water basin which forms part of the L. Victoria water basin. The Molo river water basin is approximately 35 km west of Nakuru town and has an average elevation of 2200 m above sea level. The economic activities in the area are mainly agriculture, construction and lumbering. The water basin comprises river Eburgon, River Molo and Kibunja tributary. The larger river Molo flows through Nakuru and Baringo counties before draining its water into L. Baringo one of Kenya's fresh water lakes. The river supports the livelihoods of the local communities by providing water for domestic use, small scale irrigation and livestock. The sampling points were located and marked using a geographical positioning system (GPS) version 4.82 (214).

3.2.1 Sample collection

The water and sediment samples were collected from six sampling points whose location is as shown in Figure 3.1 and Table 3.1 below located using a global information system (GIS): Kibunja tributary (K1), Rongai town (M1), Salgaa bridge (M2), river Molo (M3), river Elburgon downstream (E1) and river Elburgon upstream (E2) in three replicates. Sampling containers used for water and sediments samples were thoroughly cleaned with 10 % v/v nitric acid to remove any contaminants and ensure sample integrity. They were then rinsed several times with deionized water to remove any remaining acid residues. Before collecting the samples, the containers were washed 3-4 times with water from the exact site of sampling to avoid contamination and condition the containers. Concentrated nitric acid was added immediately after collection to water samples in one of the bottles for metal analysis to preserve the water samples.

Sediment samples were collected in duplicate from the same sampling points as the water samples using a core sampler. This method ensured consistent and representative sediment collection for subsequent analysis. The collected sediment samples were placed into plastic containers designated for heavy metals and inorganic analysis to prevent contamination and preserve sample quality. All samples were transported in an icebox to the laboratory where they will be refrigerated at 4 °C awaiting the analysis.

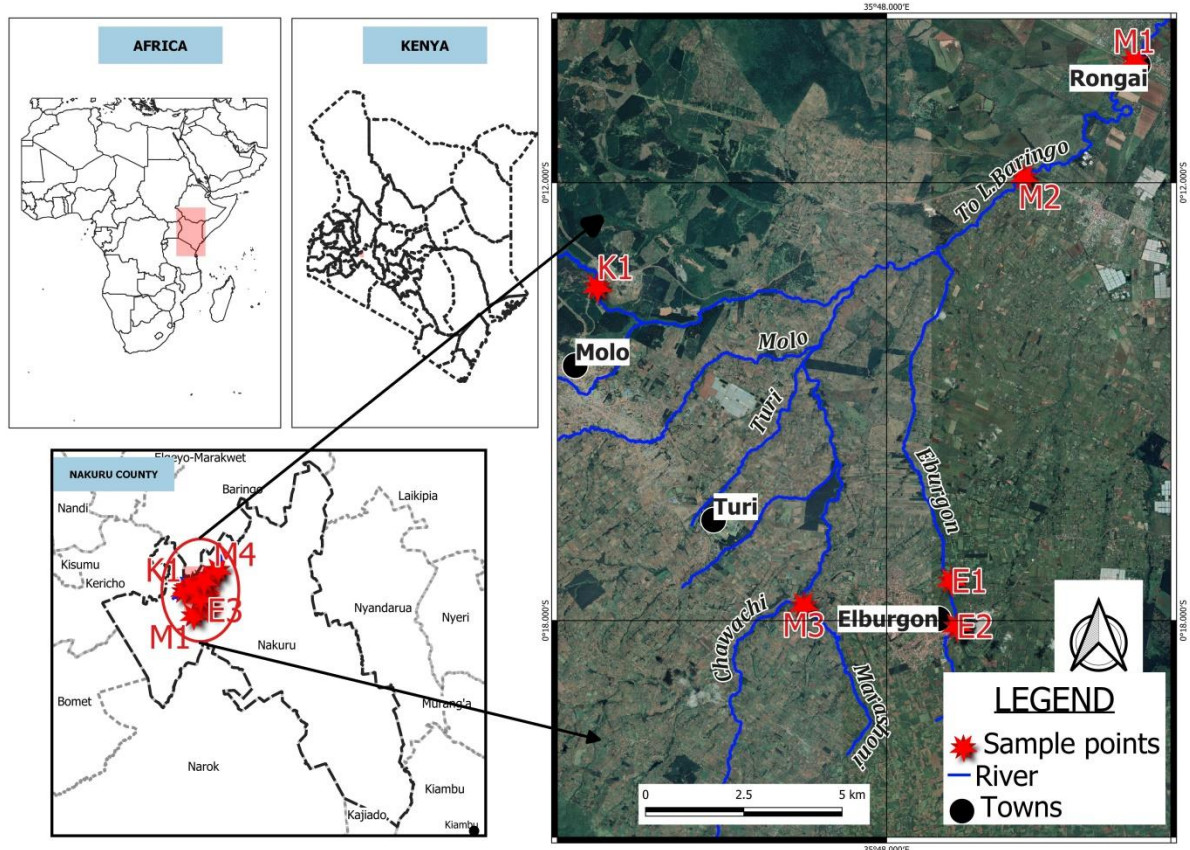


Figure 3.1: The sampled sites in the Molo water basin

Table 3.1: Geographical information system coordinates of the sampled points

| Sampling point | Location | Elevation (m) |
|----------------|---------------------|---------------|
| M1 | S0°10'20, E35°51'24 | 1876 |
| M2 | S0°11'56, E35°49'53 | 1906 |
| M3 | S0°17'48, E35°46'52 | 2444 |
| E1 | S0°16'52, E35°50'55 | 2169 |
| E2 | S0°18'5, E35°48'58 | 2404 |
| K1 | S0°13'26, E35°44'2 | 2399 |

3.2.2 Water and sediment analysis

All chemicals used in this study were sourced from Sigma-Aldrich and were of analytical grade with purity greater than 99%, ensuring the accuracy and reliability of the analyses. The reagents and analytical procedures utilized in this study follow the procedure of Laurence *et al.* (2018). Temperature, pH, electrical conductivity, salinity and TDS were determined in situ at the sampling points while concentrations of heavy metals were determined in the laboratory for both water and sediments. The concentration of chlorides, fluorides, phosphates, sulphate, hydrogen carbonate, and total carbonate in water samples were determined automatically by a titroline processor using appropriate reagents and electrodes. The detailed procedure for analysis of these parameters is described by Kwadzah and Iorhemen (2015) and Chebet *et al.* (2020) in literature.

Atomic absorption spectrophotometer (Shimadzu AA-7000 series) was used to determine concentrations of Cd, Cu, Cr, Pb, Mn and Fe in the water samples. An air-acetylene flame was used, with an acetylene flow rate of 2.0 L/min and an air flow rate of 10 L/min. This configuration ensures efficient atomization of metal ions in the samples, facilitating precise and accurate determination of metal concentrations. Background correction was done using a deuterium lamp. Burner height was operated between 8 mm to 12 mm. Biobase FP640 flame photometer was used to determine K, Ca, Na, and Mg concentration. The equipment was calibrated using standard solutions of known concentrations to ensure accuracy and precision.

Water bottom sediments were air-dried and sieved through a 2 mm sieve and thereafter sifted to isolate fine particles. About 10g of the sieved sediment samples were added to a 0.4 M solution of sodium pyrophosphate decahydrate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$) prepared in 50% hydrogen peroxide diluted with water. Hydrogen peroxide oxidized and effectively decomposed organic material present in the sediments, while sodium pyrophosphate is a dispersing agent that prevented particle aggregation. The suspension obtained was diluted using hot water and sifted through a 0.5 mm sieve. The remaining sediment in the sieve was washed, dried at 105 °C, and finally sifted through a 0.2 mm sieve and its topology investigated using a scanning electron microscope coupled with an energy dispersive X-ray spectrometer (SEMEDX) operated at 25 kV. The sediment sample was adhered to aluminium SEM stubs with carbon tape and was subsequently gold coated in a Quorum Q150 RES sputter coater in accordance with the procedure reported by Jebet *et al.* (2018). The gold coating enhances the conductivity of the samples, reducing charging effects and improving

image quality during SEM analysis. This technique allowed for detailed imaging of sediment surface features and elemental composition analysis.

3.3 Water quality index

The water quality of a water system can be expressed using a WQI which a dimensionless number is obtained from selected parameters of the water system. This study used WAWQI which has a total of six steps. The first step involves selection of the parameters that affect water quality. The second step assigns weights (W_i) to the selected parameters as given by equation 3.1.

$$w_i = \frac{k}{S_i} \tag{3.1}$$

The value of K is given by equation 3.2

$$k = \frac{1}{\sum \frac{1}{S_i}} \tag{3.2}$$

S_i is recommended standard guideline value like the limits given by WHO and USEPA. Assigning weight reflects on relative impact of a given parameter because parameters have varying impacts.

The third step comes once W_i has been assigned to parameters, the quality rating scale (Q_i) is calculated using equation 3.3.

$$Q_i = 100 \frac{V_i}{S_i} \tag{3.3}$$

Where S_i is recommended limit value and V_i is the measured value of the given parameter. Given the value of W_i and Q_i for a given parameter, the fourth step involves computing the Weighted Quality Rating (W_iQ_i) for each parameter using equation 3.4.

$$WQ = w_iQ_i \tag{3.4}$$

Given the W_iQ_i for each parameter the fifth step comes in where WQI is calculated using equation 3.5.

$$WQI = W_{pH}Q_{pH} + W_{DO}Q_{DO} \dots \dots \dots W_{Zn}Q_{Zn} \tag{3.5}$$

The last step is interpretation of the resulting WQI value to excellent, good, poor, very poor, or unsuitable categories. When water is classified as excellent or good it indicates the water is generally safe and meets most recommended standards. As the WQI value increases, moving into Poor or Very Poor categories, the water quality deteriorates, signalling potential risks to human health and aquatic ecosystems. These categories often reflect higher levels of pollutants implying the need for treatment before use. Water deemed unsuitable suggests severe contamination making it unsafe for most uses without significant remediation efforts.

This categorization is critical for environmental monitoring and management, as it guides policymakers and stakeholders in prioritizing actions to protect water resources and public health.

3.4 Water pollution index

Water pollution index is a tool used to assess pollution levels in a water body by aggregating concentrations of various pollutants into a single numerical value. WPI can accommodate more number of parameters and consequently providing more reliable results as compared to WQI because it is flexible for n number of parameters (Begum *et al.*, 2023). WPI determination begins with the calculation of pollution load index PLi of the i^{th} parameter or the standardized value of a particular parameter using equation 3.6.

$$PLi = 1 + \frac{Ci - Si}{Si} \quad (3.6)$$

where, C_i is the measured concentration or value of the i^{th} parameter, S_i is the standard or the highest permissible limit concentration or value for the respective parameter. In cases where the measured value of a parameter is zero, it is excluded from the total n parameters. The equation for calculating the PLi value of pH is dictated by the prevailing pH value. A pH value of 7 is considered neutral and when the prevailing pH value is less than 7, equation 3.7 is used for pH PLi calculation.

$$PLi(\text{pH}) = \frac{Ci - 7}{Si_a - 7} \quad (3.7)$$

where, C_i is the measured pH value and S_{i_a} is the minimum acceptable pH value. When the prevailing pH value is greater than 7, equation 3.8 is used for PLi calculation.

$$PLi(\text{pH}) = \frac{Ci - 7}{Si_b - 7} \quad (3.8)$$

where C_i is the measured pH value and S_{i_b} is the minimum acceptable pH value. When PLi for each of the parameters has been calculated, WPI with n number of parameters is calculated through summation of all the PLi and dividing it with n using expression 3.9. Table 2.4 presents various classification of water quality determined using the water pollution index parameter.

$$WPI = \frac{1}{n} \sum_{i=1}^n PLi \quad (3.9)$$

3.5 Results

3.5.1 Water quality data

The data presented in Table 3.2 shows that most of the parameters analysed are within the WHO set limits except for fluoride, potassium and sodium which are evidently more than the WHO limits in the E1, M1, M2, M3 and K1 sampling points. Elevated levels of fluorides can cause dental and skeletal fluorosis that pose serious health risk from regular consumption of the water. Dental fluorosis arises from excess fluoride exposure during tooth development from infancy up to 8 years. Skeletal fluorosis emanates from long term excessive ingestion of fluorides. (Srivastava & Flora, 2020).

Table 3.2: Results of the water basin physico-chemical parameters, anions, cations and heavy metal analysis

| Parameter | Sampling points | | | | | | WHO limits |
|--------------------------------------|-----------------|---------|----------|---------|---------|----------|------------|
| | E1 | E2 | M1 | M2 | M3 | K1 | |
| pH | 7.66 | 7.86 | 7.96 | 8.45 | 7.75 | 7.85 | 8.5 |
| σ ($\mu\text{S}/\text{cm}$) | 300.33 | 223.67 | 231.67 | 230.67 | 152.67 | 164.33 | 1500 |
| TDS (mg/L) | 196.00 | 146.33 | 151.33 | 150.67 | 100.33 | 107.00 | 1000 |
| salinity | 282.67 | 213.67 | 221.33 | 219.67 | 148.00 | 158.67 | 1000 |
| K(mg/L) | 80.00 | Nd | 76.00 | 420.00 | 620.00 | 92.00 | 100 |
| Na(mg/L) | 104.10 | 19.00 | 100.00 | 1220.00 | 1800.00 | 146.00 | 200 |
| SO_4^{2-} (mg/L) | 6.50 | 5.50 | 5.00 | 86.00 | 60.00 | 26.00 | 500 |
| NO_3^- (mg/L) | 10.66 | 3.08 | 6.16 | 4.32 | 2.09 | 1.73 | 50 |
| F (mg/L) | 0.80 | 0.30 | 4.50 | 5.30 | 4.50 | 5.30 | 1.50 |
| Cl (mg/L) | 50.00 | Nd | 75.00 | 110.00 | 75.00 | 110.00 | 250 |
| Mg (mg/L) | 0.10 | 0.60 | 4.00 | 17.00 | 12.00 | 4.00 | 100 |
| Ca (mg/L) | 25.00 | 21.00 | 7.00 | 52.00 | 44.00 | 7.00 | 250 |
| Al (mg/L) | 0.00843 | 0.034 | 0.0085 | 0.0852 | 0.013 | 0.0134 | 0.2 |
| Zn (mg/L) | 2.15 | 2.14 | 3.48 | 0.10 | 12.70 | 8.78 | 5 |
| Cu (mg/L) | 0.3615 | 0.0116 | 0.6167 | 0.8704 | 0.7006 | 0.2657 | 2 |
| Cr (mg/L) | 0.03615 | 0.00116 | 0.06167 | 0.08704 | 0.07006 | 0.02657 | 0.05 |
| Pb (mg/L) | 0.00487 | 0.00751 | 0.002275 | 0.00714 | 0.0058 | 0.000954 | 0.01 |
| Mn (mg/L) | 0.118 | 0.509 | 0.382 | 0.657 | 0.00459 | 0.317 | 0.4 |

Fe (mg/L) 0.2729 0.274 0.033 0.928 0.691 0.474 0.3

Legend: Nd – Not detected

High fluorides in the region of study can be associated with volcanic geology and mineral weathering. Gevera and Mouri (2018) reported more than 87% of the boreholes are characterized by fluoride levels higher WHO limits for safe drinking water ranging from 0.5 to 72 mg/l, with a mean of 11.08 mg/l. The high sodium and potassium can be associated with various agricultural activities and wastewater discharge from Salгаа and Sachangwan in the Molo water basin. Elevated sodium and potassium can cause hypertension and kidney issues especially for sensitive groups. Chromium was more than the WHO limit in M1, M2 and M3 whereas Mn exceeded the WHO limit in E2 and M2 sample points. Besides, Zn was above the recommended limit at M3 and K1 sampling points. Iron was also higher than the acceptable WHO limit at sampling points M2, M3 and K1. Elevated heavy metals Cr, Zn, Fe, and Mn raise a significant red flag concerning possibility of toxicity. These data when compared with WHO standards indicates general water pollution in the Molo water system.

The data in Table 3.2 were used to calculate WQI of the Molo river water basin and the obtained WQI values presented in Table 3.4 and categorization as presented in Table 3.3. Higher values indicate poorer water quality or higher concentration relative to standards. Cr, Pb, Fe, Mn, Zn, Cu, Al and F had extremely high weighted values especially Cr and Pb indicating heavy metal pollution. Interestingly, Pb, Cu, and Al concentrations were below the WHO limits in all the sampling points however the weighted values were extremely high reflecting the parameter’s relative importance and toxicity.

Table 3.3: Categorization of water suitability from sampling point based on WHO classification (Ram *et al.*, 2021)

| WQI Rating | Classification | Sampling point classification |
|------------|-----------------------------------|-------------------------------|
| 0 – 25 | Excellent | K1 |
| 25 – 50 | Slightly polluted (good) | M1 |
| 50 – 75 | Moderately polluted (poor) | E1, E2 and M3 |
| 75 – 100 | Polluted (very poor) | M2 |
| >100 | Excessively polluted (unsuitable) | |

Calculated WQI values result in values ranging from 0 to 100. These range of 0-100 is further broken down as shown in Table 3.3 to smaller ranges of 0-25 values within which represent excellent water quality, 25-50 represents slightly polluted water, obtained values 50-75 represents moderately polluted, obtained values 75-100 represents polluted water quality, and any value above 100 is excessively polluted and are regarded unsuitable for use. The sampling point K1 has excellent drinking water quality with a calculated water quality index value of 23.12. On the other hand, M1 with calculated water quality index of 39.86 is slightly polluted whereas E1, E2 and M3 reported water quality index values of 51.17, 62.64 and 73.20, respectively, and are categorized as moderately polluted water. The sampling point M2 had elevated concentrations of heavy metals especially Pb contributed 53.92 weighted values and an overall water quality index value of 94.82 of the sampling which falls in the polluted category.

Table 3.4: A summary of calculated WiQi for each parameter and the cumulative WQI for each sampling point

| Parameter | Sampling points | | | | | |
|-------------------------------|-----------------|----------|----------|----------|----------|----------|
| | E1 | E2 | M1 | M2 | M3 | K1 |
| pH | 0.039105 | 0.050954 | 0.056879 | 0.085911 | 0.044437 | 0.050362 |
| σ | 0.000101 | 7.51E-05 | 7.78E-05 | 7.74E-05 | 5.13E-05 | 5.52E-05 |
| TDS | 0.000148 | 0.000111 | 0.000114 | 0.000114 | 7.58E-05 | 8.08E-05 |
| salinity | 0.000214 | 0.000161 | 0.000167 | 0.000166 | 0.000112 | 0.00012 |
| K | 0.006043 | - | 0.00574 | 0.031723 | 0.046829 | 0.006949 |
| Na | 0.001966 | 0.000359 | 0.001888 | 0.023037 | 0.033989 | 0.002757 |
| SO ₄ ²⁻ | 1.96E-05 | 1.66E-05 | 1.51E-05 | 0.00026 | 0.000181 | 7.86E-05 |
| NO ₃ ⁻ | 0.003221 | 0.000931 | 0.001861 | 0.001305 | 0.000631 | 0.000523 |
| F | 0.268556 | 0.100708 | 1.510627 | 1.779183 | 1.510627 | 1.779183 |
| Cl | 0.000604 | - | 0.000906 | 0.001329 | 0.000906 | 0.001329 |
| Mg | 7.55E-06 | 4.53E-05 | 0.000302 | 0.001284 | 0.000906 | 0.000302 |
| Ca | 0.000302 | 0.000254 | 8.46E-05 | 0.000628 | 0.000532 | 8.46E-05 |
| Al | 0.159182 | 0.642017 | 0.160504 | 1.608818 | 0.245477 | 0.25303 |
| Zn | 0.064957 | 0.064655 | 0.10514 | 0.003021 | 0.383699 | 0.265266 |
| Cu | 0.068261 | 0.00219 | 0.11645 | 0.164356 | 0.132293 | 0.050172 |
| Cr | 10.92184 | 0.350466 | 18.63208 | 26.297 | 21.16691 | 8.027474 |
| Pb | 36.78378 | 56.72406 | 17.18339 | 53.9294 | 43.8082 | 7.205693 |

| | | | | | | |
|--|--------------|--------------|--------------|--------------|--------------|--------------|
| Mn | 0.557044 | 2.402842 | 1.803312 | 3.101507 | 0.021668 | 1.496465 |
| Fe | 2.290279 | 2.299511 | 0.276948 | 7.788124 | 5.799131 | 3.977986 |
| WQI = $\sum w_i Q_i$ | 51.17 | 62.64 | 39.86 | 94.82 | 73.20 | 23.12 |

These highlight the importance of assigning weight using objective tools rather than subjective methods, such as relying solely on expert opinion. Human settlement has also shown to affect concentration of possible pollutants. E1 a sampling located downstream of Elburgon town has elevated levels of the major anions and cations while upstream; E2 has lower concentrations of these category of pollutants.

Of the six sampling points, there was none whose drinking water quality was excessively polluted thus allowing the general categorization of the water basin as suitable for drinking. The same data in Table 3.2 was used to calculate WPI as given in Table 3.5 and interpretation done to give pollution status of area of study using Table 3.6. The WPI calculations showed that E1 and E2 had the lowest WPI values of 0.38 and 0.30, respectively which falls under excellent waters whereas M1 and K1 reported WPI values of 0.53 and 0.64, respectively and can be classified as good waters. This shows that most of the sampling points are not polluted.

Table 3.5: WPI of the various sampling points based on calculation using data from Table 3.2

| Parameter | Si | PLI per sampling point | | | | | |
|-------------|------|------------------------|----------|----------|----------|----------|----------|
| | | E1 | E2 | M1 | M2 | M3 | K1 |
| pH | 8.5 | 1.094286 | 1.122857 | 1.137143 | 1.207143 | 1.107143 | 1.121429 |
| σ | 1500 | 0.20022 | 0.149113 | 0.154447 | 0.15378 | 0.10178 | 0.109553 |
| TDS | 1000 | 0.196 | 0.14633 | 0.15133 | 0.15067 | 0.10033 | 0.107 |
| salinity | 1000 | 0.28267 | 0.21367 | 0.22133 | 0.21967 | 0.148 | 0.15867 |
| K | 100 | 0.8 | - | 0.76 | 4.2 | 6.2 | 0.92 |
| Na | 200 | 0.5205 | 0.095 | 0.5 | 6.1 | 9 | 0.73 |
| SO_4^{2-} | 500 | 0.013 | 0.011 | 0.01 | 0.172 | 0.12 | 0.052 |
| NO_3^- | 50 | 0.2132 | 0.0616 | 0.1232 | 0.0864 | 0.0418 | 0.0346 |
| F | 1.5 | 0.533333 | 0.2 | 3 | 3.533333 | 3 | 3.533333 |
| Cl | 250 | 0.2 | - | 0.3 | 0.44 | 0.3 | 0.44 |
| Mg | 100 | 0.001 | 0.006 | 0.04 | 0.17 | 0.12 | 0.04 |

| | | | | | | | |
|--|------|-------------|-------------|--------------|--------------|--------------|--------------|
| Ca | 250 | 0.1 | 0.084 | 0.028 | 0.208 | 0.176 | 0.028 |
| Al | 0.2 | 0.04215 | 0.17 | 0.0425 | 0.426 | 0.065 | 0.067 |
| Zn | 5 | 0.43 | 0.428 | 0.696 | 0.02 | 2.54 | 1.756 |
| Cu | 2 | 0.18075 | 0.0058 | 0.30835 | 0.4352 | 0.3503 | 0.13285 |
| Cr | 0.05 | 0.723 | 0.0232 | 1.2334 | 1.7408 | 1.4012 | 0.5314 |
| Pb | 0.01 | 0.487 | 0.751 | 0.2275 | 0.714 | 0.58 | 0.0954 |
| Mn | 0.4 | 0.295 | 1.2725 | 0.955 | 1.6425 | 0.011475 | 0.7925 |
| Fe | 0.3 | 0.909667 | 0.913333 | 0.11 | 3.093333 | 2.303333 | 1.58 |
| \sum PLI | | 7.22 | 5.65 | 10.00 | 24.71 | 27.67 | 12.23 |
| $WPI = \frac{1}{n} \sum_{i=1}^n PLi$ | | 0.38 | 0.30 | 0.53 | 1.30 | 1.46 | 0.64 |

Sampling points M2 and M3 on the other hand indicated highly polluted waters with WPI values of 1.30 and 1.46 calculated, respectively. High levels of chromium, lead, manganese, potassium and iron in M2 and M3 may be responsible for the observed pollution rating in the two sampling points.

Table 3.6: Water classification as per WPI (Abualhaija & Mohammad, 2021)

| WPI value | Category | Sampling points categorization |
|------------|---------------------------|--------------------------------|
| < 0.5 | Excellent water | E1 and E2 |
| 0.5 – 0.75 | Good water | M1 and K1 |
| 0.75 – 1 | Moderately polluted water | |
| >1 | Highly polluted water | M2 and M3 |

Three sampling points, E1, E2, M1, and K1, may be considered good sources of water for domestic and other uses among the six sampling stations. The average water pollution index of this sub-water basin is 0.77 which lies in the bracket of moderately polluted water.

The combined WQI and WPI assessment of water provides a robust and multidimensional picture. They both point out the need of immediate remediation and preventive measures to protect the public health and ecosystems.

3.5.2 Sediment elemental composition and topology

Sediment micrographs provide high resolution images that give details on grain shape, size, surface textures, and structure. These characteristics dictate pollutant adsorption and retention and ultimately determining how long pollutants stay in the sediments and their

transport dynamics. When coupled with energy dispersive X-ray spectroscopy (EDX), it reveals minerals present in sediments helping map pollutants distribution critical for locating pollution hotspots and sources. Valladares *et al.* (2022) conducted a comprehensive physical and chemical characterization of riverbed sediments of Moquegua River in Peru using SEMEDX. They confirmed that the sediments were primarily silicon, aluminium, sodium, and potassium.

In this study, all the sediments as reported in Table 3.7, oxygen atoms was the most prevalent owing to its presences in most organic and inorganic compounds followed by silicon. Notably sediment morphology was also determined using EDX and the finding showed the absence of heavy metal pollutants of concern which include lead, mercury, arsenic and cadmium however it showed presence of manganese and iron. Ideally, oxygen was the most abundant element in the sediments sampled in the Molo water basin, with E2, M1, and M3 posting the highest oxygen levels, respectively. On the other hand, the highest carbon level was noted in E2, M1 and M3 linked to organic matter possibly from anthropogenic activities. Silicon was the third most abundant element in all the sediment samples followed by aluminium.

The other elements such as potassium, calcium, titanium, manganese, and iron were found in significantly low amounts. The low concentrations of essential elements (K, Na, Ca, and Mg) could be attributed to their relatively high solubility in water. E1 extremely high Fe content suggests strong iron-rich sediments or contamination, while M2 and M3 have relatively lower Fe, possibly due to different sediment sources or water chemistry. This corresponds to their high concentrations in the water-phase as reported in Table 3.2.

Table 3.7: Sediment elemental composition

| Element | Sampling points | | | | | |
|---------|-----------------|------------|------------|------------|------------|------------|
| | E1 | E2 | K1 | M1 | M2 | M3 |
| C | 12.07±1.04 | 24.42±0.21 | 15.51±1.43 | 17.70±1.27 | 11.93±1.14 | 17.79±0.18 |
| O | 25.76±0.4 | 32.62±0.27 | 37.10±0.69 | 48.30±0.78 | 42.96±0.61 | 44.23±0.21 |
| Al | 2.92±0.08 | 7.93±0.10 | 7.02±0.15 | 8.19±0.15 | 9.13±0.15 | 7.21±0.09 |
| Si | 9.27±0.15 | 24.18±0.17 | 25.04±0.45 | 16.66±0.28 | 27.57±0.39 | 24.64±0.15 |
| K | 0.23±0.04 | 3.40±0.07 | 4.98±0.11 | 1.33±0.05 | 6.06±0.11 | 3.07±0.06 |
| Ca | 0.63±0.05 | 0.71±0.05 | 0.98±0.06 | 0.53±0.04 | Nd | 0.17±0.03 |
| Ti | 0.24±0.05 | 0.31±0.05 | 0.63±0.06 | 0.70±0.05 | 0.32±0.05 | Nd |
| Mn | 4.76±0.13 | 4.42±0.11 | 0.39±0.07 | Nd | Nd | Nd |

Fe 43.94±0.57 4.70±0.12 7.34±0.18 6.58±0.15 2.03±0.10 2.90±0.08

Legend: Nd – Not detected

From the micrographs in Figure 3.2, the sediments present interesting similarities but differ markedly in elemental composition. The micrographs also show sediments tightly bound together flaky sheets rolling over each other which are an indication of sequential settling from the water phase. With the exception of K1 micrograph which has a number of dark spaces, the other micrographs show minimal dark spaces signifying low porosity of the sediments.

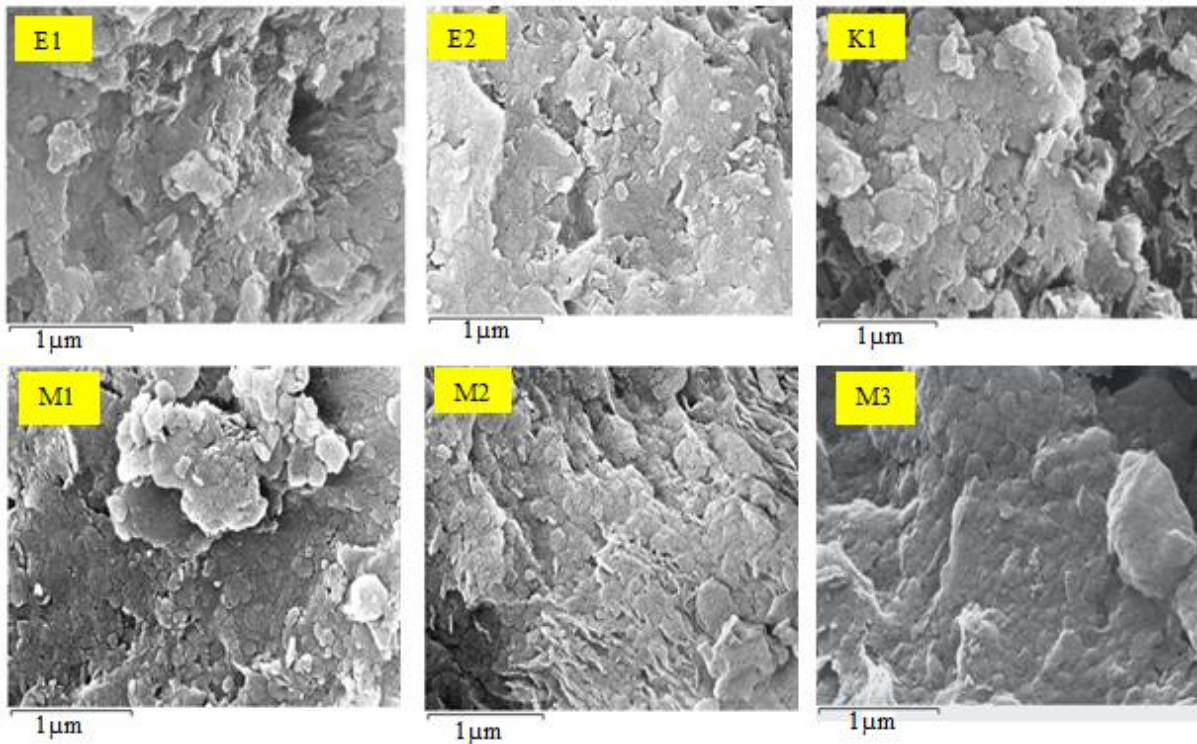


Figure 3.2: Scanning electron micrographs of sediments collected from various sampling points in the Molo water basin

Generally, the characteristics obtained from the micrographs are attributed to presences of clay particles in the sediments which are known to have particle sizes below 2μm, possess low porosity and are cohesive. This can be observed in sediments collected from M2 and M3 which show some polymeric behaviour. Although E1, E2, K1, and M1 also exhibit polymeric characteristics, some particulate nature of sediments is clear. Notably, the sediments sampled from the Molo water basin have an average size which is far much less than 1μm.

The SEM morphology visually confirms the chemical pollution trends observed through WQI, WPI, and elemental analysis. Clean sites (E1, E2, and K1) show typical natural

sediment texture while heavily polluted sites (M2, M3) exhibit compacted and layered structures due to pollutant deposition and fine particulate agglomeration. M1 shows intermediate signs of crystallization, suggesting chemical processes are active but less severe than in M2 and M3.

3.6 Discussion

This study has shown that nitrates and phosphates were within the WHO limit in all the sampling points of the Molo water basin. Nitrate concentration was below the WHO limit in all the sampling points therefore blue baby syndrome are unlikely to be significant concern in the water basin. Low phosphate levels indicate minimal domestic effluent rich in detergents that may accumulate at the water basin. Phosphates and nitrates contribute significantly to eutrophication of aquatic systems by promoting excessive algal growth (Mishra, 2023). Therefore, the low levels observed indicate a reduced risk of nutrient enrichment and subsequent eutrophication downstream in the water basin extending to lake Baringo. However it is advisable to conduct periodic monitoring to ensure these conditions remain stable. Nevertheless, water quality cannot be assessed by examining the data collected from the basin without further analysis using the state-of-the-art procedures – water quality index and water pollution indices.

Water quality is an expression that indicates the suitability of water for various uses and processes, which varies from region to region, and time to time as reported. Abdul Maulud *et al.* (2021) studied spatial and water quality during dry and rainy seasons at Kelantan river Basin in Malaysia. They found that the water quality varied from region to region and season to season. Moreover, Tian *et al.* (2019) assessed the water quality of the upper and middle streams of the Luanhe river in Northern China. They reported significant seasonal and locational variation of water quality. Each of the various uses or processes will have their own demands and influences on water quality. These demands and influences are the requirements for physical, chemical or the biological characteristics of water. Water quality can be defined by a range of natural and human influences which limit water use. The most important of the natural influences are geological, hydrological and climatic factors.

Several factors, such as the concentration of DO, bacteria levels, the amount of salt (salinity), or the amount of material suspended in the water (turbidity), the concentration of microscopic algae and quantities of pesticides, herbicides, and heavy metals present in the water system are used to measure water quality (Zeinalzadeh & Rezaei, 2017). It is clear from Table 3.2 that Zn and Cr are the major heavy metals pollutants in the Molo water basin.

Their concentrations in most sampling points especially in M1, M2, and M3, and for Cr, in M1, M3, and K1 are way above the WHO allowable limits. TDS correlates with conductivity within a factor of 0.5 to 0.75 depending on the level of salinity (M'nassri *et al.*, 2019; Poursaeid *et al.*, 2020). This correction is approximate because the organic fraction of the dissolved solids does not conduct electricity and the ionic mobility of the conductive species varies. The amount of dissolved salt gives salinity of the water which also forms part of the TDS. The nature of substances dissolved in the water determines the pH of the water which in turn determines how corrosive the water can be. The prevailing pH of water also affects bioavailability of the substances dissolved (do Nascimento *et al.*, 2021; Ondrasek & Rengel, 2021).

Water quality index was originally developed by Horton in 1965 to measure water quality by using 10 most regularly used water parameters but has been modified by different experts over time. It is a mathematical tool that simplifies the complexity of water quality data sets into a single dimensionless number that gives the water quality status of a given water system (Banda & Kumarasamy, 2020). WQI provides a single number that represents overall water quality at a certain location and time, based on some selected water parameters which allows for comparison of water quality between different rivers or water of the same river from different seasons or sampling points (Wu *et al.*, 2018). This number gives the combined impact of the many different factors that characterize the quality of water and enables comparison of the water quality in the different sampling points (Sharma *et al.*, 2020). It tells whether the overall quality of water bodies poses a potential threat to various uses of water such as water being a habitat for aquatic life, use in agriculture and livestock, recreation and aesthetics, and drinking water supplies (Liou *et al.*, 2004; Nazeer *et al.*, 2014). Notably, heavy metals are the main contributors for the high water indices realized in the water basin.

In view of this, heavy metals are very important parameters in checking the quality of water in a given source. The average WQI of the water sub-basin is 57.47, and lies in the bracket of moderately polluted water. This value gives an overall picture of the state of water in the Molo water basin. Generally, the most polluted water in the basin is those located in M2. This is conceivable if we consider that this is an area with possibly rich agricultural activity with the Nakuru-Eldoret highway passing through it. Downstream at M1 the WQI obtained was 39.86 and at M2 the value obtained was 94.82 with the two sampling points next to each other. This observation can be associated with pollution source being next to M2 which is the Eldoret-Nakuru highway. The WQI obtained from this study compares well with

the results previously reported by (Robert, 2021) in water quality assessment index for the Chania River where the highest WQI value was 89.15 and the lowest value was 19.67. Abdel-Satar *et al.* (2017) reported deterioration of Nile water quality extending from poor to marginal with respect to aquatic WQI. They also reported variation of drinking water quality from marginal to good. Ibrahim *et al.* (2018) used GIS techniques to monitor surface water quality for river Nile in Egypt and reported average water quality index values range between 58.8 and 67.2. Although these data were obtained from different geographical locations in Kenya, it is evident the data from the river Molo sub-basin agree with the WQI data reported in rivers Chania, Nile, and Nyando.

Generally WQI is reliable in assessing the general water quality of a given source. it takes into consideration a limited number of physio-chemical parameters but becomes unreliable when dealing with a large number of parameters or data sets (Mogane *et al.*, 2023). Therefore WPI is applied for physical, chemical (major metal ions) or even for biological quality assessment of water sources based on the available water quality standards for use (Tanjung & Hamuna, 2019). It gives the combined effect of general physico-chemical parameters as well as heavy metals with respect to their permissible limits thus bridging the gap left by WQI which does not factor in heavy metals in predicting the quality of water sources (Widodo *et al.*, 2019). Considering the Molo water basin, it is evident that M2 and M3 are the most polluted waters with water pollution indices of 1.3 and 1.46, respectively. All other sampling points within the basin are classified as excellent waters. This observation is remarkably consistent with the water status predicted using the water quality index (WQI) parameter.

Surface erosion, mining and various human activities including agriculture and wood treatment in a water basin introduces suspended solids and particulate matter which can be deposited as sediments, and may contain minerals and organic matter. In a water system, the deposited sediment acts as a source and sinks for organic matter and heavy metals depending on the river chemistry such pH, salinity and dissolved oxygen. Sediment is also important for the development of aquatic ecosystems especially because sediment particle size and arrangement affect sediment porosity, which is an important factor influencing sediment oxygen conditions. The presence of carbon and oxygen in all the sampling points in the Molo water basin may be an indication of the presence of organic contaminants of environmental concern. Such organic contaminants may include benzo[a]pyrene, pesticides, phenols and dioxins. These are serious organic contaminants usually associated with endocrine

malfunctions, cancer, mutagenesis, and other biological defects. High levels of oxygen in sediments may be attributed to metal oxides, metal carbonates and metal complexes.

Sediments act as a sinks for a significant number of toxic substances and should therefore be investigated alongside the water-phase. Sediments contain a record of previous pollution, which makes sediment analysis an important component in understanding the mineral deposits in the river basin and monitoring pollution of rivers and other water bodies elsewhere in the world (Gayathri *et al.*, 2021; Yan Li *et al.*, 2018). Heavy metals immobilized in the sediment become mobilized at points exposed to the water phase (Pal & Maiti, 2020). In this study the sediment analysis showed minimal differences in the obtained micrographs with all being bright with minimal dark spaces signifying sediments of low porosity. K1 sediment micrographs had elevated levels of dark spaces which can be associated to the presence of a high organic matter given the sampling point is located next to a forested area.

Metals in the river system exist in different chemical forms associated with organic, residual, exchangeable, carbonate fractions and those bound to, for instance iron oxides, manganese oxides, chromates, metal chlorides, and metal sulphates (Geng *et al.*, 2020). Factors including physical and chemical equilibrium, pH, redox reactions, oxidation states of elements and sediment attributed organic matter control heavy metal distribution and accumulation in sediments (Yuanhang Li & Gong, 2021). The mobility and bioavailability of metals in river systems is largely dependent on sediment transport dynamics which is influenced by several factors such as pH, redox potential, organic matter, temperature, dissolved organic carbon, salinity, composition of the sediment, particle size, and grain texture (Baran *et al.*, 2019).

Heavy metals accumulate in vital body organs such as kidneys, liver and the brain resulting in the disruption of normal biological functioning of the organism. High levels of heavy metals in the environment have been associated with a number of health issues. These health issues depend on the amount exposed to and the period of exposure to heavy metals. The health impacts include impaired intellectual development, gastrointestinal, cardiovascular, neurological, renal respiratory and haematological effects (Yang & Massey, 2019). In view of these health effects, WHO, the EC and US EPA have defined limits of parameters beyond which the quality of water is considered unsuitable for specific utilization. Heavy metal toxic load is also important in determining the limit at which an organism's immune system breaks down on exposure to heavy metals. It gives the concentrations of heavy metals above which etiological risks occur (Jaishankar *et al.*, 2014).

Generally, water-based pollution is one of the leading causes of death in the twenty-first century. According to the Lancet Commission on Pollution and Health, pollution-related diseases caused an estimated 9 million premature deaths in 2015, accounting for $\approx 16\%$ of all fatalities worldwide. This number is three times higher than the combined deaths from major infectious diseases, and fifteen times higher than the total number of deaths from all wars and other types of violent acts around the globe (Landrigan *et al.*, 2018). Experts also project that, under the current climate change scenario, nearly half of the world's population, including between 75 million and 250 million people in Africa, will be living in areas of significant water stress by 2030 (Nhamo *et al.*, 2019). Among the possible pollutants of water, heavy metals and POPs have attracted a lot of attention because of their toxicity even at low concentrations.

3.7 Conclusions

This study has found that the physico-chemical properties observed in the Molo river basin indicate a strong influence from heavy metals. This correlates very well with the water quality parameters; WQI and WPI reported which show that the water of the Molo river basin is significantly polluted. The high levels of heavy metals observed in the water basin compromise the water quality because they can bioaccumulate and biomagnified in living organisms to cause serious public health problems. The high concentration of heavy metals may be attributed to agricultural activities, soil erosion, and weathering of rocks in the study area. Water quality index and WPI data specifically in this basin agree to a larger extent and are therefore complementary in water quality assessment. The sediment chemistry in the study area has also predicted serious possible pollution levels likely to be caused by hazardous organics based on the high levels of carbon and oxygen incorporated in sediments. This may point to the presence of benzo[a]pyrene, dioxins, phenols, and benzene and its derivatives among other pollutants. Most sediments indicate the presence of high amounts of iron and aluminium suggesting that there is an iron and an aluminium point source which is most likely to be anthropogenic. Generally, the water basin is moderately polluted as corroborated by the two methods used to evaluate the water quality status – Water quality index and water pollution index. The findings of the Molo water basin can be extrapolated to other water basins and water bodies in different geographical locations around the world.

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CHAPTER FOUR

CONCENTRATION PROFILES OF POLYCYCLIC AROMATIC CHEMICALS IN THE MOLO WATER BASIN AND THEIR ECOLOGICAL HEALTH RISKS

Abstract

Urbanisation, modernization, and the rapid population growth have led to an increase in environmental pollution. Polycyclic aromatic hydrocarbons (PAHs), one of the categories of organic contaminants, contain two or more fused aromatic rings. They originate from incomplete combustion of organic material through pyrogenic and petrogenic sources. PAHs of pyrogenic sources are produced through anoxic combustion of fossil fuels resulting in heavy PAHs of 4–6 membered rings. Petrogenic sources include crude oils and associated by-products of their combustive emissions. Owing to their lipophilic nature PAHs readily get absorbed from the lungs following inhalation, the skin on contact and gastrointestinal tract on ingestion increasing their bioavailability after exposure. Long-term exposure to biologic effective dose may lead to acute effects, short term minor asymptomatic manifestations, or chronic effects. This study determined the concentrations of various PAHs in the Molo River water basin using a GC-MS. 2 μL of extracts in split ratio 50:1 at an injection temperature of 250 $^{\circ}\text{C}$ was injected to Agilent Technologies 7890A GC -5975C inert XL. Ultra-high purity helium mobile phase flowing at a constant flow rate of 3.3 mL/min carried sample extract mixture into a non-polar column HP-5MS 30 m \times 250 μm \times 0.25 μm . The mass spectrometer was operated on Total Ion Current Mode (TIC) on a mass scan range of 15 - 600 amu. The detected PAHs in the Molo water basin were 18 unsubstituted, 21 substituted and 14 hetero PAHs. Concentration were in the ppm levels and varied with type of PAH and location. Cumulatively unsubstituted PAHs $\sum_{18} = 216.51 \pm 0.51$ ppm, Substituted PAHs $\sum_{21} = 138.34 \pm 0.88$ ppm, Hetero-atomic $\sum_{14} = 23.86 \pm 0.35$ ppm, and a total PAH load of 378.71 ± 1.08 ppm which included six (6) PAHs listed in the 16 priority pollutants with a total BaP-TEQ of 5.14 ppm.

4.1 Introduction

Urbanisation, modernization, and the rapid population growth have led to an increase environmental pollution (Patel *et al.*, 2020). Polycyclic aromatic hydrocarbons (PAHs), one of the categories of organic contaminants, contain two or more fused aromatic rings. They originate from incomplete combustion of organic material through pyrogenic and petrogenic sources among others. PAHs of pyrogenic sources are produced through anoxic combustion of fossil fuels resulting in heavy PAHs of 4–6 membered rings. Petrogenic sources include crude oils and associated by-products of their combustive emissions which are naturally enriched with light PAHs of 2–3 membered rings such as phenanthrene, and its alkylated homologs such as dimethylphenanthrene (Marris *et al.*, 2020). The best known PAH is benzo(a) pyrene (BaP) which is used as a reference in the measurement of PAH levels in the environment with PAH profile giving the relationship between the amount of BaP and some other PAHs. They are highly lipid-soluble allowing them to be absorbed from the lung, gut, and skin of mammals leading to harmful health effects with the high-molecular-weight PAHs more detrimental to the environment and human health. They are known to have carcinogenic, mutagenic, and toxic potential making their presence in the environment a huge concern. USEPA has identified 16 PAHs as priority pollutants because of their toxic and carcinogenic properties.

Based on existing experimental data International Agency for Research on Cancer (IARC) evaluated the carcinogenic risk of PAHs to humans Benzo (a) is classified as carcinogenic to humans while dibenzo (a,h)anthracene and benzo(a)anthracene are classified as probably carcinogenic to humans. benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, naphthalene, indeno(1,2,3-cd)pyrene, chrysene, are classified as possibly carcinogenic to humans. PAHs find their way into aquatic environments through direct wet or dry deposition from the atmosphere, runoff from land, roads, pavements, roofs, guttering, and industries with naphthalene and phenanthrene being the most abundant PAHs in aquatic environment (Berríos-Rolón *et al.*, 2025) . PAHs may undergo post-emission transformation and degradation into potentially more hazardous products than the parent PAHs. The half-life of PAHs in atmosphere is the shortest as compared with half-life of PAHs in water, soil and sediments making soil, water, and sediments have the largest accumulation of PAHs (Hites, 2021)

The probability of occurrence of an undesired ecological impact upon exposure to PAHs or any other pollutants referred to ecological risk is assessed using a process that entails problem formulation, exposure analysis, effects assessment, and risk characterization

(Ankley *et al.*, 2023). A review by Liang *et al.* (2022) on distribution and ecological risks associated with PAHs in different compartments in Kenya showed a wide range of variation in concentration of the PAHs with limited data about PAHs in Kenya showed little information about PAHs' distribution characteristics and spatial and temporal distribution. Rizzi *et al.* (2023) investigated the presence of 16 priority PAHs in the Amazonian surface waters and found PAHs in all samples, with total concentrations up to 163 ng L⁻¹ with higher concentrations next to large urban areas with the calculated ecological risk posed by the PAHs in the amazon categorized as low or insignificant by the researchers. A research done by Dudhagara *et al.* (2016) on distribution, sources and ecological risk assessment of PAHs in surface sediments at Bhavnagar coast, Gujarat, India reported elevated levels of the PAHs and potentially acute and chronic health hazards.

4.2 Sources of PAHs

Sources of polycyclic aromatic hydrocarbons pollution can be broadly categorized as either natural or anthropogenic. Naturally, they occur in fossil fuels, natural forest fires produce dominantly low-ring PAHs with relatively low toxicity (Yang *et al.*, 2022), extra-terrestrial bodies (Varela, 2023), and volcanic eruptions (Nizametdinov *et al.*, 2022). These natural sources of PAHs are marginal and contribute minimally to the PAH environmental pollution. Anthropogenic sources of PAHs are a significant determinant of PAH pollution and can be classified into four groups including industrial, mobile (Huang *et al.*, 2022), domestic, and agricultural sources (Cheruiyot *et al.*, 2015).

4.3 Routes of exposure

Humans can consume PAHs via different routes, such as inhalation, dermal contact, and ingestion. PAHs present in the environment find their way into the human body through inhalation from ambient air and smoking of cigarettes, dietary intake although PAH concentration in foodstuff vary depending on the type of food with charring meat or barbecuing food over a charcoal, wood, or other type of fire reportedly increasing the concentration of PAHs, and dermal intake (Aquilina & Harrison, 2023; Bernard & Dudler, 2022; Domingo & Nadal, 2015; Seo *et al.*, 2022). Owing to their lipophilic nature they readily get absorbed from the lungs following inhalation, the skin on contact and gastrointestinal tract on ingestion increasing their bioavailability after exposure. After entry to the body, it has been reported that they concentrate in organs rich in adipose tissue making those organs serve as storage location.

4.4 Toxicity of PAHs

The health effects arising from exposure to PAHs depends on the length exposure, route of exposure, the amount of PAHs one is exposed to, pre-existing health status of the exposed person, age of the exposed individual and the toxicity of the PAHs. These health effects can be broadly classified as acute effects and the chronic effects. Acute effects are short term minor asymptomatic manifestations arising from exposure to PAHs and include symptoms such as eye irritation, skin irritation, skin inflammation, nausea, vomiting, diarrhoea and confusion. Chronic effects result from long-term exposure to PAHs and include decreased immune function, cataracts, kidney and liver damage, breathing problems, asthma-like symptoms, and lung function abnormalities. Several investigations on effects of PAHs have reported PAH-induced toxic cytotoxicity, genotoxicity, carcinogenicity, teratogenicity, developmental aberrations, cardiovascular dysfunction, endocrine disruption, immunotoxicity, and other effects in fish, amphibians, birds, and mammals.

For PAH to cause toxic effects, a biologic effective dose which is the amount of toxicant that can cause toxicity, must reach the target site or organ. At the site, PAH and DNA can react to form PAH-DNA adduct a site critical to the regulation of cell differentiation or growth causing mechanical and steric hindrance affecting the DNA-proof-reading activity of polymerase enzymes and if not repaired it leads to mutation. Metabolism of weak carcinogen PAHs makes them more potent carcinogens through generation of reactive metabolites of PAHs like epoxides and dihydrodiols which binds to cellular proteins and DNA causing biochemical disruptions and cell damage that lead to mutations, developmental malformations, tumours, and cancer. Cytochrome P450 1A1 (CYP1A1) biologically activates PAHs into active metabolites predisposing persons with a high degree of CYP1A1 inducibility to risk of PAH carcinogenesis. Nitrated polycyclic aromatic hydrocarbons (N-PAHs), sometimes from nitration of unsubstituted PAHs, are direct-acting potential mutagens and carcinogens to mammalian systems thus they have far greater toxicity than unsubstituted PAHs.

4.5 Area of study

This research focused on the Molo water basin, the upper part of Molo River which has its source at the Mau complex and flows downstream 120 km long to L. Baringo. The river serves the residents of Nakuru and Baringo counties. The Molo river and its tributaries receives domestic discharges, oil and its combustion products from oil spills and accidents in Salgaa area, and waste contaminants from farming activities in the area which contaminate

which includes some of the generally known sources of PAHs posing a risk of possible contamination with PAHs hence such water may not be fit for domestic use.

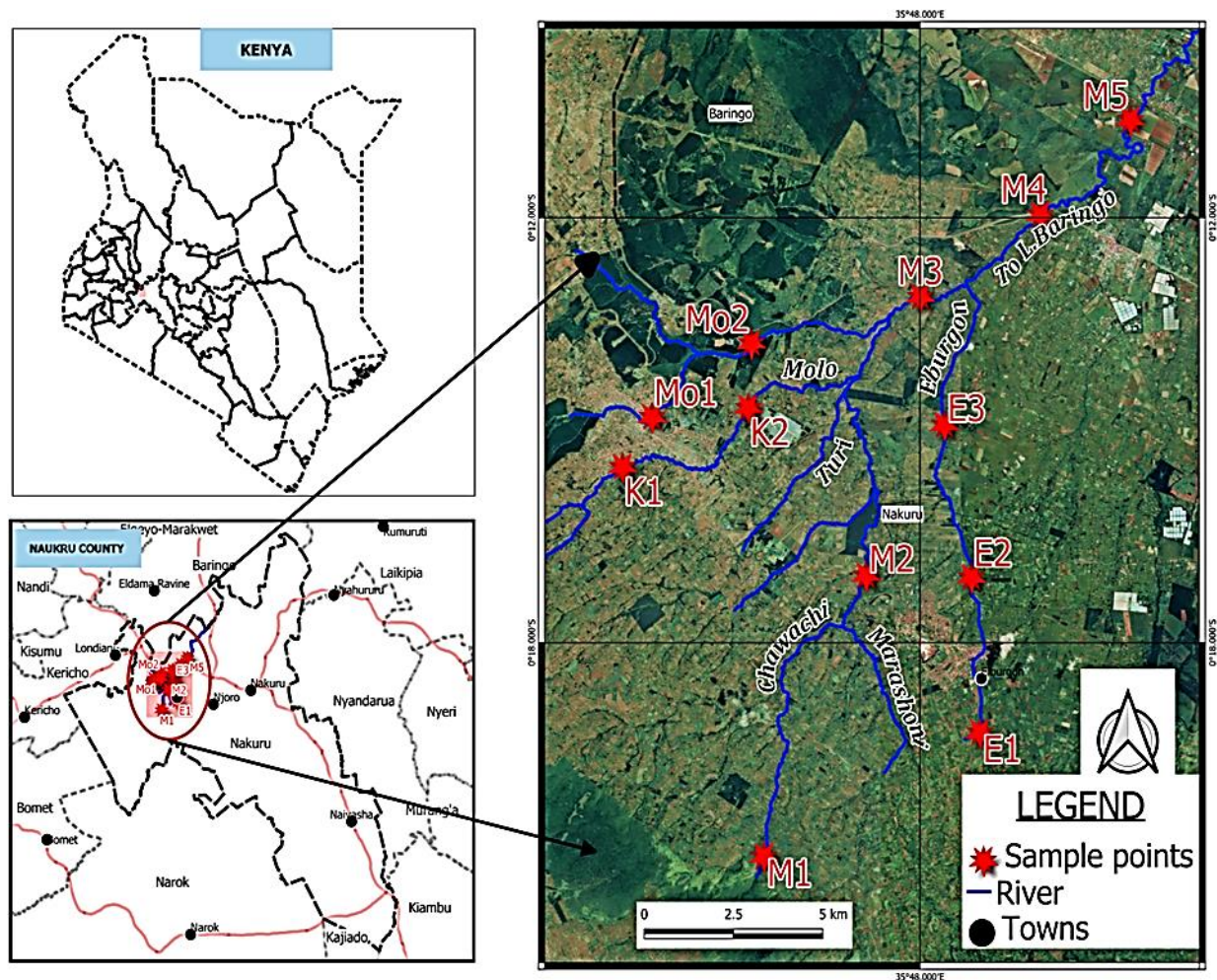


Figure 4.1: The sampling sites in the Molo water basin

The upper section of River Molo passes through towns such as Elburgon, Salgaa and Rongai. In the Molo water system, urban waste has become a serious problem along Rivers Molo, Kibunja and Elburgon. Effluents from industries, sewage from residential areas, chemical run-offs from agricultural activities, quarry activities, large and small-scale dumping of waste from towns poses serious effects on the Molo river water basin water quality. Commercialized agriculture in the region such as horticulture and large-scale farming are bound to pollute the Molo water basin.

4.6 Materials and methods

Gas chromatograph, connected to a mass spectrophotometer, and centrifuge, were used for this work. All the chemicals that were used in this study were of analytical grade.

4.6.1 Sampling and sample handling

The water samples were collected from seven sampling points, as indicated in fig 4.1, in three replicates using 2.5 L amber bottles. These sampling bottles were cleaned with 10 % v/v nitric acid and thoroughly rinsed with deionized water to remove contaminants and ensure accuracy. During sampling, these sampling bottles were washed 3-4 times with water from the exact site of sampling before taking the sample to condition them and minimize contamination. All samples were transported in an icebox to the laboratory where they were refrigerated at 4 °C awaiting the analysis (Tuit & Wait, 2020). Sampling points were located using GIS.

4.6.2 Quality assurance/Quality control

Distilled water which served as the control sample was analysed for PAHs before the analysis of water samples from Molo river water basin. Standard concentrations was prepared ensuring components of interest in the water were within the bracket concentrations of the standard termed the analysis range. Sample analysis was conducted in replicates to enhance the validity and reproducibility of the results. To one sample out of 20 samples, a known concentration of the analyte was added and the recovery of ~95% obtained was good enough to proceed with analysis (Bienvenu *et al.*, 2017).

4.6.3 Extraction procedure for PAHs from water

Pyrene-d₁₀ (100 µL of 1 ng/mL) was added to each water sample before extraction. Samples were extracted using solid-phase extraction (SPE) as described by Tais *et al.* (2007). The SPE cartridges were first conditioned with 6 mL of dichloromethane followed by 6 mL of acetonitrile and 6 mL of distilled water. Water samples (200 mL) was passed through the cartridge under a vacuum at a rate of approximately 6 mL/ min. Water residues from cartridges was eliminated by 30 min vacuum and the solvent then removed at low temperature (< 35 °C) by rotary evaporation and analysed using GC-MS.

4.6.4 Preparation of calibration standards for organic contaminants

The spike recovery method was used for validation studies by spiking with 1 µL of 100 mg/L standard mixture consisting of 16 PAHs to 500 mL pre-extracted water samples. Double-distilled water (500 mL) was pre-extracted in triplicate with 30 mL dichloromethane as a blank sample. The spiked samples was extracted and analysed. Polycyclic aromatic hydrocarbons standards were used for the calibration of the instrument (Edokpayi *et al.*, 2016).

4.6.5 GC-MS analysis for PAHs

Analysis of PAHs was carried out using a Gas Chromatograph system coupled with mass spectrometry system (GC-MS) Agilent Technologies 7890A GC -5975C inert XL whose oven temperature was set at 50 °C for 3 min then ramped to 10 °C/min to 250 °C for 2 min, then held constant at 250 °C for 20 min. Ultra-high purity (UHP, 99.999%) helium was used as the carrier gas at a constant flow rate of 3.3 mL/min. The MS was operated on Total Ion Current Mode (TIC) on a mass scan range of 15 - 600 amu. The organic extract (2 µL) was injected in the split ratio 50:1 at an injection temperature of 250 °C. Samples and standards were run through the GC-MS system, and the peak shapes and retention times compared with the compounds of interest. The column used was a non-polar column HP-5MS 30 m × 250 µm × 0.25 µm.

4.6.6 Ecological risks

Ecological risk is the likelihood that the environment might be impacted from exposure to one or more PAHs. Assessing these risks is done through three phases of problem formulation, analysis, and risk characterization (Venkatraman *et al.*, 2024). Despite the widespread nature of PAHs emanating from their numerous sources both natural and anthropogenic, they have been known to pose adverse negative effects on the environment. Several PAHs including BaP have been identified as potential carcinogens by causing mutations of DNA leading to cancer development (Cheng *et al.*, 2021).

In the environment, these PAHs exist in mixture leading to their exposure as mixtures leading to synergistic or antagonist effects coupled with their persistence and ability to bioaccumulate further exacerbates the risks.

Benzo (a) pyrene is the most extensively studied PAH and toxicological data provide sufficient basis for the risk assessment of this compound. To evaluate the carcinogenic risks posed by PAHs it is assumed that the toxicity of all PAHs can be expressed relative to the toxicity of BaP. Under this assumption, concentrations of carcinogenic PAHs are converted into Benzo(a)pyrene toxic equivalent (BaP-TEQ) or Benzo(a)pyrene mutagenic equivalent (BaP-MEQ) concentrations (Di Duca *et al.*, 2023). This assumption excludes naphthalene due to its low toxicity and carcinogenicity. This conversion uses potency equivalency factors (PEFs), with BaP serving as the index compound. By standardizing PAH concentrations in terms of BaP equivalents, these approaches provide a unified metric to assess potential carcinogenic and mutagenic risks from complex PAH mixtures (Haber *et al.*, 2022). PEFs of 21 PAHs and PAH derivatives have been derived based on data preference schemes.

Bap-TEQ and Bap-MEQ are calculated by multiplying the concentration of the found PAH with its toxicity equivalent factor relative to BaP or mutagenic equivalent factor relative to BaP as shown in equation 4.1 and 4.2.

$$\text{Bap} - \text{TEQ} = [\text{PAH}] \times \text{TEF} \quad (4.1)$$

$$\text{Bap} - \text{MEQ} = [\text{PAH}] \times \text{MEF} \quad (4.2)$$

The total Bap-TEQ and Bap-MEQ is calculated through equation 4.3 and 4.4 below

$$\text{BaP} - \text{TEQ}_{\text{total}} = \sum_{k=0}^n \text{BaP} - \text{TEQs} \quad (4.3)$$

$$\text{BaP} - \text{MEQ}_{\text{total}} = \sum_{k=0}^n \text{BaP} - \text{MEQs} \quad (4.4)$$

Table 4.1: TEF of selected PAHs (Hussain *et al.*, 2018)

| | PAH | TEF |
|-----|------------------------|-------|
| 1. | Benzo(a)pyrene | 1 |
| 2. | Anthracene | 0.01 |
| 3. | Dibenz(a,h)anthracene | 1 |
| 4. | Naphthalene | 0.001 |
| 5. | Benz(a)anthracene | 0.1 |
| 6. | Acenaphthylene | 0.001 |
| 7. | Benzo(b)fluoranthene | 0.1 |
| 8. | Acenaphthene | 0.001 |
| 9. | Benzo(k)fluoranthene | 0.1 |
| 10. | Fluorene | 0.001 |
| 11. | Indeno(1.2.3.cd)pyrene | 0.1 |
| 12. | Phenanthrene | 0.001 |
| 13. | Chrysene | 0.01 |
| 14. | Fluoranthene | 0.001 |
| 15. | Benzo(g,h,i)perylene | 0.01 |
| 16. | Pyrene | 0.001 |

Similarly, HQ can be used to assess non-carcinogens ecological risks for aquatic organisms as either acute HQ or chronic HQ. Acute HQ, is a fraction of risk assessment of peak water concentration of PAHs commonly referred to ADD over lowest tested EC50 or LC50 of aquatic organisms commonly referred to RfD from acute toxicity tests is a result of single or multiple exposure to PAHs over a short period of time (Abd Manan *et al.*, 2021).

$$\text{HQ}_{\text{acute}} = \frac{\text{peak water concentration(ADD)}}{\text{lowest tested EC50 or LC50(RfD)}} \quad (4.5)$$

On the other hand, chronic HQ is used to estimate the adverse effects that occur after long-term exposure through a fraction of average concentration of PAHs in 21 days over the lowest no observed adverse effect concentration for aquatic organisms from early life-stage or full life-cycle tests (Qin *et al.*, 2013).

$$HQ_{\text{chronic}} = \frac{\text{average concentration of PAHs in 21 days}}{\text{Aquatic invertebrate chronic toxicity NOAEC}} \quad (4.6)$$

4.7. Results and discussions

4.7.1 Unsubstituted PAHs

Table 4.1 gives a summary of unsubstituted PAHs, Table 4.2 Substituted PAHs, and Table 4.3 hetero-atomic PAHs concentration data. The toxicity of PAHs is affected by substitution and the heteroatoms present. In this study, 18 unsubstituted PAHs with molecular weight ranging between 154.21 of acenaphthene to 664.9 of benzo[fluoranthene], 21 substituted PAHs with molecular weight ranging between 142.2 of methyl-naphthalene to 258.2708 of benzo(a)anthracene-7,12-dione, and 14 heteroatomic PAHs with molecular weight ranging between 167.21 of dibenzopyrole to 234.3 of benzonaphthothio-pene, the distribution of unsubstituted PAHs was more than the substituted and heteroatomic PAHs.

USEPA priority pollutant list contains 16 pollutants which includes naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[g,h,i]perylene, indeno[1,2,3-c,d]pyrene, and dibenz[a,h]anthracene. In this study, six(6) PAHs listed in the 16 priority pollutants which include acenaphthene (M2 0.106±0.03 ppm), fluorine in all the sampling points except in M1 with concentration ranging between 0.053±0.01 ppm to 2.469±0.003 ppm, fluoranthene (in E1 9.177±0.04 ppm and K1 0.899±0.023 ppm), pyrene in all the sampling points except in E2 with concentrations ranging between 0.027±0.001 ppm and 28.689±0.025 ppm, chrysene in E1, E2, and M2, with concentrations ranging between 2.697±0.002 ppm and 10.670±0.024 ppm and benzo(a)pyrene in E2 only were reported in in the water basin.

With a total concentration of 216.51±0.51ppm of unsubstituted PAHs, pyrene at 53.65±0.08 ppm is the highest contributor followed by anthracene at 36.18±0.02 ppm. Pyrene is released to the environment and equally to water bodies from the burning of wood, gasoline exhaust, manufacture of dyes and optical brighteners, and cigarette smoke which can be associated to the human activities in the area of study.

Table 4.2: Detected unsubstituted PAHs in the Molo water basin

| PAH | PAH conc. (ppm) | | | | | | | Totals |
|--------------------|-----------------|--------------|-------------|-------------|-------------|--------------|-------------|------------|
| | E1 | E2 | K1 | K2 | M1 | M2 | M3 | |
| Acenaphthene | Nd | Nd | Nd | Nd | Nd | 0.106±0.03 | Nd | 0.106±0.03 |
| Fluorene | 0.592± 0.022 | 0.553±0.016 | 0.053±0.01 | 0.146±0.08 | Nd | 2.469±0.003 | 0.826±0.004 | 4.64±0.09 |
| Anthracene | 0.592±0.01 | Nd | 1.247±0.003 | 0.126±0.005 | 0.018±0.007 | 34.198±0.011 | Nd | 36.18±0.02 |
| Benzoazulene | 13.014±0.002 | Nd | Nd | Nd | Nd | Nd | 1.296±0.013 | 14.31±0.01 |
| Phenanthrene | Nd | 11.377±0.023 | Nd | 4.326±0.004 | Nd | Nd | 1.819±0.016 | 17.52±0.03 |
| Fluoranthene | 9.177±0.04 | Nd | 0.899±0.023 | Nd | Nd | Nd | Nd | 10.08±0.05 |
| Pyrene | 12.647±0.003 | Nd | 1.253±0.021 | 2.485±0.032 | 0.027±0.001 | 28.689±0.025 | 8.551±0.067 | 53.65±0.08 |
| 2,3-Dihydro | Nd | 6.900±0.02 | Nd | Nd | Nd | Nd | Nd | 6.9±0.02 |
| 4,5-Dihydro pyrene | 0.625±0.023 | 0.621±0.072 | 0.057±0.008 | 1.411±0.03 | Nd | Nd | 0.853±0.039 | 3.57±0.09 |
| | | | 2 | | | | | |
| benzofluorene | 1.843±0.003 | 0.329±0.004 | Nd | Nd | 0.016±0.049 | 6.055±0.07 | Nd | 8.24±0.09 |
| 5, 6-dihydro | Nd | 0.122±0.04 | Nd | Nd | Nd | Nd | Nd | 0.12±0.04 |
| benzanthracene | | | | | | | | |
| Benzanthracene | 1.382±0.08 | 2.217±0.07 | 0.320±0.034 | 0.246±0.009 | Nd | Nd | 14.856±0.45 | 19.02±0.46 |
| Benzophenanthrene | Nd | 0.165±0.003 | Nd | 0.424±0.065 | Nd | Nd | Nd | 0.59±0.07 |
| Chrysene | 2.697±0.002 | 2.740±0.005 | nd | Nd | Nd | 10.670±0.024 | Nd | 16.11±0.02 |
| Benzoxanthene | Nd | Nd | Nd | Nd | Nd | 2.930±0.03 | Nd | 2.93±0.03 |
| Benzo(a)pyrene | Nd | 0.601±0.004 | Nd | Nd | Nd | Nd | Nd | 0.60±0.004 |

| | | | | | | | | |
|--------------------|-------------------|-------------------|-------------------|------------------|--------------------|-------------------|-------------------|--------------------|
| Benzo[e]pyrene | Nd | Nd | 0.078±0.03 | Nd | Nd | Nd | Nd | 0.08±0.003 |
| Benzo[fluoranthene | Nd | 1.708±0.023 | 0.173±0.042 | 0.341±0.004 | Nd | 1.899±0.006 | 17.741±0.035 | 21.86±0.06 |
| Totals | 42.57±0.10 | 27.33±0.12 | 4.08±0.0-7 | 9.51±0.11 | 0.061±0.050 | 86.02±0.09 | 45.94±0.46 | 216.51±0.51 |

Legend: Nd – Not detected

Equally M2 at a total concentration of unsubstituted PAHs at 86.02 ± 0.09 ppm, M3 at 45.94 ± 0.46 ppm and E1 at 42.57 ± 0.10 ppm are the largest contributors of PAHs in the water basin. The high concentrations of PAHs in M2 and M3 can be associated to their proximity to the road and agricultural activities plus timber treatment and human settlement in the Elburgon for the E1.

These unsubstituted group of PAHs are strongly UV-VIS active, chemically stable, and they are hydrophobic hence adsorb strongly to soils and sediments and bioaccumulate. Their strong UV-VIS activity makes them susceptible to photo degradation into oxy-PAHs, hydroxylated-PAHs, and carbonyl compounds. Some of the degradation products can be more toxic than the parent PAHs. The toxicity of these PAHs can be in the order Oxygenated PAHs (quinones, ketones) > Hydroxylated PAHs > High molecular weight parent PAHs > Low molecular weight parent PAHs. The levels of these PAHs are comparable to studies done by Jiao *et al.* (2017) in Shanxi, China, Areguamen *et al.* (2023) Ikpoba River, South-South Nigeria. The levels of these PAHs are moderate to high compared to WHO limits.

4.7.2 Substituted PAHs

In this study, a number of Oxo-substituted PAHs which includes fluorenone 1.194 ± 0.025 ppm in E2, phenalenone 1.059 ± 0.002 ppm in M3, fluorenol of 0.470 ± 0.024 ppm at E2 and 0.85 ± 0.025 ppm in M3, anthraquinone in six sampling points ranging in between 0.176 ± 0.004 ppm to 3.664 ± 0.073 ppm, pyrenol 3.502 ± 0.32 ppm in M2, 4-[1,2-dihydroxyethyl] fluorine of 0.459 ± 0.53 ppm in M2, pyrenealdehyde in five sampling points ranging between 0.112 ± 0.034 ppm and 81.641 ± 0.045 ppm, benzoanthracenone in five sampling points ranging between 0.121 ± 0.043 ppm and 10.065 ± 0.004 ppm, Benzanthracene-7, 12-dione of 0.932 ± 0.009 ppm in E2, and benz(a)anthracene-7,12-dione of 0.111 ± 0.003 ppm in K2.

These substituted PAHs are associated with biotic and abiotic transformation of parent PAHS through oxidation through atmospheric photo-oxidation, sometimes referred to as atmospheric aging by ozone (O₃), the hydroxyl (OH) radical, nitrogen dioxide (NO₂), and the nitrate (NO₃ radical) (Hrdina et al., 2022). This aging can take place in the atmosphere and the products find their way to water bodies through deposition on the water or indirectly through deposition on soil and surface run off directs them to water bodies. Similarly, on the upper surface of water where there is sufficient light, oxidation of PAHs will take place.

Oxidized PAHs possess little lipophilicity making it hard for them to cross cell membrane hence may not enter the cells and undergo the same biochemical transformations of the parent PAH (Xiaoyang Zhang *et al.*, 2019).

Table 4.3: Detected substituted PAHs (ppm) in the Molo water basin

| PAH | Sampling points | | | | | | | Total Conc |
|-----------------------------|-----------------|-------------|-------------|-------------|----|-------------|-------------|-------------|
| | E1 | E2 | K1 | K2 | M1 | M2 | M3 | |
| Methylnaphthalene | Nd | Nd | Nd | Nd | Nd | 0.187±0.005 | Nd | 0.187±0.005 |
| Ethylidene indene | Nd | Nd | Nd | Nd | Nd | 0.115±0.012 | Nd | 0.115±0.012 |
| 1,2-Dimethyl naphthalene | Nd | Nd | Nd | Nd | Nd | 0.106±0.003 | Nd | 0.106±0.003 |
| Ethyl naphthalene | Nd | Nd | Nd | Nd | Nd | 0.065±0.01 | Nd | 0.065±0.01 |
| 1,4,6-Trimethyl-naphthalene | Nd | Nd | Nd | Nd | Nd | 0.223±0.014 | Nd | 0.223±0.014 |
| Fluorenone | Nd | 1.194±0.025 | Nd | Nd | Nd | Nd | Nd | 1.194±0.025 |
| Phenalenone | Nd | Nd | Nd | Nd | Nd | Nd | 1.059±0.002 | 1.059±0.002 |
| Methylfluorene | Nd | 0.266±0.032 | Nd | Nd | Nd | 0.792±0.027 | Nd | 1.06±0.04 |
| Fluorenol | Nd | 0.470±0.024 | Nd | Nd | Nd | Nd | 0.850±0.025 | 1.32±0.03 |
| Methyl anthracene | Nd | Nd | 0.253±0.03 | 0.102±0.38 | Nd | 8.511±0.038 | 0.924±0.056 | 9.79±0.39 |
| Methylphenanthrene | 2.497±0.023 | 2.091±0.059 | 0.188±0.03 | 0.301±0.22 | Nd | 1.851±0.037 | 2.189±0.033 | 9.12±0.24 |
| 1-Phenylnaphthalene | 1.810±0.07 | 1.744±0.005 | 0.131±0.009 | 0.176±0.006 | Nd | Nd | 1.544±0.058 | 5.41±0.09 |
| Dimethyl phenanthrene | Nd | Nd | Nd | Nd | Nd | 0.683±0.28 | Nd | 0.683±0.028 |
| Anthraquinone | 2.084±0.041 | 3.664±0.073 | 0.176±0.004 | 0.358±0.007 | Nd | 0.605±0.038 | 1.790±0.061 | 8.68±0.11 |
| Methylfluoranthene | Nd | Nd | Nd | Nd | Nd | 0.634±0.003 | Nd | 0.634±0.003 |
| Pyrenol | Nd | Nd | Nd | Nd | Nd | 3.502±0.32 | Nd | 3.502±0.32 |

| | | | | | | | | |
|---------------------------------|------------------|-------------------|------------------|------------------|----------|-------------------|-------------------|--------------------|
| 4-[1,2-Dihydroxyethyl] Fluorene | Nd | Nd | Nd | Nd | Nd | 0.459±0.53 | Nd | 0.459±0.53 |
| Pyrenealdehyde | 0.872±0.45 | 1.571±0.026 | Nd | 0.112±0.034 | Nd | 81.641±0.045 | 4.894±0.004 | 89.09±0.45 |
| Benzoanthracenone | 1.273±0.093 | 1.314±0.035 | 0.121±0.043 | 0.146±0.063 | Nd | Nd | 10.065±0.004 | 12.92±0.13 |
| Benzanthracene-7, 12-dione | Nd | 0.932±0.009 | Nd | Nd | Nd | Nd | Nd | 0.932±0.009 |
| Benz(a)anthracene-7,12-dione | Nd | Nd | Nd | 0.111±0.003 | Nd | Nd | Nd | 0.111±0.003 |
| Total | 8.54±0.47 | 12.25±0.11 | 0.87±0.06 | 1.31±0.45 | 0 | 99.87±0.69 | 23.32±0.11 | 138.34±0.88 |

Legend: Nd – Not detected

This category of PAHs has higher water solubility giving them higher bioavailability compared to unsubstituted PAHs. PAHs undergo metabolic transformation in the organisms, resulting in polar products that are destined for excretion. Metabolic transformation sometimes results in reactive metabolites that can form covalent adduct with DNA. biodegradation of alkylated PAHs has been reported to be much faster than their unsubstituted analogues as shown by alkylated phenanthrenes and pyrenes whose biodegradation rates were much faster than pyrene (Lee & Kwon, 2020).

In this study, pyrenealdehyde had the highest concentration at 89.09 ± 0.45 ppm followed by benzoanthracenone at 12.92 ± 0.13 ppm, methyl anthracene at 9.79 ± 0.39 ppm and methylphenanthrene at 9.12 ± 0.24 ppm. M1 recorded zero substituted PAH concentration which can be associated to its location in upstream with minimal human activities associated, the highest being in M2 with total substituted PAHs concentration of 99.87 ± 0.69 ppm followed by M3 with total substituted PAHs concentration of 23.32 ± 0.11 ppm which can be associated to their location proximately to the Eldoret-Nakuru highway, a busy highway that contaminates the river Molo through vehicular emissions. The basin had a cumulative concentration of substituted PAHs of $\sum_{21} = 138.34 \pm 0.88$ ppm.

4.7.3 Hetero-atomic PAHs

Once in the environment, unsubstituted PAHs react with oxidants such as NO_x , O_3 , and OH to produce nitrated or oxygenated PAHs. as substituted polycyclic aromatic nitrogen heterocycles has high polarity and polycyclic aromatic sulphur heterocycles and polycyclic aromatic oxygen heterocycles compounds are relatively less polar making them have a higher chance to bio-accumulate in the adipose tissues of living organisms (Ghosh & Mukherji, 2021).

The total average concentration of the hetero-atomic PAHs analyzed in this study was found to be $\sum_{14} = 23.86 \pm 0.35$ ppm with the highest concentration contributed by anthraquinone at 4.3 ± 0.10 ppm followed by benzoxanthene at 2.93 ± 0.02 ppm, and benzacridine at 2.86 ± 0.29 ppm with most of the others below 1ppm in the water basin. Anthraquinones are formed from PAHs in the environment through their direct combustion, degradation by atmospheric oxidants, and also found in agro-chemicals (DeLiberto & Werner, 2016) and as an additive in the soda and kraft chemical alkaline pulp processes in the paper and pulp industry (González-García *et al.*, 2010). These elevated levels of anthraquinone in the water basin can be associated with the intense agricultural activities involving maize, potatoes and flower farms in the area and the timber treatment in the area.

The bulk of the hetero-atomic PAHs (8 out of 14) are oxygenated with the other three containing nitrogen and the remaining three containing sulphur. The high ratio of oxygenated PAHs may signify the oxidation of the PAHs in the environment. In terms of sampling points, M2 at 8.48 ± 0.11 ppm and M3 at 7.54 ± 0.10 ppm are the most contaminated. Proximity of M2 to the Eldoret- Nakuru highway is exposing the water basin to a high amount of these pollutants. The slight drop in hetero-atomic PAH concentration in M2 can be associated with dilution and settling in sediments as the river flows downstream. The slightly higher levels of hetero-atomic PAHs in the Elburgon region at 3.23 ± 0.09 ppm in E1 and 3.86 ± 0.29 ppm in E2 as compared to the Kibunja area can be associated to high human activity in the Elburgon. The region has flower farms and timber treatment factories as compared to the forested area of Kibunja whose hetero-atomic PAH concentration was at K1 0.20 ± 0.01 ppm and K2 0.39 ± 0.07 ppm.

Table 4.4: Detected Hetero PAHs (ppm) in the Molo water basin

| PAH | Sampling points | | | | | | | |
|-----------------------------------|------------------|------------------|------------------|------------------|----------|------------------|------------------|-------------------|
| | E1 | E2 | K1 | K2 | M1 | M2 | M3 | Totals |
| Dibenzopyrrole | Nd | 0.178±0.02 | Nd | Nd | Nd | Nd | Nd | 0.18±0.002 |
| Dibenzofuran | Nd | 0.256±0.023 | Nd | 0.083±0.041 | Nd | 1.528±0.043 | 0.448±0.012 | 2.32±0.07 |
| 4-Methyldibenzofuran | Nd | Nd | Nd | Nd | Nd | 0.491±0.03 | Nd | 0.49±0.03 |
| 6h-Dibenzo[b,d]-pyran | Nd | Nd | Nd | Nd | Nd | 0.780±0.02 | Nd | 0.78±0.02 |
| Dibenzothiophene | 0.866±0.001 | Nd | Nd | Nd | Nd | Nd | Nd | 0.87±0.001 |
| <u>Naphtho[2,3-b]thiophene</u> | Nd | 0.797±0.034 | Nd | 0.078±0.025 | Nd | 2.079±0.065 | 0.806±0.022 | 3.76±0.08 |
| 1,2-Dimethylnaphtho [2,1-b]furan | Nd | Nd | Nd | Nd | Nd | 0.182±0.003 | Nd | 0.18±0.003 |
| 3-Methyl-dibenzothiophene | Nd | Nd | Nd | Nd | Nd | 0.182±0.046 | Nd | 0.18±0.046 |
| Anthraquinone | 1.042±0.023 | 1.832±0.069 | 0.088±0.011 | 0.179±0.054 | Nd | 0.303±0.034 | 0.895±0.002 | 4.3±0.10 |
| Benzo[b]naphtho[2,1-d]furan | 0.411±0.084 | 0.300±0.036 | Nd | 0.052±0.003 | Nd | Nd | 0.859±0.045 | 1.62±0.10 |
| Benzacridine | Nd | 0.500±0.28 | Nd | Nd | Nd | Nd | 2.363±0.078 | 2.86±0.29 |
| Benzoxanthene | Nd | Nd | Nd | Nd | Nd | 2.930±0.02 | Nd | 2.93±0.02 |
| 8-Phenylquinoline-6-carboxaldehyd | Nd | Nd | Nd | Nd | Nd | Nd | 2.170±0.032 | 2.17±0.032 |
| Benzo[b]naphtho[2,1-d]thiophene | 0.909±0.034 | Nd | 0.107±0.001 | Nd | Nd | Nd | Nd | 1.02±0.03 |
| Total concentration (ppm) | 3.23±0.09 | 3.86±0.29 | 0.20±0.01 | 0.39±0.07 | 0 | 8.48±0.11 | 7.54±0.10 | 23.86±0.35 |

Legend: Nd – Not detected

M1 which is the upstream towards Molo at 0 ppm with consistency in the low concentrations compared to the other sampling points through the other classes of PAHs. M2 showed contamination with almost all the detected PAHs in the water basin which can be associated with it being downstream and close to the highway making it prone to contamination with PAHs from the vehicles and the spills from accidents. In this study, the total concentration of PAHs detected was 378.71 ± 1.08 ppm with the unsubstituted PAHs forming a large bulk at 216.51 ± 0.51 ppm followed by substituted at 138.34 ± 0.88 ppm and lastly the hetero PAHS at 23.86 ± 0.35 ppm.

These variations can be associated with the biotic and abiotic transformation of parent PAHs in the environment. The hetero PAHs are also emitted with the parent PAHs from combustion sources (Cao *et al.*, 2022). These hetero PAHs have been reported to be more toxic than the parent PAHs (Clergé *et al.*, 2019; Lu *et al.*, 2022; Xiao Zhang *et al.*, 2022). The detection of these PAHs and their substituted congeners signifies the risk which the water user in the Molo water basin is exposed to.

4.8 Health risk assessment of PAHs

Health risk assessment of PAHs found in the area of study was determined using the BaP-TEQ and BaP-MEQ using TEF values from Table 4.1 and equation 4.1 the calculated values are as shown in Table 4.5.

Table 4.5: Calculated BaP-TEQ (ppm) for detected PAH compounds with determined TEF

| PAH | TEF | Bap-TEQ | | | | | | | Total Bap-TEQ |
|----------------------|-------|---|---|---|---|---|-----------------------|-----------------------|-----------------------|
| | | E1 | E2 | K1 | K2 | M1 | M2 | M3 | |
| Acenaphthene | 0.001 | - | - | - | - | - | 1.1×10^{-4} | - | 1.1×10^{-4} |
| Fluorene | 0.001 | 5.92×10^{-4} | 5.53×10^{-4} | 5.30×10^{-5} | 1.46×10^{-4} | - | 2.47×10^{-3} | 8.26×10^{-4} | 4.64×10^{-3} |
| Anthracene | 0.01 | 5.92×10^{-3} | - | 1.25×10^{-2} | 1.26×10^{-3} | 1.80×10^{-4} | 3.42×10^{-1} | - | 3.62×10^{-1} |
| Phenanthrene | 0.001 | - | 1.14×10^{-2} | - | 4.33×10^{-3} | - | - | 1.82×10^{-3} | 1.75×10^{-2} |
| Fluoranthene | 0.001 | 9.18×10^{-3} | - | 8.99×10^{-4} | - | - | - | - | 1.01×10^{-2} |
| Pyrene | 0.001 | 1.26×10^{-2} | - | 1.25×10^{-3} | 2.49×10^{-3} | 2.70×10^{-5} | 2.87×10^{-2} | 8.55×10^{-3} | 5.37×10^{-2} |
| Benzofluorene | 0.1 | 1.84×10^{-1} | 3.29×10^{-2} | - | - | 1.60×10^{-3} | 6.06×10^{-1} | - | 8.24×10^{-1} |
| Benzanthracene | 0.1 | 1.38×10^{-1} | 2.22×10^{-1} | 3.20×10^{-2} | 2.46×10^{-2} | - | - | 1.49×10^{-0} | 1.90×10^{-0} |
| Chrysene | 0.01 | 2.70×10^{-2} | 2.74×10^{-2} | - | - | - | 1.07×10^{-1} | - | 1.61×10^{-1} |
| Benzofluoranthene | 0.1 | - | 1.71×10^{-1} | 1.73×10^{-2} | 3.41×10^{-2} | - | 1.90×10^{-1} | 1.77 | 2.19 |
| Total Bap-TEQ | | 3.78×10^{-1} | 4.65×10^{-1} | 6.40×10^{-2} | 6.69×10^{-2} | 1.81×10^{-3} | 1.28 | 3.27 | 5.14 |

From the calculated BaP-TEQ, it is clear that M3 has the highest toxic equivalent at 3.270896 ppm followed by M2 at 1.275344 ppm while all the other sampling points having toxic equivalents below 1. Similarly, M1 had the lowest toxic equivalent at 0.001807 ppm. From BaP-TEQ calculation, the Molo river water basin had a BaP-TEQ of 5.14 ppm.

4.9 Distribution patterns of PAHs

From the distribution patterns shown in Figure 4.2, it is clear that M2 and M3 shows high levels of pollution with M1 showing the least. The pollution source can be associated with the region surrounding M2 from this observation. The regions of sampling points M2, M3, E1 and E2 are marked with human settlement and its associated human activities like agriculture and municipal waste which has been shown to be sources of PAHs.

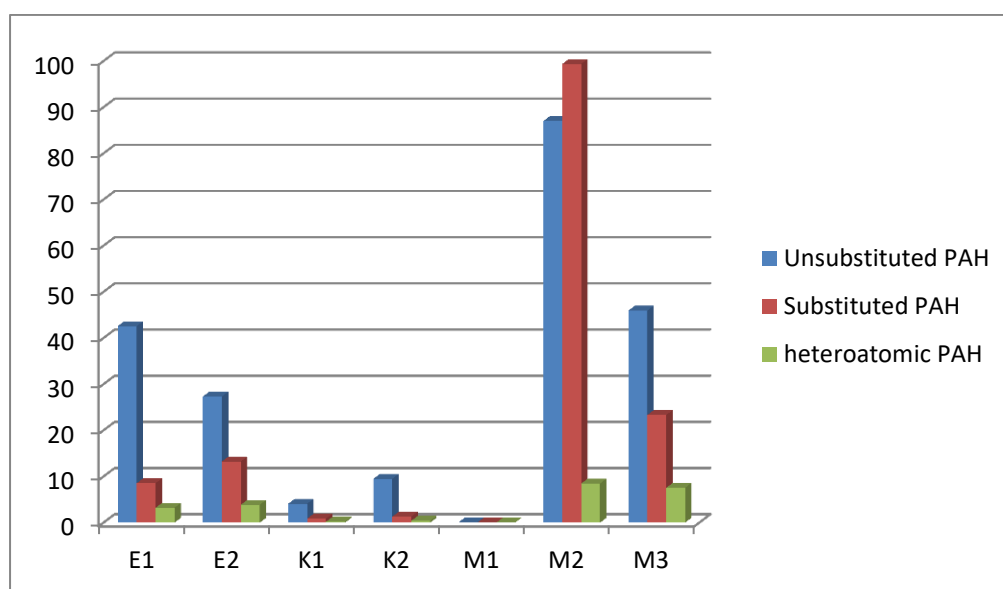


Figure 4.2: PAH distribution patterns in the Molo River water basin

4.10 PAHs diagnostic ratios

A diagnostic ratio is a binary ratio method of determining source of PAHs where the ratios of pairs of frequently found PAH emissions are compared. The diagnostic ratio can be altered sometimes to take care of reactivity of some PAHs with the environmental components like oxides of nitrogen degradation of PHs during and after sampling. This approach has been widely used however sometimes it gets limited by its inability to differentiate some sources single headedly due to the closeness of the ratios.

Table 4.6 gives a summary of how to use diagnostic ratios to identify the source of PAHs in the Molo river water basin. With reference to the PAH in Table 4.6, diagnostic ratios for the Molo water basin were calculated and the results were as shown in Table 4.7.

Table 4.6: Diagnostic ratio interpretation table

| Diagnostic Ratio formula | Diagnostic Ratio Value | PAH Source |
|--------------------------|------------------------|-------------------------------|
| | <0.5 | Petrol Emissions |
| FL/(FL+PRY) | >0.5 | Diesel Emissions |
| | <0.1 | Petrogenic |
| ANT/(ANT+PHE) | >0.1 | Pyrogenic |
| | <0.4 | Petrogenic |
| | 0.4-0.5 | Fossil Fuel Combustion |
| | >0.5 | Grass, Wood, Coal, Combustion |
| FLA/(FLA+PYR) | | |
| | ~0.5 | Fresh Particles |
| BaP/(BaP+BeP) | >0.5 | Photolysis |

With respect to FL/(FL+PRY), it can be clearly seen that the PAHs in the basin are of petrol emissions. This due to the prevalence of FL/(FL+PRY) ratios below 0.5 except in K2 which reported a ratio of 1.0 way above 0.5 leading to the conclusion that they are of diesel emissions.

Table 4.7: Calculated Diagnostic ratio for the Molo river water basin

| PAH | PAH Conc (ppm) | | | | | | | |
|---------------|----------------|------|------|------|------|------|------|------|
| | E1 | E2 | K1 | K2 | M1 | M2 | M3 | |
| FL/(FL+PRY) | 0.04 | 1.00 | 0.04 | 0.06 | 0.00 | 0.08 | 0.09 | 0.08 |
| ANT/(ANT+PHE) | 1.00 | 0.00 | 1.00 | 0.03 | 1.00 | 1.00 | 0.00 | 0.67 |
| FLA/(FLA+PYR) | 0.42 | | 0.42 | 0.00 | 0.00 | 0.00 | 0.00 | 0.16 |
| BaP/(BaP+BeP) | | 1.00 | 0.00 | | | | | 0.89 |

ANT/(ANT+PHE) were greatly above 0.1 associated with pyrogenic sources in E1, K1, M1, and M2 more than 50% of the sampling points. E2, K2, and M3 were below 0.1 associating them to petrogenic sources. With respect to FLA/(FLA+PYR), the sources were petrogenic and fossil fuel combustion in E1 and K1. Data for BaP/(BaP+BeP) were minimal however the available data associated PAHs in E2 to be resulting from photolysis of PAHs, K1 as fresh PAHs and the Molo river water basin as having PAHs resulting from photolysis.

4.11 Limitations of the study

This study has painted a picture of the levels of PAHs however the study has been limited by the single season sampling which cannot allow us to tell whether there is a seasonal variation. Similarly, the levels of PAHs in the sediments were not determined limiting an important source identification since the sediments are a sink of pollutants in water bodies. The above limitations were compounded by financial incapacity with respect to financing extended sampling, proper security during sampling, transportation, analysis and access to paid literature.

4.12 Conclusions

The Molo water basin is an important water resource for the human settlement around it and the environment. Despite the huge importance of the water basin, no documented study on the levels of PAHs in the water basin had been done. This study has provided a baseline on the levels of PAHs in the basin which is exposed to a myriad of human activities with the potential of introducing the pollutants in the study to the environment. A number of unsubstituted, substituted and heteroatom PAHs were detected in the water basin including six(6) PAHs listed in the 16 priority pollutants which include acenaphthene (M2 0.106 ± 0.03 ppm), fluorine ranging between 0.053 ± 0.01 ppm to 2.469 ± 0.003 ppm, fluoranthene (E1 9.177 ± 0.04 ppm and K1 0.899 ± 0.023 ppm) , pyrene ranging between 0.027 ± 0.001 ppm and 28.689 ± 0.025 ppm, chrysene ranging between 2.697 ± 0.002 ppm and 10.670 ± 0.024 ppm and benzo(a)pyrene in E2 only were reported in in the water basin. Elevated concentration of PAHs detected in the water samples implies Molo water basin is contaminated with PAHs. It is clear that M2 and M3 shows high levels of pollution with M1 show the least with pyrogenic and petrogenic sources being the most prevalent of the sources of PAHs. The ability of these organic contaminants to bio-accumulate and bio-magnify in the food chain poses health risk to aquatic life, livestock drinking from the basin and contamination of the L. Baringo where the basin is draining. Further studies need to be done on the water basin to determine the levels of other organic contaminants and also extent it downstream to where it drains to L. Baringo. This will give a comprehensive picture of the general water quality of the basin.

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CHAPTER FIVE

GENERAL DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS

5.1 General discussion

God through his wisdom created the earth giving it perfect conditions, with a delicate equilibrium balance, for life to thrive. Water is a critical resource for sustenance of life from time immemorial. Overtime, human population has increased exponentially prompting them to find ways of exploiting the available resources to meet the relatively increasing human needs. Human exploitation of natural resources coupled with natural phenomena like volcanic activities and production of man-made resources has led to the destabilization of the natural composition of water resources. Climate change and the ever increasing demand from the rising human and animal population are continuously increasing pressure on water resources. In September 2015, the United Nations general assembly adopted a set of 17 SDGs to end poverty, protect the planet and ensure prosperity for all to promote prosperity while protecting the planet.

Human exposure to water pollutants even at low concentrations is associated with various health effects such as endocrine disruption, reproductive and respiratory system effects, mutagenic and carcinogenic effects, immunologic, neurological effects and cardiovascular disorders among others with severity of the effects depending on age, habits, health conditions and rate of exposure. The health impacts vary from one pollutant to another and also from organ to organ.

Quality of water varies significantly depending on the source, time, and geographical location with the different uses having differing quality requirements. Assessment of water quality uses several indices which include WQI and WPI which takes into account different physical, chemical and biological quality parameters. This study was carried out in the Molo river water basin, an agricultural area, in Nakuru county which drains to Lake Baringo in Baringo County with the Nakuru – Eldoret highway passing through the basin with several vehicle accidents reported around Salgaa and the Sachangwan areas. This study has helped in understanding the pollutants that compromise the quality of water in the Molo river water basin, its environs and summarize the general water quality status of the Nile water basin. A review of the current status of water quality in the Nile water basin was done, In the Molo River water basin the physical parameters, heavy metal and PAH levels were determined

From the review of the Nile water basin, it was found out that the basin is greatly influenced by human settlement contributing towards the deterioration of water quality over

time. Municipal waste has negatively impacted as was indicated by pharmaceutically active compounds, high conductivity, and Biochemical oxygen demand. Agriculture also is contributing to pollution in the Nile basin as evidenced by reported pesticides, OCPs, and PCBs, in the water basin. Heavy metal, one of the major contaminant of the water basin has been largely attributed to industrial activities, mining and municipal with little contribution from the soil. Most of the water quality parameters in the basin are still within the recommended levels however caution is paid to the high levels of cadmium, aldrin and dieldrin as reported. Sediments of the water basin have played well the role of acting as a sink of pollutants from their relatively high concentration of pollutants as compared to the pollutants in the water column limiting transport of pollutants downstream. Micro-plastics have also been reported in the water basin severely exposing aquatic animals from the basin to pollutants levels that pose risks to their survival. These finding point at the need of instituting policies, laws and regulations to govern the management of the transboundary water resource with an aim of mitigating the already out of limits pollutants and prevent the within limits pollutants from crossing the limits. There is need also to do public sensitization on the consequence human activities on water quality.

This study has found that the physico-chemical properties observed in the Molo river basin indicate a strong influence from heavy metals. This correlates very well with the water quality parameters; WQI and WPI reported which show that the water of the Molo river basin is significantly polluted. The high levels of heavy metals observed in the water basin compromise the water quality because they can bioaccumulate and biomagnify in living organisms to cause serious public health problems. The high concentration of heavy metals may be attributed to agricultural activities, soil erosion, and weathering of rocks in the study area. The calculated WQI and WPI of the Molo river water basin agree to a larger extent serving as a mean of complimenting each other. The sediment chemistry in the Molo river water basin predicted serious possible pollution levels likely to be caused by hazardous organics based on the high levels of carbon and oxygen incorporated in sediments. This may point to the presence of benzo[a]pyrene, dioxins, phenols, and benzene and its derivatives among other pollutants. Most sediments indicate the presence of high amounts of iron and aluminium suggesting that the there is an iron and an aluminium point source which is most likely to be anthropogenic. Generally, the water basin is moderately polluted as corroborated by the two methods used to evaluate the water quality status – Water quality index and water pollution index. A number of unsubstituted, substituted and heteroatom PAHs were detected in the water basin including six (6) PAHs listed in the 16 priority pollutants which include

acenaphthene, fluorine, fluoranthene, pyrene, chrysene, and benzo(a) pyrene with concentration ranging between 0.018 ppm to 34.198 ppm. Elevated concentration of PAHs detected in the water samples implies Molo water basin is contaminated with PAHs. It is clear that M2 and M3 shows high levels of pollution with M1 show the least with pyrogenic and petrogenic sources being the most prevalent of the sources of PAHs. The ability of these organic contaminants to bio-accumulate and bio-magnify in the food chain poses health risk to aquatic life, livestock drinking from the basin and contamination of the L. Baringo where the basin is draining.

5.2 Conclusions

The rise of human population with the diminishing natural resources is posing a huge threat to human survival on earth. Human adaptation to these diminishing resources has led to various technological advancement which has produced a number of synthetic materials like the plastics, engine based means of transport, concentrated human settlement, industrialization, modern agricultural practices, and modern medicine among others. From the study, the following findings were made:

- i. The Molo water basin concentration levels of Cr, Pb, Mn, and Fe were reported outside the WHO limits for drinking water pointing to anthropogenic pollution since these elements are utilised in a number of human activities including agriculture, industry and the auto-mobiles.
- ii. The sediments of the Molo river water basin are tightly bound together flaky sheets rolling over each other with average size far much less than $1\mu m$. The sediments are dominated by oxygen, carbon and silicon with a notable absence of lead, mercury, arsenic and cadmium heavy metal contaminants of concern however presence of manganese and iron suggests natural weathering from clay particles and can point to oxidizing conditions.
- iii. The Molo river water basin is contaminated with PAH with concentration levels of unsubstituted PAHs at 216.51 ± 0.51 ppm, substituted PAHs at 138.34 ± 0.88 ppm, and hetero PAHs 23.86 ± 0.35 ppm total giving a total concentration of PAHs detected at 378.71 ± 1.08 ppm with a BaP-TEQ of 5.14 ppm. These PAHs can be associated with the Eldoret-Nakuru highway, agricultural and timber treatment in the Molo water basin.

5.3 Recommendations

Sustainable exploitation of water resources for the good of human life and the environment calls for approaches that ensure that foster longevity and safety of these resources. From the study the following recommendations are made:

- i. Human activities have to be regulated to reduce the risk of contaminating water resources. Regular monitoring of water quality is done to provide a baseline data, arrest pollution at early stages to prevent exposure of populations and organisms to life threatening pollutants, the data be used in decision in policy and making.
- ii. On water resources that cut through more than one country like the Nile water basin and Molo river water basin, the transboundary bodies and policies made must be ensured to be legally binding and enforceable. This ensures comprehensive protection and sustainable management of the water resources.
- iii. This study also recommends more studies that covers more than a season and on emerging pollutants like the micro-plastics since they pose an environmental degradation individually and through sorption and eventual concentration of the organic contaminants.

5.4 Suggestions for further studies

Following the findings of elevated levels of PAHs in the Molo river water basin in this study, it is suggested that periodic studies be done on the water basin to monitor the levels of PAHs both in the water and the river sediments.

APPENDICES

Appendix A: A review of the current status of the water quality in the Nile water basin

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REVIEW

Open Access



A review of the current status of the water quality in the Nile water basin

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Abstract

Background Water contamination has become one of the most challenging problems to clean water supply and infrastructure in the twenty-first century. Accordingly, access to clean water is limited by negative impacts of climate change and pollutants of varying health risks. Overtime, global population has experienced an exponential growth, which has put pressure on the limited water resources. At least 3 billion people globally rely on water whose quality is largely unknown.

Main body of the abstract The Nile water basin, found in East and Central Africa, covers 11 countries including DRC, Tanzania, South Sudan, Kenya, Uganda, Burundi, Egypt, Ethiopia, Eritrea, Sudan, and Rwanda. The Nile River flows through it before draining its water into the Mediterranean Sea in Egypt. Nile River water was pivotal for the ancient civilization in the Sudan and Egypt through provision of fertile soil and water for irrigation, drinking, fishing, animal husbandry, and channel of transport and in modern times, on top of the historical utilization, for generation of hydro-electric power leading to conflict and cooperation over the shared water resources. Literature on water quality in the Nile water basin is summarized, using the traditional review method to point out gaps, compare the water quality with other areas and suggest recommendations based on the findings of this study. The Nile water basin has been contaminated by numerous pollutants such as toxic heavy metals and organic contaminants, therefore pushing the resident water quality above the World health organization (WHO) acceptable guidelines for drinking water, agricultural irrigation, and aquatic life support. Cases of contamination outside the recommended limits of cadmium in little Akaki River in Ethiopia, aldrin and dieldrin in the Tanzanian side of L. Victoria and other areas clearly show contamination above the WHO limits in the Nile water basin.

Short conclusion The effect of fish cages, micro-plastics, heavy metals, organic contaminants and suspended sediment load primarily from human activities like agriculture, industries and municipal wastes is continuously contaminating the Nile basin water toward poor quality water status. Consequently, interventions like transboundary laws and regulations to mitigate the risks must be enforced.

Keywords Water, Transboundary laws, Acceptable guidelines, Nile basin water, Micro-plastics

Appendix B: The use of water quality index and water pollution index in assessing the water quality and suitability of the river Molo water basin, Kenya

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The use of water quality index and water pollution index in assessing the water quality and suitability of the river Molo water basin, Kenya

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Abstract

Water quality assessment has become a very essential scientific procedure for qualifying water for drinking and general purpose use, and better public health policy on clean water supply. Various tools have been employed to determine the status of water systems for drinking, industrial and general use. For the purpose of this study, water quality index (WQI) and the recently developed water pollution index (WPI) have been adopted to evaluate the water of the Molo water basin. The world health organization (WHO) has defined limits of these parameters beyond which the quality of water is considered unsuitable for a specific use. The study was carried out in December, 2021 during the dry season. In this contribution, pH, conductivity, TDS, salinity, major cations and anions, and selected heavy metals were explored. Of the major cations Na reported the highest concentration at 1800 mg/L whereas in the anion category, the Cl gave the highest concentration at 110 mg/L. The highest pH, TDS and salinity were 8.5, 146.33, and 282.67, respectively. The data obtained were used to determine the water quality index (WQI) and water pollution index (WPI) of the Molo water basin based on the world health organization (WHO) standards. The average WQI obtained was 57.47 indicating that the water is slightly polluted. Also the average WPI obtained was 0.77 indicating that the water from the water basin is not of good quality. Sediment morphology and composition was also determined using energy dispersive X-ray spectroscopy (EDS). The findings showed the presence of heavy metal pollutants of concern which include lead, manganese and copper. Therefore, with respect to WQI, WPI and sediment morphology, the water basin is significantly polluted. There is need therefore for the government and health authorities to formulate policies aimed at regulating pollution activities which may endanger the Molo water basin.

Keywords: Pollution; Sediment; Water pollution index; Water quality index

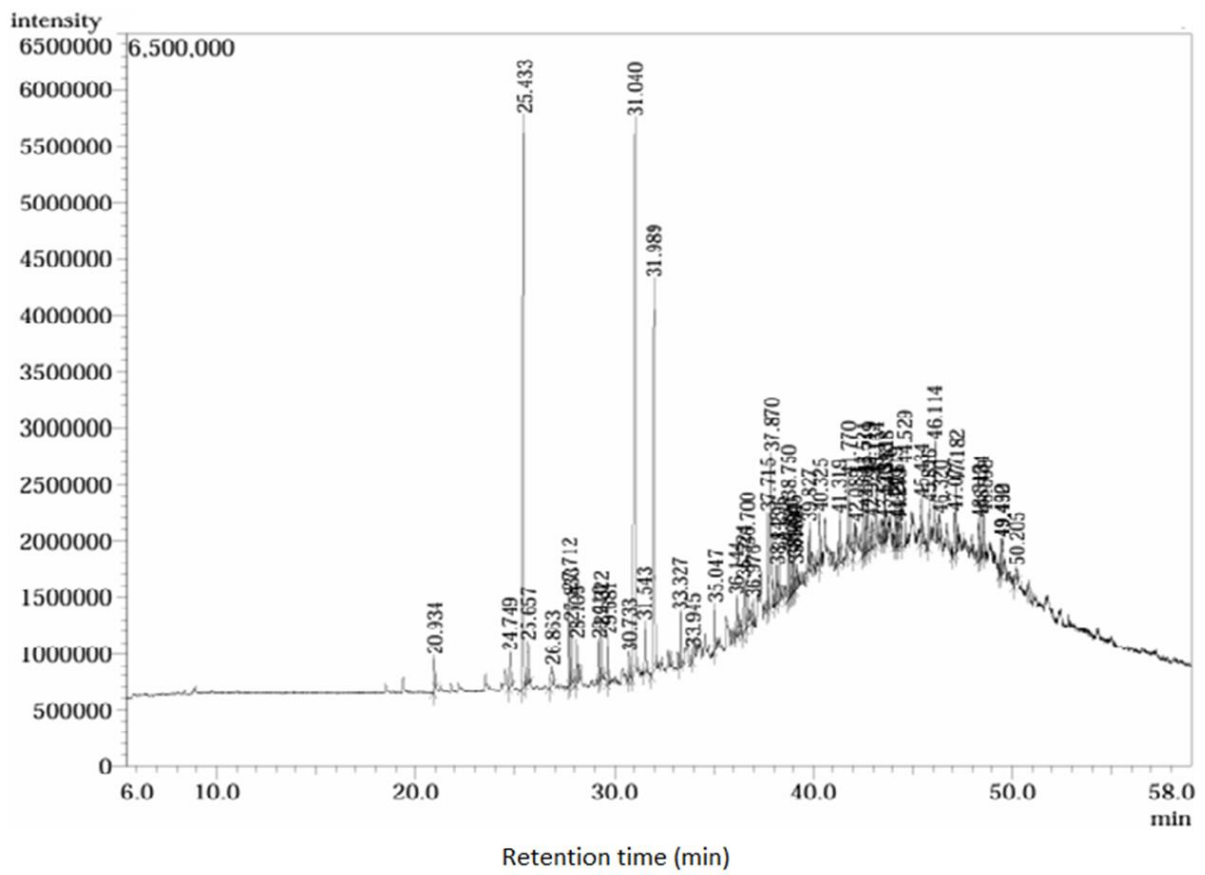
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Appendix C: Sample chromatogram




Appendix D: NACOSTI research permit


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