



RESEARCH PAPER

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# 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 21<sup>st</sup> 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.



Furthermore, most heavy metals are known to exist in a variety of oxidation states, which influence their bioactivity and biotoxicity (Engwa et al., 2019; Riaz et al., 2023; Kaur et al., 2023).

Groundwater and soil contamination with heavy metals as a result of fast industrialization and urbanization have attracted a lot of attention in the study of water quality in the recent times (Pandiarajan et al., 2023). Ground water (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 sought-after 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; Hassan and Mohammed, 2023). However, the rate at which various anthropogenic and natural activities are currently contaminating the groundwater resource has equally raised serious concerns. The environment and public health 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; the extent of chemical farming, mining activities and industrial waste discharge. Toxic metals may bio-accumulate in plants and animals before finding their way up the food chain (Akhtar et al., 2021).

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 biological functioning, but the concentrations at which they are received in soil, water, or food by either plants or animals, and humans, are not necessarily within the WHO safe limits. Nevertheless, 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 forms. Increased supply of these elements, on the other hand, will cause toxicity in plants, microorganisms, and including higher order animals such as man (Fraga, 2005). Some of the detrimental heavy metals include Pb, Cr and Cd, which are especially toxic to higher order animals due to Zn inhibition in enzymes and subsequent bio-accumulation in bodily tissues (Perić-Mataruga et al., 2017). As a result of human activities 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 systems. The bioavailability and extent of a metal's biohazardity of oxidation state must be determined regardless of whether a metal 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).

Clay-derived sediments in particular are effective at adsorbing and holding onto heavy metals over extended periods of time (Van Poucke et al., 2020). However, when soil is physically disturbed during drilling and when the pH of water changes, sediments emerge to be a source of heavy metals, thus 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 practices during crop production (Sandeep et al., 2019). This chiefly happens when polluted land is watered or when groundwater is used for agricultural purposes. The initial standard for determining the presence of heavy metal pollutants in the environment was to evaluate the salinity of the soil or ground water (Adimalla, 2021). Data for statistical analysis are generated from the findings of ground water chemical investigation (Islam et al., 2021). Heavy metal analysis in ground water and soil sediment determines the extent 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 etiological health problems and illnesses in humans, including cholera, diarrhea, dysentery, typhoid, polio, guinea worm, and skin infections (Syafudin et al., 2021). Numerous researches have highlighted the need to improve management conditions that would support drinking water quality improvement. The primary purpose of this study is to investigate the quality of ground water in the Kerio Valley basin, which is the primary source of drinking and agricultural

water for the Baringo. The discovery of oil deposits in the Kerio Valley prompted oil explorers to drill wells in search of hydrocarbons. The residents of Baringo County have relied heavily on borehole water systems for many decades. Therefore, 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).

### Experimental Reagent

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 collected from eight boreholes, namely; KV1, KV2, KV3, KV4, KV6, KV7, KV8, and KV9, along the Kerio Valley water basin and used without further treatment.

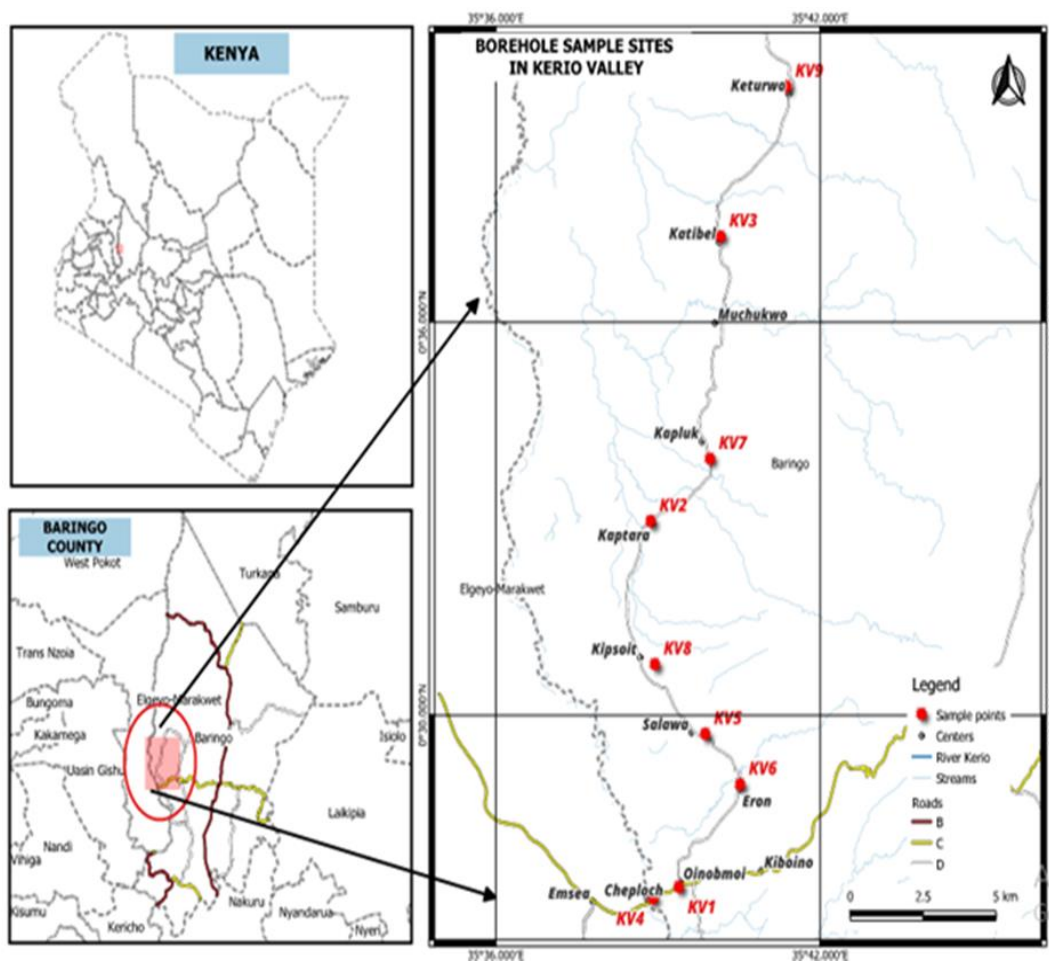


Fig 1. A map of Kerio Valley showing borehole water sampling sites

### Sample collection

The water samples were collected during the dry season from eight sampling points in three replicates using 1 L sterilized plastic containers and filtered using Whatman filter paper number 4 and acidified with nitric acid in order to maintain the pH of the samples to within less than 2 for heavy metal analysis. The major water quality parameters were determined in situ using a portable multi-parameter meter, Temp/pH/TDS/EC meter (model MI 1399) and included temperature, pH, electrical conductivity, and total dissolved solids. Sampling points were located using a global information system (GIS) model Wacos Intuos Pro.

### Sample treatment

100 mL of water sample were measured and poured into a 500 mL beaker. 2 drops of concentrated nitric acid were then added to the sample using a teat pipette. A 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 2 hours and refluxed before cooling for 30 minutes. 10 mL of the solution were measured and poured into a 100 mL flat bottomed flask. The solution was then be made to the mark with distilled water.

### **The study area**

Kerio Valley is located in the Rift valley Western segment part of Baringo County in in the Kenyan Rift Valley system. Baringo County is one of the 47 counties in Kenya and is considered an Arid County which suffers scarcity of water and basic resources required to better living standards. Kerio valley lies between 35°20'E and 00°10'N and covers an area of ~ 50 Km<sup>2</sup>. The source of drinking water in the county is largely borehole water and river water suspected to contain a range of micro-ionic species and hydrocarbons. 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 systems. Fig. 1 presents a map of the study area.

### **Heavy metal analysis**

The groundwater samples that were typical of the residential, commercial, and industrial areas were chosen for heavy metal analysis. Analytical graded concentrated HNO<sub>3</sub> was used to digest groundwater samples for 30 minutes while AAS was used to determine the concentrations of heavy metals and major cations in water samples. Aliquots 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 use in calibration of the atomic absorption spectrophotometer. The concentration levels of Cd, Cr, Pb, Mn, and Co in the worked- up samples were then profiled using AAS.

### **Results and discussion**

Table 1 presents the physico-chemical parameters from nine sampling locations along the Kerio Valley water basin. The pH ranged from 7.88 and 9.74. The pH obtained from 3 boreholes; KV<sub>4</sub>, KV<sub>7</sub>, and KV<sub>9</sub> were 9.51, 8.58, and 9.74, respectively, which were noted to be higher than that recommended by the WHO for irrigation and drinking – 6.5-8.5 pH units.

**Table 1:** Physico-chemical water quality parameters of borehole water of the Kerio Valley water basin

Borehole	Temp. (°C)	pH	Electrical Conductivity (µS)	TDS (mg/L)
KV <sub>1</sub>	22.4±0.2	8.2± 0.3	320±5	156±2
KV <sub>2</sub>	22.6±0.3	8.03±0.2	271±4	136±2
KV <sub>3</sub>	25.8±0.2	8.34±0.3	371±7	185±3
KV <sub>4</sub>	26.3±0.3	9.51±0.4	188±2	93±2
KV <sub>6</sub>	26.4±0.2	8.50±0.3	102±2	51±2
KV <sub>7</sub>	26.4±0.4	8.58±0.3	102±2	51±1
KV <sub>8</sub>	27.2±0.3	8.50±0.3	375±5	187±2
KV <sub>9</sub>	34.7±0.6	9.74±0.5	118±3	59±2
WHO	15.0	6.5- 8.0	1500	1000

The temperatures were measured and found to range between 22.4 and 34.7 °C and thus were above the recommended temperature of 15°C which reportedly encourages the growth of undesirable organisms and could exacerbate corrosion problems, taste, odor, and colour. Water that is between 4.4 and 18.3 °C is commonly preferred by domestic animals (Chebet et al., 2020). 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 and should not exceed WHO limit of 1500  $\mu$ S.

**Table 2.** Heavy metal concentration in selected borehole water

Heavy metal	Concentration in parts per million (ppm)								
	KV1	KV2	KV3	KV4	KV6	KV7	KV8	KV9	WHO
Cr	0.17	0.21	0.18	Nd	0.09	0.13	0.14	0.37	0.05
Pb	0.40	0.63	10.72	0.67	0.28	0.53	0.26	0.49	0.3
Mn	1.52	0.93	0.41	0.98	0.03	0.06	1.86	0.47	1.3
Cd	0.25	0.26	0.29	0.22	0.28	0.27	0.26	0.29	0.003
Co	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	

Nd – Not detected

Chromium concentrations in the water ranged from 0.09 to 0.37 ppm with KV9 having the highest concentration as reported in Table 2. Chromium concentration in all groundwater samples tested was found to be above the WHO recommended limit of 0.05 ppm in drinking water (Sharma et al., 2012). In most cases chromium compounds are utilized in various industrial operations despite their environmental risks and hence get into water bodies when waste water is discharged as effluent (Mishra et al., 2019). The chromium hexavalent form is known to be more mobile in the soil environment than the trivalent form and is not only toxic but also a precursor for cancer and other serious ailments (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 may damage the liver and kidneys in high concentrations, although chromate dust is a well-known carcinogen (Monga et al., 2022).

Lead levels in borehole water samples varied from 0.26 to 10.72 ppm as shown in in Table 2. The amount of lead in the groundwater samples KV6 and KV8 is within the WHO-recommended 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 and rocks possibly rich in lead. The corresponding concentration of lead in other borehole water increased from KV1, KV9, KV7, KV2 and KV4 with 0.40, 0.49, 0.53, 0.63, and 0.67, respectively. Their respective concentration registered a higher amount compared to WHO limit in drinking water and therefore may render most of the borehole water in the basin unsafe for use. It is imperative to note that, if lead is ingested in significantly high levels, it can cause hypertension, fatigue, irritability, anemia, behavioral abnormalities, and intellectual impairment (Mason et al., 2014). Continuous exposure to lead, particularly soluble salts or the potent oxide such as PbO<sub>2</sub>, can have negative effects on the kidneys and the nervous system (Boldyrev, 2018).

Cadmium concentrations in water ranged from 0.22 to 0.29 ppm with KV4 recording the least concentration, whereas KV3 and KV9 recording similar concentration levels. The amount of cadmium in groundwater samples exceeds the WHO-recommended limit for all the samples analyzed (Table 2). The maximum cadmium concentration in a groundwater sample taken in an industrial region near the drilled well was 0.29 ppm which is about hundred times higher than the WHO recommended limit. The high levels of cadmium concentration recorded may have resulted 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 observed in the boreholes of Kerio Valley (Bhagure and Mirgane, 2011). Significant amounts of cadmium may result in symptoms like nausea, vomiting, breathing problems, cramping, and loss of consciousness (Pandey, 2013). Anemia, anosmia, cardiovascular illnesses, renal issues, and

hypertension can result from prolonged exposure to toxic heavy metals (Zahra and Kalim, 2017). The health issues associated with adverse exposure of cadmium have been widely witnessed in the region of study in yester years before the onset of hydrocarbon exploration.

The concentration of manganese in the water samples analyzed ranged from 0.03 to 1.86 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 observed to have concentrations of 0.03, 0.06, 0.41, 0.47, 0.93, and 0.98, respectively, in an increasing order as reported in Table 2. Remarkably, manganese is a trace mineral that the body requires in very small amounts. The liver, kidneys, pancreas, and the bones are where it is most commonly found in the body (Silva et al., 2019). Manganese aids in the formation of bones, connective tissue, blood clotting components, and sex hormones. However, a neurological disorder called manganism, which has symptoms like tremors, trouble walking, and facial muscle spasms, can be brought about by manganese toxicity in excess (Sachse et al., 2019). It is therefore essential to watch the levels of manganese as well as other heavy metals in drinking water to avoid health problems.

### Conclusions

Most of the physico-chemical parameters of groundwater quality in the Kerio Valley basin are within WHO allowable limits with the exception significantly high temperatures in KV9, and high pH levels in KV4 and KV9. Moreover, the groundwater tests from the Kerio Valley basin revealed high levels of electrical conductivity and total dissolved solids. The elevated concentration of these parameters in the groundwater resource could be attributed to home and industrial sewage discharge. Because of mining activities, the Kerio Valley water basin witnessed high values of total dissolved solids and possible alkalinity. The concentration of heavy metals in groundwater for chromium, lead, manganese, and cadmium was found to be higher than the WHO limit in most boreholes water samples. A high concentration of heavy metals in groundwater can affect ecosystems, plants and animals, as well as cause health issues in humans. The main causes of contamination in this basin are industrial discharge, random disposal of hazardous waste water, release of untreated municipal effluents into the soil and use of fertilizers in crop production. Data from heavy metal analyses in groundwater and soil suggest that lead, chromium, cadmium and manganese are more mobile and may seep into groundwater systems. KV9 borehole water posted extremely high levels of lead and cadmium and therefore should be decommissioned.

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#### **Author Contributions**

FKL, JKK and FIO conceived the concept, wrote and approved the manuscript.

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#### **Competing interest**

The authors declare no competing interests.

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Not applicable.





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