## RESEARCH ARTICLE



# Arsenic in Groundwater Sources and Skin Cancer Prevalence in Meru County, Kenya

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#### ABSTRACT

Natural contamination of groundwater by arsenic (As) derived from the Earth's crust is a common global phenomenon. The World Health Organization (WHO) has set a safe limit of 10 µg/L for As in drinking water. Arsenic toxicity causes serious human health problems, especially dermal lesions and skin cancers. Other associated effects include lungs, bladder, prostate, liver, and kidney cancers; cardiovascular diseases; diabetes mellitus; encephalopathy; and adverse pregnancy outcomes. This study investigated the levels of arsenic in groundwater sources and the 5-year prevalence of skin cancer in Meru County, Kenya. Four springs and twenty-five water boreholes were analysed for arsenic using inductively coupled plasma-optical emission spectrometry (ICP-OES). The As levels ranged from <2.94 to 85.4  $\pm$  8.3  $\mu$ g/L. All the four springs were found to be free from As contamination whereas eight boreholes (32%) had >10 µg/L As. Most of the affected springs were in Buuri sub-county, and the same area had a high prevalence of skin cancers, with 8 per 100,000 persons five times higher than the national prevalence. The findings showed an underlying potential health risk of As-induced cancers from the use of contaminated groundwater, and follow-up epidemiological studies are recommended. Mitigation and remediation measures against chronic As exposure are necessary to safeguard inhabitants of this region.

Keywords: Arsenic, contamination of groundwater, epidemiological studies, prevalence of skin cancer.

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### 1. Introduction

Arsenic is a metalloid element with the chemical symbol As and atomic number 33 in the periodic table. Arsenic is ubiquitous in the Earth's crust and ranks 20th in abundance among the elements [1]. Inorganic As is a major natural pollutant in groundwater globally, posing a serious risk to human health, especially in developing countries [2]. The World Health Organization (WHO) has recommended a safe limit of 10 µg/L As in drinking water [3]. The element is extremely toxic to humans and a well-known carcinogen, mutagen, and teratogen. It is ranked first in the 2019 priority list of hazardous substances by the Agency for Toxic Substances and Disease Registry (ATSDR). It is classified as Group 1 (carcinogenic to humans) by the International Agency for Research on

Natural As contamination of groundwater has been reported for more than a century in many parts of the world, which is attributed to the widespread existence of As in the Earth's crust [5]. The most affected countries are in Asia (Bangladesh, China, and India) and Latin America, including Argentina, Chile, and Mexico [6], [7]. In Africa, high As groundwater has been reported in Botswana, Burkina Faso, Ethiopia, Ghana, Morocco, Nigeria, South Africa, Tanzania, Togo, and Zimbabwe [8], [9].

The mobilization of As in groundwater is primarily from natural sources, and the mechanism involved depends on the geological formation of a given region [10], [11]. However, anthropogenic activities in mining areas can contribute to further mobilization of As. High As levels in groundwater occur in shallow unconsolidated sediment aquifers. The reductive dissolution of As-bearing iron (III) oxyhydroxide (FeOOH) to soluble iron (II) species plays a major role in releasing the sorbed As into

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the groundwater. Another release mechanism involves dissociation of As from arsenopyrite (FeAsS) under oxidizing conditions, as shown in (1) [12].

$$4\text{FeAsS}_{(s)} + 6\text{H}_2\text{O}_{(l)} + 11\text{O}_{2(g)} \rightarrow 4\text{FeSO}_{4(aq)} + 4\text{H}_3\text{AsO}_{3(aq)}$$
 (1)

Arsenic mobilization is also achieved by an exchange mechanism for the adsorption sites of the oxyhydroxides between As and other compatible anions such as PO<sub>4</sub><sup>3-</sup>, NO<sub>3-</sub>, and HCO<sub>3-</sub>. In addition to redox conditions, other factors that control the release of As in aquifers include pH, temperature, and solution composition [13], [14].

Two inorganic As species are predominant in natural waters: arsenite (AsO<sub>3</sub><sup>3-</sup>) and arsenate  $(AsO_4^{3-})$  with oxidation states +3 and +5, respectively. Arsenite species  $(As^{3+})$ , which occur mostly under reducing conditions, is more toxic than arsenate species (As<sup>5+</sup>). However, trace amounts of less toxic methylated (organic) arsenic species such as monomethylarsonic acid (MMA), CH<sub>3</sub>AsO(OH)<sub>2</sub>, and dimethylarsinic acid (DMA), (CH<sub>3</sub>)<sub>2</sub>AsO(OH), may exist in drinking water. Most As compounds have no smell or taste in water and are not easily detectable when drinking contaminated water [15].

An estimated 230 million people in about 108 countries worldwide are facing health risks linked to the long-term use of As-polluted groundwater [11]. People are mostly exposed to As by using polluted water for drinking, food preparation, and crop irrigation. High As levels in groundwater has been associated with the development of skin, lung, bladder, kidney, liver, and prostate cancers. Other health conditions encountered as a result of As toxicity include dermal lesions, hyperpigmentation (skin, hair, and nails), cardiovascular diseases, diabetes mellitus, encephalopathy, and adverse birth outcomes such as pre-term births, birth defects, still births, and spontaneous abortions. These arsenic-related health conditions are collectively known as arsenicosis [16]–[18], [7].

Arsenic toxicity is primarily caused by the ability of As to induce oxidative stress in the body. This leads to the formation of free radicals (reactive oxygen species), that attack proteins, DNA, and lipids. As<sup>3+</sup>, which is five times more potent than As<sup>5+</sup>, binds to the thiol group, causing interference with body functions. On the other hand, As<sup>5+</sup> is predominantly deposited in the skeleton where it replaces phosphate  $(PO_4^{3-})$  in the  $Ca_3(PO_4)_2$  (apatite crystal) in bones. The mechanism of  $As^{5+}$  induced toxicity follows this route of PO<sub>4</sub><sup>3-</sup> replacement during glycolysis, which affects adenosine triphosphate (ATP)

According to the 2022 Global Cancer (GLOBOCAN) observatory report [20], Kenya has a 44,726 annual incidence of cancer with 29,317 deaths and 102,152 prevalence cases (5-year) against a total population of 56,215,224. The top five cancers in Kenya are breast, cervix uteri, prostate, esophagus, and colorectal cancers. Cancer is the third among the leading causes of death in Kenya after infectious and cardiovascular diseases. The cancer burden in Kenya is not uniformly distributed and seems to follow a pattern whereby some counties have a higher burden in particular areas, whereas some cancer types have been noted to cluster around certain geographical areas. Hence, cancer control interventions and research must align with local or regional trends. This approach can guide prevention, early detection and treatment efforts sub-nationally [21].

Meru County lies in the volcanic region of Mt. Kenya. It has 11 permanent rivers, 12 shallow wells, 30 protected springs, 2 water pans, 16 dams, and 242 boreholes. These are the major sources of water for domestic use, irrigation, and livestock production [22]. Many boreholes are sunk in the dry parts of the area, especially in Buuri sub-county, to provide additional water sources where the flow of perennial rivers is insufficient. A previous study by Mungai et al. [23] showed As contamination in some naturally occurring carbonated mineral springs located in many parts of Meru County, which was attributed to the geology of the area, characterized by volcanic and sedimentary rocks. Volcanic rocks are a common source of geogenic As which can detrimentally affect groundwater quality [24]. Cutaneous or dermatological effects characterized by skin lesions (melanosis and keratosis) are the most common initial manifestations of As toxicity derived from groundwater sources. Skin cancers and Bowen's disease also occur in patients with arsenicosis [25], [19]. The current study investigated the status of arsenic levels in some frequently used water springs and boreholes in relation to the prevalence of skin cancer in Meru County.

# 2. Materials and Methods

### 2.1. Study Area

Meru County is situated in central Kenya on the eastern and north-eastern slopes of Mt. Kenya volcano and lies on the equator. The Nyambene volcanic hills occupy the north eastern part of the county (Fig. 1).

A total of four (S1-S4) springs and twenty-five (B5-B29) boreholes were investigated. The sampling sites are bound by latitudes of -0.004657 and 0.286540, and longitudes of 37.522705 and 37.871757.

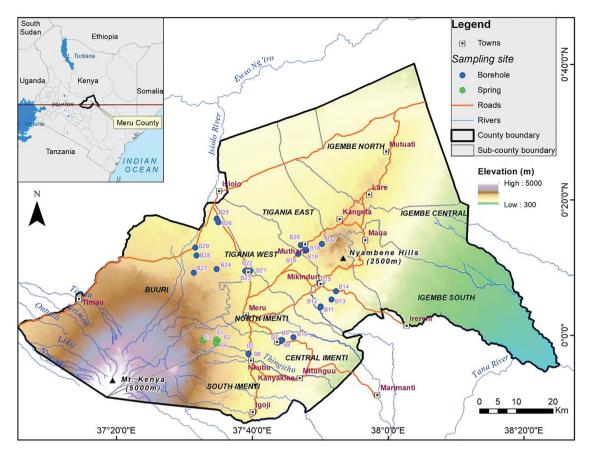


Fig. 1. Location map of sampling sites in Meru County, Kenya.

The County is divided into 11 sub-counties, which are Imenti South, Imenti Central, Imenti North, Buuri East/West, Tigania East/Central, Igembe South, Igembe Central, and Igembe North. The area covers approximately 7,006.3 km<sup>2</sup> with a total human population of 1,544, 866 according to the 2019 Kenya population and housing census [26]. This represented approximately 3.2% of the Kenyan population, which was 47,564,296. The geology of the area is almost entirely volcanic, dominated by basaltic rocks along with trachytes, phonolites, and kenytes [27]. Mt. Kenya and the Nyambene Range are key water towers in the region. Most dry areas in the county rely on groundwater abstraction by both hand-dug and drilled wells.

## 2.2. Materials and Instruments

#### 2.2.1. Materials

The materials included questionnaires, 0.45 µm filters, 300 mL polyethylene terephthalate (PET) bottles, gloves, pH buffers 4 and 7, deionized water, concentrated nitric acid (HNO<sub>3</sub>), concentrated perchloric acid (HClO<sub>4</sub>) and 1000 mg/L arsenic standard reference material solution (H<sub>3</sub>AsO<sub>4</sub>) in 0.5 mol/L HNO<sub>3</sub> traceable to the National Institute of Science and Technology (NIST). All reagents were analytical grade.

# 2.2.2. Instruments

The instruments included a portable pH meter (HANNA instruments: HI 98129, Bertoki, Slovenia), block digester (JP Selecta Bloc-digest: Attiki, Greece), and inductively coupled plasma-optical emission spectrometer (ICP-OES Thermo Scientific iCAP 7000 series: Waltham, USA).

## 2.3. Data Collection

Ethical approval for this study was granted by the Meru University Institutional Research Ethics Review Committee (Approval number MIRERC030/2024), and a research license was acquired from the National Commission for Science, Technology and Innovation (license number NACOSTI/P/24/39156), in Kenya. This study was supported by the County Government of Meru. Skin cancer data in Meru County for a 5-year period from 2019 to 2023 was provided by the Cancer Registry at the Meru Teaching and Referral Hospital (MeTRH). Water samples were collected from four natural springs, which were regularly used by the community, and twenty-five private boreholes

for laboratory analysis of As. Household heads from the sampled boreholes filled questionnaires to provide information related to the use and properties of their groundwater sources.

#### 2.4. Inclusion and Exclusion Criteria

The respondents were required to be adults aged 18 years and above, residents of Meru County, heads of households, and have a water borehole in their homes. The participants signed informed consent forms. Respondents who did not show interest in or declined to participate in the study were excluded.

#### 2.5. Selection of Water Sampling Sites

A non-random water sampling was undertaken with priority given to the sub-counties lying strategically between the foothills of Mt. Kenya and Nyambene Range volcanoes. The exercise was performed during the dry season in September and October 2024. Twenty-nine water sources were investigated from four different sub-counties, consisting of four springs and twenty-five boreholes. All four springs (S1-S4) were located in Imenti Central highlands bordering Mt. Kenya. A total of six boreholes (B6-B10) were drawn from Imenti Central, five boreholes (B11-B15) in Tigania Central, five boreholes (B5-B20) in Tigania East, and nine boreholes (B21-B29) in Buuri. Three samples were collected from each water source using clean 300 mL polyethylene terephthalate (PET) bottles. The samples were filtered through a 0.45 µm pore diameter membrane filter and treated with 1 mL of analytical grade nitric acid (HNO<sub>3</sub>) to prevent the precipitation and adsorption of analytes on the walls of the bottles. The samples were transported to the laboratory within 24 h and refrigerated at 4°C to prevent volume changes. The water temperature and pH were measured in situ. Fig. 2 shows two boreholes among the sampled boreholes.

### 2.6. Analysis of Arsenic

Arsenic was analysed using inductively coupled plasma-optical emission spectrometry (ICP-OES) procedure for water analysis, adapted from the EPA method 200.7. The analysis was conducted in collaboration with an accredited Analytical Chemistry Laboratory at the Kenya Plant Health Inspectorate Service (KEPHIS). To 45 mL of each water sample, 9 mL HNO<sub>3</sub> and 4 mL HClO<sub>4</sub> were added to a digestion tube and allowed to react for 5 min. The samples were then heated in a block digester at 95°C for 90 min. After cooling, the samples were quantitatively transferred to a 250 mL volumetric flask and filled to the mark using deionized water. The instrument was calibrated with external standards ranging from 0-50 µg/L, and As was analysed in triplicate at 189.04 nm by axial mode. The limit of detection (LOD) for As was derived from the calibration curve for the standards and blank. The regression equation was y = 0.3485x - 0.9879, with  $R^2 = 0.9941$ . LOD =  $y_B + 3s_B$ , where  $y_B$  was given by the intercept (a = -0.9879) and  $s_B$  was estimated by the statistic  $s_{\nu/x}$  for the standard deviations of the y-residuals [28]. By applying this method, the LOD for As was established to be 2.94 µg/L. To evaluate the stability of the method, four different water samples were spiked with 30 μg/L of As, and the percentage recoveries ranged from 78.0% to 96.7%.





Fig. 2. (A) Boreholes B10 (hand-dug well <10 m deep) and (B) B19 (drilled tube well >50 m deep) in Imenti Central and Tigania East sub-counties, respectively.

#### 3. RESULTS AND DISCUSSION

#### 3.1. Results

The levels of As at the investigated sites are listed in Table I. Three samples (A, B, and C) were analysed separately from each of the 29 water sources. The samples were analysed in triplicate (n = 3)and their relative standard deviations (RSD) were calculated.

From the water analysis in Table I, most of the pH values (5.6–8.1) were near the neutral point and the temperatures (13.2°C-28.4°C) were close to the ambient temperature of the surrounding environment. As levels in the four springs (S1–S4) were below the detection limit ( $<2.94 \mu g/L$ ). Eight boreholes (32%) contained As levels above the WHO safe limit (10 µg/L) for drinking water. In nine boreholes (36%), water samples had As  $\geq$ 2.94 µg/L (above the detection limit) but <10 µg/L, and eight boreholes (32%) had As levels below the limit of detection. Buuri comprised 50% of the boreholes exceeding the permissible limit, Imenti Central 25%, Tigania Central 12.5% and Tigania East 12.5%. The As levels in all three samples from borehole B09 were >10 μg/L. The highest As level was 85.4 μg/L for sample A from borehole B24.

Table II summarises the number of skin cancers (melanoma and non-melanoma) recorded in Meru County, categorized by sub-county, from 2019 to 2023 (5 years). Buuri sub-county had the highest prevalence of skin cancer with 8 cases per 100,000 persons.

## 3.2. Discussion

The three water samples (A, B and C) were not homogeneous, as indicated by the different levels of As recorded for each site in Table I. Water discharged from the springs was safe for drinking, while 32% of the investigated borehole water sources posed a health risk to the community due to As exposure above 10 µg/L. Buuri had the most contaminated boreholes since eight out of the nine boreholes (B21-B29) sampled in the area had As ranging from  $3.07 \pm 3.9 - 85.4 \pm 8.3 \,\mu\text{g/L}$ .

Most of the boreholes (19 of 25), as indicated in Table I, were deep (>50 m), and only six boreholes were in the range of 10-30 m. It shows that half (4 out of 8) of the boreholes with high levels of As above the 10 µg/L safe limit were relatively shallow, 10–30 m deep. This means that shallow wells have a higher As contamination risk compared to deeper wells. The dissolution of As-bearing minerals from volcanic sedimentary aquifers in this region could be a key source of elevated As levels in most shallow groundwater sources, especially in plain areas. A study in the Huaihe River Plain, China, by Xu et al. [29] found that proportion of As was 9.77% and 2.85% in shallow and deep groundwater samples, respectively. The As concentrations were higher in plain areas than in hilly areas, and some As hazard areas possessed high cancer rates. Aquifers are poorly flushed in flat, low-lying areas where groundwater flow is sluggish, and any As released from the sediments following burial accumulates in groundwater.

The near-neutral pH values reported, ranging from 5.6 to 8.1, enhance the reductive dissolution of Fe/Mn oxyhydroxides with the subsequent release of adsorbed As species into the water [30]. Groundwater from tube-wells in Bangladesh reported As levels above 10 μg/L in 59 out of 64 districts, which caused detrimental health effects on people. Mobilization was associated with the reduction of metal oxyhydroxides such as FeOOH and MnOOH, arsenopyrite (FeAsS) oxidation and ion exchange mechanisms [31]. In rural Burkina Faso, As concentrations in 14% of 1498 samples from water wells were above 10 μg/L, and approximately 560,000 people were potentially exposed to high As groundwater. The source of As was linked to geology, which consists of schists and volcanic bedrock of the Birimian Formation [32].

pН As  $(\mu g/L) \pm RSD$ , LOD = 2.94  $\mu g/L$ Borehole/Spring GPS coordinate Depth (m) Temp.(°C) Latitude/Longitude Sample A Sample B Sample C S1\*\* -0.012633, 16.9 7 1 < 2.94 < 2.94 < 2.94 37.581155 S2\*\* -0.010550,18.2 6.7 < 2.94< 2.94 < 2.94 37.577632 S3\*\* -0.011470.0 13.2 6.8 < 2.94 < 2.94 < 2.9437.545452 S 4\*\* -0.019545, 0 16.1 6.5 < 2.94 < 2.94< 2.94

37.576692

TABLE I: Analysis of As (µg/L) in Water Samples from Meru County, Kenya

TABLE I: (CONTINUED)

	GPS coordinate Latitude/Longitude	Depth (m)	Temp.(°C)	pН	As $(\mu g/L) \pm RSD$ , LOD = 2.94 $\mu g/L$		
	_				Sample A	Sample B	Sample C
B5	-0.045467, 37.657515	>50	22.0	7.5	<2.94	<2.94	<2.94
В6	-0.046360, 37.657057	>50	21.2	8.1	<2.94	<2.94	<2.94
В7	-0.018602, 37.729347	20–30	25.7	7.9	$13.32 \pm 7.9^*$	<2.94	<2.94
В8	-0.012790, 37.740380	10–20	26.2	7.9	<2.94	<2.94	<2.94
В9	-0.011603, 37.736743	10–20	29.0	7.5	$18.15 \pm 6.2^*$	$19.56 \pm 3.7^*$	$10.14 \pm 7.8^*$
B10	-0.004657, 37.767612	<10	25.2	7.3	<2.94	<2.94	<2.94
B11	0.070610, 37.834233	>50	24.0	7.0	<2.94	<2.94	<2.94
B12	0.069220, 37.839207	>50	24.2	7.1	$4.55 \pm 1.9$	<2.94	<2.94
B13	0.087708, 37.860842	>50	25.2	7.2	<2.94	<2.94	$8.17 \pm 3.1$
B14	0.108493, 37.871757	>50	23.5	6.6	<2.94	$3.62 \pm 2.2$	<2.94
B15	0.130008, 37.832487	20–30	25.1	6.2	<2.94	$23.79 \pm 2.3^*$	<2.94
B16	0.199830, 37.779160	10–20	22.7	7.1	$4.42 \pm 2.9$	<2.94	<2.94
B17	0.224537, 37.837163	10–20	19.5	7.7	$13.3 \pm 9.3^*$	<2.94	<2.94
B18	0.209045, 37.799143	>50	23.3	7.0	<2.94	<2.94	<2.94
B19	0.211475, 37.797033	>50	22.5	6.6	<2.94	<2.94	$6.22 \pm 7.7$
B20	0.221672, 37.785553	>50	24.2	7.9	<2.94	<2.94	<2.94
B21	0.158133, 37.660872	>50	27.9	6.8	<2.94	<2.94	$12.92 \pm 9.9^*$
B22	0.159165, 37.656425	>50	23.8	6.9	<2.94	<2.94	<2.94
B23	0.157993, 37.649072	>50	22.3	6.3	<2.94	<2.94	$3.07 \pm 3.9$
B24	0.162595, 37.643445	>50	24.7	6.0	$85.4 \pm 8.3^*$	$6.63 \pm 5.5$	<2.94
B25	0.286540, 37.579017	>50	27.8	5.8	<2.94	$4.25 \pm 8.0$	$13.26 \pm 1.1^*$
B26	0.277872, 37.583060	>50	28.4	5.9	$7.01 \pm 6.7$	$4.52 \pm 5.2$	<2.94
B27	0.153778, 37.522705	>50	26.9	6.4	$4.65 \pm 5.4$	$4.29 \pm 8.1$	$4.06 \pm 6.3$
B28	0.196440, 37.529398	>50	25.9	6.0	<2.94	$6.08 \pm 6.5$	<2.94
B29	0.215535, 37.526430	>50	24.8	5.6	<2.94	$17.82 \pm 3.5^*$	$7.79 \pm 1.1$

Note: \*Above the 10 µg/L safe limit set by the World Health Organization (WHO).

High levels of As contamination in groundwater are likely to pose significant health risks in the study region. From the results in Table II, there were 81 skin cancer prevalence cases in Meru County for a 5year period (2019–2023) against a total population of 1,544,866, equivalent to 5.2 cases per 100,000. In the Global Cancer (GLOBOCAN) Observatory Report 2022, Kenya had 712 skin cancer prevalence (5year) against a total population of 56, 215, 224 which is approximately 1.3 cases per 100,000 [20]. This shows that the prevalence of skin cancer in Meru County is five times higher than that at the national level. The prevalence was the highest in Buuri sub-county, where a greater number of As-contaminated boreholes were found. Therefore, As contamination of groundwater and the prevalence of As-induced

<sup>\*\*</sup>Spring.

Kenya population census 2019 Number of skin cancers 5-Year Prevalence (2019–2023) Per 100,000 Sub-County Imenti South 206.506 15 Imenti Central 133,818 9 6 12 7 Imenti North 177,567 Buuri East/West 157,360 13 8 Tigania West 139,961 7 Tigania Central/East 177,279 Igembe South 161,646 5 3 11 5 Igembe Central 221.412 4 2 Igembe North 169.317 1.544.866 81 46 Total

TABLE II: THE 2019 KENYA POPULATION CENSUS AND SKIN CANCER CASES (2019–2023) IN MERU SUB-COUNTIES

cancers require further understanding, which can be achieved through epidemiological studies of the target populations where groundwater is commonly used. Epidemiological studies in Argentina, Chile, Mexico, Japan, Taiwan, and Bangladesh have associated high arsenic levels in drinking water with skin, kidney, lung, and bladder cancer [33]. About 8.81 million people in Mexico are exposed to dangerous levels of As in groundwater and 13,070 cases of different types of cancers are expected due to chronic As exposure. The arid states of north-central Mexico are the most affected [34].

Various principles can be applied to remove As from contaminated groundwater, including oxidation, chemical coagulation, adsorption, nano-filtration, and electrocoagulation [35]-[37]. The application of these methods depends on the As removal efficiency, level of pollution and affordability. Other alternative safety measures include the use of deep wells, which have relatively lower Ascontaminated groundwater than shallow wells, sourcing water from rivers and springs, or using rainwater harvesting supplies. Moreover, laboratory testing of all groundwater sources and aquifer sediments could be a crucial step in the early warning of contamination in high As hazard zones to prompt mitigation measures.

In addition to initiating epidemiological studies to establish causation between As toxicity and skin cancer, more groundwater sources in the region should be investigated in future. Similarly, an in-depth geological survey of Mt. Kenya region could help to understand the rock formations, geochemical processes and hydrogeology with regard to As mobilization in groundwater.

### 4. Conclusions

In this study, the status of As in groundwater sources in Meru County was investigated. The results showed that the water discharged from the surface springs was safe for consumption. Approximately one-third of the investigated water boreholes were contaminated with As above the 10 µg/L WHO guideline value for drinking-water quality. Buuri sub-county had the majority of contaminated boreholes, and a high number of skin cancers have been reported in the area. This implies that there is a high potential for As-induced cancers in Meru County, and further epidemiological studies are needed on the target populations, which largely rely on groundwater sources. Both mitigation and remediation measures against chronic As exposure are necessary to assist the affected communities.

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#### CONFLICT OF INTEREST

The authors declare that they do not have any conflict of interest.

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