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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, 1,3,5trimethylbenzene, 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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1. Introduction

Groundwater pollution can occur as a result of human activities such as hydraulic oil mining, agriculture, and mineral exploration, as well as natural processes such as vulcanicity [1]. Additionally, surface water conditions have a significant impact on groundwater quality and vice versa [2]. Therefore, it is essential to note that another source of groundwater contamination is surface water bodies that recharge the groundwater system. These include 'natural' recharge sources such as lakes and rivers, and 'man-made' recharge sources such as urban runoff infiltration, artificial recharge wells, and injection wells for hydrocarbon exploration, as is the case in the Kerio Valley water basin. Excess mineralization makes groundwater unsafe for animal and human consumption if not properly treated. In general, it is critical to consider the interaction of all sources and pathways of environmental pollution in the assessment and monitoring of ground water quality [3]. Stakeholders have made a sustained attempt to drill water wells in the Kerio Valley rift system, ostensibly to provide the communities that inhabit this region with clean and accessible water for drinking, laundry, and irrigation. For this reason, several boreholes have been sunk in the past decade [4]. However, the realization that the Kerio Valley geological system harbors significant hydrocarbon deposits has put into question the safety of the borehole water in the area. Interestingly, there have been no assessment and monitoring strategies conducted on the borehole water many years after drilling to ascertain its quality and safety.

Although about 70% of the earth is water, clean water is scarce mainly because of pollution-related problems and other anthropogenic activities including mining and agricultural

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ISSN 2153-2249 (Print) / ISSN 2153-2257 (Online) – Copyright © 2023 The Authors – Atlanta Publishing House LLC – Printed in the USA. This work is published and licensed by Atlanta Publishing House LLC – CC BY NC – Some Rights Reserved. https://dx.doi.org/10.5155/eurichem.14.3.337-347.2458 practices. For this reason, groundwater in the form of wells, springs, and rivers has become the most reliable source of water for most of the world's population [5]. Ground water can be defined as water located beneath the earth surface and is primarily formed through down seepage of surface water into hydrological subsurface systems [6]. 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 [7]. All these activities may lead to contamination of aquifer systems, which ultimately alters the quality of water available for human use and agricultural practices [1]. Xylenes (benzene derivatives) play an important role in the extraction of oil and natural gas as excellent emulsion breakers [8].

The Kerio Valley basin in the Kenyan Rift system receives moderate rainfall annually, although most of this rain water drains into rivers and lakes in the region through surface runoff and feeder streams. Consequently, the boreholes in the Kerio Valley basin are the main sources of water for domestic and agricultural activities. The safety of these underground water bodies has not been evaluated before despite concerns of suspected pollution from mining activities, and currently exploratory wells being undertaken in the area in search of hydrocarbons. The suitability of groundwater for use depends mainly on the amount and concentration of constituent minerals in the water, which can be altered by natural or anthropogenic activities [9]. 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 [10]. This technology uses several toxic chemicals throughout the drilling process, which may result in contamination of groundwater [11]. Therefore, the possibility of finding organic compounds in the aquifer system is significantly high. In this process, approximately 91% of the chemicals used during extraction remain beneath the surface of the ground and are transported by aquifer systems to nearby wells, boreholes, and springs by hydraulic gradient [12]. In addition, the waste water recovered from the hydraulic fracturing process ends up mixing with ground water, causing serious contamination and thus altering the quality of the water. In most cases, waste water is stored in open pits that can easily leach organic chemicals and heavy metals into groundwater. Additionally, poor treatment and disposal of waste water may lead to organic contamination of nearby water bodies, such as rivers and streams. Furthermore, chemical spills during transport and poor handling can result in water contamination through runoff or leaching of waste rich in organic contaminants [13].

The oil exploration and mining activity in the study region is suspected to be the leading source of contamination, probably due to leaching, surface runoff of waste water, chemical spillage, and poor waste-water disposal mechanisms. Chemicals used in the oil drilling and exploration process include xylene, benzene, formaldehyde, 2-butoxyethanol (2-BE), naphthalene, and ethylbenzene [14]. These chemicals are a potential source of toxicity and may alter the chemical composition and quality of groundwater [15]. 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 [16]. Consequently, the disturbance caused by the fracturing process leads to the mixing of naturally occurring trace metals and organic substances with groundwater. Approximately 91% of the chemicals used during oil extraction are retained subsurface, hence contaminating groundwater [17]. Consequently, geological processes within the ground intensify the extent to which the water table is contaminated. On the other hand, the toxicity and mutagenic characteristics of trace metals are increased through technogenic activities that occur in mining sites. For example, during poor disposal or discharge of waste water, leaching and flocculation may occur, thus affecting underground water through underground seepage along fracturing channels [18].

The current chemical mode of farming, the spontaneous growth of industries and the increase in urbanization are precursors of the serious accumulation of organic contaminants in ground and surface water, which have increased significantly in recent years [19]. Despite the fact that aquitards control the contamination of groundwater [20], the hydraulic fracturing employed by oil exploration and other mining activities in the Kerio Valley region breaks underground hydro systems and thus permits the entry of chemical contaminants into groundwater [21]. The levels of organic contaminants in selected borehole water in the Kerio Valley water basin will inform policy and public health authorities on the safety of water drawn from the boreholes.

This study focuses on evaluating the hazardous organic contaminants that compromise water quality in the Kerio Valley water basin. Of significant importance are polycyclic aromatic hydrocarbons, which are well-established toxins and precursors to cancer in water systems. The detection of the most reactive polycyclic aromatic hydrocarbons (PAHs) including 2,3-dihydrofluoranthene, fluoranthene, and azulene at remarkably high concentrations in most of the sampled boreholes is a clear indication that the Kerio Valley groundwater system is not safe for both domestic and commercial applications. However, periodic water quality monitoring of the Kerio Valley water regime is very essential in order to inform both environmental and public health concerns on water quality.

2. Experimental

2.1. Reagents

The reagents used in this study were of analytical grade (purity \ge 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 1).

2.2. Sample collection

Groundwater samples were collected in duplicate from four sampling points, namely; KV1, KV2, KV3, and KV4 (Figure 1) using 2-L sterilized aluminum containers. Samples were collected during the dry season of December 2022. 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 [22]. 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) [23].

2.3. Sample treatment

The sample was filtered using filter paper to remove debris. 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. Approximately 500 mL of water from each sampling point was filtered using Whatman no 2 filter paper and cleaned using a C18 cartridge.



Figure 1. A map of the Kerio Valley basin showing borehole sampling sites.

The extraction process was carried out for 24 h, after which the extract was filtered and cleaned using a solid phase extraction technique. The extracts were preconcentrated with a rotor vapor 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 [23,24]. 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 aqueous phase was drawn and discarded, while the organic phase was preconcentrated to about 10 mL using a rotor evaporator. The same procedure was applied to all water samples in the extraction of organics. The extract was characterized using Gas chromatograph-mass spectrometry.

2.4. GC/MS characterization of organic pollutants

Samples collected from groundwater in the Kerio Valley boreholes were passed through 10 mL dichloromethane solution (DCM), filtered using a filter paper (Whatman no. 10) and characterized using Agilent 6890 Gas chromatograph hyphenated with an Agilent mass selective detector (MSD) 5890 series following the method developed by [25]. About 1 uL of the filtered sample was injected into a GC column (DB-5MS, 30 m \times 250 um \times 0.5 μ m). The temperature of the injector port was set at 200 °C to allow the transformation of organic species into the gas phase prior to MS analysis. The temperature programming was applied at a heating rate of 15 °C for 10 minutes, holding for 3 minutes at 200 °C, followed by a heating rate of 20 °C for 5 minutes, and holding for 10 minutes at 300 °C. An 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 incurporated into Agilent's MSD Chemstation [22]. 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.

2.5. 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 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 1.

3. Results and discussion

Because groundwater is a major source of drinking water in the Kerio Valley and many regions in Kenya, a thorough assessment of the possible influences of oil drilling fluids on groundwater and drinking water quality is a major concern. Groundwater needs protection as a natural water body. In Kenya, locals mainly use groundwater with limited groundwater contamination evaluation reports based on the United States Environmental and Protection Agency (US EPA) limit values for safe drinking water. From the results obtained from this study, benzene derivatives including xylenes and PAHs such as naphthalene, anthracene, chrysene, fluoranthene, and pyrene were identified in most of the borehole samples. Moreover, long-chain hydrocarbons and cyclohydrocarbons were also identified in all sampled boreholes. Other identified organic pollutants were benzo[a]azulene, 1H-indene, phenanthrene, and 2,3-dihydrofluoranthene. It can be seen that benzene derivatives were dominant in all samples except the case of KV2. Table 1 summarizes some of the major organic pollutants identified in the Kerio Valley borehole water.

3.1. Benzene derivatives in the Kerio Valley borehole water

Numerous specific organic chemicals are used during hydraulic fracturing activities [26]. A comprehensive study was conducted in northwest China to candidly clarify whether these compounds can enter shallow groundwater aquifers and negatively affect local water quality after injection into deep shale horizons in search of hydrocarbons [27].

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

Table 1. Major organic contaminants were found in the Kerio Valle boreholes.

Table 2. Distribution and concentration of benzene derivatives in 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 [28]
	1-Ethyl-3-methylbenzene	7.32	20.47±1.53	0.7 [29]
	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 [28]
	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	-

During the extraction of hydrocarbons, a mixture of diethylbenzene and ethylxylene is usually used because it is a suitable solvent mixture and a constituent of gasoline. These compounds are preferred because they are resolved into fractions in a mixture of crude oil extracts. As reported in Table 2, 1,3,5-trimethylbenzene, 1-ethyl-3-methylbenzene, 1,3-di ethylbenzene, 1-ethyl-3,5-dimethylbenzene, 1-methyl-2-propyl pentylbenzene were present in KV1. KV2 contained 1-(dode cycloxy)-2-nitrobenzene among other contaminants, while 1,3,5-trimethylbenzene, 1,2,4,5-tetramethylbenzene, and 1-ethyl-3,5-dimethylbenzene and 1-ethyl-3,5-dimethylbenzene were present in the KV3 sample. 1,2,4,5-tetramethylbenzene were present in KV4.

The most prevalent among benzene derivatives is 1-ethyl-3,5-dimethylbenzene. According to Table 2, 1-ethyl-3,5-di methylbenzene had a concentration of 2.84, 9.85, and 8.4 ppm for all samples analyzed of KV1, KV3, and KV4, respectively. Evidently, KV3 had the highest concentration, followed by KV4 and finally KV1, which had a concentration four times lower than that of KV3. The presence of 1-ethyl-3,5-dimethylbenzene in the study area confirms that it is adversely being used by the hydrocarbon exploration companies, and KV3 being nearer to the drilling point recorded the highest concentration. Furthermore, KV4 may receive drilling effluent due to poorly managed waste water from various drilling points, and this can increase their concentration of organic contaminants 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 [30].

3.2. Polycyclic aromatic hydrocarbon contaminants in the borehole water

Polycyclic aromatic hydrocarbons (PAHs) are a group of more than 100 different chemicals that are released from burning coal, oil, gasoline, trash, tobacco, wood, or other organic substances, such as charcoal-broiled meat [31]. PAHs are known to occur naturally in crude oil and smoke and ash

from forest fires and are often found as products of incomplete combustion, especially in incinerators [32]. Naphthalene was the dominant organic pollutant in the KV1 water sample with a concentration of 5.00 ppm. Naphthalene is a common environmental contaminant found in urban air, soil, and water, and can also be produced by certain industrial processes such as the manufacture of dyestuffs and explosives, which in this case is suspected to originate from mining sites in the Kerio Valley region [33]. The toxicity and effects of naphthalene on human health are of concern due to its potential for widespread exposure [34]. KV4 borehole water, which is a major source for both irrigation and domestic use, is highly contaminated with pyrene, fluoranthene, phenanthrene, anthracene, 8,9-dihydrofluoranthene, and benzo(a)azulene, as can be deduced from Table 3. The health effects of these PAHs on humans have been observed to depend on the level and duration of exposure, as well as individual factors such as age, sex, and preexisting health conditions [35]. The findings revealed varying concentrations of various PAHs, with pyrene, fluoranthene, and phenanthrene exhibiting the highest concentrations above the allowable limits of US EPA in KV4. However, the KV1 results posted a significantly lower concentration of azulene, naphthalene, 1-methyl-1H-indene, 1H-indene, and chrysene in decreasing order of concentration (Table 3). The findings imply that KV1 and KV4 were mainly contaminated with a significant concentration of PAHs, some of which have been implicated in serious biological risks. The detection of cyclopenta-fused PAHs (fluoranthene, benzo(a)azulene, and azulene) is an indication of toxicity in water since these compounds are more bioactive than other PAHs without cyclopentafused rings [36]. For example, azulene and its derivatives were found to be present in KV1 and KV4 borehole water samples. This compound is predicted to block both the Na⁺ and Ca²⁺ channels expressed in cardiac and vascular smooth muscles [37]. In particular, anthracene was detected in the KV4 borehole water sample at significant concentrations as reported in Table 3.

In many cases, PAHs have been identified in groundwater near various mining sites due to poorly managed waste effluence that may mix with water bodies and are associated with negative health impacts, although their varied concentrations are of considerable interest [43].

Borehole	Organic pollutant	Retention time (min)	Concentration (ppm)	US EPA limits (ppm) 0.02 [38]	
KV1	Naphthalene	11.71	5.00±0.85		
	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 [39]	
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 [40]	
	8,9-Dihydrofluoranthene	31.90	11.06±0.98	-	
	Pyrene	30.96	23.14±2.05	0.05 [41]	
	Fluoranthene	32.50	18.54±1.89	0.04 [42]	



Figure 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).

Many PAHs have been classified in the same group of carcinogens; however, not all PAHs have the same toxicity in humans. In particular, the structure and substituent groups present in PAHs determine their etiological risks. Based on the US EPA limits, it is evident from Table 3 that most PAHs were above the permissible limits. These included chrysene in the KV1 borehole, which was nearly 3000 times above the US EPA's allowed limits for drinking water, and anthracene in KV4, which was ~20 times higher than the allowed limit. Other PAHs that were above the US EPA limits were pyrene and fluoranthene that were approximately 463 and 265 times, respectively. The sample chromatogram showing the main PAHs of interest identified in the Kerio Valley borehole water is presented in Figure 2.

Table 2 Distribution and concentration of DAHs in selected hereboles

Pyrene is a natural component of coal tar, gasoline, pesticides, and asphalt [44]. From the reported data, it is clear that the concentration of pyrene in the KV4 water borehole was significantly (23.14 ppm) in contrast to 50 ppb in drinking water according to US EPA allowed limits [45]. According to studies in the literature, pyrene is toxic to aquatic organisms at concentrations lower than the reported values in surface water [46]. Pyrene has the ability to damage cell DNA and affects endocrine activity [47]. Another PAH detected is fluoranthene in KV4, recording a concentration of 18.54 ppm, which is above the US EPA allowed limit [48]. From previous studies carried out in the St. Louis Park aquifer considered to be contaminated by coal tar, it was found that fluoranthene concentration increased as mining progressed, confirming the high concentration of fluoranthene due to the continued mining activities that take place in the area [49]. The potential for pyrene and fluoranthene to accumulate in aquatic sediments is of great concern, which could pose a risk to organisms living in the bottom of lakes and rivers. Furthermore, naphthalene was found in the water sample obtained from KV1 with a concentration of 5.00 ppm. Although the results obtained are higher than the US EPA limits and it bioaccumulates in the human body, which eventually may result in negative health impacts. The results recorded in Tables 2 and 3 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 0.54, 2.32, and 4.38 ppm, respectively, for KV1 in addition to dibenzyl(diethyl)stannane, whose concentration in KV2 is 0.55 ppm. These concentrations are of great concern due to their toxic nature and have been widely associated with cancer. Anthracene constituted a higher concentration of 12.72 ppm and is well known to cause a number of health problems for humans.

3.3. 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. For the case of KV2 and KV3, it was realized that they had nearly equal peak area of about 265081 volts-min. Tridecane is an essential component of oil and may have entered groundwater during the hydraulic fracturing process or drilling processes, or any other anthropogenic activities taking place in the area [50]. Undecane and tetradecane were the other organic compounds determined in all water samples. KV1 was found to have the highest peak intensities for undecane and tetradecane and was predictably the highest concentration. The concentration of undecane and tetradecane increased in the KV2, KV3, and KV4 boreholes correspondingly. It should be noted that undecane occurs naturally in sedimentary rocks and forms a major portion of oil and as a result of anthropogenic activities such as mining and can enter groundwater systems [51]. The dimethylundecane isomers were also another organic that was prevalent in all water samples. KV3 had the highest peak intensity and therefore the most dominant suspected organic pollutant, while KV2 recorded the lowest concentration among all the boreholes considered in this work. Clearly, the KV3 borehole showed that the concentration of dimethylundecane was 5 times and 1.5

Borehole	Symbol	Organic pollutant	Retention time (min)	Peak intensity (a.u.)
KV1	i	n-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
	х	<i>n</i> -Undecane	8.42	265081
	xi	2,4-Dimethyldecane	9.35	89831
	xii	2,7-Dimethylundecane	9.68	89831
	xiii	11-Methyldodecane	12.10	265081
	xiv	7-Butyldocosane	14.43	368337
	XV	3,5-Methydodecane	12.47	265081
	xvi	3,4,5,6-Tetramethyloctane	9.35	89831
KV3	m	n-Tridecane	8.65	220853
	n	<i>n</i> -Undecane	8.42	500084
	0	2,8-Dimethylundecane	8.55	500084
	р	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	а	<i>n</i> -Tridecane	8.65	478437
	b	<i>n</i> -Undecane	8.42	478437
	с	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	n Figogono	10.65	115272

Table 4. Legend for Figure 2 on long chain hydrocarbon pollutants.





Figure 3. Long chain hydrocarbon distribution in (a) KV1, (b) KV2, (c) KV3, and (d) KV4 boreholes.

times those reported in KV2 and KV1, respectively. Their presence in borehole water may be a potential hazard to human because it has been known to be a tumor promoter even at low concentrations [52]. The peak intensities for the long-chain hydrocarbons determined from this study are reported in Figure 3 and Table 4.

Dimethyldecane isomers were observed in samples collected from the KV4 borehole and were shown to have the highest concentration. The relative concentration of dimethyldecane in KV4 was approximately 5 times that in KV2 and approximately 1.5 times that found in KV1 and KV3. Other organic compounds identified were 5-sec-butylnonane and 4-

ethyl-5-methylnonane. Both of these compounds were not identified in KV2. 5-Sec-butylnonane was found to have the least peak intensity, making its concentration three times lower than that of KV1 and KV3. Furthermore, in KV4, 4-ethyl-5methylnonane had the highest peak intensity of approximately 1.5 times that exhibited in the KV1 borehole. Most of the aliphatic hydrocarbons realized in this study may originate from crude oil found in the Kerio Valley and may have accidentally entered the groundwater system during various anthropogenic activities in the region.



Figure 4. Relative concentration profiles of cyclic hydrocarbons in the KV1, KV2 and KV3 boreholes.

In this study, the peak intensity of a particular suspected organic pollutant on the gas chromatograph is the major determinant of the number of compounds present in a sample, since it is directly proportional to the actual concentration of the compound. In this regard, the areas of the peaks obtained in each compound were compared to represent the concentration. There are several hundreds of hydrocarbon compounds in all water samples analyzed, ranging from KV1, KV2, KV3 to KV4, possibly due to the existence of a hydrocarbon subsurface 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) [53]. Total petroleum hydrocarbons are used to describe the mixtures of organic compounds found in crude oil that have the potential to be the most toxic and can contaminate groundwater and make them unsuitable for use in homes and other commercial purposes, including irrigation [54]. Figure 4 shows the variation in the

peak intensities for the cyclic hydrocarbons identified in the boreholes under study.

Only KV4 registered one cyclic hydrocarbon, ((1-ethyl propyl)cyclohexane), which implies that this borehole is less contaminated with potential risk cyclic hydrocarbons compared to boreholes KV1, KV2 and KV3. Investigations on cycloaliphatic hydrocarbons using GC/MS clearly showed that *n*-cyclohexane was present in all water samples at different concentration levels. For example, KV3 was approximately 15 times that of KV4 and 2 times that reported in KV1. Since ncyclohexane is a nonpolar compound used in various industries, it can be confirmed that mining companies in the Kerio Valley region may have used this solvent during the exploration of hydrocarbon hydraulic fracturing, which may have led to the leaching of waste water and runoff to aquitards. It is possible that the KV3 borehole is closer to the mining exploration area and thus receives a significant amount of this compound during the fracturing process.

Cyclic dodecane was obtained in all samples analyzed in the KV1, KV2, and KV3 boreholes with varied concentrations, except in KV4, where its presence was not detected. For example, the relative concentration of cyclic dodecane in KV1 is approximately 4 times that of KV2 and about 10 times that of KV3. From previous research done by Fu et al., 2022, various companies apply cyclic dodecane in search of hydrocarbons as a solution to nonpolar organic compounds, stabilizers, temporary sealants, and more so as a water repellant, thus easing the transport and protection of solutes on deeper aqueous surfaces during the extraction of hydrocarbons [55]. These findings are in total agreement that cyclic dodecane is being applied during mining in the Kerio Valley in search of hydrocarbons despite its persistent and potential to bioaccumulate in the environment, which may cause serious environmental and public health problems.

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

Petroleum plays an important role in modern society as a major source of fuel and raw materials for various manufacturing industries, including pharmaceutical industries. It is the main energy source for the heating, transportation, and manufacturing industries, in addition to being a raw material for plastic and synthetic rubber [56]. Most products containing total petroleum hydrocarbons (TPHs) can be easily burnt. Being a major component of oil, natural gas, and pesticides, hydrocarbons have enormously contributed to the greenhouse effect and climate change, depleted ozone, reduced the photosynthetic ability of plants, and increased the occurrence of cancer and respiratory disorders in humans. These organic contaminants cause serious damage to the environment through oil spills, which is the most important cause of environmental degradation, aquatic toxicology, and water poisoning. Once released into the aquatic environment, certain petroleum hydrocarbon fractions exhibit high toxicity and have been associated with the induction of serious health problems in humans, including cancer [49]. For saturated hydrocarbons, the chain length is highly correlated with direct toxicity. Fractions of lower molecular weight structures have been shown to be more toxic due to their high bioavailability in the environment [57].

However, the larger saturated-chain hydrocarbons have an increased mutagenic potential. The toxicity of unsaturated hydrocarbon structures is not as predictable and may be influenced by reactive functional groups, the solubility of water and the membrane, the viscosity and interactions of these compounds with the membrane and with the constituents of the membrane [58]. When TPH is released into the environment through wastewater discharge, accidents, industrial releases, oil spills, or leaks, and enters when it into the soil, it moves from the soil to the groundwater and some microorganisms may break them down into smaller fractions such as aldehydes, ketones, ethers and esters while some may evaporate into the atmosphere [59]. All of these contaminants will eventually percolate into boreholes, as well as surface water, including rivers and lakes. However, others may remain in the soil for longer periods of time and will ultimately be broken down by other organisms found in the soil to more toxic organics, thus causing a hazardous health effect [60]. Drinking water containing petroleum hydrocarbons can cause stomach upset, stomach cramps, nausea, vomiting, and diarrhea [61]. It may also cause throat and mouth irritation. However, if it enters the lungs, it can cause pneumonia-like conditions in addition to permanent lung damage and, eventually, cardiac arrest [62]. Some hydrocarbons can cause other health effects, such as coma, seizures, irregular heart rhythms, or damage to the kidneys or liver [63]. PAHs are often found in facilities that were previously involved in creosote coking and wood preservative

production sites, as well as in former manufactured gas plants that used coal as feedstock [64].

Most regulatory bodies analyze PAHs such as anthracene, benz(a)anthracene, dibenz(a,h)anthracene, fluoranthene, naphthalene, phenanthrene, and pyrene, since exposure to these PAHs is linked to lung, liver, and skin cancers [34]. Phenanthrene has been classified as a Group 3 carcinogen by the IARC, implying that it has limited evidence of carcinogenicity in humans [65]. However, animal studies have shown that exposure to phenanthrene can cause tumors in various organs, including the lungs, liver, and skin [66]. Long-term exposure to phenanthrene can increase the risk of cancer in humans, particularly in individuals with high levels of exposure.

Studies have shown that an azulene-based synthetic drug has beneficial cardiovascular effects and may be helpful in the treatment of arrhythmias and relaxation of venous tissues, thus improving circulation [67]. Multiple ion channel blocking effects of these azulene-based drugs are considered to be largely responsible for antiarrhythmic and vasorelaxant actions [68]. Azulene extracts used in skin creams to reduce puffiness and wrinkles on the skin have also gained popularity in the health industry. However, studies have shown that azulene can be photoreactive after irradiation with ultraviolet (UV) and visible light, causing a mutagenic compound that may cause more harm to life if it enters the human biological system [69].

Anthracene and its derivatives are known to be toxic to humans and the environment, and exposure to anthracene has been linked to a variety of health problems [70]. Anthracene is a carcinogen and mutagen that has been shown to cause tumors in animals. It is toxic to the kidneys, causing damage and even kidney failure in severe cases [61]. This is because anthracene can accumulate in the kidneys and cause oxidative stress, leading to cell injury and aberrations [71]. In addition to these deleterious risks, anthracene can cause neurological problems such as headache, dizziness, and confusion [72]. Continuous exposure to anthracene can cause reproductive problems, such as infertility and miscarriage [61]. This is because anthracene can interfere with hormone production and cause DNA damage in reproductive cells [73].

Naphthalene is in most cases used to make dyes, explosives, toilet deodorants, insecticides, lubricants, PVC piping, and is a potential part of the chemical suite used in natural gas development [74]. Although naphthalene can dissolve to some extent in water, it is mixed with water during hydraulic fracturing of oil to act not only as a biocide but also weakly attached to soil particles [75]. Moreover, it occurs naturally in crude oil and coal tar and can be found in diesel fuel, jet fuel, gasoline, kerosene, gasoline station waste water, and lubricating oils [48]. This may be the genesis of naphthalene in groundwater. If ingested, naphthalene may cause liver and kidney damage and may cause methemoglobinemia, bluish discoloration of the skin, convulsions and death, severe digestive tract irritation with abdominal pain, nausea, vomiting, diarrhea, and anemia and other blood abnormalities [76].

4. Conclusions

This study has shown that Kerio Valley water boreholes are significantly contaminated with organic pollutants. Although some boreholes were sampled, it is possible to extrapolate that most of the borehole water in this region is contaminated by organic pollutants and may not be suitable for human consumption, in addition to being unsafe for irrigation purposes. Interestingly, in the KV1 borehole, phenanthrene and azulene had significantly higher concentrations than other PAHs, reporting 5.00 and 7.20 ppm, respectively. However, KV4 showed high concentration profiles of pyrene, fluoranthene, and phenanthrene at 23.14, 18.54 and 14.14 ppm, respectively. From these findings, the KV4 borehole is by far the most polluted of all the boreholes investigated in this work. In contrast, KV2 and KV3 were less polluted. It is also noted that all of the boreholes investigated exhibited a high level 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 nundecane, while 7-butyldocosane was dominant in KV3. Regarding cyclic hydrocarbons, n-nonyl cyclopropane had the highest concentration profile in KV1, while 3-cyclohexylundecane was prevalent in KV2. Remarkably, long-chain and cyclic hydrocarbons were by far the most dominant organics in all of the boreholes sampled. When assessing the human and environmental impact, it is often not practically possible to estimate the damages contributed to the existing exposure. Significant consideration must be given to the impacts of possible water pollution during hydrocarbon exploration and any other mining activities. It is paramount to adapted monitoring strategies and procedures for ground and surface waters as well as ambient air by health authorities. Studies in groundwater have shown significant associations between leachates from hydraulic fracturing processes and observed health effects. Since human exposure is largely described in epidemiological studies using various distance measures as a surrogate, the challenge for future studies will be not only to use measured concentrations of pollutants but also to use the kinetics 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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Conflict of interest: The authors declare that they have no conflict of interest. Ethical approval: All ethical guidelines have been adhered to. Sample availability: Samples of the compounds are available from the

corresponding author. Data availability: Data associated with the findings of this study are available

from the corresponding author upon reasonable request.

CRediT authorship contribution statement GR

Conceptualization: Joshua Kiprotich Kibet; Methodology: Joshua Kiprotich Kibet, Festus Kipkemoi Langat; Software: Joshua Kiprotich Kibet; Validation: Francic Inyangala Okanga, John Onyango Adongo, Joshua Kiprotich Kibet; Formal Analysis: Festus Kipkemoi Langat, Joshua Kiprotich Kibet, Francis Inyangala Okanga; Investigation: Festus Kipkemoi Langat, John Onyango Adongo; Resources: Joshua Kiprotich Kibet, Francis Inyangala Okanga; Data Curation: John Onyango Adongo, Johua Kiprotich Kibet; Writing - Original Draft: Festus Kipkemoi Langat; Writing - Review and Editing: Joshua Kiprotich Kibet, John Onyango Adongo; Visualization: Francis Inyangala Okanga, Joshua Kiprotich Kibet; Supervision: Joshua Kiprotich Kibet; Supervision: Joshua Kiprotich Kibet; Francis Inyangala Okanga, Joshua Kiprotich Kibet; Supervision: Joshua Kiprotich Kibet, Francis Inyangala Okanga, Okanga, Project Administration: Joshua Kiprotich Kibet, Francis Inyangala Okanga.

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