

**ORGANIC CONTAMINANTS AND HEAVY METAL ANALYSIS IN THE
GROUNDWATER OF KERIO VALLEY WATER BASIN, BARINGO COUNTY,
KENYA**

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**A Thesis Submitted to the Graduate School in Partial Fulfilment of the Requirements for
the Master of Science Degree in Chemistry of Egerton University**

EGERTON UNIVERSITY

JUNE, 2024

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

I dedicate this thesis to my lovely wife Judy Chepkemoi, my parents Mr. Kiplangat Mosonik and Mrs. Linner Mosonik, my siblings, my daughter (Ivana Chemutai), and my sons (Maxwell Kibet and Brian Kipkorir) for giving me the opportunity to develop into the person I am today. I also dedicate this work to them.

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ABSTRACT

Many harmful effects of human activities below the surface of the earth have a negative impact on groundwater quality, as many mineral- and oil-rich places can attest to. The impacts may include enhanced risks of cancer and genetic aberrations. Therefore, research on the determination of physico-chemical characteristics, heavy metals and organic pollutants in groundwater from boreholes of Kerio Valley water basin near commercial oil exploratory wells is fundamental. A solid phase extraction technique was used to extract water samples from specific boreholes in the Kerio Valley water basin of Baringo County. The water samples were then analyzed for organic contaminants using a gas chromatograph interfaced with a mass spectrograph detector. Out of the 4 boreholes sampled, 3 contained benzene derivatives, mainly xylene, 1,3,5-trimethylbenzene, 1-ethyl-3-methylbenzene, 1-methyl-2-propylpentylbenzene, and polycyclic aromatic hydrocarbons such as naphthalene, phenanthrene, fluoranthene, azulene, and pyrene. Furthermore, long-chain hydrocarbons were found in varied quantities in all groundwater samples. Benzene derivative concentrations ranged from 2.84 ± 1.04 to 20.47 ± 1.53 ppm. However, polycyclic hydrocarbons exhibited the highest concentrations of all organic pollutants, with pyrene giving a concentration of 23.14 ± 2.05 ppm, fluoranthene (18.54 ± 1.89 ppm), phenanthrene (14.13 ± 1.60 ppm) and anthracene (12.72 ± 1.20 ppm). In accordance with the results, 3-methyl-2,3-dihydro-1-benzofuran predominated in all samples, with concentrations ranging from 0.070 ± 0.28 to 9.390 ± 1.12 ppm compared to 0.28 ppm WHO permitted limits. Heavy metals were analysed in groundwater samples using atomic absorption spectroscopy (AAS). The results showed that the boreholes have remarkably high concentrations of lead, cadmium, and chromium. Interestingly, Pb was found to have a concentration profile ranging from 0.26 ± 0.01 to 10.76 ± 0.22 ppm, Cd ranges from 0.22 ± 0.01 to 0.29 ± 0.03 ppm, Mn posting high concentration of 1.86 ± 0.04 ppm in KV8 water sample, while Cr concentration ranged from 0.09 ± 0.002 to 0.37 ± 0.03 ppm. According to the results of this study, borehole water in the Kerio Valley basin is contaminated and may be hazardous for human consumption. The reported concentration levels were several times greater than the guidelines of the United States Environmental Protection Agency (USEPA) and the World Health Organization (WHO). Consequently, it is vital to establish a policy framework for the assessment and monitoring of water quality in the region, as well as propose intervention methods to assure a clean water supply for the well-being of inhabitants of the Kerio Valley water basin.

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LIST OF ABBREVIATIONS AND ACRONYMS

2-BE	2-Butoxyethanol
AAS	Atomic Absorption Spectrometer
EC	Electrical Conductivity
EDTA	Ethylenediamine tetraacetic acid
GC-MS	Gas Chromatography-Mass Spectrometry
GIS	Global Information System
GW	Groundwater
HM	Heavy Metals
KVWB	Kerio Valley Water Basin
PAHs	Polycyclic Aromatic Hydrocarbons
TDS	Total Dissolved Solids
WHO	World Health Organization
XRD	X-Ray Diffraction

CHAPTER ONE

INTRODUCTION

1.1 Background Information

Water is an essential natural resource whose importance to human existence and natural ecosystems cannot be overstated, hence the quote "water is life." Although water occupies over 70% of the earth's surface, pure water is in short supply due to pollution and other anthropogenic activities such as mining and agricultural practices. As a result, groundwater (GW) in the form of wells, springs, and rivers has become the most dependable supply of water for the vast majority of the world's population (Amiri *et al.*, 2022). Groundwater is water under the earth's surface that is created predominantly through down seepage of surface water into hydrological sub-surface processes. Nonetheless, the eminence of GW in a given area is heavily influenced by natural and anthropogenic processes as well as the quantity of chemical farming and industrial waste discharge. All of these activities has the potential to contaminate aquifer systems, which would lower the quality of water that is available for use in agriculture and human consumption (Barbieri *et al.*, 2021).

The Kerio Valley basin in the Kenyan Rift system receives modest rainfall each year. Rain water drains into the region's rivers and lakes (River Kerio and Lake Kapnarok) via surface runoffs and feeder streams making the area experience scarcity of water. As a result, boreholes in the Kerio Valley basin serve as the primary source of water for home and agricultural purposes as a mitigation plan by Kerio Valley Development Authority (KVDA) to resolve constant conflict witnessed in yester years. Despite concerns about suspected pollution from commercial mining companies in pursuit of hydrocarbons and fluorspar, the safety of these subsurface water systems has never been assessed. The quantity as well as the concentration of constituent minerals in water, which can be altered by natural or artificial processes, primarily determines the suitability of groundwater for human use (Serianz *et al.*, 2020). Oil explorers employ hydraulic fracturing technique to drill exploratory wells in order to maximize geological survey of crude oil and hydrocarbon gases. Throughout the drilling process, this technology employs a number of harmful compounds, which may contaminate GW (Wattenberg *et al.*, 2015). The

likelihood of detecting heavy metals (HM) and organic compounds in the aquifer system is extremely high.

Mining activities in this region are a major source of contamination, most likely through leaching, surface runoff of waste water, chemical spillage, and inadequate waste-water disposal devices (G. Chen *et al.*, 2021). Xylenes, benzene, formaldehyde, 2-butoxyethanol (2-BE), naphthalene, and ethylbenzene are among the compounds used in oil drilling and exploration. These substances are possible toxins that can change the chemical composition and quality of GW (Goldstein *et al.*, 2014). The hydraulic fracturing method is used during the oil extraction process to remove the oil molecules in the bedrock surface beneath the earth's crust (Adeola *et al.*, 2022). The fracturing process causes the mixing of naturally occurring HM and organic compounds with GW. Nearly 91% of the chemicals used in oil extraction remain beneath the subsurface, contaminating GW (Mambwe *et al.*, 2021). Geological processes beneath the ground exacerbate the extent to which the water table is poisoned. Heavy metal toxicity and mutagenicity, on the other hand, are amplified by technogenic processes that occur in mining sites. For instance, in the event that wastewater is improperly disposed or discharged, leaching and flocculation can occur, affecting subsurface water through underground seepage along fracture channels as well as surface runoffs (Gogoi *et al.*, 2018).

A scientific method of locating unusual concentrations of potentially dangerous or dangerous metals in the natural ecosystem is known as HM analysis. Heavy metals' bioactivity, bioavailability, biotoxicity, and bioaccumulation are all influenced by a variety of variables, including solubility, chemical behaviour, volatility, and the level of anthropogenic activity in a specific area (Jeong *et al.*, 2023). Analysis of the concentration and identification of HM in water systems have become crucial due to their biological, environmental, and metabolic biohazardous nature. According to numerous studies, HM and metal complexes are more hazardous than other metals, posing a danger to the environment and people in general (Vardhan *et al.*, 2019). Heavy metals including lead, cadmium, chromium, manganese, and cobalt (Pb, Cd, Cr, Mn, and Co) form the basis of this study. Organics such as benzene, methylbenzene, xylenes, and polycyclic aromatic hydrocarbons (PAHs) were investigated.

The principal aim of this work was to explore the quality of GW in Kerio Valley basin, which is the major source of livelihood for the people of Baringo. The borehole water systems have served the residents of the Baringo County for many years until the discovery of oil deposits along the valley, which prompted oil explorers to drill wells in search of hydrocarbons. This is an anthropogenic activity that may have affected the quality of GW and thus may have made water unsafe for human, plant, animals, and agricultural use. Most of the contaminants originating from oil exploration surveys may be carcinogenic as well as mutagenic (Anyanwu *et al.*, 2020). Previously, there was an outcry due of discharge to raw effluent into the River Kerio. This resulted to miscarriages among domestic animals and humans. This phenomenon, although well known to the residents of Kerio Valley has not been documented. Studies on HM and hazardous organics on the Kerio Valley water basin is scarce in literature. This scarcity hinders the establishment of comprehensive understanding of the quality of GW in the area of study.

1.2 Statement of the problem

The world in the present day has been facing water contamination problems occasioned by HM, inorganic, and organic contaminants. In Kerio Valley water basin, the main source of water is GW. However, the water currently available may be unsafe for use due to contamination by mining activities such as exploratory drilling in search of hydrocarbons and fluorspar mineral. This is attributed to the anthropogenic activities from oil exploratory wells that are known to use toxic chemicals during the extraction of crude oil and explosives used during fluorspar mining. Most of these chemicals remain beneath the earth surface for many years and are constantly channeled to the nearby wells and rivers either by underground seepage or fractured tunnels. Heavy metals, for instance, are known to cause undesirable effects to humans and animals even at very low concentration. Their non-biodegradable nature, HM bio-accumulate in the body tissues, ultimately leading to death depending on the nature, quantity and bioactivity of HM. This work aims at identifying quantitatively organic pollutants, and HM that are present in the GW in the Kerio Valley water basin.

1.3 Objectives

1.3.1 General objective

To investigate the quality of GW in the Kerio Valley water basin near commercial oil exploratory wells in Baringo County.

1.3.2 Specific objectives

- i. To characterize the concentration of organic contaminants in the GW of the Kerio Valley water basin.
- ii. To quantify the concentration of furans and phenolic-based contaminants in the boreholes water of Kerio Valley water basin.
- iii. To analyze the concentration profiles of heavy metals in the boreholes of Kerio Valley water basin.

1.4 Research questions

- i. Will the concentration of organic contaminants (benzene, xylenes, naphthalene, anthracene, and pyrene) be significantly different in GW of selected boreholes of the Kerio Valley water basin?
- ii. Will the concentration of furans and phenolic-based contaminants be significantly different in boreholes water of the Kerio Valley water basin?
- iii. Will the levels of heavy metals (lead, chromium, nickel, and cadmium) present in the selected boreholes of Kerio water basin differ significantly?

1.5 Justification of the study

Quality assessment of GW is important in ascertaining the levels of HM and organics in borehole water, and soil sediments in the hydrological basin with the primary focus of remediating detrimental effects of water contaminants. Heavy metal deposition from commercial oil companies is an anthropogenic activity which may initiate water and soil contamination. The ultimate health effects of such activities include enhanced risk of cancer and other associated diseases that affect the general human population, plant, and other natural ecosystems such as microorganisms. Studies on heavy metals and hazardous organics on the Kerio Valley water basin is scarce in literature which has ultimately hindered the establishment of comprehensive understanding of the quality of GW in the area of study. The contamination of water by waste

materials from industries is a serious concern and as a result the water around this region has become a sink for heavy metals and organics. This has drastically affected the health of plants, animals and the general physical integrity of the residents living in the Kerio Valley basin. Considering the mutagenic properties of toxic heavy metals and their derivatives, a number of people may have suffered from cancer, strange sicknesses, and mental illness from this area. In this regard, this study was fundamental in unraveling the potential contaminants in soil and GW systems which is of concern to the people of Kerio Valley.

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CHAPTER TWO

LITERATURE REVIEW

2.1 Groundwater chemistry

Groundwater is water found beneath the earth surface and commonly produced by surface water seeping into hydrological subsurface processes. Currently, GW is increasingly becoming the principal supply of fresh water in most developing countries. Based on the underground geological constituents, GW is obtained from aquifers which act as a sub-surface store that ends up supplying water to wells and springs (Ejaz *et al.*, 2022). In most cases, the chemical composition, pH, colour, and taste of water is altered by the nature and composition of the rocks and unconsolidated sediments (Umamageswari *et al.*, 2019). The presence of openings and unconsolidated materials in the bedrock determines the amount of runoff water percolating the water table (Hayashi, 2020). The runoff water plays a significant role in replenishing sub-surface aquifers. There is always an interchange between GW and surface water especially at the valleys and depressions (Su *et al.*, 2020). This intersection depends on the season of the year, for instance during the dry season GW replenishes the surface water in the rivers and streams through underground seepages whereas during the wet seasons, surface water (floods) seeps into the ground water with all manner of surface chemicals or contaminants from anthropogenic activities (Chakraborty & Chakraborty, 2021).

The hydraulic conductivity and transmissivity is mainly used to determine the measure of quality and quantity of the contaminants being transported through the aquifer systems either to surface water or to the GW (Medici & West, 2021). For instance, the current chemical way of farming, spontaneous expansion of industry, and rising urbanization threaten substantial accumulation of heavy metals in ground and surface waters in which their concentration in the same water have been noted to be continuously rising in the past few years (Feng *et al.*, 2022). Even though the aquitards control the adulteration of GW (Han *et al.*, 2021), hydraulic fracturing employed during oil exploration and fluorspar mining breaks the aquitards, thus permitting the entry of chemical contaminants to the GW systems. Therefore, heavy metals - mainly from industrial discharges, agricultural chemicals, and atmospheric wet depositions from automobile

emissions - finally reach the ground water through penetration of aquitards (Chakraborty *et al.*, 2023).

2.2 Hydraulic fracturing and water contamination

Hydraulic fracturing is a chemical and mechanical method employed by oil and gas drilling companies to access maximum amounts of hard-to-get oils and gas under a rocky surface (Moska *et al.*, 2021). In this process, the injection of high amounts of water, fracturing chemicals, and sand to the ground aims at fracturing the rock to allow the flow of oil to the surface (Agarwal & Kudapa, 2023). The hydraulic fracturing technique creates vertical and horizontal tunnels beneath the surface of the earth which are used to pump water, hydraulic chemicals, and sand used in oil extraction process (Q. Li *et al.*, 2020). This method may vary depending on the position and depth of the oil reserve. The composition and the chemical used during the oil exploration have not been bound to any regulation and thus use of toxic chemicals during the process is a major precursor for water contamination (Crini *et al.*, 2018).

Contamination of clean water with fracturing chemicals, oil, and naturally occurring toxic HM such as lead, cadmium, chromium and nickel is a serious concern to WHO. Approximately 91% of the chemicals employed in the extraction process remain beneath the earth surface and are transferred by underground water to surrounding wells, boreholes, and springs by hydraulic gradient (Rafiee *et al.*, 2022). Additionally, the wastewater obtained from the hydraulic fracturing process mixes with GW, resulting in significant pollution and altering composition. In most cases, wastewater is held in open pits, which can easily leak chemicals and HM into the GW. Equally, poor wastewater management and disposal can result in HMs and organic contamination of surrounding water bodies, such as rivers and streams. Furthermore, accidental releases of chemicals during transit and improper disposal cause water quality issues either through runoff or leaching (Babuji *et al.*, 2023).

2.3 Organic pollutants in groundwater systems

The pollution of GW may occur as a result of human activities such as hydraulic oil mining, agriculture as well as mineral mining and some from natural processes like vulcanicity (Bayabil *et al.*, 2022). Excess mineralization renders GW harmful for animal and human consumption unless properly treated.

2.3.1 Silica

During oil extraction process, sand enriched with silica is pumped into the well at high pressure (H. Liu *et al.*, 2021). The oil beneath the parent rocks then flows out through an opening created and is held by sand. Although this component ensures maximum extraction of oil and natural gases located beneath hard rocks, silica (a major component of sand) is well known for its carcinogenic and mutagenic nature (Chen *et al.*, 2023). Previous studies have confirmed that most elderly mining workers complain of lung diseases and this problem reflects back to the huge quantity of sand (silica) used in the extraction of hydrocarbons (Samuels *et al.*, 2022). Despite all this, the most recent fracturing technique entails use of large amount of silica dust in fracturing at the expense of workers' health and the environment (Kalam *et al.*, 2021).

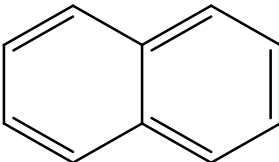
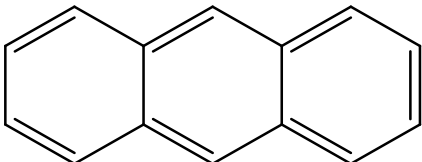
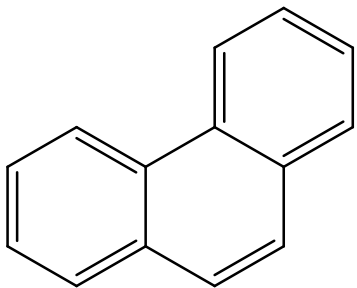
2.3.2 Polycyclic aromatic hydrocarbon (PAHs)

Polycyclic aromatic hydrocarbon are emitted to the environment mainly by anthropogenic activities associated with pyrolysis of organic matter, automobile exhausts, wastewater discharges from mining industries, wood, and combustion of petroleum products (Ali *et al.*, 2021). Additionally, PAHs occur naturally through volcanic eruption and emerge as important components of crude oil (Farrington, 2020). All these sources ultimately deliver PAHs to fresh water. For instance, most rivers near heavy industries are potential receptors of their effluents as well as runoffs from urban and agricultural farms, thus making the sediments within rivers as sinks for PAHs. Groundwater is also highly contaminated by PAHs either through natural underground disturbances or techno-genic activities of mining and well digging, thus rendering fresh water unfit for human use (Buzmakov *et al.*, 2023). PAHs in Table 2.1 are the most renowned grave organic compounds in the environment because of their mutagenic and carcinogenic nature. These organic compounds are persistent in the environment leading to bioaccumulation and bio amplification in case it enters into the food chain (Borgå *et al.*, 2022). It is reported that continuous long term exposure to air containing PAHs in particulates may eventually result in lung cancer and other associated diseases (Manisalidis *et al.*, 2020).

Naphthalene is aromatic hydrocarbons that is contained in a larger percentage in crude oil and coal tar (Zhe *et al.*, 2021). It is notated that naphthalene is produced by burning cigarettes smoke, forest fires, and car exhaust. Additionally, PAHs undergo biochemical degradation

resulting to naphthalene derivative such as anthracene and phenanthrene that are potential cause of cancer (Jouyban *et al.*, 2020). Although it is used as pesticide in most developing countries, naphthalene is linked to development of hemolytic anemia, kidney and liver damage. This is because of naphthalene metabolic products such as alpha-naphthol (Scruggs *et al.*, 2022).

Table 2. 1 : Polycyclic aromatic hydrocarbon (PAHs) in groundwater (Ogbuagu *et al.*, 2011)

Name	Molecular structure
Naphthalene	
Anthracene	
Phenanthrene	

2.3.3 Oxygenated organic hydrocarbons in groundwater

Oxygenated hydrocarbons are compounds having oxygen atom within their straight chain or cyclic rings as shown in Table 2.2. The presence of compounds with heteroatoms in drinking water interacts with biological tissues, giving them different health impacts. Carbonyl functional groups do not increase mutagenic properties of these compounds; however, their oxyl radical can cause serious cellular damages leading to cell malfunctions. Some of these compounds are discussed herein. 2-butoxyethanol (2-BE) is one of the chemical components whose major function in hydraulic fracturing fluid is to hasten foaming process (surfactant) (Manz & Carter,

2018). This chemical is a core contaminant especially when it gets in contact with soil, sediments or water. Its biological health effects include hemolysis (destruction of red blood cells), and extensive damage to the body organs such as liver, bone marrow, and spleen (Corrons *et al.*, 2021). Moreover, it is carcinogenic as well as mutagenic (Bhattacharyya *et al.*, 2018). Therefore, its study in underground water systems is very important in determining water quality.

Formalin is an artificially produced simple aldehyde with a chemical formula of formaldehyde. It is usually used as biocides or preservative in aqueous solution for control of bacteria that are prone to polymer attack (Bharti *et al.*, 2022). Although the government has restrained the use of this chemical due to its carcinogenic nature (linked to leukemia and nasopharyngeal cancer), most companies prefer using it as a biocide, taking advantage of little knowhow of workers and inhabitants (Subha Ranjani, 2022). Formaldehyde poses serious danger to the inhabitants near the oil exploration sites when wastewater spills from fracking fluid get into water bodies.

Phenolic compounds are organic pollutants usually found in wastewater of textile, paper, coal, petroleum, chemical, and petrochemical industries at significantly high percentage (Prabakar *et al.*, 2018). The major reason behind this is inadequate treatment of wastewater discharged to water bodies hence impose environmental contamination of surface- and groundwater (Sahani *et al.*, 2022). Phenolic compounds mainly from petroleum wastewater are very toxic to aquatic organisms and causes high oxygen demand to the receiving water mass (Panigrahy *et al.*, 2022). For this case, therefore, refiners and regulatory agencies have been constantly monitoring the amount of phenolic compounds as a parameter of quality of water. Usually effected at every effluence points of very large industries, especially refining industries because wastewater originating from oil production and refineries are believed to contain high concentration of phenols (Eldos *et al.*, 2022).

Chlorophenols were initially used as reliable disinfectants and wood preservative agents until their deleterious nature was discovered (Bjerketorp *et al.*, 2018). Pentachlorophenol use has been restricted in most countries as it is a potential carcinogen and mutagen but it is readily found in wooden crates, cardboards, papers, and containers, which may contaminate edible foods

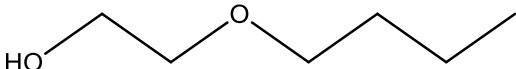
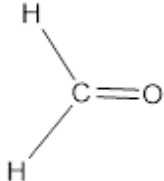
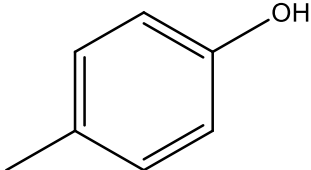
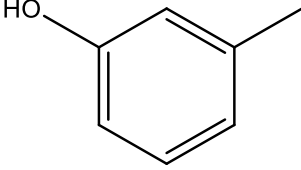
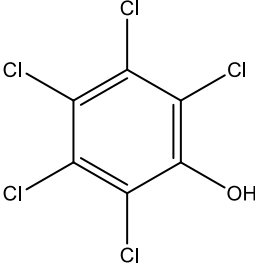
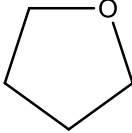
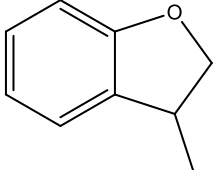
by mobility and finally to the entire food chain (Cook *et al.*, 2022). Additionally, pentachlorophenol persists longer in water and soil sediments, thus affecting the taste and odour of fresh water even at low concentrations (Bettinetti *et al.*, 2018). It is also noted that chlorinated phenols are easily given out during fresh water chlorination and it is, therefore, necessary to examine chlorinated water regularly (Zhang *et al.*, 2022).

Moreover, nitrophenols are photochemically produced in the atmosphere from unburned hydrocarbon fumes emerging from vehicle exhausts (Le Breton *et al.*, 2019). These contaminants are finally deposited into the soil and consequently interacts with GW either by dry or wet deposition to the environment. From literature, biological method of wastewater treatment is the most efficient and effective method of reducing phenolic contamination although it is influenced by p^H , dissolved oxygen, nutrients present in the water and temperature (Romola *et al.*, 2021). Among the phenolic contaminants most likely to be found in water or oil exploration fields include *p*-cresol and *m*-cresol.

Furan has been identified as a potential groundwater contaminant due to its widespread use and persistence in the environment. Moreover, furan can enter the groundwater through industrial discharges, spills, and leaks from storage tanks (Langat *et al.*, 2024). Once in the groundwater, furan can travel great distances and contaminate large volumes of water. It is also known to persist in the environment, which means that it can remain in the groundwater for a long time (Kanan & Samara, 2018). Consequently, exposure to furan-contaminated groundwater can pose a risk to human health. Tetrahydrofuran has been classified as a potential human carcinogen, which suggests that it may result in cancer. 3-methyl-2,3-dihydro-1-benzofuran has been associated to long-term liver, kidney, and lung damage as well as reproductive system harm.

Furan-contaminated groundwater remediation can be a challenging and expensive operation. Air stripping, activated carbon adsorption and chemical oxidation are prevalent techniques. These techniques work well to remove furan from groundwater but can be expensive and time-consuming (Lele *et al.*, 2023). Furan-containing products need to be handled and disposed of carefully in order to avoid groundwater contamination. Furan-using industries have adequate spill containment and storage procedures in place to avoid unintentional discharges.

Table 2.2: Oxygenated organic hydrocarbons in groundwater (O'Reilly *et al.*, 2019)

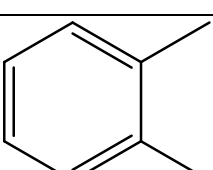
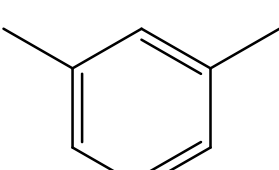
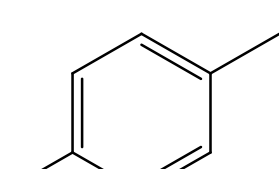
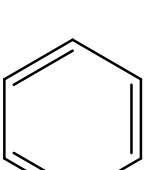
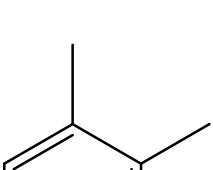
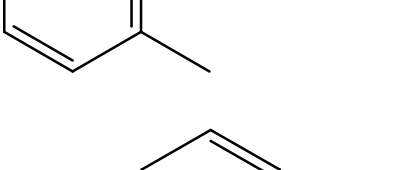
Name	Molecular structure
2-butoxyethanol (2-BE)	
formaldehyde	
<i>p</i> -cresol	
<i>m</i> -cresol	
pentachlorophenol	
tetrahydrofuran	
3-methyl-2,3-dihydro-1-benzofuran	

2.3.4 Xylenes and benzene derivative in groundwater

Xylenes (dimethyl substituted benzenes) play a significant role in oil and natural gas extraction as excellent emulsion breaker (Onojake & Waka, 2021). Nonetheless, 1,2-dimethylbenzene, 1,3-dimethylbenzene, and 1,4-dimethylbenzene in Table 2.3 are increasingly being replaced with propylene glycol, especially in sites near mass of fresh and salty water. This is because of its grave effects on human and natural ecosystems but is still widely used in most extraction sites found in third world countries (Carpenter, 2016).

Benzene, is an organic substance well recognized globally as a hazardous toxic chemical capable of initiating and accelerating cancer, specifically associated with leukemia in addition to breast and urinary tract cancers (Hanif *et al.*, 2021). Despite the hazardous nature of benzene, it is used in fracturing fluids as a surfactant since it is capable of decreasing liquid surface tension, thereby easing fluid and extracts passage up the surface along the fixed pipes (Davoodi *et al.*, 2023). Furthermore, benzene is relatively inert and, therefore, plays a significant role in inhibiting corrosion and rusting in pipes (Khan *et al.*, 2021). Moreover, benzene naturally occurs in crude oil in varied concentrations depending on the nature of the bed rock in which oil or gas occurs and the type of fracturing fluid used (Al-Ghouthi *et al.*, 2019). Gasoline, cooking oil and other refine products contain benzene because of its crude oil occurrence and extensive use as antiknock in engine fuels (Amaral *et al.*, 2021). This has rendered employees of hydrocarbon exploration companies vulnerable to occupational exposure diseases through release to the environment (Abereton *et al.*, 2023). Important benzene derivatives associated with oil exploration include 1,2,3-trimethylbenzene and 1,3-diethylbenzene as presented in Table 2.3.

Table 2.3: Xylenes and benzene derivative in groundwater (Lotte Ask Reitzel & Bjerg, 2005)

Name	Molecular structure
1,2-dimethylbenzene	
1,3-dimethylbenzene	
1,4-dimethylbenzene	
Benzene	
1,2,3- trimethylbenzene	
1,3-diethylbenzene	

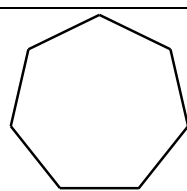
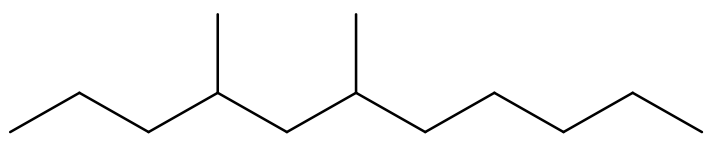
2.3.5 Oil components in groundwater

Fossil fuel is the most Stable and reliable source of energy that is commonly used in the world and especially in developing countries (Ebhotu & Jen, 2020). In spite of the magnificent use of petroleum, there have been escalating problems of GW and soil pollution by products of hydrocarbons (Shaheen *et al.*, 2022). This occurs through residual leaching of saturated hydrocarbon by water that flows to the water table by gravity and finally to the GW. Accidental spillage, underground tanks leakages, and industrially treated and untreated discharges of chemical derivatives and hydrocarbon waste to the water bodies. Furthermore, the residual hydrocarbons saturated near water table may finally reach the GW either through disturbances caused by geological hydraulic fracturing of oil (Woda *et al.*, 2018), human activity in hand-dug bore holes and wells, or natural fluctuation of water table (Baloyi & Diamond, 2019). Notably, water contamination is the overall serious world concern especially in areas with scarcity of water resource such as Kerio Valley basin. Although most petroleum hydrocarbons are known to decompose, cycloalkanes and branched alkanes do not easily decompose either aerobically or anaerobically (Nishiwaki *et al.*, 2018). The current problem calls for better techniques for treating soil and water before it is used for domestic purposes, and agricultural practices in order to minimize public and environmental health impacts (Wu *et al.*, 2019). Petroleum is composed of a number of hydrocarbons with unique characteristics of molecules, which ultimately give its physical and chemical properties as observed from viscosity and colour (Ambaye *et al.*, 2022).

Naphthenes are saturated cycloalkanes containing one or more carbon rings (Batchamen Mognol *et al.*, 2022). Naphthenes constitute the greatest percentage of saturated hydrocarbons in crude oil (Montes *et al.*, 2019). Cycloalkanes such as cycloheptane are known to have higher boiling points compared to other petroleum hydrocarbons (Landera *et al.*, 2022). Table 2.4 present naphthenes and long chain alkanes for example 4,6-dimethylundecane. They are least biodegraded due to their stable structures (Chunyan *et al.*, 2023) and complexity, hence remain the main organic pollutants in oil fields and water systems. However, not much health complaints associated to such compounds have been reported (X. Liu *et al.*, 2022). Naphthenes persistence in the environment may ultimately poses serious negative human health impacts such as respiratory problems, digestion discomfort and tumours (Loyeh & Mohsenpour, 2020).

Therefore, oil refining companies have made good use of these natural products through catalytic cracking into diesel, kerosene, jet fuel, and lubricants among others. Nowadays, naphthenes are increasingly becoming the major value determinant of petrochemical and technical property of petroleum products (Adebiyi, 2022).

Table 2. 4: Oil components in groundwater (Cozzarelli *et al.*, 2022)

Name	Molecular structure
cycloheptane	
4,6-dimethylundecane	

2.4 Heavy metal analysis

In the 21st century, industrialization has become the forefront of economic growth in developing countries. This has adversely increased fresh water demand for use in the industries and may result in elevated wastewater and sewage emission in recent days (Posselt *et al.*, 2018). Nevertheless, most governments have formed agencies and enacted strict regulation governing wastewater, sewage disposal and treatments, and direct disposal of untreated effluent to rivers and water bodies. Effluents from industries are rich in toxic heavy metals which are non-biodegradable. This property enables heavy metals to remain in water and soil sediments for decades and is currently associated with cancer and other diseases (Buszewski *et al.*, 2018).

Additionally, heavy metal from anthropogenic sources discharged to water bodies are usually in particulate or solution form and thus can easily undergo reaction and result into organometallic compounds of which their bioaccumulation, bio-mobility, and biohazardity have been reported before. Furthermore, most HM are known to exist in a wide range of oxidation states which determines their bioactivity and bio-toxicity (Baruah *et al.*, 2019). For example, Cr

(VI) has been found to be nearly 100 times more toxic than Cr (III). Moreover, Cu^+ is highly toxic compared to other oxidation states of copper (Cu) – Cu^{2+} and Cu^0 (Y.-X. Li *et al.*, 2018). Notably, studies reveal that the free hydrated ion is the most toxic and usually easily adsorbed by biological systems (Feng *et al.*, 2022).

The heavy elements considered essential for animals and plants include Fe, Mn, Zn, B, Cu and Mo. These elements are needed in small quantities by both plants and animals for effective and efficient body function. Nonetheless, deficiencies of these elements may lead to retarded growth and body malfunction to plants and animals respectively (Jomova *et al.*, 2022). These deficiencies are as a result of exhaustion in soils, thus extremely low concentrations of these elements, and presence of the same elements in insoluble form. On the other hand, elevated supply of these elements will result in toxicity to the plants, microorganism and animals (Shotyk *et al.*, 2019). Some of the toxic heavy metals are Pb and Cd, and are particularly toxic to higher order animals through inhibition of Zn in the enzymes and consequent bioaccumulation in the body tissues (Perić-Mataruga *et al.*, 2019). Copper, Nickel and Cobalt on the other hand are more toxic to plants than animals and are termed “phytotoxic” (Chaudhary *et al.*, 2018).

Pollution of fresh water from human activities such as mining and smelting and accumulation from natural bio-geological processes has resulted in constant increase of the essential and toxic heavy elements which out of speciation research are in excess supply compared to expected amounts for a particular soil or water system. Whether an element is present naturally in the soil and water sources or has been introduced by human making, it is of great importance to determine the bioavailability and extent of biohazardous state of the element. This property is related to the mobility and uptake by plants and animals (Mykolenko *et al.*, 2018). Oxidation state of pollutant also influences greatly the extent of extraction in soil and water by the chemical treatments. The concentration of the element at any one time in the soil and water solution often seems a better measurement of availability and level of contamination of pollutant in question.

Sediments, especially from clay soil, are excellent heavy metal adsorbents and can retain for long periods of time (Tack & Egene, 2019). However, sediments become a source of heavy metal by releasing them to water in case of occurrence of physical disturbance of soil during

drilling or change in pH of water, thus contaminating fresh water and hence pose potential health risks to both humans and animals (Xu *et al.*, 2022). Agricultural activities are also potential sources of heavy metal (Sun *et al.*, 2019). This mainly occurs through irrigation of contaminated soil or use of GW in agricultural activities. The salinity of soil and GW were previously the parameters for heavy metal contamination in the environment (Mahammad *et al.*, 2022). As the population grows, there is a greater need for clean water.

The significance of GW utilized in agriculture, animal husbandry, and industry has increased as a result of problems including climate change, wastewater, and heavy metal concentration in water (Hojnik *et al.*, 2020). The most current literature reports provide insight into the significance of heavy metal concentration in water. Additionally, it is extremely impressive to examine the heavy metal content of water and sediments as well as related variations, anomalies, and harmful effects. Data for statistical analysis are created from the findings of GW chemical analysis (Yang *et al.*, 2020). Heavy metal analysis in GW and soil sediment determines not only the degree of pollution and the impact of heavy metals' bioavailability and origin in the human habitat but also predicting its fate in aquatic ecosystems (Sarker *et al.*, 2020).

Groundwater has emerged as the most coveted and dependable source of drinking water for the growing human population as a result of increasing contamination of freshwater bodies (Priyan, 2021). However, the rate at which various anthropogenic and natural activities are currently contaminating the groundwater resource has equally raised a concern. The environmental health and that of consumers are greatly impacted by poor water quality (Giri, 2021). According to numerous scientific studies, drinking water that has been contaminated can cause a wide range of harmful health issues and illnesses in humans, including cholera, diarrhea, dysentery, typhoid, polio, guinea worm, and skin infections (Shah *et al.*, 2023).

It has been noted by a number of scholars that there is a need to increase the management conditions that would support the enhancement of drinking water quality. Evaluating the drinking water quality in GW or surface water is one of the fundamentals requirements for making knowledgeable decisions and plans for managing and protecting drinking water quality (Carvajal *et al.*, 2021). In this regard, this study was to investigate the quality of groundwater in

Kerio Valley basin, which is the primary source of drinking and agricultural water for residents of Baringo. Evaluating the quality of groundwater is one of the fundamental criteria for developing informed decisions and plans for maintaining and safeguarding drinking water quality in area of concern.

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CHAPTER THREE

ORGANIC CONTAMINANTS IN THE GROUNDWATER OF THE KERIO VALLEY WATER BASIN, BARINGO COUNTY, KENYA

Abstract

Various adverse impacts caused by human activities under the earth's surface have had a substantial impact on groundwater quality. This is evidenced in several places rich in mineral and hydrocarbon reserves, as well as agricultural and industrial processes. The possible etiological implications may include increased risks for cancer and genetic abnormalities. The purpose of this study was to detect and determine the concentration profiles of various organic contaminants in wells located along the Kerio Valley water basin near the exploratory wells for hydrocarbons and mining activities. The research was conducted during the dry season of December 2022. Water samples from boreholes were collected, subjected to solid phase extraction, and characterized using a gas chromatograph interfaced with a mass spectrograph detector. The results indicate that benzene derivatives, which were mainly xylene, 1,3,5-trimethylbenzene, 1-ethyl-3-methylbenzene, 1-methyl-2-propylpentylbenzene and polycyclic aromatic hydrocarbons such as naphthalene, phenanthrene, fluoranthene, azulene, and pyrene, were found in most of the boreholes sampled. Furthermore, all groundwater samples contained long-chain hydrocarbons in variable concentrations. The concentration of the benzene derivatives ranged from 2.84 ± 1.04 to 20.47 ± 1.53 ppm. However, polycyclic hydrocarbons exhibited the highest concentrations of all organic pollutants, with pyrene giving a concentration of 23.14 ± 2.05 ppm, fluoranthene (18.54 ± 1.89 ppm), phenanthrene (14.13 ± 1.60 ppm) and anthracene (12.72 ± 1.20 ppm). According to this research's findings, most borehole water in the Kerio Valley basin is contaminated and may be hazardous for human consumption. Most of the stated concentration levels were many times greater than the US EPA standards. As a result, it is required to create a policy framework for assessing and monitoring water quality in the region and recommend immediate measures to maintain a safe water supply for inhabitants.

3.1 Introduction

Human activities like hydraulic oil mining, agriculture, and mineral exploration, as well as natural phenomena like vulcanicity, can lead to groundwater pollution (Akhtar *et al.*, 2021). Additionally, surface water conditions have a significant impact on groundwater quality and vice versa (Haque *et al.*, 2021). Surface water bodies that recharge the groundwater system can contribute to groundwater contamination. These include 'natural' recharge sources like lakes and rivers, as well as 'man-made' recharge sources including urban runoff infiltration, artificial recharge wells, and injection wells for hydrocarbon exploration, as shown in the Kerio Valley watershed. Excess mineralization renders groundwater potentially hazardous for animal and human consumption if not treated appropriately. In general, the assessment and monitoring of ground water quality must take into account the interaction of all sources and channels of environmental degradation (Stuart *et al.*, 2012). Stakeholders have made a concerted effort to drill water wells in the Kerio Valley rift system, ostensibly to supply clean and accessible water for drinking, laundry, and agriculture. As such, several boreholes have been drilled in the previous decade (Davies *et al.*, 2014). However, the realization that the Kerio Valley geological structure harbours considerable hydrocarbon concentrations has called into question the safety of the borehole water in the area. Interestingly, no assessment or monitoring procedures have been implemented on borehole water many years after drilling to guarantee its quality and safety. Thus, the purpose of this study was to uncover the level of organic pollutants in the sampled borehole water, which can subsequently be extrapolated to include other boreholes within the Kerio Valley basin.

Although water covers over 70% of the earth's surface, unadulterated water is in short supply due to pollution and other anthropogenic activities that include mining and agriculture. As such, groundwater in the form of wells, springs, and rivers has become the most dependable supply of water for almost all of the world's population (Sarker *et al.*, 2021). Groundwater can be defined as water located beneath the earth's surface and is primarily formed through down seepage of surface water into hydrological subsurface systems (Jolly *et al.*, 2008). However, the quality of groundwater in a given area is largely dependent on natural and anthropogenic activities; the extent of chemical agriculture and industrial waste effluent (Burri *et al.*, 2019). All

these activities may lead to contamination of aquifer systems, which ultimately alters the quality of water available for human use and agricultural practices (Akhtar *et al.*, 2021). Xylenes (benzene derivatives) play an important role in the extraction of oil and natural gas as excellent emulsion breakers (Hajivand & Vaziri, 2015).

The Kerio Valley basin in the Kenyan Rift system receives considerable rainfall each year, however most of this rainwater flows into the rivers and lakes via surface runoff and feeder streams. Consequently, boreholes in the Kerio Valley basin are the primary sources of water for domestic and agricultural use. These subsurface water bodies have never been evaluated for safety. This is amid worries about suspected pollution from mining activities, and currently exploration for hydrocarbons. The suitability of groundwater for use depends mainly on the quantity and concentration of constituent minerals in the water, which can be affected by natural or human activities (Cicek, 2021). In the exploration of hydrocarbons, hydraulic fracturing technology to drill exploratory wells in order to maximize the geological survey of crude oil and hydrocarbon gases is applied (Chengzao *et al.*, 2012). This technology uses several toxic chemicals throughout the drilling process, which may result in contamination of groundwater (Gordalla *et al.*, 2013). Therefore, the possibility of finding organic compounds in the aquifer system is significantly high. Approximately 91% of the chemicals employed in the extraction process remain beneath the earth surface and are transferred by underground water to surrounding wells, boreholes, and springs by hydraulic gradient (Ossai *et al.*, 2020). Furthermore, the wastewater obtained from the hydraulic fracturing process mixes with groundwater, creating significant contamination thus affecting the quality of the water. Most wastewater is held in open pits, which allow organic compounds and heavy metals to leak into groundwater. Moreover, improper wastewater treatment and disposal may result in organic contamination of surrounding water bodies such as rivers and streams. Accidental releases of chemicals during transportation and poor wastewater treatment can result in water contamination through runoff or leaching of trash high in organic pollutants (He *et al.*, 2022).

The research indicates that oil exploration and mining activity is suspected to be the main source of contamination, most likely owing to leaching, surface runoff of wastewater, chemical spillage, and inadequate wastewater disposal techniques. Chemicals employed in the oil drilling

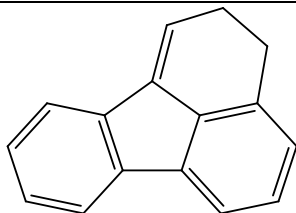
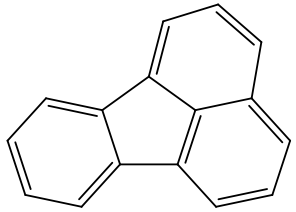
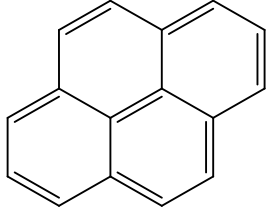
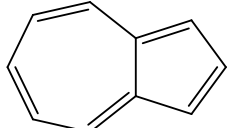
and exploration process include 1,2-dimethylbenzene, benzene, formaldehyde, 2-butoxyethanol, naphthalene, and 1,3-diethylbenzene, outlined in tables in chapter two (Koelmel *et al.*, 2022). These hydraulic fluids are a possible cause of toxicity and may change the chemical composition and quality of groundwater (Shin *et al.*, 2020). During the process of oil extraction, the hydraulic fracturing technology uses a significant amount of water to remove the oil molecules from the bedrock surface beneath the earth's crust (Badjadi *et al.*, 2023). Consequently, the disturbance caused by the fracturing process leads to the mixing of naturally occurring heavy metals and organic substances with groundwater. Approximately 91% of the hydraulic chemicals employed during oil extraction are retained under subsurface, hence contaminating groundwater (Bombino *et al.*, 2021). Consequently, geological processes within the ground exacerbate the extent to which the water table is poisoned. On the other hand, technogenic activities at mining sites increase the toxicity and mutagenic properties of trace metals. For example, during improper disposal or release of wastewater, leaching and flocculation may occur, influencing subsurface water via underground seepage along fracture channels (Nigam & Kumar, 2022).

Precursors to the major build-up of organic pollutants in ground and surface water, which has expanded dramatically in recent years, include the current chemical agricultural method, the unplanned expansion of industry, and the rise in urbanization (Ritter, 2002). Despite the fact that aquitards governs the contamination of groundwater (Wu *et al.*, 2015), the hydraulic fracturing technology employed by oil exploration and other mining activities in the Kerio Valley region penetrates underground hydro systems, and thus allows the entry of chemical contaminants into groundwater (Pan & Wang, 2015). The levels and concentration of organic pollutants in chosen borehole water from the Kerio Valley water basin will help policymakers and public health officials determine the safety of borehole water.

This study aimed on assessing the hazardous organic contaminants that compromise water quality in the Kerio Valley water basin. Of significant importance are polycyclic aromatic hydrocarbons (PAHs) presented in Table 3.1, which are well-established toxins and precursors to cancer whenever they enter to body systems. The most reactive PAHs including 2,3-dihydrofluoranthene, fluoranthene, pyrene, and azulene were detected in high concentrations in most of the sampled boreholes. This clearly indicates that the Kerio Valley groundwater system

is unsafe for both residential and commercial use. Hence, periodic water quality monitoring is very essential in order to establish comprehensive understanding of the quality of GW in Kerio Valley water regime of concern to both environment and public health.

Table 3. 1: Organic contaminants in groundwater

Name	Molecular structure
2,3-dihydrofluoranthene	
fluoranthene	
pyrene	
Azulene	

3.2 Experimental

3.2.1 Reagents

The reagents used in this study were of analytical grade (purity $\geq 99\%$). Methanol and hexane were purchased from Sigma Aldrich, Inc., St. Louis, MO, USA. Groundwater samples

were obtained from four boreholes, namely; KV1, KV2, KV3, and KV4, along the Kerio Valley water basin and used without further treatment (Figure 3.1).

3.2 Sample collection

Groundwater samples were collected randomly in duplicate from four sampling points near to oil exploratory wells, namely; KV1, KV2, KV3, and KV4 (Figure 3.1) using 2-L sterilized aluminum containers. . Samples were collected during the dry season of December 2022 through electrical pumping of borehole water. The sampling points were located using a global information system (GIS). All necessary safety procedures, such as the use of gloves, sterilized shoes, and laboratory equipment, were observed during sample collection (J. Kibet *et al.*, 2012). The samples were transported in a cooler box to the laboratory, where they were refrigerated at 4 °C prior to treatment and analysis according to the procedure adopted by Laurence *et al.* (2018).

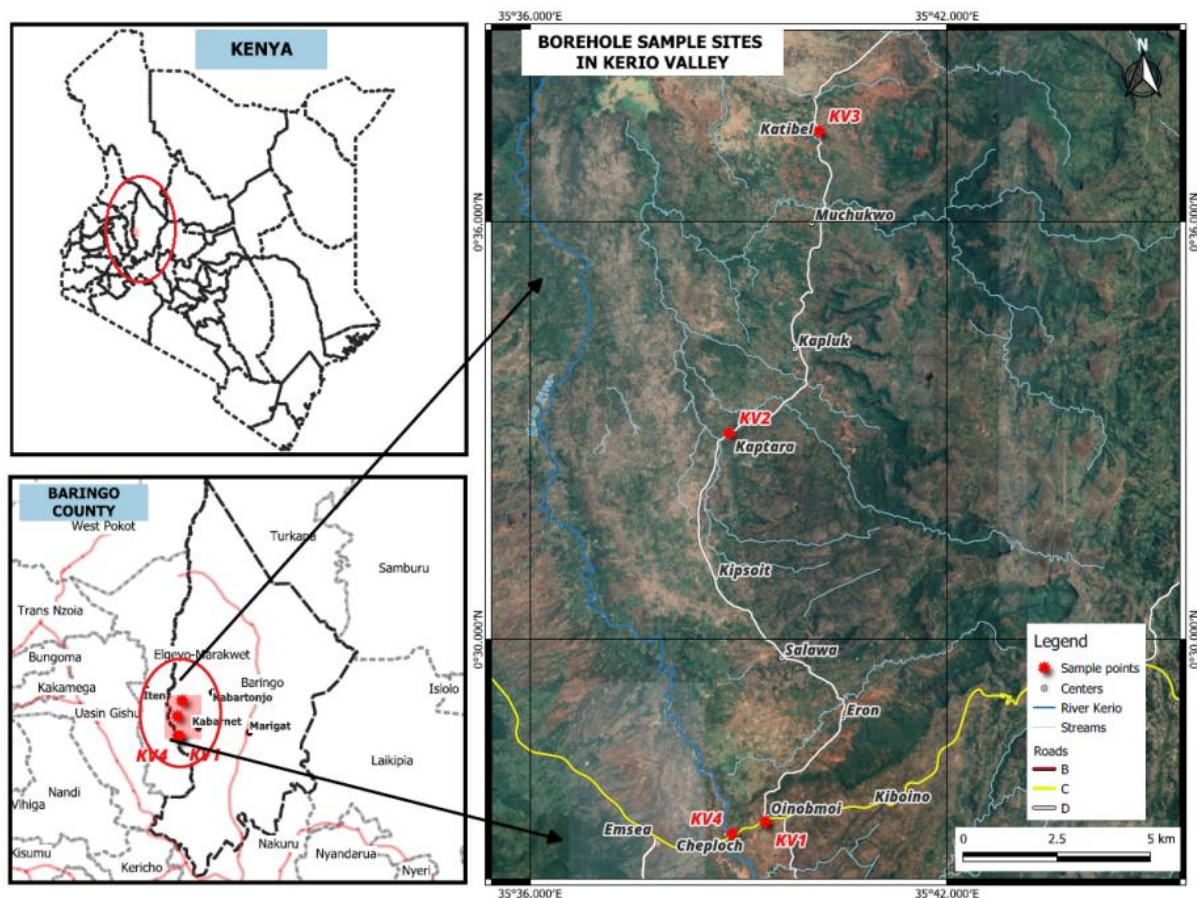


Figure 3.1:A map of the Kerio Valley basin showing borehole sampling sites.

Kerio Valley is located in the Rift Valley part of Baringo County in Kenya. Baringo County is bordered by Turkana County and West Pokot County to the north, Samburu County and Laikipia County to the east, Nakuru County and Kericho County to the south, Uasin Gishu County to the south west and Elkeiyo Marakwet to the west. The Kerio valley lies between 35°20'0"E and 0°10'0"N and covers an area of ~50 km². It is home to Kenyans whose economic activities include farming, fishing, and mining. The map of the study area is presented in Figure 3.1.

3.3 Sample treatment

Approximately 500 mL of water from each sampling point was filtered using Whatman no 2 filter paper and cleaned using a C18 cartridge to remove debris. About 300 mL of water sample was poured into a 500 mL separating funnel followed by 100 mL of a binary mixture of *n*-hexane and methanol in the 1:1 ratio. The mixture was then shaken for 10 minutes to reach homogeneity and allowed to stand for 30 minutes. The mantle was supplied with a heat source operating at temperatures between 60 and 80 °C. This low-temperature range is recommended to avoid the decomposition of thermally labile molecular components. The extraction process was carried out for 24 h, after which the extract was filtered and cleaned using a solid phase extraction technique. The aqueous phase was drawn and discarded, while the organic phase was preconcentrated to about 10 mL using a rotary evaporator and then packed in 2 mL amber vials for analysis using a gas chromatograph hyphenated to a mass spectrometer (GC/MS). For quality assurance/quality control analysis, a mixture containing pure 1 µg/L benzene, naphthalene, and pyrene was run through GC/MS under conditions similar to those of samples reported elsewhere (Kibet *et al.*, 2015; Laurence *et al.*, 2018). The recovery was 95, 98 and 102%, respectively. This result was good enough to validate the reliability of the Agilent 6890/5890 GC/MS instrument. Three replicate analyzes were performed to ensure repeatability of the findings. The same procedure was applied to all water samples in the extraction of organics. The extract was characterized using Gas chromatograph–mass spectrometry.

3.4 GC-MS characterization of organic pollutants

The extract was characterized using Agilent 6890 Gas chromatograph hyphenated with an Agilent mass selective detector (MSD) 5890 series following the method reported in literature

(Bosire, 2016). About 1 μL of the filtered sample was injected into a GC column (DB-5MS, 30 m \times 250 μm /0.25 mm \times 0.5 μm). The temperature of the injector port was set at 200 $^{\circ}\text{C}$ to allow the transformation of organic species into the gas phase prior to MS analysis. The carrier gas was ultra-high pure (UHP) helium (99.999 %) and the flow rate was 3.3 mL min^{-1} . The temperature programming was applied with initial temperature set at 50 $^{\circ}\text{C}$ followed by a heating rate of 15 $^{\circ}\text{C}/\text{min}$ for 10 minutes, holding for 3 minutes at 200 $^{\circ}\text{C}$, followed by a heating rate of 20 $^{\circ}\text{C}/\text{min}$ for 5 minutes, and holding for 10 minutes at 300 $^{\circ}\text{C}$. Electron impact ionization energy of 70 eV was used during ionization. Molecular products were identified using the National Institute of Science and Technology software (NIST, USA) and confirmed by the enhanced data software incorporated into Agilent's MSD Chemstation (J. Kibet *et al.*, 2012). To ensure that the correct compounds were reported, the standards of pure compounds were run through the GC-MS under similar conditions, and the retention times and peak shapes were found to match with remarkable accuracy.

3.5 Results and discussion

Table 3.2 summarizes some of the major organic pollutants identified in the Kerio Valley borehole water. According to the findings of this investigation, benzene derivatives comprising xylenes and PAHs such as naphthalene, anthracene, chrysene, fluoranthene, and pyrene were found in the majority of borehole samples. Furthermore, all of the boreholes analysed contained long-chain hydrocarbons and cyclohydrocarbons. Other organic contaminants found were benzo[a]azulene, 1H-indene, phenanthrene, and 2,3-dihydrofluoranthene. Benzene derivatives were prevalent in all samples except KV2.

Table 3. 2: Major organic contaminants found in the Kerio Valley boreholes.

Class of contaminants	Name	Retention time (min)	Molar mass unit (g/mol)
Benzene derivatives	1,3,5-Trimethylbenzene	6.035	120.19
	1-Ethyl-3-methylbenzene	8.040	120.19
	1,4-Dimethylbenzene	8.190	106.16
	2-Ethyl-1,4-Dimethylbenzene	8.945	134.22
	1,2,4,5-Tetramethylbenzene	8.880	134.22
	1,2,3,5-Tetramethylbenzene	8.880	134.22
Polycyclic aromatic hydrocarbons	Naphthalene	30.965	128.17
	Phenanthrene	25.395	178.23
	Benz(a)azulene	25.395	178.23
	Azulene	11.705	128.17
	Anthracene	25.395	178.23
	2,3-Dihydrofluoranthene	25-395	204.27
	Fluoranthene	30.965	202.26
	Pyrene	30.965	202.25
1H-Indene	11.705	116.16	

3.6.1 Benzene derivatives in the Kerio Valley borehole water

Numerous specific organic chemicals are used during hydraulic fracturing activities (Rosenblum *et al.*, 2017). A comprehensive investigation was done in northwest China to candidly establish whether these substances can infiltrate shallow groundwater aquifers and adversely damage local water quality following injection into deep shale horizons in quest of hydrocarbons (H. Zhang *et al.*, 2023). A mixture of diethylbenzene and ethylxylene is commonly employed in hydrocarbon extraction since it is a suitable solvent and a constituent of gasoline. These chemicals are popular because they can be fractionated in a crude oil extract mixture. As reported in Table 3.3, 1,3,5-trimethylbenzene, 1-ethyl-3-methylbenzene, 1,3-diethylbenzene, 1-ethyl-3,5-dimethylbenzene, 1-methyl-2-propylpentylbenzene were present in KV1. KV3 sample contained 1,3,5-trimethylbenzene, 1,2,4,5-tetramethylbenzene, and 1-ethyl-3,5-dimethylbenzene while 1,2,4,5-tetramethylbenzene and 1-ethyl-3,5-dimethylbenzene were present in KV4.

Table 3. 3: Distribution and concentration of benzene derivatives in KV1, KV2, KV3, and KV4 boreholes

Borehole	Organic pollutant	Retention time (min)	Concentration (ppm)	US EPA limits (ppm)
KV1	1,3,5-Trimethylbenzene	6.04	18.21 ± 1.25	0.005 (Adenuga <i>et al.</i> , 2014)
	1-Ethyl-3-methylbenzene	7.32	20.47 ± 1.53	0.7 (Dietert & Hedge, 1996)
	1,3-Diethylbenzene	8.04	14.78 ± 1.04	-
	1-Ethyl-3,5-dimethylbenzene	8.95	2.84 ± 0.08	-
	1-Methyl-2-propylpentylbenzene	5.90	7.94 ± 0.35	-

KV2	Not detected	-	-	-	
KV3	1,3,5-Trimethylbenzene	6.04	4.58 ± 0.28	0.005	(Adenuga <i>et al.</i> , 2014)
	1,2,4,5- Tetramethylbenzene	8.98	1.24 ± 0.04	-	
	1-Ethyl-3,5- dimethylbenzene	8.95	9.85 ± 0.92	-	
KV4	1,2,4,5- Tetramethylbenzene	8.98	2.58 ± 0.06	-	
	1-Ethyl-3,5- dimethylbenzene	8.95	8.40 ± 1.12	-	

The most predominant among benzene derivatives is 1-ethyl-3,5-dimethylbenzene. According to Table 3.3, 1-ethyl-3,5-dimethylbenzene had a concentration of 2.84 ± 0.08 , 9.85 ± 0.92 , and 8.40 ± 1.12 ppm for all samples analyzed of KV1, KV3, and KV4, respectively. Evidently, KV3 had the largest concentration, followed by KV4, and finally KV1, which had a concentration nearly four times lower than KV3. The presence of 1-ethyl-3,5-dimethylbenzene in the research region suggests that it is being utilized adversely by hydrocarbon exploration companies, with KV3 having the highest concentration due to its proximity to the drilling point. Furthermore, KV4 may have received drilling effluent from numerous drilling points due to poor wastewater management, which might elevate the concentration of organic pollutants in the boreholes. The 1,3,5-trimethylbenzene concentration was found to be 4 times that of KV3, although it was not found in the KV4 borehole. The difference in their respective concentrations may be attributed to the nature of the crude oil in the area, as well as the ability of the compound to get access to shallow aquifers from leaking hydraulic fracture tunnels (Deziel *et al.*, 2022). KV2 registered no benzene derivatives because it is slightly far away from the drilling site.

3.6.2 Polycyclic aromatic hydrocarbon contaminants in the borehole water

Polycyclic aromatic hydrocarbons (PAHs) are a group of more than 100 distinct compounds that are released from burning coal, oil, gasoline, trash, tobacco, wood, or other organic substances, such as charcoal-broiled meat (Aslam *et al.*, 2023). PAHs are known to occur naturally in crude oil and smoke and ash from forest fires and are often detected as products of incomplete combustion, especially in incinerators (Cheng *et al.*, 2023). Distribution and concentration of PAHs in the sampled boreholes is provided in Table 3.3. Naphthalene was the dominant organic pollutant in the KV1 water sample with a concentration of 5.00 ± 0.85 ppm.

Naphthalene is a prevalent environmental contaminant found in urban air, soil, and water, and it can also be produced by specific industrial operations such as the fabrication of dyestuffs and explosives, which in this case is suspected to emanate from mining sites in the Kerio Valley region (Gearhart-Serna *et al.*, 2018). Naphthalene's toxicity and impact on human health are of concern owing to its potential for widespread exposure (Oz, 2022). KV4 borehole water, which is the main source for both irrigation and domestic use, is extremely contaminated with pyrene, fluoranthene, phenanthrene, anthracene, 2,3-dihydrofluoranthene, and benzo[a]azulene, as can be inferred from Table 3.4.

Human health consequences from exposure to these PAHs have been found to vary depending on individual factors such as age, sex, and preexisting medical disorders, as well as the level and duration of exposure (Das & Ravi, 2022). The results showed that different PAHs were present in different amounts, with pyrene, fluoranthene, and phenanthrene exhibiting the greatest concentrations exceeding US EPA permissible limits in KV4. However, in decreasing order of concentration, the KV1 data showed a substantially lower concentration of azulene, naphthalene, 1-methyl-1H-indene, 1H-indene, and chrysene (Table 3.4).

According to the results, KV1 and KV4 were primarily contaminated with a significant quantity of PAHs, some of which have been linked to grave biological hazards. Since cyclopenta-fused PAHs (benzo[a]azulene, azulene, and fluoranthene) are more bioactive than other PAHs without cyclopenta-fused rings, their presence in water is indicative of toxicity (Reizer *et al.*, 2022). For example, azulene and its derivatives were found to be present in KV1

and KV4 borehole water samples. The anticipated effect of this chemical is to block the Na⁺ and Ca²⁺ channels that are expressed in smooth muscles of the heart and blood vessels (Argiolas *et al.*, 2023). In particular, anthracene was detected in the KV4 borehole water sample at significant concentrations as reported in Table 3.4.

Table 3.4: Distribution and concentration of PAHs in selected boreholes

Borehole	Organic pollutant	Retention time (min)	Concentration (ppm)	US EPA limits (ppm)
KV1	Naphthalene	11.71	5.00 ± 0.85	0.02 (Valero-Navarro <i>et al.</i> , 2009)
	Azulene	11.98	7.20 ± 1.00	-
	1H-Indene	10.65	2.32 ± 0.02	-
	1-Methylene-1H-indene	12.20	4.38 ± 0.05	-
	Chrysene	34.04	0.54 ± 0.01	0.0002 (Mirzaee & Sartaj, 2022)
KV2	Dibenzyl(diethyl)stannane	42.77	0.55 ± 0.01	-
KV3	Not detected	-	-	-
KV4	Phenanthrene	25.20	14.13 ± 1.60	-
	Benzo[a]azulene	25.39	10.15 ± 1.15	-
	Anthracene	26.55	12.72 ± 1.20	0.3 (Bruzzoniti <i>et al.</i> , 2010)

2,3-Dihydrofluoranthene	31.90	11.06 ± 0.98	-
Pyrene	30.96	23.14 ± 2.05	0.05 (Oyekunle <i>et al.</i> , 2021)
Fluoranthene	32.50	18.54 ± 1.89	0.04 (Akinsanya <i>et al.</i> , 2020)

Although their diverse amounts are of great interest, PAHs have frequently been found in groundwater close to different mining sites as a result of improperly managed waste effluent that may mix with water bodies and have detrimental effects on human health (Howard *et al.*, 2021). While several PAHs have been categorized as carcinogens, not all of them are equally hazardous to humans. The etiological dangers associated with PAHs are specifically determined by their structure and substituent groups. Table 3.4 illustrates clearly that the majority of PAHs were above the allowable levels based on US EPA guidelines. These included anthracene in KV4, which was around 20 times higher than the permitted limit, and chrysene in the KV1 borehole, which was almost 3000 times higher than the US EPA's permitted threshold for drinking water.

Other PAHs that exceeded the US EPA limits include pyrene and fluoranthene that were approximately 463 and 265 times, respectively. The sample chromatogram in Figure 3.2 depicts the main PAHs of interest identified in the Kerio Valley borehole water.

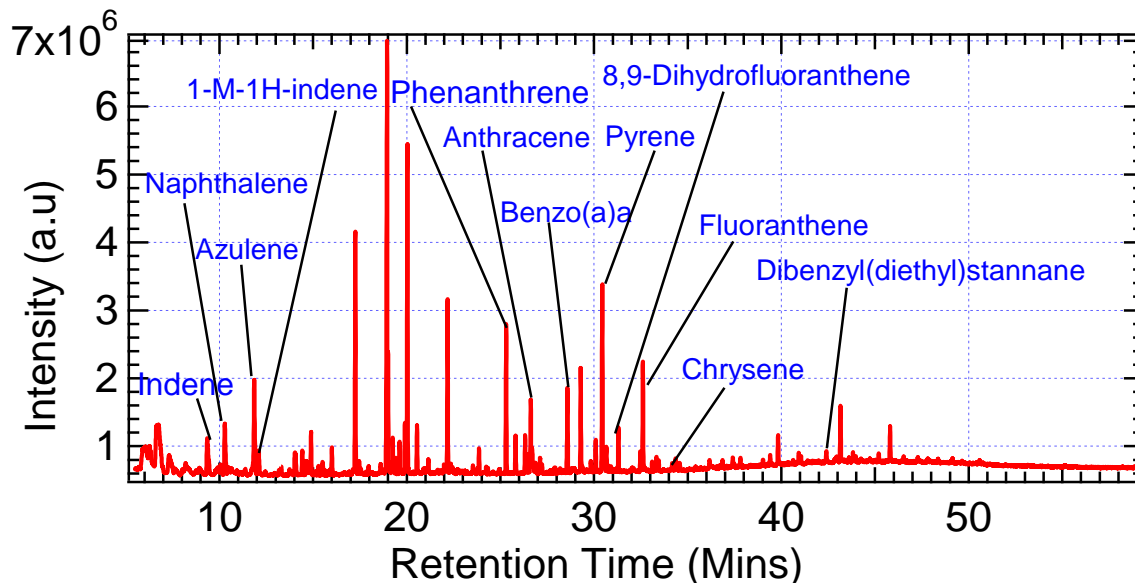


Figure 3. 2: Sample chromatogram showing the identification of major PAHs in the Kerio Valley borehole water (The abbreviation benzo[a]a is benzo[a]azulene, while 1-M-1H-indene is 1-methylene-1H-indene).

Pyrene is a natural component of coal tar, gasoline, pesticides, and asphalt (Li *et al.*, 2011). From the reported data, it is clear that the concentration of pyrene in the KV4 water borehole was significantly higher (23.14 ± 2.05 ppm) in contrast to 50 ppb in drinking water according to US EPA allowed limits (Kovalev *et al.*, 2016). Studies in the literature show that pyrene is hazardous to aquatic life at concentrations lower than the reported levels in surface water (Yang *et al.*, 2021). Pyrene has the ability to damage cell DNA and affects endocrine activity (Y. Zhang *et al.*, 2016). Another PAH detected is fluoranthene in KV4, recording a concentration of 18.54 ppm, which is above the US EPA allowed limit (Onyidinma *et al.*, 2021). Previous research in the St. Louis Park aquifer, which is thought to be contaminated by coal tar, it revealed that the concentration of fluoranthene rose as mining developed, confirming the high concentration of fluoranthene is caused by the ongoing mining activities in the area (Ferne *et al.*, 2018). The accumulation of pyrene and fluoranthene in aquatic sediments is an important concern since it could endanger creatures living at the bottom of lakes and rivers.

Furthermore, naphthalene was found in the water sample obtained from KV1 with a concentration of 5.00 ± 0.85 ppm. Additionally, it bioaccumulates in the human body and

eventually has detrimental effects on health, regardless of whether the results are greater or lower than the US EPA standards. The results recorded in Tables 3.3 and 3.4 strongly point out that the mining activities in the area are possibly the main source of benzene derivatives and PAHs with other anthropogenic sources such as farming, forest fires, or pyrolysis of fuel by vehicles as minor sources. The corresponding concentrations of chrysene, 1-H-indene, and 1-methylene-1H-indene are 0.544 ± 0.01 , 2.32 ± 0.02 , and 4.38 ± 0.05 ppm, respectively, for KV1 in addition to dibenzyl(diethyl)stannane, whose concentration in KV2 is 0.55 ± 0.01 ppm. Owing to their hazardous nature and extensive correlation with cancer, these concentrations pose a serious threat. Anthracene, which is known to cause several health issues in humans, established a higher concentration profile of 12.72 ± 1.20 ppm.

3.6.3 Distribution of aliphatic hydrocarbons in the Kerio Valley borehole water

The tridecane from the KV1 sample was found to have the highest peak intensity followed by KV4 as shown in Figures 3.3 and Table 3.5. It emerged that the peak areas of KV2 and KV3 were almost equal, at around 265081 volts-min. Tridecane, an essential component of oil, may have gotten into the groundwater as a result of borehole drilling process, hydraulic fracturing, or any other anthropogenic activity going on in the surrounding area (Tao *et al.*, 2022). Undecane and tetradecane were the additional organic chemicals detected in all water tests. KV1 had the highest peak intensities for undecane and tetradecane and, therefore, the highest concentration. The concentrations of undecane and tetradecane increased in the KV2, KV3, and KV4 boreholes, respectively. It should be mentioned that undecane occurs naturally in sedimentary rocks and forms a significant component of oil, and as a result of anthropogenic activity such as mining, and can enter groundwater systems (Skvortsov, 2020). Another organic substance found in all water samples was dimethylundecane isomers. Dimethylundecane showed the highest peak intensity of all the samples collected from KV3, making it the most dominating suspected organic pollutant, while KV2 had the lowest concentration of any borehole investigated in this study.

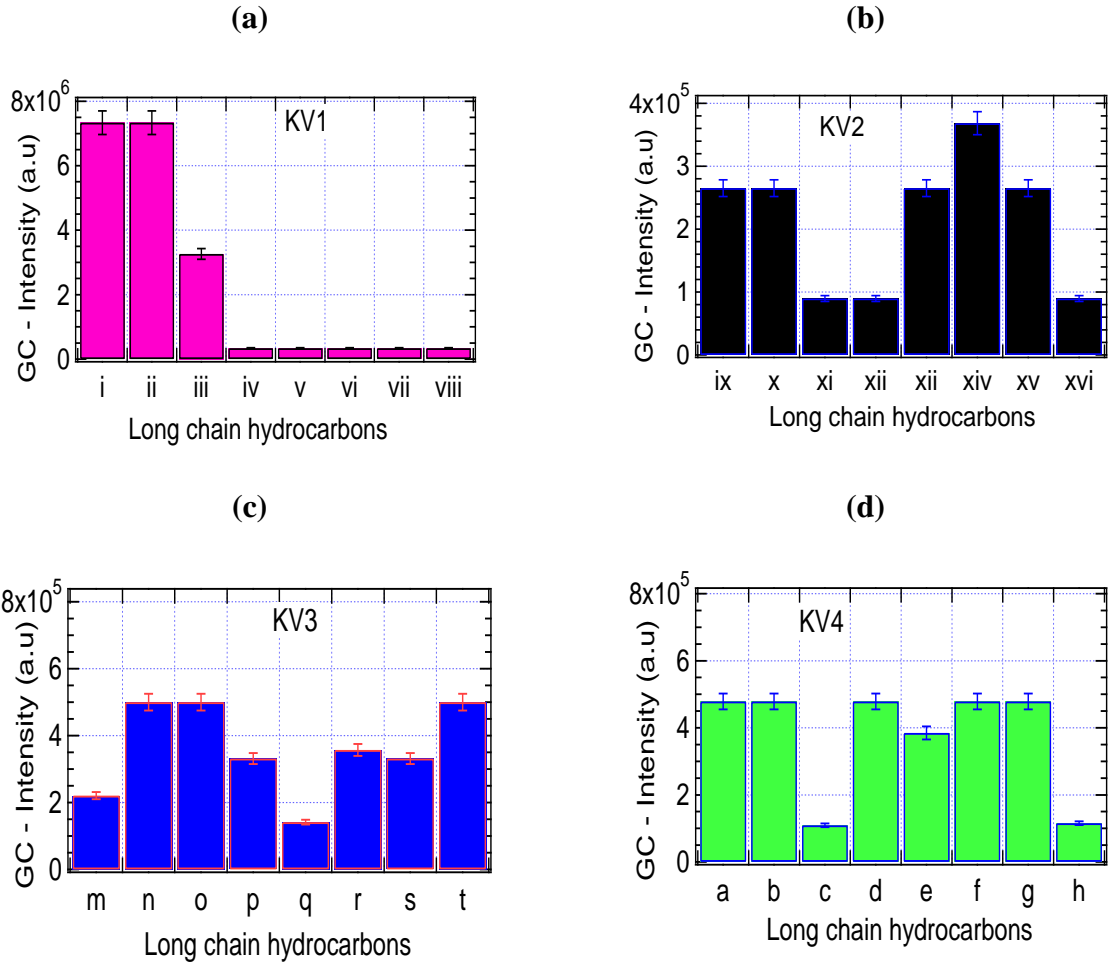


Figure 3. 3: Sample peak intensities for the major long-chain hydrocarbons for (a) KV1, (b) KV2, (c) KV3, and (d) KV4

Clearly, the KV1 borehole showed that the concentration of dimethylundecane (iii) was 36 times and 6.5 times those reported in KV2 (xii) and KV3 (o), respectively. Because of their proven ability to induce tumour growth even at low quantities, their presence in borehole water may pose a risk to human health (Elsamahy *et al.*, 2023). The peak intensities for the long-chain hydrocarbons determined from this study are reported in Figures 3.3 and Table 3.5.

Table 3. 5: List of identified long chain hydrocarbon pollutants

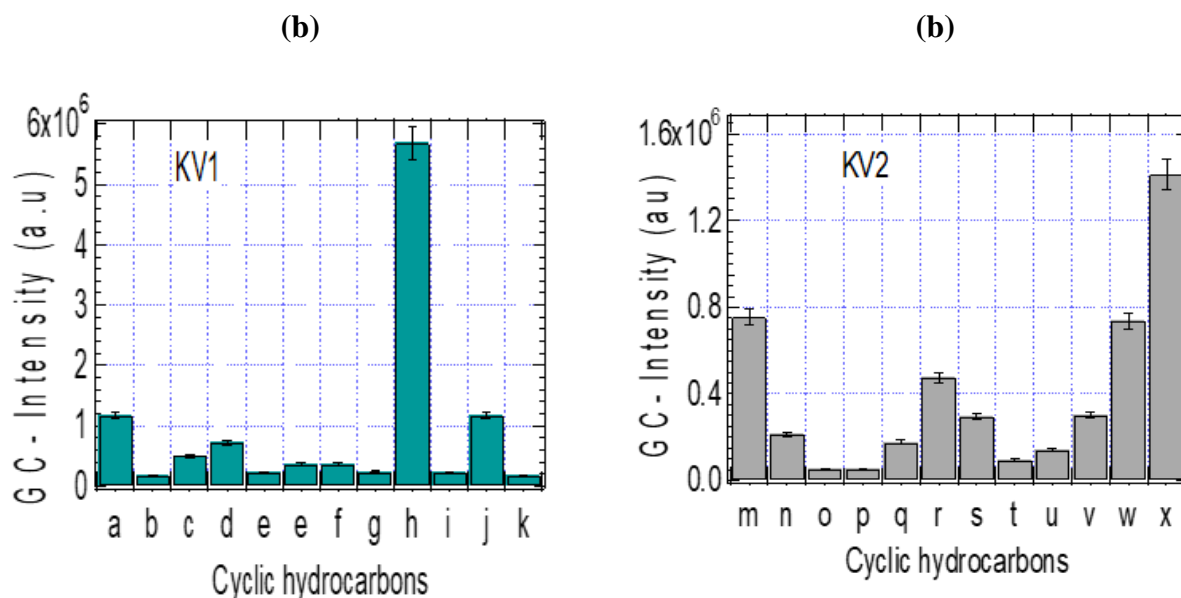
Borehole	Symbol	Organic pollutant	Retention time (min)	Peak intensity (a.u.)
KV1	i	<i>n</i> -Tridecane	8.65	7333623
	ii	<i>n</i> -Undecane	8.42	7333623
	iii	4,6-Dimethylundecane	9.350	3261313
	iv	3,7-Dimethyldecane	10.49	338043
	v	5-Sec-butylnonane	11.62	338043
	vi	2,3-Dimethyldecane	10.36	338043
	vii	5-Butylnonane	10.80	338043
	viii	2,3,6,7-Tetramethyloctane	11.75	338043
KV2	ix	Tridecane	12.10	265081
	x	<i>n</i> -Undecane	8.42	265081
	xi	2,4-Dimethyldecane	9.35	89831
	xii	2,7-Dimethylundecane	9.68	89831
	xiii	11-Methyl dodecane	12.10	265081
	xiv	7-Butyldocosane	14.43	368337
	xv	3,5-Methyl dodecane	12.47	265081
	xvi	3,4,5,6-Tetramethyloctane	9.35	89831
KV3	m	<i>n</i> -Tridecane	8.65	220853

	n	<i>n</i> -Undecane	8.42	500084
	o	2,8-Dimethylundecane	8.55	500084
	p	3,7-Dimethyldecane	11.15	331314
	q	4-Methyldodecane	35.02	141410
	r	4-Ethyl-5-methylnonane	18.26	356822
	s	5-Sec-butylnonane	11.62	331314
	t	11-Methyldodecane	8.41	500084
KV4	a	<i>n</i> -Tridecane	8.65	478437
	b	<i>n</i> -Undecane	8.42	478437
	c	5-Sec-butylnonane	11.62	109572
	d	6-Ethyl-2-methylnonane	8.78	478437
	e	2,8-Dimethyldodecane	13.67	384969
	f	2,4-Dimethyldecane	8.42	478437
	g	2,9-Dimethylundecane	8.56	478437
	h	<i>n</i> -Eicosane	19.65	115373

Dimethyldecane isomers were detected in samples obtained from the KV4 borehole and found to be the most concentrated. The concentration of dimethyldecane in KV4 was approximately 5 times that of KV2, and 1.5 times that of KV1 and KV3. Other chemical substances found included 5-sec-butylnonane and 4-ethyl-5-methylnonane. Both of these substances were not detected in KV2. 5-Sec-butylnonane was found to have the lowest peak intensity in KV4, with a concentration three times lower than that of KV1 and KV3. Moreover,

the peak intensity of 4-ethyl-5-methylnonane in KV4 was roughly 1.5 times higher than that observed in the KV1 borehole. Most of the aliphatic hydrocarbons identified in this study may have originated from crude oil discovered in the Kerio Valley. They might have unintentionally gotten into the groundwater system due to other human activities.

In this study, the peak intensity of a specific suspected organic pollutant on the gas chromatograph is the most important determinant of the concentration of compounds present in a sample because it is directly proportional to the actual content of the chemical. In this regard, the areas of the peaks produced in each compound were compared to determine the concentration. All water samples analysed included hundreds of hydrocarbon compounds ranging from KV1, KV2, KV3, and KV4, possibly indicating the presence of a hydrocarbon subsoil in the Kerio Valley region. Their presence is of great significance for oil exploration companies, as they may be attributed to total petroleum hydrocarbons (TPHs) (Inyang *et al.*, 2018). Total petroleum hydrocarbons refer to the mixtures of organic compounds that make up crude oil that possess the highest potential for toxicity, hence posing a risk to groundwater and rendering it unfit for residential and commercial applications, such as irrigation (Fatehbasharзад *et al.*, 2022). Figure 3.4 and Table 3.6 show the variation in the peak intensities for the cyclic hydrocarbons identified in the boreholes under study.



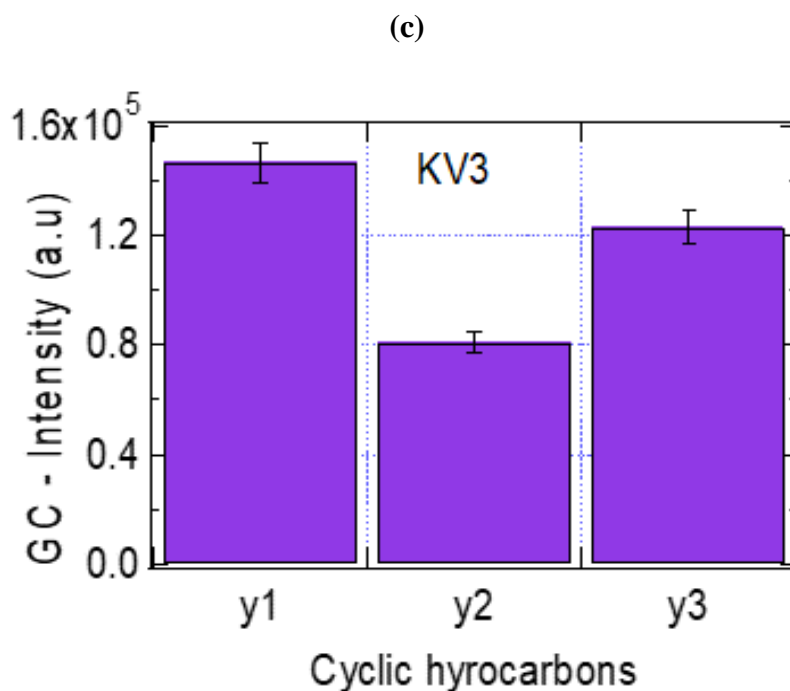


Figure 3. 4: Variation in the samples peak intensities for the cyclic hydrocarbons obtained from (a) KV1, (b) KV2, and (c) KV3

Table 3. 6: List of identified cyclic hydrocarbon pollutants

Bore hole	Pollutant symbol	Organic pollutant	Retention time (min)	Peak Intensity (volt-min)
KV1	a	1,1,2-Trimethylcyclododecane	16.005	1179305
	b	1-Isopropyl-1-methyl-2-nonylcyclopropane	21.870	69623
	c	1,1,3,3-Tetramethylcyclopentane	26.875	500266
	d	1,2,2-Trimethylbutylcyclohexane	27.115	723639
	e	1,2,4,5-Tetraethylcyclohexane	32.720	229125
	f	5-Cyclohexylundecane	44.245	367726

	g	5-Cyclohexyltridecane	44.245	367726
	h	1,2,3-Trimethylcyclohexane	10.940	238043
	i	<i>n</i> -Nonylcyclopropane	11.860	5682421
	j	1-Methyl-2-(3-methyl)cyclopropane	15.415	231340
	k	1-Methyl-2-octylcyclopropane	16.005	1179305
	l	Methylcyclodecane	17.125	180103
KV2	m	<i>n</i> -Nonylcyclopropane	11.860	753764
	n	1-Sec-butyl-1-(2-methylbutyl)cyclopropane	14.630	213891
	o	1,1,3-Trimethylcyclopentane	13.880	54479
	p	1,2-Dimethylcyclooctane	13.880	54479
	q	1-Methyl-2-(3-methylpentyl)cyclopropane	24.195	190670
	r	Cycloheptane	15.805	475577
	s	1,1,2-Trimethylcyclododecane	16.010	296587
	t	2-Cyclopropylhexane	16.720	94842
	u	Methylcyclodecane	20.895	140706
	v	1-Isopropyl-1-methyl-2-nonylcyclopropane	22.060	301776
	w	7-Cyclohexyltridecane	39.270	737265
	x	3-Cyclohexylundecane	40.870	1413115
KV3	y1	3,5,5-Trimethyl-1-cyclohexane	6.485	146416

y2	1,2-Dimethylcyclohexadecane	47.880	80782
y3	1,1,2-Trimethylcyclododecane	8.550	122843

In contrast to boreholes KV1, KV2, and KV3, borehole KV4 only recorded one cyclic hydrocarbon, (1-ethylpropyl) cyclohexane, suggesting that this borehole is less contaminated with potentially dangerous cyclic hydrocarbons. GC/MS analyses of cycloaliphatic hydrocarbons given in Table 3.6 clearly showed the presence of n-cyclohexane at varying concentrations in all water samples. For instance, KV3 was roughly 15 times higher than KV4 and twice as high as KV1 data. Since n-cyclohexane is a nonpolar molecule that is used in many different industries, it is verifiable that mining companies in the Kerio Valley area may have applied this solvent when exploring hydrocarbon, and may have resulted in wastewater leaching and runoff into aquitards. The KV3 borehole may have obtain a substantial quantity of this compound during the hydraulic fracturing process because it is located closer to the mining exploration area.

Cyclic dodecane was found in all samples analysed in the KV1, KV2, and KV3 boreholes at varying amounts, with the exception of KV4, where it was not detected. For example, the relative concentration of cyclic dodecane in KV1 is roughly 4 times that of KV2, and 10 times that of KV3. From previous research done by Fu *et al.*, (2022), various industries use cyclic dodecane in search of hydrocarbons as a solution to nonpolar organic compounds, stabilisers, temporary sealants, and more so as a water repellent, thereby simplifying the movement and protection of solutes on deeper watery surfaces during the extraction of hydrocarbons (Fu *et al.*, 2022). These results entirely agree that, despite its persistence and ability to bioaccumulate in the environment and pose a threat to public health and the environment, cyclic dodecane is used in the Kerio Valley mining process in quest of hydrocarbons.

3.7 The public health concerns of organic pollutants in the Kerio Valley borehole water

Petroleum is a significant resource in modern society since it provides fuel and raw materials for a variety of manufacturing companies, including the pharmaceutical industry. It is the main source of energy for the heating, transportation, and industrial industries, as well as a raw material for plastic and synthetic rubber (Engels *et al.*, 2013). Most products containing total petroleum hydrocarbons (TPHs) are easily combustible. Hydrocarbons, as important components

of oil, natural gas, and pesticides, have significantly contributed to the greenhouse effect and climate change, depleted ozone, impaired plant photosynthetic ability, and raised the incidence of cancer and respiratory illnesses in people. The organic pollutants listed in Table 3.2 causes significant environmental damage through oil spills, which are the leading source of environmental degradation, aquatic toxicity, and water pollution. Certain petroleum hydrocarbon fractions that are released into the aquatic environment are highly hazardous and have been linked to major health concerns in humans, including cancer (Ferne *et al.*, 2018). The chain length of saturated hydrocarbons has a strong direct toxicity correlation. It has been demonstrated that fractions with lower molecular weight structures are more hazardous because of their increased environmental bioavailability (Logeshwaran *et al.*, 2018).

However, the larger saturated-chain hydrocarbons presented in Table 3.5 have an increased mutagenic potential. Unsaturated hydrocarbon structures have unpredictable toxicity. The solubility, viscosity, and interactions of these substances with the membrane and its constituents are frequently altered by reactive functional groups (Truskewycz *et al.*, 2019). When TPH is released into the environment through wastewater discharge, accidents, industrial releases, oil spills, or leaks, and enters the soil, it moves from the soil to the groundwater, where some microorganisms may break them down into smaller fractions such as aldehydes, ketones, ethers, and esters, while others may evaporate into the atmosphere (Saravanan *et al.*, 2021). Eventually, all of these pollutants will percolate into surface water, such as rivers and lakes, and boreholes. Others, on the other hand, might stay in the soil for extended periods of time and eventually be converted into more harmful organics by soil-dwelling creatures, which could have a negative impact on health (Cao *et al.*, 2023).

Drinking water containing petroleum hydrocarbons can cause stomach upset, stomach cramps, nausea, vomiting, and diarrhea (Priyadarshane *et al.*, 2022). It may also cause inflammation in the throat and mouth. If it penetrates the lungs, it can cause pneumonia-like illnesses, lasting lung damage, and, eventually, cardiac arrest (Shrestha *et al.*, 2021). Some hydrocarbons can cause unconsciousness, seizures, abnormal cardiac rhythms, or damage to the kidneys or liver (Kuppusamy *et al.*, 2020). The PAHs listed in Table 3.1 are frequently detected in facilities that were once involved in the production of wood preservative and creosote coking,

as well as in former manufactured gas plants that used coal as a feedstock (G. Zhang *et al.*, 2020).

According to regulatory agencies, the PAHs in Table 3.4 are carcinogenic. These include phenanthrene, pyrene, benz[a]anthracene, dibenz[a,h]anthracene, fluoranthene, naphthalene, and naphthalene since exposure to these PAHs has been connected to malignancies of the liver, lung, and skin (Oz, 2022). Phenanthrene has been classified as a Group 3 carcinogen by the International Agency for Research on Cancer (IARC), implying that it has limited evidence of carcinogenicity in humans (Lee & Choi, 2023). However, animal studies have shown that exposure to phenanthrene can cause tumors in various organs, including the lungs, liver, and skin (Mallah *et al.*, 2022). Long-term exposure to phenanthrene can increase the risk of cancer in humans, particularly in individuals with high levels of exposure.

Studies have revealed that an azulene-based synthetic medication has good cardiovascular effects and may be useful in the treatment of arrhythmias and relaxing of venous tissues, therefore increasing circulation (Bakun *et al.*, 2021). Multiple ion channel blocking effects of these azulene-based drugs are considered to be largely responsible for antiarrhythmic and vasorelaxant actions (Hou *et al.*, 2022). In the medical field, azulene extracts, which are utilised in skin treatments to minimise wrinkles and puffiness, are becoming more and more popular. But research has revealed that azulene in Table 3.4 can become photoreactive when exposed to UV and visible light, creating a mutagenic substance that could be more harmful to life if it gets into the human body (Struwe *et al.*, 2011).

Anthracene and its derivatives are considered hazardous to humans and the environment, and exposure to anthracene has been associated with various health concerns (Sahoo *et al.*, 2020). Anthracene, shown in Table 3.4, is a carcinogen and mutagen linked to animal tumors. It is harmful to the kidneys, causing damage and even renal failure in serious cases (Priyadarshanee *et al.*, 2022). This is because anthracene may accumulate in the kidneys and develop oxidative stress, resulting to cell damage and abnormalities (Abadi *et al.*, 2023). In addition to these deleterious risks, anthracene can cause neurological problems such as headache, dizziness, and confusion (Ielo *et al.*, 2023). Continuous exposure to anthracene can cause reproductive problems, such as infertility and miscarriage (Priyadarshanee *et al.*, 2022). This is because

anthracene can interfere with hormone production and cause DNA damage in reproductive cells (Kim & Kim, 2016).

Naphthalene in Table 3.4 is most commonly used for making dyes, explosives, toilet deodorants, insecticide, lubricants, and polyvinyl chloride (PVC) pipes, and it is a potential part of the chemical suite utilized in natural gas extraction (El-Khateeb, 2022). During hydraulic fracturing of oil, naphthalene is mixed with water to function as a biocide and to weakly conform to soil particles, even though it can dissolve in water to some extent (Wollin *et al.*, 2020). Additionally, it can be found in diesel fuel, jet fuel, gasoline, kerosene, and gasoline station wastewater as well as lubricating oils. It also occurs naturally in crude oil and coal tar (Onyidinma *et al.*, 2021). This may clarify the reason why naphthalene appears in groundwater. If consumed, naphthalene can trigger liver and kidney damage, along with methemoglobinemia, bluish discoloration of the skin, convulsions and death, severe digestive tract irritation with abdominal discomfort, nausea, vomiting, diarrhea, anemia, and other blood abnormalities (Deo *et al.*, 2016).

3.8 Conclusions

This investigation discovered that Kerio Valley water boreholes are heavily contaminated with organic pollutants. Although only a few boreholes were analyzed, it is plausible to infer that most of borehole water in this region is contaminated. Consequently, borehole water is not suitable for human consumption as well as irrigation purposes. Interestingly, in the KV1 borehole, naphthalene and azulene had significantly higher concentrations than other PAHs, reporting 5.00 ± 0.85 and 7.20 ± 1.00 ppm, respectively. However, KV4 showed high concentration profiles of pyrene, fluoranthene, and phenanthrene at 23.14 ± 2.05 , 18.54 ± 1.89 and 14.14 ± 1.60 ppm, respectively. Based on these findings, the KV4 borehole is by far the most polluted of the boreholes examined in this study. It is also reported that all of the boreholes studied displayed a high quantity of aliphatic hydrocarbons, both long-chain and cyclic. Evidently, the long-chain hydrocarbons with the highest concentration profiles in KV1, KV2, and KV4 were *n*-tridecane and *n*-undecane, while 7-butyldocosane was dominant in KV3. Regarding cyclic hydrocarbons, *n*-nonylcyclopropane had the highest concentration profile in KV1, while 3-cyclohexylundecane was prevalent in KV2. Surprisingly, long-chain and cyclic

hydrocarbons were the most prevalent organics in all boreholes analyzed. During hydrocarbon exploration and other mining activities, the potential for water pollution must be carefully taken into account. It is paramount to adapt monitoring strategies and procedures for ground and surface waters as well as ambient air by health authorities. Groundwater studies have found substantial associations between leachates from hydraulic fracturing procedures and reported health impacts. Since human exposure is typically characterized in epidemiological studies using various distance measures as a surrogate, future studies must deal with the problem of using not only recorded pollutant concentrations but also the dynamics of fracturing fluid beneath the surface. The use of fracturing chemicals with toxic organic compounds remains a problem for humans and the environment.

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CHAPTER FOUR

FURAN AND PHENOL BASED CONTAMINANTS IN THE BOREHOLE WATER QUALITY OF THE KERIO VALLEY WATER BASIN, KENYA

Abstract

Organic water contaminants taken by humans and animals over time may result in enhanced risk for cancer and genetic abnormalities, and hence possible etiological effects. The purpose of this study was to detect and determine the concentration profiles of furan- and phenol-based contaminants in the wells situated along the Kerio Valley water basin close to the exploration wells for hydrocarbons and mining activities. The samples were collected during the dry season of December, 2022. The water samples from the boreholes were extracted using a solid phase extraction procedure and characterized using a gas chromatograph interfaced with a mass selective detector. Based on the findings, furan derivatives, mainly 3-methyl-2,3-dihydro-1-benzofuran, were predominant in all the samples with its concentration profile ranging from 0.070 ± 0.28 to 9.390 ± 1.12 ppm compared to 0.28 ppm World Health Organization Maximum Residual Limits (WHO MRL). Imperatively, KV1 was also polluted with 2.64 ± 0.34 ppm of 2-furanmethanol which emerged as twice the WHO permissible limits in drinking water, in addition to 2-methyltetrahydro-2-furanol and 2-(dichloromethyl)tetrahydrofuran in elevated concentration. Moreover, 3,5-bis(1,1-dimethylethyl)phenol was predominant in KV1 and KV2 with 5.99 ± 0.82 and 0.074 ± 0.01 ppm respectively. 3-(1,1-dimethylethyl)-4-methoxyphenol posted the highest concentration profile of 9.40 ± 1.20 ppm in KV1 which is about four times WHO limits in drinking water, hence more contaminated compared to other boreholes. According to the study's findings, the most of the borehole water in the Kerio Valley basin is contaminated with furans and phenolic compounds and may not be safe for human consumption as well as irrigation. Most of the concentration levels that were recorded were significantly higher than WHO standards. To ensure that residents have access to clean water, it is required to develop a policy framework for the evaluation and monitoring of water quality in the area and to suggest immediate action.

4.1 Introduction

Because of persistent and emerging water pollutants clean water supply has become one of the greatest challenges witnessed in the 21st century. For this reason, ground water has been considered the greatest source of portable water globally and the most frequently used for public water supply. This is because groundwater is significantly harder to pollute than surface water although it is more difficult to clean when it is polluted (Pavlidis & Tsihrintzis, 2018). It is imperative to note that water supply issues are of utmost concern globally, especially in situations of water scarcity. Since so many aspects of life depend heavily on water, it is essential to keep the water clean in order to safeguard the environment, ecosystems, and the people (Singh *et al.*, 2020). For decades, groundwater has been the primary source of water in the Kerio Valley basin for both domestic and irrigation activities.

There are two sources of groundwater pollution globally; either through human activities, or it can occur naturally. Numerous human activities, including farming, industry, and mining, can have a negative impact on groundwater quality (J. Wu & Sun, 2016). Some of the human activities that can cause water contamination include hydraulic fracturing during the exploration of hydrocarbons and mining of minerals of economic value – an activity that has been going on in the Kerio valley water basin for more than five decades. Hydraulic fracturing, used in conjunction with deep horizontal drilling, enables the extraction of natural gas and crude oil from so-called unconventional reservoirs, where they are trapped in tiny rock pores rather than flowing naturally (Jew *et al.*, 2022). Fracturing fluid is injected into the borehole under high pressure during this operation. The fluid then induces cracks in the rock via penetrating pipe's perforations in the horizontal borehole. Proppants, or beads with a diameter of approximately 1 mm, such as sand or ceramic, are employed into the drills with other fracturing fluid. Their purpose is to "prop" the pores open when the liquid medium is withdrawn after pressure release. Water is often employed as the liquid media (Zhang *et al.*, 2019). Fracturing fluids contain chemical additives, which are often added to the water on-site at the drilling location, to maintain the proppants suspended in the liquid phase as they travel down to the horizontal pipe until they are deposited in the fissures (Peers De Nieuwburgh, 2020).

In earlier research, the influence of petroleum refinery wastewater on the quality of water in Nigeria's Niger Delta was examined. The findings revealed that waters mixed with the discharged effluent had negative effects on aquatic life (Balogun *et al.*, 2019). Furthermore, long-term exposure to these harmful hydrocarbons and compounds such as phenols can be carcinogenic and result in a variety of serious health problems in people, including infections of the lungs, liver, kidneys, and vascular system (Barbosa Jr *et al.*, 2023). Because they are soluble in water and persistent, these contaminants have the potential to enter groundwater. Phenolic chemicals are among the most worrisome persistent pollutants and are mostly produced by the catalytic cracking and fractionation of crude oil in petroleum refineries. In addition, the desalted effluent, wastewater from extraction sites, the neutralized wasted caustic waste streams, and tank water are the other sources of total phenolic compounds in the petrochemical effluents. Numerous phenolic chemicals are reportedly released into the environment every year. The normal level of phenols in the waste streams that are discharged might vary, depending on the industrial source of the effluent (Ahmed *et al.*, 2021). This is despite the fact that the release of untreated effluents containing phenol pollutants into the environment, even at low concentrations, can result in the threat to aquatic life and ecosystem harmony as well as the contamination of soil, groundwater, and other surface waters (Akpan & Bassey, 2020).

The main source of phenolic compounds water contamination from an agricultural source is the use of pesticides, insecticides, and herbicides (Idowu *et al.*, 2022). The detection of phenol, several chlorophenols, including 2,4-dichlorophenol, among others in the aquatic environment has been linked to the degradation of some of these pesticides. These herbicides include 2,4-dichlorophenoxyacetic acid, 4-chloro-2-methylphenoxyacetic acid, and 2,4,5-trichlorophenoxyacetic acid. Pentachlorophenol, another pesticide that is widely used in the agricultural sector, eventually breaks down into other chlorophenols with fewer chlorine substituents (Leung *et al.*, 2019).

Another source of phenolic compounds entering groundwater is through the influents and effluents from municipal waste treatment facilities, domestic waste disposals as well as leachates from municipal solid waste landfills (El Fadili *et al.*, 2022). From previous studies, cresols have been found in leachates from a municipal waste disposal site and are believed to result from the

byproducts of incineration (Kumar *et al.*, 2023). Similar to 2,4,6-trichlorophenol, 4-tertrabutylphenol, and bisphenol A, which were all observed in leachates and are thought to originate from fly ash whereas 4-tert-octylphenol was found in landfill leachates and was thought to originate from combustion events (Kotowska *et al.*, 2020). Municipal garbage disposal sites have been shown to include some chlorophenols, 4-nonylphenol, and phenol (Ateş & Argun, 2021). As a result, the discharge of untreated leachates from landfills, the discharge of incineration byproducts such solid fly ash, and the discharge of incombustible materials into neighbouring water bodies all contribute to the pollution of the environment.

China (Yongwu Wu *et al.*, 2021), Brazil (Ramos *et al.*, 2021), Egypt (El-Naggar *et al.*, 2022), South Africa (Yahaya *et al.*, 2019), India (Othmani *et al.*, 2022), and Malaysia (Lim, 2022) have all published findings about the presence of these priority pollutants in their water bodies. Only a few nations, most notably those in North America (the USA and Canada) and Europe, have successfully dealt with the issue of phenolic contamination in their water supplies. Because of this, there have not been many reports of these contaminants in their water bodies over the past ten years. A few countries in Asia and Africa, such as China, India, South Africa, and Egypt, on the other hand, have significant concentrations of phenolic compounds, which may be a sign of their countries' expanding industrialization. Additionally, a number of developed countries have established permissible concentration limits for the presence of these phenolic compounds in their water, particularly drinking water. For instance, countries in Europe set the maximum level of chlorophenols in drinking water at 0.005 g L^{-1} (Saxena *et al.*, 2017) while Canada limits them at 0.005 g L^{-1} (Yichen Wu *et al.*, 2022). Despite the fact that these phenolic compounds are widely used in industries, and particularly for agricultural purposes in Africa, there is a lack of information on their presence in water bodies and drinking water sources within the continent. Consequently, no limit has been established for these priority pollutants in aquatic environments in Kenya and other African countries.

It is reasonable to assume that leachates from urban waste treatment facilities are not the sole source of phenols in the groundwater of the Kerio Valley. Effluents from the mining and oil exploration industries as well as agricultural practices are also thought to be significant contributors. It is believed that oral exposure to phenol is very hazardous to humans (Chowdhary

et al., 2020). Chronically exposed humans have reported symptoms such as anorexia, weight loss diarrhea, vertigo, salivation, dark urine colour, and effects on the blood and liver. Animals have had muscular spasms, trouble walking, and even death after ingesting water with incredibly high phenol concentrations. The phenols are definitely cancer-causing to people (Thakur & Kumar, 2022). The quality of this drinking water from boreholes in Kenya and especially the Kerio Valley, with respect to phenolic chemicals, is largely unidentified since the water is not pre-treated before consumption.

Furan has been identified as a potential groundwater contaminant due to its widespread use and persistence in the environment. Moreover, furan can enter the groundwater through industrial discharges, spills, and leaks from storage tanks (Encarnaç o *et al.*, 2019). Once in the groundwater, furan can travel great distances and contaminate large volumes of water. It is also known to persist in the environment, which means that it can remain in groundwater for a long time (Miglioranza *et al.*, 2022). Consequently, exposure to furan-contaminated groundwater can pose a risk to human health. Furan has been classified as a potential human carcinogen, which suggests that it may result in cancer. Furan has been associated to long-term liver, kidney, and lung damage as well as reproductive system harm (Helal *et al.*, 2022).

Furan-contaminated groundwater remediation can be a challenging and expensive operation. Air stripping, activated carbon adsorption and chemical oxidation are prevalent techniques. These techniques work well to remove furan from groundwater but can be expensive and time-consuming (Naha *et al.*, 2023). Furan-containing products need to be handled and disposed of carefully in order to avoid groundwater contamination. Furan-using industries should have adequate spill containment and storage procedures in place to avoid unintentional discharges. Regular monitoring of groundwater near areas where furan is used or stored can also help identify and prevent contamination (Khobragade, 2019). The existence of furans in groundwater and their possible consequences on human health and the environment are the subject of numerous ongoing studies. For instance, Zhang *et al.* (2020) researched on the "Furan occurrence in groundwater from a contaminated site and its potential health risk." This study investigated the occurrence of furans in groundwater samples collected from a contaminated site in China. The authors found that furan concentrations exceeded the drinking water standard in

some samples and calculated the potential health risk to humans through ingestion and dermal exposure. Moreover, Faccio *et al.* (2019) investigated the "Furan contamination of groundwater in an industrial area in Italy." This study assessed the levels of furans in groundwater samples collected from an industrial area in Italy. The authors found that furan concentrations were higher in samples from the contaminated site compared to a control site and suggested that furan contamination may be linked to industrial activities in the area.

Environmental scientists typically concentrate on the fate, transport, and impact of petroleum hydrocarbons when assessing the environmental impact of oil spills and drilling. The environmental effects of oil spills into groundwater are thought to be reduced by several weathering processes such as biodegradation, photooxidation, and physical weathering (Wang *et al.*, 2021). Hydrocarbons can, however, be transformed into compounds that may be important for the environment through processes like biodegradation and photochemistry. When evaluating the risk of an oil spill, these transformation products are often overlooked (Ward & Overton, 2020). It is imperative to know that oxygenated hydrocarbons are prevalent for longer periods of time hence considered as persistent in the environment and, therefore, increase the likelihood of bioaccumulation in ecosystems as well as in the human body (Kirkok *et al.*, 2020). On oxygenated hydrocarbons, there is limited statistical data readily available currently on persistence, bioaccumulation, and toxicity (PBT). Therefore, in light of these regulatory requirements, it is crucial to screen the representative chemical families of oxygenated hydrocarbons.

Numerous furan and furan-like chemicals have undergone *in vivo* and *in vitro* tests to determine their extent of pollution in water systems. Studies on chronic exposure in mammals have shown that furans are linked to poor reproductive results, birth abnormalities, hepatotoxicity, immunosuppression, and carcinogenicity. Mice that consumed furan throughout their entire lives got thyroid and liver cancer. Rats that were similarly exposed got liver, lung, tongue, hard palate, and nose cancers (Cholico, 2019). The detection of furan and phenol-based pollutants at extremely high quantities in most of the examined boreholes is unequivocal evidence that the Kerio Valley groundwater system is unsafe for both domestic and commercial use. However, periodic water quality monitoring of the Kerio Valley water regime is extremely important to inform both environmental and public health concerns about water quality.

4.2 Material and methods

4.2.1 Reagents

Analytical grade (purity $\geq 99\%$) reagents were employed in this study. Methanol and hexane were purchased from Sigma Aldrich, Inc., St. Louis, Missouri, USA through its subsidiary, Kobian, Kenya. Groundwater samples were obtained from four boreholes namely, KV1, KV2, KV3, and KV4 along Kerio Valley Water Basin and used without further treatment.

4.3 Sample treatment

Approximately 500 mL of water from each sampling point was filtered using Whatman no 2 filter paper and cleaned using a C18 cartridge to remove debris. About 300 mL of water sample was poured into a 500 mL separating funnel followed by 100 mL of a binary mixture of *n*-hexane and methanol in the 1:1 ratio. The mixture was then shaken for 10 minutes to reach homogeneity and allowed to stand for 30 minutes. The mantle was supplied with a heat source operating at temperatures between 60 and 80 °C. This low-temperature range is recommended to avoid the decomposition of thermally labile molecular components. The extraction process was carried out for 24 h, after which the extract was filtered and cleaned using a solid phase extraction technique. The aqueous phase was drawn and discarded, while the organic phase was preconcentrated to about 10 mL using a rotary evaporator and then packed in 2 mL amber vials for analysis using a gas chromatograph hyphenated to a mass spectrometer (GC/MS). Exactly 20 μL of pure stock furan-D4 solution was diluted to 10 mL in methanol to result in a solution of 2.0 ppm which was evaluated for quality assurance/quality control. Under instrumental circumstances that have been previously designed (Christine *et al.*, 2018), 2 L of the solution combination was injected into the GC-MS. To guarantee the repeatability of the results, three replicate analyses were carried out. For the extraction of organics, the same method was used on all water samples. Gas chromatograph-mass spectrometry was used to characterize the extract in three replicates.

4.4 GC-MS characterization of furan and phenol-based contaminants in borehole water

Following a procedure from literature (Langat *et al.*, 2023), samples taken from groundwater in the Kerio Valley boreholes were extract and characterized using Agilent 6890 Gas chromatograph hyphenated with an Agilent mass selective detector (MSD) 5890 series.

About 1 μL of the filtered sample was injected into a GC column (DB-5MS, 30 m \times 250 μm /0.25 mm \times 0.5 μm). The temperature of the injector port was set at 200 $^{\circ}\text{C}$ to allow the transformation of organic species into the gas phase prior to MS analysis. The carrier gas was ultra-high pure (UHP) helium (99.999 %) and the flow rate was 3.3 mL min^{-1} . The temperature programming was applied with initial temperature set at 50 $^{\circ}\text{C}$ followed by a heating rate of 15 $^{\circ}\text{C}/\text{min}$ for 10 minutes, holding for 3 minutes at 200 $^{\circ}\text{C}$, followed by a heating rate of 20 $^{\circ}\text{C}/\text{min}$ for 5 minutes, and holding for 10 minutes at 300 $^{\circ}\text{C}$. Electron impact ionization energy of 70 eV was used during ionization. The National Institute of Science and Technology software (NIST, USA) was used to identify the molecular products, and the improved data program built within the Agilent MSD Chemstation provided further confirmation according to Kibet *et al.* (2012). Standards of pure compounds were run through the GC-MS under same circumstances to ensure that the proper compounds were reported, and it was discovered that the retention periods and peak shapes matched with outstanding precision.

4.5 Method validation

To ensure repeatability and reproducibility of this study, standards of pure compounds in each category (phenols and furans) were prepared and found to be linear with correlation coefficient, $r \geq 0.989$. In order to determine the accuracy of the GC-MS, spiked borehole samples were used. The relative recovery experiments at various concentrations were assessed and relative recovery values ranged between 88.5% and 105.6% suggesting commendable accuracy. The sensitivity of the GC-MS method was evaluated by computing the limits of detection (LOD) and quantification (LOQ). Ten (10) separate blank solutions were prepared and analyzed. The determination of LOD and LOQ was performed following the protocol advanced by the International Union of Pure and Applied Chemistry (IUPAC) (Manousi & Zachariadis, 2020) using the equations 1 and 2.

$$\text{LOD} = 3 \left(\frac{\delta}{s} \right) \quad (1)$$

$$\text{LOQ} = 10 \left(\frac{\delta}{s} \right) \quad (2)$$

where, s is the slope of the calibration curve for each element, δ = standard deviation of the measurements of the blank solution.

The calibration curves for each compound were constructed by plotting the peak area of the optimum GC-area counts to the concentration of the standard solution. Next, the least square linear regression analysis was performed to determine the slope, intercept and coefficients.

4.6 Study area

Kerio Valley is located in the Rift valley part of Baringo County in Kenya. Baringo County is bordered by Turkana County and West Pokot County to the north, Samburu County and Laikipia County to the east, Nakuru County and Kericho County to the south, Uasin Gishu County to the south west and Elkeiyo Marakwet to the west as shown in (figure 4.1). Kerio Valley lies between 35°20'0"E and 0°10'0"N and covers an area of ~ 50 Km². It is home to Kenyans whose economic activities include farming, fishing, and fluorspar mining and hunting. The source of drinking water is largely boreholes suspected to contain a range of micro-ionic species and hydrocarbons which has not been explored before. Evidently, the quality of water may be affected by rock weathering and waste materials from mining sites that may result in the release of toxic chemicals into both the environment and the aquatic system.

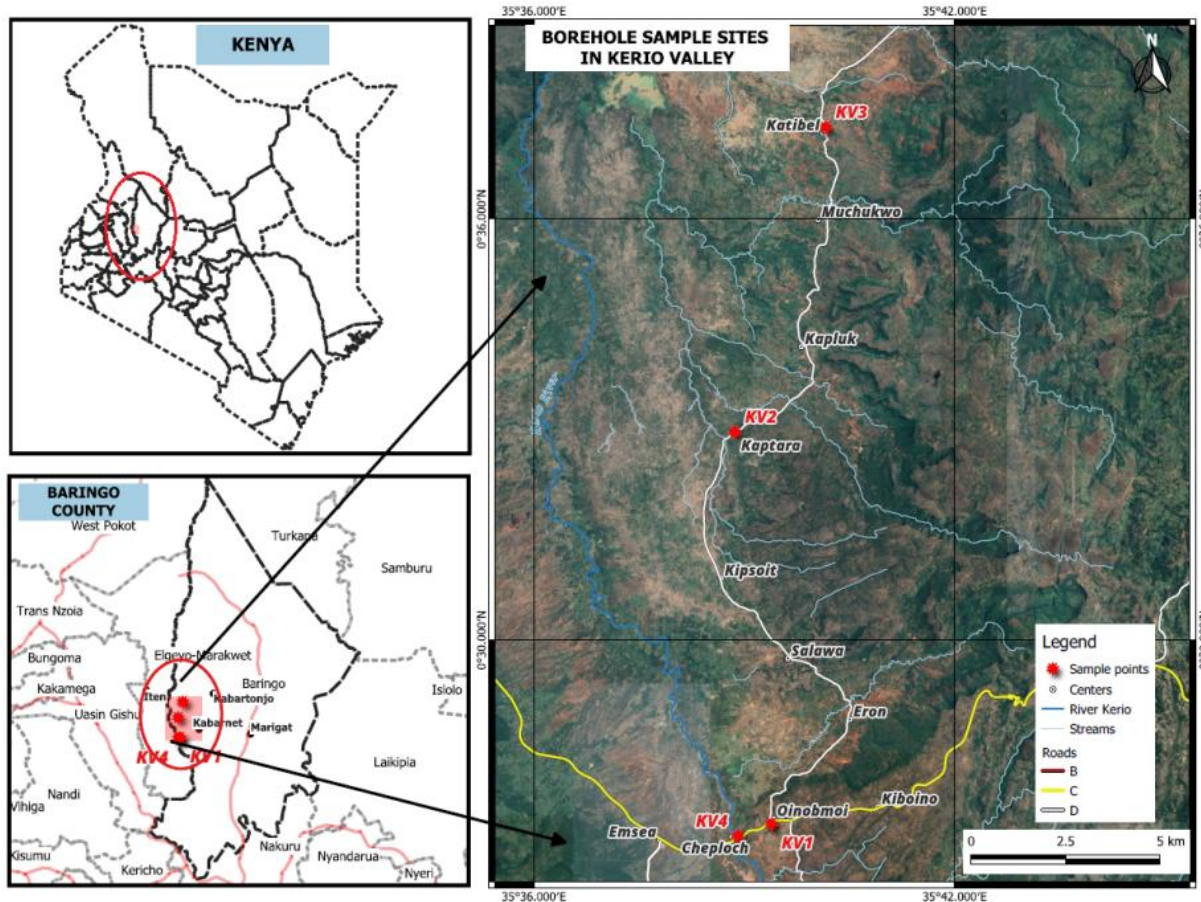
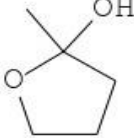
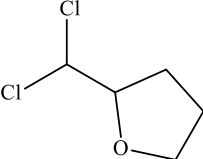
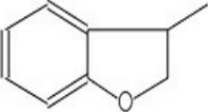
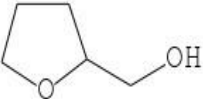
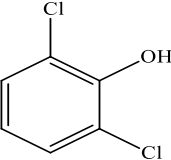
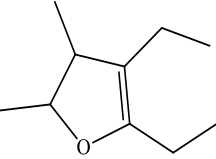
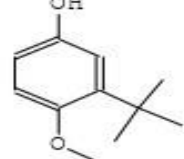
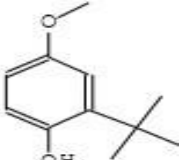


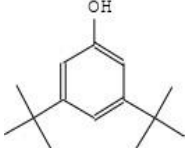
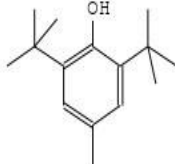
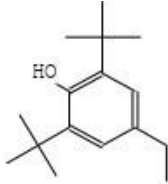
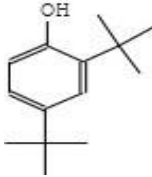
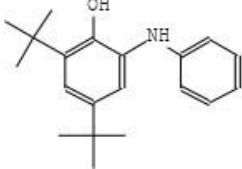
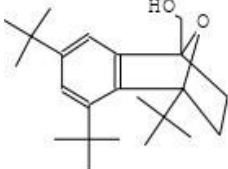
Figure 4.1:A map of the Kerio Valley basin showing extended borehole sampling sites

4.7 Results and discussion

The primary water sources for agricultural and domestic use in the Kerio Valley basin are boreholes. Despite worries about possible pollution from mining companies and the current exploratory wells being drilled in the vicinity to look for hydrocarbons, the safety of these underground water bodies has not previously been assessed. Based on the findings of this study, furan derivatives such as 2-butyltetrahydrofuran, 2-(dichloromethyl)tetrahydrofuran, 4,5-diethyl-2,3-dimethyl-2,3-dihydrofuran, 2-furanmethanol, 2-methyltetrahydro-2-furanol, 3-methyl-2,3-dihydro-1-benzofuran, 1-(5-ethyltetrahydro-2-furanyl)-3,3-dimethyl-2-butanone, and 5-isopropenyl-3-isopropyl-2,2-dimethyl-2,5-dihydrofuran were present in varied concentration as reported in Table 4.1 constituting of molecular structure, gas-chromatography retention time and their respective molar masses.

Table 4.1: Major furan and phenol based contaminants in borehole water

Name	Molecular structure	RT (min)	Molar mass
2-methyltetrahydro-2-furanol		6.41	102.13
2-(dichloromethyl)tetrahydrofuran		8.18	120.58
3-methyl-2,3-dihydro-1-benzofuran		9.82	143.18
2-furanmethanol		10.31	126.15
2,6-dichlorophenol		13.13	163.00
4,5-diethyl-2,3-dimethyl-2,3-dihydrofuran		17.46	154.25
3-(1,1-dimethylethyl)-4-methoxyphenol		18.95	180.24
2-(1,1-dimethylethyl)-4-methoxyphenol		19.04	180.24

3,5-bis(1,1-dimethylethyl)phenol		20.10	206.33
2,6-bis(1,1-dimethylethyl)-4-methylphenol		22.16	220.35
2,6-bis(1,1-dimethylethyl)-4-ethylphenol		25.81	234.38
2,4-bis(1,1-dimethylethyl)phenol		40.10	278.50
2-anilino-4,6-di-tert-butylphenol		43.19	297.44
1,4-epoxynaphthalene-1(2H)-methanol		46.18	344.27

4.7.1 Furan-based contaminants in Kerio Valley borehole water

Based on the findings of this study, 2-(dichloromethyl)tetrahydrofuran was found in borehole water KV1 and KV3 with concentration of 0.177 ± 0.02 and 0.045 ± 0.01 ppm respectively lower than the WHO limit of 2.0 ppm allowed in drinking water as shown in Table 4.2. Tetrahydrofuran from literature is a solvent well known to be used in the production of adhesives as used by oil explorers among other significant usage such as production of rubber, resins, plastics, dyes, lacquers, spandex, PVC pipe, and packaging materials (Marques *et al.*,

2020). Significantly, tetrahydrofuran spreads readily through soil, but it also releases into the atmosphere and decomposes swiftly there.

Table 4.2: Distribution of furan-based contaminants in borehole water

Borehole	Furan derivative	Peak area	Conc. (ppm)	WHO limits (ppm)
KV1	3-methyl-2,3-dihydro-1-benzofuran	18799902	9.390 ± 1.12	0.28
	4,5-diethyl-2,3-dimethyl-2,3-dihydrofuran	1746304	0.873 ± 0.09	-
	2-furanmethanol	5289018	2.64 ± 0.34	0.20
	2-methyltetrahydro-2-furanol	626037	0.313 ± 0.06	2.00
	2-(dichloromethyl)tetrahydrofuran	353998	0.177 ± 0.02	2.00
KV2	3-methyl-2,3-dihydro-1-benzofuran	473647	0.237 ± 0.02	0.28
KV3	3-methyl-2,3-dihydro-1-benzofuran	426800	0.213 ± 0.05	0.28
	2-(dichloromethyl)tetrahydrofuran	91051	0.045 ± 0.001	2.00
KV4	3-methyl-2,3-dihydro-1-benzofuran	139890	0.070 ± 0.001	0.28

Due to its ease of transition from water to air and potential for biodegradation, tetrahydrofuran has a lower concentration in surface water (Yang *et al.*, 2020). This explains why it was not found in KV4 water sample. Tetrahydrofuran can be found in quite high concentrations in groundwater due to the fact that it is difficult to degrade in groundwater and challenging to move from groundwater to soil and rock, thus higher potential to accumulate even beyond the WHO standard (Takai *et al.*, 2022). Therefore, the difference in concentrations of KV1 and KV4 depends on their distance from exploratory wells injected with the chemical even though not registered in KV2 depending on their rate of percolation in soil and biodegradation with time. It is, therefore, imperative noting that their respective concentrations for 2-(dichloromethyl)tetrahydrofuran in KV1 is highest compared to that of KV3 as shown in Table 4.2.

Interestingly, 4,5-diethyl-2,3-dimethyl-2,3-dihydrofuran emerged in KV1 to have concentration of 0.873 ± 0.09 ppm, which seemingly used during the oil exploration in the nearby drills and may have contaminated groundwater. Additionally, 2-furanmethanol and 2-methyltetrahydro-2-furanol were obtained to be concentrated in KV1 with 2.64 ± 0.34 ppm and 0.313 ± 0.06 ppm respectively compared to WHO standard in drinking water of 0.2 ppm as reported in Table 4.2. Notably, these organic compounds are solvent for tanning agents, dyes, and resins apart from being used in cement, sealants, and the polymers furan and urea-formaldehyde (Palaniappan *et al.*, 2020). The most significant application is in the production of poly(furfuryl alcohol) resins for sand-based cores and molds in foundries, as well as for the production of plastics, cements, mortars, binders, and adhesives during oil exploration in addition to fungicide and weed killer though it is possibly carcinogenic to human (Pizzi & Ibeh, 2022). Generally, the genesis of these organic contaminants in borehole may be attributed to exploratory activities, chemical farming and poor wastewater management in the study area, and thus elevating the concentration thirteen times beyond WHO standard of 2-furanmethanol.

4.7.2 Phenol-based contaminants in Kerio Valley borehole water

The distribution of phenol-based contaminants was analyzed and tabulated in Table 4.3

Table 4.3: Distribution of phenol-based contaminants in borehole water

Borehole	Phenolic derivative	Peak intensity	Conc. (ppm)	WHO limits (ppm)
KV1	3-(1,1-dimethylethyl)-4-methoxyphenol	18799902	9.40 ± 1.20	2.50
	2,6-bis(1,1-dimethylethyl)-4-methylphenol	2216468	1.11 ± 0.07	0.10
	3,5-bis(1,1-dimethylethyl)phenol	11980737	5.99 ± 0.82	2.70
	2-(1,1-dimethylethyl)-4-methoxyphenol	185802	0.09 ± 0.002	2.50
	2,6-bis(1,1-dimethylpropyl)-4-methylphenol	267685	0.134 ± 0.03	0.10
	2,6-bis(1,1-dimethylethyl)-4-ethylphenol	1385247	0.69 ± 0.05	10.40

KV2	3,5-bis(1,1-dimethylethyl)phenol	127934	0.074 ± 0.01	2.70
	1,4-epoxynaphthalene-1(2H)-methanol	5607812	2.804 ± 0.15	0.30
KV3	2-analino-4,6-di-tert-butylphenol	146523	0.073 ± 0.001	2.00
KV4	2-analino-4,6-di-tert-butylphenol	206743	0.103 ± 0.02	2.00
	2,6-dichlorophenol	117190	0.06 ± 0.001	0.001

In order to ascertain the relative contributions of drinking water to overall exposure and potential risks to human health, a thorough analysis of bis-phenol compounds concentrations was carried out in borehole water from area of study. From the results, it is clear that KV1 is endowed with bis-substituted phenols such as 3,5-bis(1,1-dimethylethyl)phenol, 2,6-bis(1,1-dimethylethyl)-4-methylphenol, 2,6-bis(1,1-dimethylethyl)-4-ethylphenol, and 2,6-bis(1,1-dimethylpropyl)-4-methylphenol, in the order of decreasing concentration of 5.99 ± 0.82 , 1.11 ± 0.07 , 0.69 ± 0.05 and 0.134 ± 0.03 ppm respectively as presented in Table 4.3 above. It is significant to note that 3,5-bis(1,1-dimethylethyl)phenol concentration is twice the WHO limits of contaminant in drinking water as used by the inhabitants and approximately fifty times more than the concentration in KV2. Nonetheless, 2,6-bis(1,1-dimethylethyl)-4-methylphenol and 2,6-bis(1,1-dimethylpropyl)-4-methylphenol concentration in groundwater of KV1 is 1.11 ± 0.07 and 0.314 ± 0.03 ppm respectively as reported in Table 4.3 . This concentration is significantly higher than the WHO maximum limit in drinking water even though 2,6-bis(1,1-dimethylpropyl)-4-methylphenol was lower than the lethal concentration limit in aquatic environment.

Mainly 3-(1,1-dimethylethyl)-4-methoxyphenol and 2-(1,1-dimethylethyl)-4-methoxyphenol were also prevalent in borehole water KV1. The toxicology of these pollutants in human include; liver and kidney damage, skin discoloration, eye damage and may also result in vision impairment as adversely witnessed in the Kerio Valley region (Program, 2004). The concentration of these pollutants is 9.40 ± 1.2 and 0.09 ± 0.002 ppm respectively as compared to WHO limit of 2.5 ppm as illustrated in Table 4.3. Nonetheless, 2,6-dichlorophenol and 2-analino-4,6-di-tert-butylphenol emerged in KV4 water sample in concentration of 0.06 ± 0.001 ppm and 0.103 ± 0.02 ppm respectively. More importantly, these pollutants are toxic at elevated

concentration in aquatic environment, and thus discharges from mining industries as well as continuous chemical method of farming need to be inspected more often in order to mitigate challenges posed to the environment (Pan *et al.*, 2011). Apart from other pollutants in KV2, 1,4-epoxynaphthalene-1(2H)-methanol posted a higher concentration of 2.804 ± 0.15 ppm which is about nine times more than the WHO limits (0.3 ppm) for oral ingestion as reported in Table 4.3 above. All these pollutants in borehole water is as a result of poorly managed waste water and discharges from mining companies within Kerio Valley region , municipal waste as well as continuous chemical farming taking place in the area.

4.8 Conclusions

According to the findings of this investigation, the Kerio Valley water boreholes are heavily contaminated with furan- and phenol-based organic pollutants. Although some boreholes near the hydrocarbon exploratory wells were analyzed, it is possible to believe that the majority of borehole water in this region is adversely contaminated by these organic pollutants and may be unfit for human consumption, in addition to being unsuitable for irrigation. Interestingly, 3-methyl-2,3-dihydro-1-benzofuran and 2-furanmethanol showed much greater quantities than other furan-based pollutants in the KV1 borehole, with 9.390 ± 1.12 and 2.64 ± 0.34 ppm, respectively. The concentration is significantly higher compared to WHO permissible limit. Moreover, KV1 had significant 3-(1,1-dimethylethyl)-4-methoxyphenol, 3,5-bis(1,1-dimethylethyl)phenol, and 2,6-bis(1,1-dimethylethyl)-4-methylphenol concentration profiles of 9.40 ± 1.2 , 5.99 ± 0.82 , and 1.11 ± 0.07 ppm, respectively. However, KV4 had elevated 2,6-dichlorophenol concentration of 0.06 ppm which is approximately sixty-times the WHO recommended levels in drinking water. According to this data, the KV1 and KV4 boreholes are by far the most polluted of all the other boreholes analysed in this study. When examining the human and environmental impact, it is usually impossible to identify the losses produced by the current exposure. The impacts of potential water pollution must be carefully considered throughout hydrocarbon exploration and any other mining activity. Surface and groundwater monitoring methods and programmes, as well as ambient air monitoring, must be modified by health authorities. Groundwater studies have indicated a high link between reported health consequences and hydraulic fracturing leachates as well as other mining activities taking place

beneath the Earth's surface. Since epidemiological studies typically describe human exposure using various distance measures as a surrogate, the challenge for future studies will be to not only use measured concentrations of pollutants but also to use the kinetics and characterization of organic pollutants during hydraulic fracturing and mining activities beneath the surface. For both humans as well as the environment, the use of explosives and the fracturing of chemicals with hazardous organic compounds continue to be detrimental.

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CHAPTER FIVE

HEAVY METAL ANALYSIS IN THE GROUNDWATER OF KERIO VALLEY WATER BASIN, BARINGO COUNTY, KENYA

Abstract

Kerio Valley region is among Kenya's industrialized areas in which mining activities takes place to date. The area's water environment is under extreme stress as a result of extensive mining and growing urbanization. However, no effort has been made to investigate the groundwater contamination caused by heavy metals. Large volumes of wastewater from homes, mining industries, and municipal effluence resulting from industrialization and urbanization are then dumped into natural water bodies such as rivers and dams in this area. In this study, groundwater samples were taken from boreholes near exploratory drills and several indicators of water quality were examined in groundwater samples. Eight samples for heavy metals were examined in groundwater samples using atomic absorption spectroscopy (AAS). The analytical results show that the boreholes near industrial region have revealed very high concentrations of total dissolved solids, higher electrical conductivity and relatively alkaline water. High concentrations of lead, cadmium, and chromium were noted in all the samples while manganese was concentrated in KV1 and KV8 water samples. Interestingly, Pb was found to have a concentration profile ranging from 0.26 ± 0.01 to 10.76 ± 0.22 ppm. Moreover, Cd posted an average concentration of 0.26 ± 0.03 ppm which is approximately eighty times the WHO allowed limits in drinking water. Furthermore, Cr concentration ranged from 0.09 ± 0.002 to 0.37 ± 0.03 ppm compared to 0.05 ppm permitted WHO limits. Contrary to the expectation, Co was not detected in all the water samples analyzed. In summary, the indiscriminate disposal of hazardous wastewater from mining industries could be the primary source of groundwater contamination. A comparison of groundwater results with WHO recommendations reveals that the majority of borehole water sampling stations are significantly contaminated with heavy metals. Chromium, cadmium, and lead have been found in borehole water samples.

5.1 Introduction

In the twenty-first century, industrialization has risen to the forefront of economic growth in developing countries. This has boosted fresh water demand for industrial usage and may have resulted in enhanced wastewater and sewage emissions in recent days (Posselt *et al.*, 2020). Nonetheless, most governments have established agencies and passed severe regulations managing wastewater, sewage disposal and treatment, and direct discharge of untreated effluent into rivers and aquatic bodies. These industrial effluents are high in hazardous heavy metals that are non-biodegradable. This feature allows heavy metals to stay in water and soil sediments for decades and is currently linked to cancer and other disorders (Ugochukwu *et al.*, 2022). Furthermore, heavy metals from anthropogenic sources discharged to water bodies are typically in particle or solution form, making them easily reactive and resulting in organometallic compounds, the bioaccumulation, bio-mobility, and biohazardity of which have previously been observed. Furthermore, most heavy metals are known to exist in a variety of oxidation states, which influence their bioactivity and biotoxicity (Engwa *et al.*, 2019).

Groundwater and soil contamination with heavy metals as a result of fast industrialization and urbanization have garnered a lot of attention as of late. Groundwater (GW) can be defined as water located beneath the earth surface and is primarily formed through down seepage of surface water into hydrological sub-surface systems. Notably, groundwater has emerged as the most coveted and dependable source of drinking water for the growing human population as a result of increasing contamination of surface water bodies (Zhao *et al.*, 2021). However, the rate at which various anthropogenic and natural activities are currently contaminating the groundwater resource has equally raised a concern. The environmental health and that of consumers are greatly impacted by poor water quality (Pradhan *et al.*, 2022). Nonetheless, the quality of GW in a given area largely depends on natural activities and anthropogenic activities, extent of chemical farming, and industrial waste effluent. All these activities may lead to contamination of aquifer systems which ultimately alters the quality of water available for human use and agricultural practices. These elements may bioaccumulate in plants and animals before finding their way up the food chain to humans (Ali & Khan, 2018).

Heavy elements considered important for animals and plants include Fe, Mn, Zn, B, Cu, and Mo. These elements are required in modest amounts by both plants and animals for effective and efficient body function. Nonetheless, deficits in these components may result in plant and animal growth retardation and physiological malfunction (Zoroddu *et al.*, 2019). These deficits are triggered by soil exhaustion, which results in extremely low concentrations of these elements, as well as the presence of these elements in insoluble form. Increased supply of these elements, on the other hand, will cause toxicity in plants, microorganisms, and animals (Fraga, 2005). Some of the detrimental heavy metals are Pb and Cd, which are especially toxic to higher order animals due to Zn inhibition in enzymes and subsequent bioaccumulation in bodily tissues (Perić-Mataruga *et al.*, 2017). As a result of human activity such as mining and smelting, essential and toxic heavy elements that, according to speciation research, are in excess supply compared to expectations for a particular soil or water, have increased continuously in fresh water. The bioavailability and extent of the element's biohazardity of oxidation state must be determined regardless of whether an element is naturally occurring in the soil and water sources or has been artificially introduced because this property is connected to the mobility and uptake by plants and animals (Eliseeva, 2019). The degree to which a contaminant is extracted chemically from soil and water depends significantly on its level of oxidation. The concentration of the element at any one time in the soil and water solution often seems a better measurement of availability and level of contamination of pollutant in question.

Clay-derived sediments in particular are effective at adsorbing and holding onto heavy metals over extended periods of time (Van Poucke *et al.*, 2020). But when soil is physically disturbed during drilling and when the pH of water changes, sediments emerge to be a source of heavy metals, contaminating fresh water and posing serious health concerns to both people and animals (Russell *et al.*, 2023). Heavy metals may also be released during agricultural processes (Sandeep *et al.*, 2019). This primarily happens when polluted land is watered or when groundwater is used for agricultural purposes. The initial criteria for determining the presence of heavy metal pollutants in the environment was the salinity of the soil and ground water (Adimalla, 2021). The most recent literature research shed light on the significance of heavy metal concentration in water. It is also fascinating to see the variations, abnormalities, and

negative consequences related with heavy metal content in water and sediments. Data for statistical analysis are generated from the findings of ground water chemical investigation (Islam *et al.*, 2021). Heavy metal analysis in groundwater and soil sediment determines the amount of pollution, the impact of a heavy metal's bioavailability and source on the human environment, and the prognosis in aquatic ecosystems (Bhuyan *et al.*, 2019).

Numerous scientific studies have demonstrated that drinking contaminated water can cause a wide range of harmful health problems and illnesses in humans, including cholera, diarrhea, dysentery, typhoid, polio, guinea worm, and skin infections (Syafudin *et al.*, 2021). Numerous academics have highlighted the need to improve management conditions that would support drinking water quality improvement. The primary purpose of this study was to investigate the quality of groundwater in the Kerio Valley basin, which is the primary source of water for the Baringo people. Prior to the discovery of oil deposits in the valley, which prompted oil explorers to dig wells in search of hydrocarbons, the Baringo County population relied on borehole water systems for many years. Evaluating drinking water quality in groundwater is one of the fundamental criteria for developing informed decisions and plans for maintaining and safeguarding drinking water quality in the area of concern (Al-Tohamy *et al.*, 2022).

5.2 Experimental

5.2.1 Reagents

The reagents used in this study were of analytical grade (purity $\geq 99\%$). Concentrated nitric acid was purchased from Sigma Aldrich, Inc., St. Louis, MO, USA. Groundwater samples were obtained from nine boreholes, namely, KV1, KV2, KV3, KV4, KV5, KV6, KV7, KV8, and KV9, along the Kerio Valley water basin and used after treatment with approximately 1mL of concentrated nitric acid.

5.2.2 Sample collection

The water samples were collected during the dry season from nine sampling points in three replicates using 1 L sterilized plastic containers and filtered using Whatman filter paper number 41 and acidified with nitric acid to maintain the pH of the samples less than two for heavy metal analysis. The major water quality parameters considered for the examination in situ

are pH, electrical conductivity, and total dissolved solids. Sampling points were located using a global information system (GIS).

5.3 Sample treatment

Exactly 100 mL of water sample were measured and poured into a beaker. To the sample, 5 mL of concentrated nitric acid were then measured and added to the sample. The hot plate was adjusted to heat the sample in the beaker at 85 °C. The sample was covered using aluminium foil during the heating process. Heating proceeded continuously for about 30 minutes then filtered and transferred to 250 mL volumetric flask for reflux process. Refluxing was done for two hours before cooling for 30 minutes. Accurately 10 mL of the solution were measured and poured into a 100 mL flat bottomed flask. The solution was then made to the mark with distilled water.

5.4 Heavy metal analysis

The groundwater samples that were typical of the residential, commercial, and industrial areas were chosen for heavy metal analysis. Analytical grade concentrated HNO₃ was used to digest groundwater samples for 30 minutes. Atomic absorption spectroscopy (AAS) was used to determine the concentrations of heavy metals in water samples. Solutions of 0.50, 1.00, 1.50, 2.00, 2.50, 3.00, 3.50, 4.00, 4.50 and 5.00 mg/L were prepared by appropriate dilution of 1000 mg/L of each metal ion solution for used in calibration the AAS. The levels of Cd, Cr, Pb, Mn, and Co in the worked-up samples were then profiled using AAS.

5.5 Study area

Kerio Valley is located in the Rift valley part of Baringo County in Kenya. Baringo County is bordered by Turkana County and West Pokot County to the north, Samburu County and Laikipia County to the east, Nakuru County and Kericho County to the south, Uasin Gishu County to the southwest and Elkeiyo Marakwet to the west. Kerio valley lies between 35°20'0"E and 0°10'0"N and covers an area of ~ 50 Km². It is home to Kenyans whose economic activities include farming, fishing, and fluorspar mining and hunting. The source of drinking water is largely bore holes suspected to contain a range of micro-ionic species and hydrocarbons which has not been explored before. Evidently, the quality of water may be affected by rock weathering and waste materials from mining sites that may result in the release of toxic chemicals into both the environment and the aquatic system.

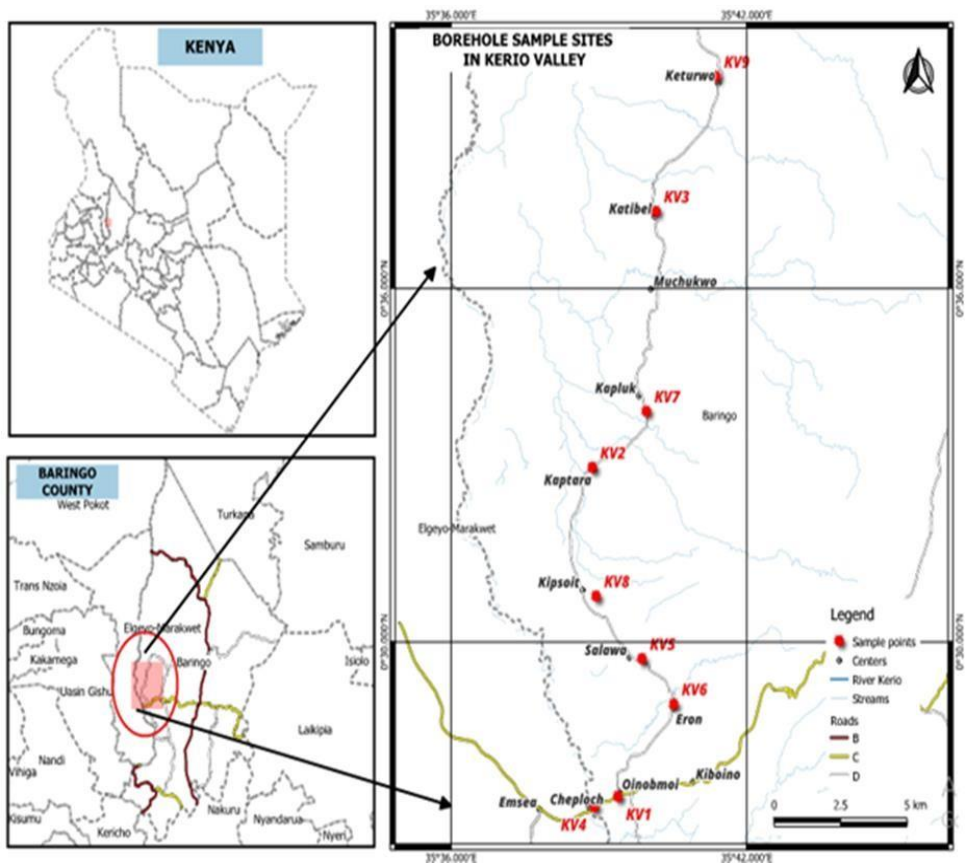


Figure 5.1: A map of the Kerio Valley basin showing extended borehole sampling sites for heavy metals

5.6 Result and discussion

Table 5.1 provides the physico-chemical parameters from thirteen sampling locations along the Kerio Valley water basin. The pH ranged from 8.03 ± 0.02 and 9.74 ± 0.08 . The pH values obtained from boreholes namely; KV4, KV7, and KV9 are higher than what the World Health Organization (WHO) recommends for irrigation and drinking water (6.5-8.5). The temperatures were measured and obtained to range between 22.4 ± 2.2 and 34.7 ± 2.8 °C and thus are above the recommended temperature of 15 °C which reportedly encourage the growth of undesirable organisms and could exacerbate issues with corrosion, taste, odour, and colour. Water that is between 4.4 and 18.3 °C is commonly preferred by cattle. Animal productivity is impacted when temperatures rise above 27 °C because of decreased water and feed intake rates.

Electrical conductivity, which is determined by the presence of ions, their total concentration, mobility, valence, relative concentrations, and temperature, is a metric to evaluate the cleanliness of water.

Table 5. 1: Water quality parameters of borehole water of Kerio Valley water basin

Borehole	Temp. (°C)	pH	TDS (mg/L)	Elec. Cond. (µS)
KV1	22.4± 2.2	8.20± 0.04	320± 11	156± 9
KV2	22.6± 2.4	8.03± 0.02	271± 12	136± 6
KV3	25.8± 1.7	8.34± 0.06	371± 18	185± 8
KV4	26.3± 1.6	9.51± 0.03	188± 10	93± 3
KV6	26.4± 2.1	8.50± 0.02	102± 5	51± 1
KV7	26.4± 2.2	8.58± 0.03	102± 4	51± 1
KV8	27.2±2.1	8.50± 0.06	375± 22	187± 8
KV9	34.7± 2.8	9.74± 0.08	118± 8	59± 2

Chromium concentrations in the water ranged from 0.09± 0.002 to 0.37± 0.03 ppm with KV9 having the highest concentration as presented in Table 5.2. Chromium concentration in groundwater is beyond the WHO recommended limit of 0.05 ppm in drinking water. In most cases chromium compounds were utilized in various industrial operations despite their environmental concern and hence get into water bodies when water is discharged (Mishra *et al.*, 2019). The chromium hexavalent form is known to be more mobile in the soil environment than the trivalent form and is more hazardous (Di Palma *et al.*, 2015). However, metabolism of lipids and proteins as well as the maintenance of a normal glucose tolerance factor both depend on the trace element chromium even though chromium damages the liver and kidneys in high quantities, and chromate dust is a well-known carcinogen (Monga *et al.*, 2022).

Lead levels in borehole water samples varied from 0.26 ± 0.01 to 10.72 ± 0.22 ppm as illustrated in Table 5.2 above. The amount of lead in the groundwater sample KV6 and KV8 is within the WHO-recommended acceptable limit. However, the concentration of lead in borehole water sample KV3 is about 35 times higher than the WHO acceptable limits. In this regard, it shows that the borehole may be receiving waste water as well as the sewages discharged from mining industries which is in agreement with the observation made by other researchers. The corresponding concentration of lead in other borehole water increased from KV1, KV9, KV7, KV2 and KV4 with 0.40 ± 0.06 , 0.49 ± 0.01 , 0.53 ± 0.03 , 0.63 ± 0.05 , and 0.67 ± 0.01 respectively as shown in Table 5.2. Their respective concentration registered a higher amount compared to WHO limit in drinking water and, therefore, may render water unsafe for use. It is imperative to know that, lead is a persistent in human body and is eligible to causes hypertension, fatigue, irritability, anemia, behavioral abnormalities, and intellectual damage (Mason *et al.*, 2014). Continuous exposure to lead, particularly soluble salts or the potent oxide such as PbO_2 , can have negative effects on the kidneys and neurological system (Boldyrev, 2018).

Cadmium concentrations in water ranged from 0.22 ± 0.01 to 0.29 ± 0.03 ppm with KV4 and KV3 equally to KV9 posting the least and highest concentration. The amount of cadmium in groundwater samples exceeds the WHO-recommended limit for all the samples analyzed. The maximum cadmium concentration in a groundwater sample taken in an industrial region near drilled point is 0.29 ± 0.03 ppm which is about hundred times higher. High levels of cadmium concentration may result from landfills that have been contaminated with sewage or from the discharge of industrial waste. The widespread use of PVC plastics, nickel cadmium batteries, pesticides, motor oil, and the disposal of sludge in landfills are all possible causes of high cadmium levels (Bhagure & Mirgane, 2011). Significant amounts of cadmium may result in symptoms like nausea, vomiting, breathing problems, cramping, and loss of consciousness. Anemia, anosmia (loss of sensation of tiny), cardiovascular illnesses, renal issues, and hypertension can all result from prolonged exposure to the metal (Zahra & Kalim, 2017).

The value of manganese in water sample analyzed ranged from 0.03 ± 0.001 to 1.86 ± 0.04 ppm. The concentration in KV1 and KV8 were significantly higher than WHO-recommended limit. On the other hand, KV6, KV7, KV3, KV9, KV2, and KV4 were found to have a

concentration of 0.03 ± 0.001 , 0.06 ± 0.004 , 0.41 ± 0.02 , 0.47 ± 0.01 , 0.93 ± 0.07 , and 0.98 ± 0.08 ppm respectively in an increasing order as reported in Table 5.2. Manganese is a trace mineral that the body requires in very small amounts. The liver, kidneys, pancreas, and bones are where it is most commonly found (Silva *et al.*, 2019). Manganese aids in the formation of bones, connective tissue, blood clotting components, and sex hormones in the body. However, a neurological disorder called manganism, which has symptoms like tremors, trouble walking, and facial muscle spasms, can be brought on by manganese toxicity in excess (Sachse *et al.*, 2019). It is therefore imperative to watch the levels of manganese as well as other heavy metals in drinking water to avoid health issues.

Table 5.2: Heavy metal concentration in borehole water

Heavy Metal	Concentration in parts per million(ppm)								
	KV1	KV2	KV3	KV4	KV6	KV7	KV8	KV9	WH O
Cr	0.17 ± 0.02	0.21 ± 0.03	0.18 ± 0.01	ND	0.09 ± 0.02	0.13 ± 0.03	0.14 ± 0.01	0.37 ± 0.03	0.05
Pb	0.40 ± 0.06	0.63 ± 0.05	10.72 ± 0.22	0.67 ± 0.01	0.28 ± 0.02	0.53 ± 0.03	0.26 ± 0.01	0.49 ± 0.01	0.3
Mn	1.52 ± 0.07	0.93 ± 0.07	0.41 ± 0.02	0.98 ± 0.08	0.03 ± 0.01	0.06 ± 0.04	1.86 ± 0.04	0.47 ± 0.01	1.3
Cd	0.25 ± 0.04	0.26 ± 0.02	0.29 ± 0.03	0.22 ± 0.01	0.28 ± 0.01	0.27 ± 0.02	0.26 ± 0.02	0.29 ± 0.03	0.00
Co	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	0.00

Legend: Nd means not detected

5.7 Conclusions

Groundwater tests from the Kerio Valley region revealed high levels of electrical conductivity and total dissolved solids. The elevated concentration of these parameters in the

groundwater Table could be attributed to home and industrial sewage discharge. Because of mining activities, the Kerio Valley water basin region had high values of total dissolved solids and alkalinity. The quantity of heavy metals in groundwater for lead, chromium, manganese, and cadmium is higher than the WHO limit. A high concentration of these metals in groundwater can affect ecosystems, plants, and animals, as well as cause health issues in humans. The main causes of contamination dispersal by rains and wind in industrial sites are the random disposal of hazardous trash and the release of untreated effluents into the soil. Data from heavy metal analyses in groundwater and soil suggest that lead, chromium, cadmium, and manganese are more mobile and reach groundwater.

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CHAPTER SIX

GENERAL DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS

6.1 General discussion

This study examines the quality of groundwater in Kerio Valley basin, which is the major source of livelihood for the people of Baringo. The borehole water systems have served the residents of the Baringo County for many years until the discovery of oil deposits along the valley, which prompted oil explorers to drill wells in search of hydrocarbons. This is an anthropogenic activity that affected the quality of groundwater and thus unsafe for human, plant, animals, and agricultural use. Most of the contaminants originating from oil exploration surveys are carcinogenic as well as mutagenic. Studies on heavy metals and hazardous organics on the Kerio Valley water basin is scarce in literature thus hinders the establishment of comprehensive understanding of the quality of groundwater in the area of study. This study was motivated by the need to characterize the concentration of organic contaminants, quantify the concentration of furan and phenol-based contaminants and to analyse the concentration profile of heavy metals in the boreholes of Kerio Valley water basin. The following observations were made based on the research questions formulated in this study:

- iv. The concentration of organic contaminants (benzene, xylenes, naphthalene, anthracene, and pyrene) was significantly different in groundwater of selected boreholes of the Kerio Valley water basin.
- v. The concentration of furans and phenolic-based contaminants was significantly different in boreholes water of the Kerio Valley water basin.
- vi. The levels of heavy metals (lead, chromium, nickel, and cadmium) present in the selected boreholes of Kerio water basin differ significantly.

The experimental part of this study involved sampling and extraction of organics in groundwater by pouring about 300ml of water into a 500ml separating funnel followed by 100 mL of a binary mixture of *n*-hexane and methanol in the 1:1 ratio. The mixture is then shaken for 10 minutes to reach homogeneity and allowed to stand for 30 minutes. The mantle was supplied with a heat source operating at temperatures between 60 and 80 °C for 24 hours. The extract was filtered and cleaned using a solid phase extraction technique. The aqueous phase was drawn and

discarded, while the organic phase was preconcentrated to about 10 mL using a rotary evaporator and then packed in 2 mL amber vials for analysis using a gas chromatograph hyphenated to a mass spectrometer (GC/MS). For quality assurance/quality control analysis, a mixture containing pure 1 µg/L benzene, naphthalene, and pyrene was run through GC/MS under conditions similar to those of samples. The reagents used in this study were of analytical grade (purity \geq 99%) purchased from Sigma Aldrich, Inc., St. Louis, MO, USA. The recovery was 95, 98 and 102%, respectively. This result was good enough to validate the reliability of the Agilent 6890/5890 GC/MS instrument. Three replicate analyzes were performed to ensure repeatability of the findings. The same procedure was applied to all water samples in the extraction of organics which include furan and phenol-based contaminants. Exactly 20 µL of pure stock furan-D4 solution was diluted to 10 mL in methanol to result in a solution of 2.0 ppm which was evaluated for quality assurance/quality control. The calibration curves for each compound were constructed by plotting the peak area of the optimum GC-area counts to the concentration of the standard solution. Next, the least square linear regression analysis was performed to determine the slope, intercept and coefficients.

For heavy metal analysis, exactly 100 mL of water sample were measured and poured into a beaker. To the sample, 5 mL of concentrated nitric acid were then measured and added to the sample. The hot plate was adjusted to heat the sample in the beaker at 85 °C. The sample was covered using aluminium foil during the heating process. Heating proceeded continuously for about 30 minutes then filtered and transferred to 250 mL volumetric flask for reflux process. Refluxing was done for two hours before cooling for 30 minutes. Accurately 10 mL of the solution were measured and poured into a 100 mL flat bottomed flask. The solution was then made to the mark with distilled water. Atomic absorption spectroscopy (AAS) was used to determine the concentrations of heavy metals in water samples. Solutions of 0.50, 1.00, 1.50, 2.00, 2.50, 3.00, 3.50, 4.00, 4.50 and 5.00 mg/L were prepared by appropriate dilution of 1000 mg/L of each metal ion solution for used in calibration the AAS. The levels of Cd, Cr, Pb, Mn, and Co in the worked-up samples were then profiled using AAS. Calibration curves were then plotted from the standard solution which is used to determine the concentration of specific heavy metal in the sample.

6.2 Findings of the study

6.2.1 Organic contaminants in the groundwater of the Kerio valley water basin, Baringo County, Kenya

According to the findings of this investigation, benzene derivatives comprising xylenes and PAHs such as naphthalene, anthracene, chrysene, fluoranthene, and pyrene were found in the majority of borehole samples. Furthermore, all of the boreholes analysed contained long-chain hydrocarbons and cyclohydrocarbons. Other organic contaminants found were benzo[a]azulene, 1H-indene, phenanthrene, and 2,3-dihydrofluoranthene. Benzene derivatives were prevalent in all samples except KV2. The most predominant among benzene derivatives is 1-ethyl-3,5-dimethylbenzene with concentration ranging from 2.84 ± 0.08 to 8.40 ± 1.12 ppm for samples analyzed. Evidently, KV3 had the largest concentration, followed by KV4, and finally KV1, which had a concentration nearly four times lower than KV3. The presence of 1-ethyl-3,5-dimethylbenzene in the research region suggests that it is being utilized adversely by hydrocarbon exploration companies, with KV3 having the highest concentration due to its proximity to the drilling point. Furthermore, KV4 receives drilling effluent from numerous drilling points due to poor wastewater management, thus elevates the concentration of organic pollutants in the boreholes. The 1,3,5-trimethylbenzene concentration of KV1 was found to be 4 times that of KV3, although it was not found in the KV4 borehole. The difference in their respective concentrations is attributed to the nature of the crude oil in the area, as well as the ability of the compound to get access to shallow aquifers from leaking hydraulic fracture tunnels.

According to the results, KV1 and KV4 were primarily contaminated with a significant quantity of PAHs, some of which have been linked to grave biological hazards. Since cyclopenta-fused PAHs (benzo[a]azulene, azulene, and fluoranthene) are more bioactive than other PAHs without cyclopenta-fused rings, their presence in water is indicative of toxicity. All PAHs examined were above the allowable levels based on US EPA guidelines. These included anthracene in KV4, which was around 20 times higher than the permitted limit, and chrysene in the KV1 borehole, which was almost 3000 times higher than the US EPA's permitted threshold for drinking water. Moreover pyrene and fluoranthene that were approximately 463 and 265 times, respectively. The corresponding concentrations of chrysene, 1-H-indene, and 1-

methylene-1H-indene are 0.544 ± 0.01 , 2.32 ± 0.02 , and 4.38 ± 0.05 ppm, respectively, for KV1 in addition to dibenzyl(diethyl)stannane, whose concentration in KV2 is 0.55 ± 0.01 ppm. Owing to their hazardous nature and extensive correlation with cancer, these concentrations pose a serious threat. Anthracene, which is known to cause several health issues in humans, established a higher concentration profile of 12.72 ± 1.20 ppm.

Undecane and tetradecane were among the organic contaminants detected in all water tests. KV1 had the highest peak intensities for undecane and tetradecane and, therefore, the highest concentration. The concentrations of undecane and tetradecane increased in the KV2, KV3, and KV4 boreholes, respectively. Another organic substance found in all water samples was dimethylundecane isomers. Dimethylundecane showed the highest peak intensity of all the samples collected from KV3, making it the most dominating suspected organic pollutant, while KV2 had the lowest concentration of any borehole investigated in this study.

GC/MS analyses of cycloaliphatic hydrocarbons clearly showed the presence of n-cyclohexane at varying concentrations in all water samples. For instance, KV3 was roughly 15 times higher than KV4 and twice as high as KV1 data. Since n-cyclohexane is a nonpolar molecule that is used in many different industries, it is verifiable that mining companies in the Kerio Valley area may have applied this solvent when exploring hydrocarbon, and may have resulted in wastewater leaching and runoff into aquitards. The KV3 borehole may have obtain a substantial quantity of this compound during the hydraulic fracturing process because it is located closer to the mining exploration area. Cyclic dodecane was found in all samples analysed in the KV1, KV2, and KV3 boreholes at varying amounts, with the exception of KV4, where it was not detected. For example, the relative concentration of cyclic dodecane in KV1 is roughly 4 times that of KV2, and 10 times that of KV3. These results entirely agree that, despite its persistence and ability to bioaccumulate in the environment and pose a threat to public health and the environment, cyclic dodecane is used in the Kerio Valley mining process in quest of hydrocarbons.

6.2.2 Furan and phenol-based contaminants in the borehole water quality of the Kerio valley water basin, Kenya

Based on the findings of this study, 2-(dichloromethyl)tetrahydrofuran was found in borehole water KV1 and KV3 with concentration of 0.177 ± 0.02 and 0.045 ± 0.01 ppm respectively lower than the WHO limit of 2.0 ppm allowed in drinking water. The difference in concentrations of KV1 and KV3 depends on their distance from exploratory wells injected with the chemical even though not registered in KV2 depending on their rate of percolation in soil and biodegradation with time. Interestingly, 4,5-diethyl-2,3-dimethyl-2,3-dihydrofuran emerged in KV1 to have concentration of 0.873 ± 0.09 ppm, which seemingly used during the oil exploration in the nearby drills and may have contaminated groundwater. Additionally, 2-furanmethanol and 2-methyltetrahydro-2-furanol were obtained to be concentrated in KV1 with 2.64 ± 0.34 ppm and 0.313 ± 0.06 ppm respectively compared to WHO standard in drinking water of 0.2 ppm.

From the results, it is clear that KV1 is endowed with bis-substituted phenols such as 3,5-bis(1,1-dimethylethyl)phenol, 2,6-bis(1,1-dimethylethyl)-4-methylphenol, 2,6-bis(1,1-dimethylethyl)-4-ethylphenol, and 2,6-bis(1,1-dimethylpropyl)-4-methylphenol, in the order of decreasing concentration of 5.99 ± 0.82 , 1.11 ± 0.07 , 0.69 ± 0.05 and 0.134 ± 0.03 ppm. It is significant to note that 3,5-bis(1,1-dimethylethyl)phenol concentration is twice the WHO limits of contaminant in drinking water as used by the inhabitants and approximately fifty times more than the concentration in KV2. Nonetheless, 2,6-bis(1,1-dimethylethyl)-4-methylphenol and 2,6-bis(1,1-dimethylpropyl)-4-methylphenol concentration in groundwater of KV1 is 1.11 ± 0.07 and 0.314 ± 0.03 ppm. This concentration is significantly higher than the WHO maximum limit in drinking water even though 2,6-bis(1,1-dimethylpropyl)-4-methylphenol was lower than the lethal concentration limit in aquatic environment. Apart from other pollutants in KV2, 1,4-epoxynaphthalene-1(2H)-methanol posted a higher concentration of 2.804 ± 0.15 ppm which is about nine times more than the WHO limits (0.3 ppm) for oral ingestion. All these pollutants in borehole water is as a result of poorly managed waste water and discharges from mining companies within Kerio Valley region, municipal waste as well as continuous chemical farming taking place in the area.

6.2.3 Heavy metal analysis in the groundwater of the Kerio valley water basin, Baringo County, Kenya

The physico-chemical parameters from thirteen sampling locations along the Kerio Valley water basin. The pH ranged from 8.03 ± 0.02 and 9.74 ± 0.08 . The pH values obtained from boreholes namely; KV4, KV7, and KV9 are higher than what the World Health Organization (WHO) recommends for irrigation and drinking water (6.5-8.5). The temperatures were measured and obtained to range between 22.4 ± 2.2 and $34.7 \pm 2.8^\circ\text{C}$ and thus are above the recommended temperature of 15°C which reportedly encourage the growth of undesirable organisms and could exacerbate issues with corrosion, taste, odour, and colour. Electrical conductivity, which is determined by the presence of ions, their total concentration, mobility, valence, relative concentrations, and temperature, is a metric to evaluate the cleanliness of water.

Chromium concentrations in the water ranged from 0.09 ± 0.002 to 0.37 ± 0.03 ppm with KV9 having the highest concentration. Chromium concentration in groundwater is beyond the WHO recommended limit of 0.05 ppm in drinking water. Lead levels in borehole water samples varied from 0.26 ± 0.01 to 10.72 ± 0.22 ppm. The amount of lead in the groundwater sample KV6 and KV8 is within the WHO-recommended acceptable limit. However, the concentration of lead in borehole water sample KV3 is about 35 times higher than the WHO acceptable limits. Cadmium concentrations in water ranged from 0.22 ± 0.01 to 0.29 ± 0.03 ppm with KV4 and KV3 equally to KV9 posting the least and highest concentration. The amount of cadmium in groundwater samples exceeds the WHO-recommended limit for all the samples analyzed. The maximum cadmium concentration in a groundwater sample taken in an industrial region near drilled point is 0.29 ± 0.03 ppm which is about hundred times higher. High levels of cadmium concentration may result from landfills that have been contaminated with sewage or from the discharge of industrial waste. The value of manganese in water sample analyzed ranged from 0.03 ± 0.001 to 1.86 ± 0.04 ppm. The concentration in KV1 and KV8 were significantly higher than WHO-recommended limit. On the other hand, KV6, KV7, KV3, KV9, KV2, and KV4 were found to have a concentration of 0.03 ± 0.001 , 0.06 ± 0.004 , 0.41 ± 0.02 , 0.47 ± 0.01 , 0.93 ± 0.07 , and 0.98 ± 0.08 ppm respectively in an increasing order.

6.3 Conclusions

This study has revealed that Kerio Valley water boreholes are considerably contaminated with organic pollutants and heavy metals. Although some boreholes were analyzed, it is safe to observe that the majority of borehole water in this region is contaminated by deleterious pollutants and may be dangerous for human consumption, in addition to being unsafe for irrigation.

- i. The Kerio Valley water boreholes are heavily contaminated with organic contaminants. Interestingly, naphthalene and azulene showed much greater quantities than other PAHs in the KV1 borehole, with 5.00 ± 0.85 and 7.20 ± 1.0 ppm, respectively. However, KV4 had significant pyrene, fluoranthene, and phenanthrene concentration profiles of 23.14 ± 2.05 , 18.54 ± 1.89 , and 14.14 ± 1.60 ppm, respectively. According to these data, the KV4 borehole is by far the most polluted of all the boreholes studied in this study. KV3 was less contaminated with PAHs. It is also worth noting that all of the boreholes examined contained a high concentration of aliphatic hydrocarbons, both long chain and cyclic. Clearly, n-tridecane and n-undecane had the largest concentration profiles in KV1, KV2, and KV4, while 7-butylidocosane was dominating in KV3. In terms of cyclic hydrocarbons, KV1 exhibited the largest concentration profile of n-nonyl cyclopropane, whereas KV2 had a higher concentration profile of 3-cyclohexylundecane. Surprisingly, long-chain and cyclic hydrocarbons were the most prevalent organics in all boreholes examined. It is frequently impossible to determine the harm caused by existing exposure when considering the human and environmental consequences.
- ii. Remarkably, 3-methyl-2,3-dihydro-1-benzofuran and 2-furanmethanol showed much greater quantities than other furan based pollutants in the KV1 borehole, with 9.390 ± 1.12 and 2.64 ± 0.34 ppm, respectively. The concentration is significantly higher compared to WHO permissible limit. Moreover, KV1 had significant 3-(1,1-dimethylethyl)-4-methoxyphenol, 3,5-bis(1,1-dimethylethyl)phenol, and 2,6-bis(1,1-dimethylethyl)-4-methylphenol concentration profiles of 9.40 ± 1.2 , 5.99 ± 0.82 , and 1.11 ± 0.07 ppm, respectively. However, KV4 had elevated 2,6-dichlorophenol concentration of 0.06 ppm which is approximately sixty-times the WHO recommended levels in drinking

water. According to these data, the KV1 and KV4 boreholes is by far the most polluted of all the other boreholes analysed in this study.

- iii. This work established that the pH values were high, indicating that the water is alkaline, probably due to mining activities and fertilizer application in surrounding farms near the study region, as well as other anthropogenic sources. Additionally, the Kerio Valley region's groundwater assessments indicated significant levels of electrical conductivity and total dissolved solids. The higher concentrations of these parameters in the groundwater Table could be ascribed to wastewater discharge from mining industries as well as agricultural activities. The amount of heavy metals in groundwater is higher than the WHO limit for chromium and cadmium in all the analysed water samples. A high concentration of these metals pollutants in groundwater can harm ecosystems, plants, and animals, as well as humans hence resulting to significant levels of total dissolves solids and elevated electrical conductivity.

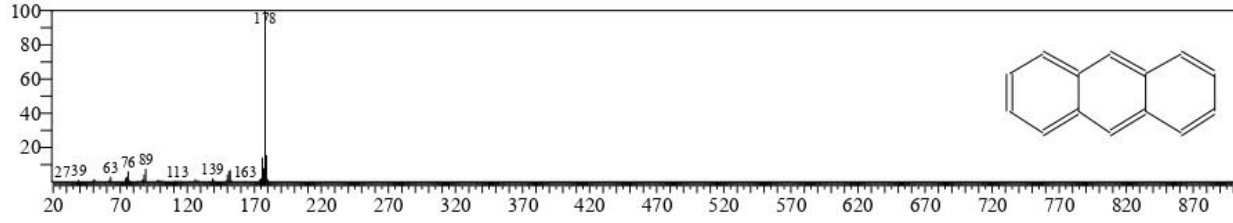
6.4 Recommendations

- i. It is paramount to adapt regular monitoring strategies and procedures for groundwater health authorities. Studies in groundwater have shown significant associations between leachates from hydraulic fracturing processes and observed health effects. Therefore, it is crucial to continuously assess the quality of groundwater for environmental monitoring and public safety.
- ii. This approach has given a starting point for classifying dangerous contaminants. The challenge for future research will be to not only use measured concentrations of pollutants but also to use the kinetics and characterization of fracturing fluid beneath the surface. The usage of harmful organic compounds as fracturing chemicals continues to be a problem for humans and the environment. Finally, the study established a foundation for further research into the relationship between hydraulic fracturing and groundwater quality, allowing for future remediation and preventative measures to be done once the relationship is fully established.

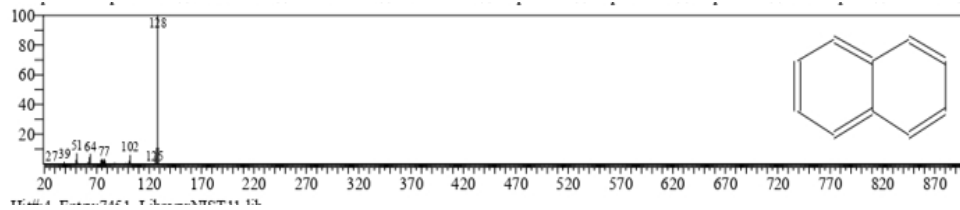
APENDICES

Appendix I: Mass spectra of selected PAHs

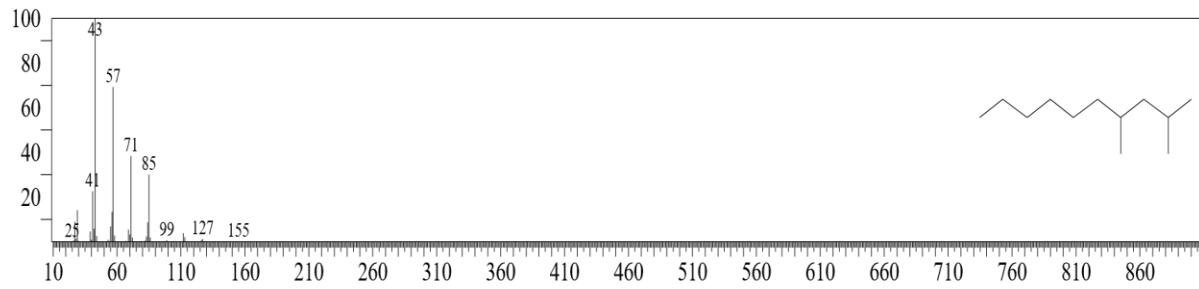
Anthracene



Naphthalene

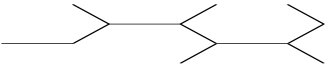


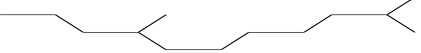

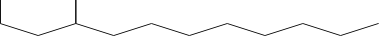
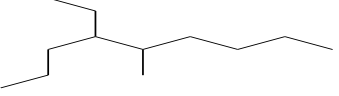
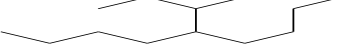
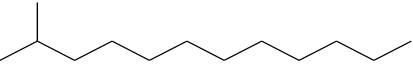
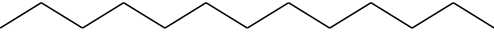
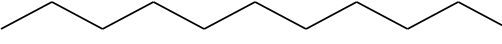
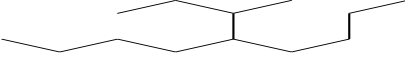
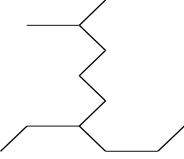
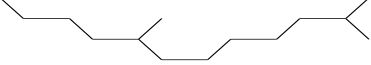




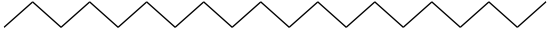
Aliphatic Hydrocarbons



Appendix II: Long chain hydrocarbon organic pollutants

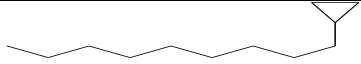
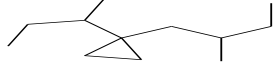
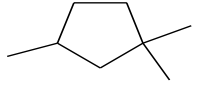
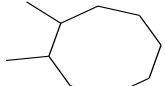
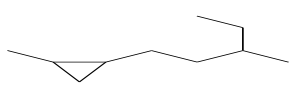
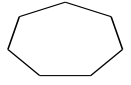

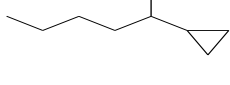
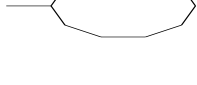
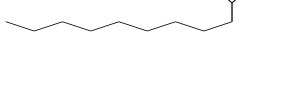
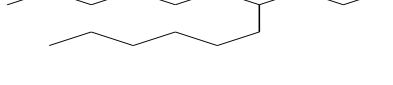
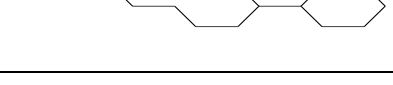
Borehole	Symbol	Organic pollutant	Molecular structure	Molar mass
KV1	I	n-tridecane		184.37
	Ii	n-undecane		156.31
	Iii	4,6-dimethylundecane		184.36
	Iv	3,7-dimethyldecane		170.33
	V	5-sec-butylnonane		184.37
	Vi	2,3-dimethyldecane		170.33
	Vii	5-butylnonane		184.36
	Viii	2,3,6,7-tetramethyloctane		170.33
KV2	Ix	Tridecane		184.37
	X	n-undecane		156.30
	Xi	2,4-dimethyldecane		170.34
	Xii	2,7-dimethylundecane		184.36
	Xiii	11-methyldodecane		216.36
	Xiv	7-butyldecosane		226.44

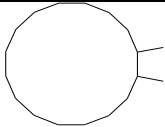
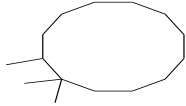
	Xv	3,5-methyldodecane		
	Xvi	3,4,5,6-tetramethyloctane		170.33
KV5	M	n-tridecane		184.37
	N	n-undecane		156.30
	O	2,8-dimethylundecane		184.22
	P	3,7-dimethyldecane		170.33
	Q	4-methyldodecane		184.36
	R	4-ethyl-5-methylnonane		170.33
	S	5-sec-butylnonane		184.37
	T	11-methyldodecane		216.36
KV13	A	n-tridecane		184.37
	B	n-undecane		156.30
	C	5-sec-butylnonane		184.37
	D	6-ethyl-2-methylnonane		170.33
	E	2,8-dimethyldodecane		226.44
	F	2,4-dimethyldecane		170.34

G	2,9-dimethylundecane		184.36
H	n-eicosane		182.55

Appendix III: Long chain cyclic hydrocarbon organic pollutants

Borehole	Pollutant symbol	Organic pollutant	Molecular structure
KV1	A	1,1,2-trimethylcyclododecane	
	B	1-isopropyl-1-methyl-2-nonylcyclopropane	
	C	1,1,3,3-tetramethylcyclopentane	
	D	1,2,2-trimethylbutylcyclohexane	
	E	1,2,4,5-tetraethylcyclohexane	
	F	5-cyclohexylundecane	
	G	5-cyclohexyltridecane	
	H	1,2,3-trimethylcyclohexane	
	I	n-nonylcyclopropane	
	J	1-methyl-2-(3-methyl)cyclopropane	
	K	1-methyl-2-octylcyclopropane	
	L	Methylcyclodecane	

KV2	M	n-nonylcyclopropane	
	N	1-sec-butyl-1-(2-methylbutyl)cyclopropane	
	O	1,1,3-trimethylcyclopentane	
	P	1,2-dimethylcyclooctane	
	Q	1-methyl-2-(3-methylpentyl)cyclopropane	
	R	Cycloheptane	
	S	1,1,2-trimethylcyclododecane	
	T	2-cyclopropylhexane	
	U	Methylcyclodecane	
	V	1-isopropyl-1-methyl-2-nonylcyclopropane	
	W	7-cyclohexyltridecane	
	X	3-cyclohexylundecane	
KV5	yl	3,5,5-trimethyl-1-cyclohexane	

y2	1,2-dimethylcyclohexadecane	
y3	1,1,2-trimethylcyclododecane	

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Organic contaminants in the groundwater of the Kerio Valley water basin, Baringo County, Kenya

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RESEARCH ARTICLE



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ABSTRACT

Currently, groundwater is largely becoming the main source of fresh water in most developing countries. However, various deleterious impacts resulting from anthropogenic activities beneath the earth's surface have significantly affected groundwater quality, as evidenced in several areas endowed with mineral and hydrocarbon deposits, agricultural activities, and industrial processes. The possible etiological impacts may include cancer and genetic aberrations which result from the toxic effects of organic waterborne contaminants ingested by humans and animals over time. The motivation behind this study was to identify and determine the concentration profiles of various organic pollutants in the wells located along the Kerio Valley water basin near the exploratory wells for hydrocarbons and mining activities. Therefore, this study is necessary in unraveling the level of organic contaminants in the sampled borehole water, which can then be extrapolated to cover other boreholes within the Kerio Valley basin. The study was carried out during the dry season of December 2022. The water samples from the boreholes were extracted using a solid phase extraction procedure and characterized using a gas chromatograph interfaced with a mass selective detector. The findings indicate that benzene derivatives which were mainly xylenes, 1,3,5-trimethylbenzene, 1-ethyl-3-methylbenzene, 1-methyl-2-propylpentylbenzene and polycyclic aromatic hydrocarbons such as naphthalene, phenanthrene, fluoranthene, azulene, and pyrene were found in most of the boreholes sampled. Furthermore, long-chain hydrocarbons were present in all groundwater samples with varying concentrations. The concentration of benzene derivatives ranged from 2.84 to 20.47 ppm. However, polycyclic hydrocarbons exhibited the highest concentrations of all organic pollutants, with pyrene giving a concentration of 23.14 ppm, fluoranthene (18.54 ppm), phenanthrene (14.13 ppm) and anthracene (11.06 ppm). According to the findings reported in this study, most of the borehole water in the Kerio Valley basin is contaminated and may be unsafe for drinking. Most of the reported concentration levels were several times higher than the standards of the U.S. Environmental and Protection Agency. However, it is necessary to develop a policy framework on the assessment and monitoring of water quality in the region and propose urgent measures to ensure a clean water supply for the benefit of residents.

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Appendix VI: Progress in Chemical and Biochemical Research Article

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Progress in Chemical and Biochemical
Research

Journal homepage: www.pcbiochemres.com



Original Research Article

Furan and Phenol-Based Contaminants in the Borehole Water Quality of the Kerio Valley Water Basin, Kenya



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ABSTRACT

Clean water supply and infrastructure is one of the greatest challenges of the 21st century as a result of persistent and emerging water pollutants. The purpose of this study was to determine the concentration profiles of furan and phenol-based contaminants in the boreholes located in the Kerio Valley water basin. The water samples from the boreholes were extracted using a solid phase extraction procedure and characterized by a gas chromatograph interfaced with a mass-selective detector. Based on the findings of this study, 3-methyl-2,3-dihydro-1-benzofuran was significantly present in all the borehole with a concentration of 9.390 ± 1.12 , 0.23 ± 0.02 , 0.213 ± 0.05 , and 0.070 ± 0.28 ppm in decreasing order of KV1, KV2, KV3, and KV4, respectively, alongside with 2-furanmethanol and 2-methyltetrahydro-2-furanol. The abbreviation KV denotes the sample was collected in Kerio Valley borehole. According to the findings of the present study, the majority of the borehole water in the Kerio Valley basin is contaminated and may not be safe for human consumption. To ensure that residents have access to clean water, it is necessary to develop a policy framework for the evaluation and monitoring of water quality in the area and to suggest immediate remediation action.



RESEARCH PAPER

OPEN ACCESS

Heavy Metal Analysis in the Ground Water of Kerio Valley Sub-Water Basin, Baringo County, Kenya

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Abstract

Water contamination in the Kerio valley basin has been attributed mainly to the mining activities along the valley, which include Fluorspar mining and exploration of hydrocarbons. Accordingly, the water environment in the region has come under extreme stress as a result of extensive mining industries and growing urbanization. This study focused on the contamination of borehole water by selected toxic heavy metals of environmental and public health concern. Considerably large volumes of wastewater from domestic, mining industries and municipal waste resulting from industrialization and urbanization are discharged into natural water bodies such as rivers and dams in this area, which ultimately seep into ground water systems. Groundwater samples were taken from boreholes near exploratory wells and several indicators of water quality were examined in groundwater samples which revealed very high concentrations of total dissolved solids, high electrical conductivity and relatively alkaline water. Eight heavy metals were analyzed in groundwater samples using atomic absorption spectroscopy (AAS). The analytical results show that the groundwater has unusual high concentrations of lead varying from 0.26 to 10.72 ppm, cadmium ranged from 0.22 to 0.29 ppm, chromium ranged from 0.09 to 0.37 ppm while manganese had high concentration in KV1 and KV8 borehole water samples posting 1.52 and 1.86 ppm respectively. The indiscriminate disposal of hazardous waste water from industrial and mining areas could be the primary source of groundwater contamination. A comparison of groundwater results with the World Health Organization (WHO) recommended levels show that the majority of borehole water sampling stations are significantly contaminated with heavy metals. Chromium, cadmium and lead have been found in borehole water samples. The main causes of contamination in this basin is industrial discharge, random disposal of hazardous waste water and the release of untreated municipal effluents into the soil, in addition to use of fertilizers in crop production.

Keywords: Kerio Valley; Groundwater; Heavy metals; Lead; Cadmium; Municipal waste

Introduction

Water contamination in the 21st century as a result of industrialization, mining activities and indiscriminate waste discharge into water bodies has reached unprecedented levels. These activities have compromised water quality, clean water supply, and infrastructure (Posselt et al., 2020). Accordingly, most governmental authorities have established agencies that are mandated to pass and enact severe regulations to managing wastewater discharge, sewage disposal and treatment, into rivers and aquatic water bodies. This feature allows heavy metals to stay in water and soil sediments for decades and is currently linked to cancer and other biological disorders (Ugochukwu et al., 2022). Moreover, heavy metals from anthropogenic sources discharged to water bodies are typically in particle or solution form, making them easily reactive and resulting in the formation of toxic organometallic compounds. Heavy metals exhibit bioaccumulation, bio-mobility and biohazardity causing serious etiological risks to biota and the general environment.

