Research

# Human health risk assessment of microbial contamination and trace metals in water and soils of Chileka Township, Blantyre, Malawi

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#### Abstract

This study assessed nutrients and microbial contamination in water and soil samples from Chileka Township, Blantyre City, Malawi. Elevated total and fecal coliforms (1300 cfu/100 mL and 290 cfu/100 mL) in groundwater (GW), and (34,000 cfu/100 mL and 8000 cfu/100 mL) in surface water (SW) were found, representing a risk of exposure to waterborne disease. While the criteria in the Malawi Standard for raw groundwater was mostly met, water from only 20% of the boreholes complied with the WHO requirements. Nitrate (NO<sub>3</sub><sup>--</sup>) and Cl<sup>--</sup> (47.8 mg/L and 263 mg/L) exceeded the WHO limits in GW. Cadmium (Cd) occurred in a few cases at concentrations up to 0.217 mg/L and 0.138 mg/L in GW and SW. Lead (Pb) and Cr were below detection limits, while Mn (0.319 mg/L and 0.640 mg/L) in GW and SW, and Fe (6.92 mg/L) in SW compromised taste. Though bacteriologically unfit for raw consumption by humans, both GW and SW chemically met FAO-acceptable limits for irrigation, and standards for livestock watering. The NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> maximum concentrations in soil were 58.9 mg/kg and 506 mg/kg, respectively. Lead (Pb) and Cd were not detected whereas Cr, Zn, Cu, Mn and Fe in soil were 27.7 mg/kg, 190 mg/kg, 60.4 mg/kg, 1307 mg/kg and 6552 mg/kg, respectively. Magnesium (Mg), Ca, Na and K were 20,523 mg/kg, 22,334 mg/kg, 544 mg/kg and 5758 mg/kg, respectively in soil. The human health risk assessment results, on the other hand, showed that at least 30% (6 out of 20) of the GW samples and 60% (3 out 8) of the SW samples had HI > 1 for adults, children and infants, indicating existence of non-carcinogenic risk. Similarly, at least 15% (3 out 20) of the GW samples and 18% (1 out of 8) of the SW samples had CR > 0.001 for adults, children and infants, suggesting a risk of developing cancer during a lifetime due to Cd exposure. Though both GW and SW are generally of good chemical quality, chronic exposure to nitrate and cadmium is a health risk in the area. The current trace metal levels are not worrisome, but soil nitrate and phosphate may need regular monitoring.

Keywords Fecal coliforms · Trace metals · Microbial contamination · Nutrients · Groundwater · Likhubula River

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#### 1 Introduction

Globally, environmental soil-water transfer of contaminants affects water guality thereby limiting community access to safe and clean water. However, both groundwater (GW) and surface water (SW) are key to human livelihood worldwide. While GW is generally the source of piped water supply in Europe, it is indispensable to support rural livelihood in Sub-Saharan Africa because of the added potential of possible use for agricultural purposes [1]. In the global quest, under the sustainable development goals of the United Nations (UN), for universal and equitable access to safe water by 2030, the intrusion into drinking water sources of contaminants of both geogenic and anthropogenic origin remains a major drawback [2]. Therefore, deliberate efforts are necessary to preserve the ecological integrity of water resources through a balance between exploitation for human benefit and protection against polluting influences. Although GW is relatively inexpensive for rural water supply in Sub-Saharan Africa, often having a satisfactory chemical profile and good microbial properties that require little or no treatment prior to human consumption, its guality is still susceptible to compromise by contaminants [3]. In the interest of public health, the World Health Organization (WHO) recommends limits for selected contaminants in drinking water [4]. Clean water, safe for drinking, is that which conforms to prescribed standards in terms of its chemical and microbial properties. In Malawi, common pollutants in both GW and SW include nutrients, trace metals and bacteria [5, 6]. These may originate in the soil and get transported downward into GW or laterally into SW bodies by surface runoff, and can be exchanged between GW and SW [7–10].

In both urban and rural environments, GW and SW might be contaminated with pathogens, nutrients, and trace metals, and the situation is worse in developing countries due to poor implementation of environmental management strategies. Although the natural subsoil profiles possess some potential of attenuating microbial and chemical contaminants originating from the surface [11], these contaminants are still capable of being mobilized under certain conditions. Thus, the contaminants eventually leach into GW, and shallow aquifers are frequently more exposed to contamination. Similarly, soil erosion and runoff processes on the land surface may constitute a vehicle transporting contaminants adsorbed to soil particles into SW. Microbial contamination of drinking water is responsible for water-borne diseases such as cholera, dysentery, typhoid and bilharzia [12]. Excess nutrients i.e., phosphate (PO<sub>4</sub><sup>3-</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) cause eutrophication and fish kill in freshwaters [13], the latter has also been linked to blue baby syndrome (methemoglobinemia) in infants [14], and to livestock poisoning [15]. Excessive concentration of lead (Pb), cadmium (Cd), and chromium (Cr) in drinking water is toxic to humans whereas iron (Fe), copper (Cu), zinc (Zn), and manganese (Mn) compromise the aesthetic quality of drinking water in addition to affecting plants and animals, and the suitability of water for irrigation, and support of aquatic life [3, 16, 17]. In soil, the fate of contaminants is described by the natural attenuation processes of biodegradation, diffusion, dilution, sorption, volatilization and chemical and biochemical stabilization, including uptake by vegetation and animals [18]. Similarly, a contaminant that enters a body of water can be transported within the water body, volatilized or transported into the atmosphere, sorbed into the soil, dissolved into or precipitated out of the water, degraded by photolysis, or transformed by biodegradation. Contaminants that are not degraded by natural systems end up bio-accumulating in organisms. Generally, water pollution depletes aquatic ecosystems.

Groundwater is, like in other developing countries, still key to rural water supply in Malawi, with 62% of the national population relying on boreholes [19]. However, due to limited monitoring, water quality data is still fragmented and inadequate, with less than 20% of the 27,913 boreholes of the country tested before use in 2014 [6, 20]. Rural and peri-urban areas often offer cheaper livelihoods subsidized by agricultural activities and are home to the larger proportion of the population. Although mandated to provide potable water to residents of both the city and the outskirts, Blantyre Water Board (BWB) already faces capacity challenges to service city dwellers adequately. Therefore, expansion of service to the surrounding rural and peri-urban areas, including Chileka Township, is unlikely to happen soon. Currently, the people of Chileka mostly use raw GW for drinking purposes while the Likhubula River, which runs through the area and drains into the country's mighty Shire River from which BWB draws water for treatment and subsequent distribution, largely provides water for non-potable uses. Cholera outbreaks have constituted a public health problem in Malawi, and Chileka in particular, in recent years [21, 22], implicating sources of drinking water among other possible routes of exposure. Faecal coliforms are predictors of the risk of waterborne diarrhoeal diseases that constitute a major cause of morbidity and mortality in developing countries [23]. In the semi-urban community of Chileka, drinking water of good quality is essential for not only human health but supporting livelihoods through agriculture. The purpose of this research, therefore, was to assess, in both GW and SW (Likhubula River), and in associated soils from Chileka Township, the extent of microbial (total and feacal coliforms), trace metal (Pb, Cd, Cr, Fe, Cu, Mn and Zn), nutrient (NO<sub>3</sub><sup>--</sup> and PO<sub>4</sub><sup>3--</sup>), chemical and organic matter (COD and BOD<sub>5</sub>) contamination, including mineral (Ca, Mg, Na, and K) content against prescribed standards.



#### 2 Materials and methods

#### 2.1 Description of the study area

Malawi is a landlocked country located in South-Eastern Africa with a dense population. It is bordered by Tanzania to the North, Zambia to the North-West with Mozambique joining it on the East, South and West. The country has a tropical climate consisting of a dry season lasting from May to October and a wet (rainy) season extending from November to April. Chileka Township is a peri-urban area approximately 70 square miles (181.3 km<sup>2</sup>) situated about 16 km northwest of Blantyre city on a plain between the Shire Highlands and the Shire River, within latitudes 15.350–16.015° S and longitudes 34.725–35.125° E. The study area (Fig. 1) comprised eight villages, namely; Mpasuka, Magombo, Masitala, Kapitao, Gova, Gopani, Mapemba, and Singano where purposively selected 10 boreholes and four sites in Likhubula River were sampled (Fig. 1). Being a typical rural community, anthropogenic activities constituting sources of soil and water pollution within the area include indiscriminate waste disposal, cultivation of riverbanks, use of fertilizers, manures and pesticides, brick kilns, and sanitation facilities (pit latrines and septic tanks).

#### 2.2 Collection of water and soil samples

A purposive sampling strategy was employed to select 10 boreholes (BH1 to BH10), and four sites (LK1 to LK4) in Likhubula River based on intensity of use by the community, surrounding land use activities, and accessibility for easy transportation of samples in both seasons. The water samples were collected in both the dry season (October, 2016) and the rainy season (February, 2017), once in each, following standard methods [24, 25]. At each sampling site, two sets of triplicate water samples were collected, filtered, and stored in new pre-cleaned polyethylene bottles. The first sample-set was acidified with HNO<sub>3</sub> (to pH 2) for analysis of major cations while the second was stored unacidified for analysis of major anions. A separate sample for microbiological analysis was collected at each site. Before collection of this sample, each borehole was flame-sterilized with cotton wool lit after being soaked in 70% methanol. Consistently, at each borehole, water was pumped to waste for 30 s before sample collection to release any trapped water and thus ensuring collection of water freshly drawn from the aquifer. The general surroundings of the boreholes, including wellhead protection



Fig. 1 Map showing the study area (Chileka) in Blantyre, Malawi



were assessed by visual examination and observation. All samples were, after on-site determination of non-conservable parameters, stored and transported on ice in a cooler box to the laboratory for subsequent analyses. In order to assess possible influence of soil contaminants on water quality, a soil sample of 500 g was collected at 0–20 cm and 20 cm–40 cm depths within a radius of 25 m of each borehole, and of each SW sampling point in crop fields near the river banks. The soil samples were taken using a hand-operated auger and collected in plastic bags [26].

#### 2.3 Physicochemical analysis of water samples

All non-conservable parameters (temperature, pH, turbidity, EC, and TDS) were measured in-situ (Table 1). The water samples were analyzed by the methods in APHA (1999) [24] as follows: for chloride (Cl<sup>¬</sup>) by the argentometric method (4500-Cl<sup>-</sup> B), phosphate ( $PO_4^{3^-}$ ) by the vanadomolybdophosphoric acid colorimetric method (4500-P C), chemical oxygen demand (COD) by the open-reflux titrimetric method (5220B), and biochemical oxygen demand (BOD<sub>5</sub>) by iodometric methods (5210B and 4500-O D). Bicarbonate (HCO<sub>3</sub>) was determined by the titrimetric method (AOAC 920.194) [25], and nitrate ( $NO_3^{-}$ ) by the sodium salicylate method [27]. Metals and mineral elements (Ca, Mg, Na, K, Cd, Cu, Cr, Fe, Mn, Pb and Zn) were determined by flame atomic absorption spectrometry (3111B). The trace metal detection limits of the GBC 732 model AAS used were 0.003 mg/L for cadmium, 0.025 mg/L for Cu, 0.001 mg/L for Pb, 0.005 mg/L for Zn, 0.002 mg/L for Mn, 0.003 mg/L for Cr, and 0.005 mg/L for Fe. Table 1 describes the equipment used in the laboratory analyses.

#### 2.4 Microbiological analysis of water samples

The water samples were, immediately after collection, analyzed for total and feacal coliform bacteria using the membrane filtration technique (9222B) as in APHA [24]. A sample of water was passed through a presterilised 0.45 µm membrane filter. This filter was then placed in a petri dish containing membrane lauryl sulphate broth (MLSB), and subsequently incubated for 24 h at 37 °C. At the end of the incubation period, the filter was examined. Bacteria trapped on the membrane grew into colonies that were counted, and a bacterial density was calculated. All yellow-coloured colonies on the filter were identified as feacal coliforms. Total coliforms were pink to dark red in colour, and had a green metallic surface sheen. The colonies were enumerated and expressed in terms of colony forming units (CFU) per 100 mL. This was calculated using the formulae below.

Colonies/100 mL = (100 mL x colony count)/sample volume used.

#### 2.5 Analytical methods used in the laboratory for soil samples

The soil samples were air-dried, crushed and passed through a 2-mm sieve. Next, a representative sample of about 200 g of the sieved soil was retained by coning and quartering, and stored in clean plastic bottles in readiness for analysis [26]. Soil pH was determined in a 1:1 (soil: water) suspension using a digital pH meter [28]. Soil NO<sub>3</sub><sup>--</sup> was determined by the sodium salicylate method in a 1:5 (soil: water) extract [27, 29]. To estimate total phosphorus, the soil samples were digested using the Perchloric Acid Digestion procedure described by O'Halloram & Cade-Menum [30]. Phosphorus was then determined in an aliquot of the clear supernatant by the Vanadomolybdophosphoric Acid Colorimetric Method (4500-P C) as in APHA [24]. Metals and mineral elements (Ca, Mg, Na, K, Cd, Cu, Cr, Fe, Mn, Pb and Zn) were extracted from soil samples following the Acid Digestion Procedure described by Bamgbose [28], and recovered by filtration through a Whatman 42 filter paper. The diluted extract was analysed for metals by Flame Atomic Absorption Spectrometry (3111B) as in APHA [24]. The precision, expressed as the relative standard deviation (RSD), of the analytical procedures ranged

Parameter	Equipment	Model	Manufacturer	Country
Temperature and pH	Digital pH meter	WE30200	Wagtech International	UK
EC and TDS	Digital EC/TDS meter	MP-4	HACH Company	USA
Turbidity	Portable turbidimeter	HACH 2100Q	HACH Company	China
$NO_3$ and $PO_4$	UV/Visible Spectrophotometer	Spectronic 20	Milton Roy Company	USA
Fe, Pb, Ca, Mg, Na, K, Cd, Cr, Cu, Zn and Mn	Atomic absorption spectrophotometer	GBC 732	Scientific equipment Pty Ltd	Australia

 Table 1
 Equipment used during water quality analysis in the present study



from 5 to 10%. Further, calculated recoveries of the metals from the spiked water samples were found to be within the range 90–110%. Throughout the analysis, blanks were run and, where necessary, corrections applied. All the observations were recorded in duplicate and average values are reported. The elemental concentration in soil of the measured species was expressed (on a dry weight basis) in milligrams of the element per kilogram of soil extracted.

#### 2.6 Data analysis

#### 2.6.1 Statistical analysis

The data obtained was entered and processed in IBM SPSS v20 software and the statistical comparison of mean values in water quality and soil parameters were done at 5% level of significance. It should be noted that before performing any statistical test, the data was first subjected to a homogeneity test to determine whether it was normally distributed or not. If the data was not normally distributed, then the common technique of taking the log of the data embedded in SPSS statistics was employed to transform non-normal distributed data into normal distributed in order to apply two-sample t-tests. The variations were further illustrated by box-and-whisker plots. The parameter values obtained in this study were compared to thresholds prescribed by both the World Health Organization (WHO), and the Malawi Bureau of Standards (MBS) for drinking water, and to literature and available regional standards for soil parameters. Canonical correspondence analysis (CCA) biplot, and hierarchical agglomerative cluster analysis (HCA) were invoked on the water data to examine correlation between the parameters. The correlation between species in GW, SW and topsoil was examined using Pearson's correlation.

#### 2.6.2 Human health risk (HHR) assessment of drinking water

The HHR assessment, established by the United States Environmental Protection Agency (USEPA), is a widely used tool for evaluating human health risk. Nitrate and cadmium concentrations were selected for HHR assessment in this study because the other toxics (Cr and Pb) were below detection in water. Both nitrate and cadmium primarily enter the human body through ingestion. Therefore, the rate of pollutant ingestion into the human body through drinking water was evaluated by calculating the chronic daily intake (*CDI*), hazard quotient (*HQ*), hazard index (*HI*), and carcinogenic risk (*CR*).

#### 2.6.3 Hazard quotient

The adverse effects of exposure to nitrate as a non-carcinogenic pollutant was evaluated using HQ) calculated as follows:

$$HQ = \frac{CDI}{RfD}$$
(1)

where *RfD* is the reference dosage (1.6 mg/kg/day for nitrate, and 0.0005 mg/kg/day for cadmium) [31, 32]. The chronic daily intake (*CDI*) was calculated using the following equation:

$$CDI = \frac{C \times IR \times EF \times ED}{BW \times AT}$$
(2)

where "*C*" is the measured concentration of the contaminant ( $NO_3^-$  or Cd) in the water (mg/L), "IR" is the rate at which a person drinks water (2 L/day for adults, 1.5 L/day for children, and 0.8 L/day for infants, "*ED*" is the duration of exposure in years (40 years for adults, 10 years for children, and 1.0 year for infants, "*EF*" is the exposure frequency in days (d) (365 days for adults, children, and infants, "*BW*" is the average body weight in kg (70 kg for adults, 20 kg for children, and 10 kg for infants, and "AT" is the average time (14,600 days for adults, 3650 days for children, and 365 days for infants), according to [33].

#### 2.6.4 Hazard index

The following equation was used to determine the *HI* of nitrate and cadmium associated with the HQ values, defined as the sum of the *HQ* of these measured parameters.



 $HI = \sum \left( HQ_{nitrate} + HQ_{cadmium} \right)$ (3)

If HQ > 1, carcinogenic health impacts are said to potentially exist whereas HQ < 1 indicates none. Similarly, HI < 1 indicates a minimal or non-existent risk of adverse non-cancer health, whereas HI > 1 denotes a high risk. Chronic risk (HQ or HI) is categorised as negligible (where HQ or HI < 0.1), low (where  $0.1 \le HQ$  or HI < 1), medium (where  $1 \le HQ$  or HI < 4), and high (where HQ or  $HI \ge 4$ ) [34].

#### 2.6.5 Carcinogenic risk

In the case of exposure to carcinogens, *CR* estimates a person's lifetime risk of developing any sort of cancer [35] calculated by the following formula:

$$CR = CDI \times SF$$
 (4)

where, "SF" (038 mg/kg/day for Cd) is the cancer slope factor [36]. The "CR" is described as ranging from very low (where  $CR < 1 \times 10^{-6}$ ) to very high (where  $CR > 1 \times 10^{-3}$ ) [34].

#### **3** Results and discussion

Table 2Total coliform andfaecal coliform densities inGW and SW samples

#### 3.1 Microbial characteristics of the water samples

Coliform bacteria constitute a useful indicator of microbial quality and can signal presence of pathogenic organisms in drinking water. The results of analysis of GW samples (BH01 to BH10) and SW samples (LK01 to LK04) for total coliforms and feacal coliforms are presented in Table 2. The WHO recommends a 0 cfu/100 mL maximum limit for total and faecal coliform count in drinking water [4]. Site BH03 was a protected shallow well (Table 2) and the higher bacterial densities were probably due to seepage and compromised well-head protection observed at this site. Out of all samples analyzed (n = 20) in the two seasons, 60% did not meet the WHO standard, having tested positive for coliform colonies, with faecal

Site/Sample ID	DRY SEASON		RAINY SEASON	
	Total coliforms (cfu/100 mL)	Faecal coliforms (cfu/100 mL)	Total coliforms (cfu/100 mL)	Faecal coliforms (cfu/100 mL)
BH01	0	0	170	0
BH02	0	0	0	0
BH03*	1300	290	300	70
BH04	130	0	170	100
BH05	17	0	220	0
BH06	0	0	130	0
BH07	0	0	160	80
BH08	0	0	0	0
BH09	0	0	140	0
BH10	36	12	70	0
LK01	16000	2300	24000	3100
LK02	24000	3600	34000	8000
LK03	19000	2900	26000	5000
LK04	13000	1400	11000	3000

BH denotes a GW site

\*BH03 is a protected shallow well

LK denotes SW (Likhubula River) site

For each parameter in each season, n = 10 for GW and n = 4 for SW



coliform colonies observed in 25% of the samples. Only two sites (BH02 and BH08) consistently produced samples that met the WHO limit in both seasons while 50% complied with the threshold of 50 cfu/100 mL prescribed in the Malawi Standard for raw GW [37]. More boreholes were contaminated in the rainy season than in the dry season probably due to transfer of microbes through recharge [38]. However, the seasonal variation of both total coliform and faecal coliform counts was not statistically significant (Table 3) due to dilution. Thus, this research found that GW was mostly bacteriologically contaminated and, therefore, a potential source of risk of exposure to water-borne diseases.

In Likhubula River, all samples (n = 8) complied with neither the WHO standard nor the national standard MS 733:2005 [37] for GW. The total coliform and faecal coliform densities showed that SW was grossly contaminated bacteriologically, and that it could not be consumed without prior treatment for risk of water-borne diseases. The variation in microbial pollution between seasons was not statistically significant (Table 3) for total coliforms probably due to dilution during the rainy season. These results are consistent with the findings of another study conducted in Blantyre's Lunzu Township [39]. Sources of microbial contamination in the river include animal dung and human faeces washed from the banks into the river. A comparison of GW and SW (Tables 4 and 3) shows that in both seasons both total coliforms and feacal coliforms were significantly higher (p < 0.05) in density in SW.

#### 3.2 Physical characteristics of water samples

The physical parameters of GW and SW samples from Chileka are shown in Table 5, and illustrated in Fig. 2. The values are compared to limits prescribed by the WHO. Though not particularly regulated in water intended for drinking, temperature may, especially if excessively high or low, compromise palatability. The temperatures recorded in both seasons in the present study were below the 30 °C threshold proposed by WHO and, therefore, not worrisome though slightly higher than those reported in a similar study in Blantyre [40]. Except at BH02 where an acidic pH falling outside the WHO range (6.5-8.5) was recorded in the dry season, the rest of the samples complied with the criteria. All samples complied with the WHO threshold of 1500 µS/cm for electrical conductivity (EC). On the other hand, except at BH02 in the dry season, all samples (n = 20) in both seasons met the WHO threshold of 600 mg/L for TDS. Therefore, based on Table 6, GW in the area may be classified as freshwater [41, 42]. Total hardness (TH) values were above the acceptability limit of 500 mg/L [4] only at few sites (BH02, BH05, and BH08). Hardness of water due to magnesium and calcium content is characterized by precipitation of soap scum, and by the need for excessive amounts of soap to achieve cleaning during washing [4]. Total hardness (TH) (as CaCO<sub>3</sub>) being in the range 119–859 mg/L (Table 5) shows that the GW may be categorized as ranging from moderately hard to very hard (Table 7) [41]. All samples registered turbidity values within the WHO limit of 5 NTU. Generally, GW physical parameters mostly conformed to standards, rendering the waters mostly acceptable in both seasons.

SW registered temperatures that were regular and reasonably comparable to those reported in a similar study in Mudi River in Blantyre [9]. All pH values (n = 8) recorded in two seasons fell within the WHO range (6.5–8.5). The WHO threshold of 750  $\mu$ S/cm for electrical conductivity (EC) was exceeded by all dry season samples probably due to concentration of salts resulting from reduced flow volume in the river. On the other hand, all samples (n = 8) met the WHO limit for TDS. Based on Table 6, the water from Likhubula River may be classified as freshwater. All total hardness (TH) values were below the WHO threshold of 500 mg/L and may be classified as ranging from moderately hard to very hard (Table 7) [41]. Table 3 shows significant seasonal variation (p < 0.05) of EC, TDS and TH, all being lower during the rainy season due to dilution as recorded in similar studies [45]. All turbidity values exceeded the 5 NTU limit recommended by WHO. This high turbidity was mostly due to disturbance of the water caused by brick-making activities along the banks during the dry season, and by cultivation during the rainy season. Turbidity was significantly higher (p < 0.05) during the rainy season due to runoff. A comparison of GW and SW (Tables 4 and 3) shows that TH was significantly higher (p < 0.05) in GW during the rainy season, and that while temperature, EC and TDS were significantly higher (p < 0.05) in SW during the dry season, pH and turbidity were higher (p < 0.05) in SW in both seasons.

#### 3.3 Chemical parameters of water quality

The results of chemical analysis of GW samples are presented in Table 8 (BH01 to BH10) and illustrated in Fig. 3. Nutrients  $(NO_3^{-1} \text{ and } PO_4^{3^{-1}})$  were detected in all GW samples (n = 20). All samples complied with the WHO requirement for  $NO_3^{-1}$  in drinking water (Table 8) implying no health risk. The values recorded in this study also compare reasonably with those reported previously in the neighbouring Machinjiri rural area of Blantyre [40]. In natural waters,  $NO_3^{-1}$  usually falls below 10 mg/L [46]. Nitrate concentrations above 13 mg/L in GW are rather excessive and a probable result of



		MD				MC			
		DRY SEASON	RAINY SEASON			DRY SEASON	RAINY SEASON		
Parameter	Statistical comparison	Mean±SD	Mean±SD	t. test	Sig	Mean±SD	Mean±SD	t. test	Sig
Temperature (°C)	DS vs RS	27.01 ± 0.73	27.17±0.73	- 0.490	0.630	27.95±0.52	26.30±1.48	2.105	0.080 <sup>ns</sup>
Н	DS vs RS	$6.84 \pm 0.45$	$7.01 \pm 0.36$	- 0.949	0.355	$7.92 \pm 0.27$	$8.00 \pm 0.19$	- 0.473	0.653 <sup>ns</sup>
Turbidity (NTU)	DS vs RS	$0.435 \pm 0.086$	$0.572 \pm 0.523$	- 0.822	0.431	$117.65 \pm 91.85$	$556.50 \pm 130.20$	- 5.508	0.002*
Electric conductivity (µS/cm)	DS vs RS	$490.20 \pm 244.86$	$476.20 \pm 175.67$	- 0.147	0.885	$882.50 \pm 25.42$	$316.50 \pm 22.43$	33.391	0.001*
TDS (mg/L)	DS vs RS	$325.60 \pm 170.28$	$311.30 \pm 124.33$	- 0.214	0.833	$598.00 \pm 16.83$	$202.25 \pm 15.22$	34.880	0.001*
Total hardness (as CaCO <sub>3</sub> , mg/L)	DS vs RS	$370.60 \pm 227.42$	$355.00 \pm 168.88$	- 0.174	0.864	$311.50 \pm 95.97$	$143.75 \pm 25.32$	3.380	0.015*
Calcium (Ca) (mg/L)	DS vs RS	79.29±54.51	$72.00 \pm 35.70$	- 0.354	0.728	$49.80 \pm 13.63$	$24.63 \pm 3.95$	3.549	0.012*
Magnesium (Mg) (mg/L)	DS vs RS	$41.90 \pm 23.10$	$42.64 \pm 20.02$	- 0.077	0.940	$45.48 \pm 15.77$	$19.93 \pm 4.48$	3.117	0.021*
Sodium (Na) (mg/L)	DS vs RS	$23.07 \pm 9.20$	$16.51 \pm 8.04$	1.697	0.107	$11.60 \pm 1.77$	$12.02 \pm 1.89$	- 0.329	0.754 <sup>ns</sup>
Potassium (K) (mg/L)	DS vs RS	$0.197 \pm 0.148$	$9.05 \pm 2.31$	- 12.084	0.001*	14.74±18.43	$60.15 \pm 76.58$	- 1.153	0.293 <sup>ns</sup>
Bicarbonate (HCO <sub>3</sub> <sup>-</sup> ) (mg/L)	DS vs RS	$17.82 \pm 6.96$	$19.88 \pm 7.76$	- 0.626	0.539	$23.63 \pm 4.64$	$12.85 \pm 1.03$	4.529	0.004*
Chloride (Cl <sup>-</sup> ) (mg/L)	DS vs RS	$53.18 \pm 73.99$	$30.43 \pm 46.14$	- 0.825	0.420	$137.25 \pm 37.02$	$21.03 \pm 2.15$	6.269	0.008*
Nitrate (NO <sub>3</sub> <sup>-</sup> ) (mg/L)	DS vs RS	$26.00 \pm 12.76$	$20.31 \pm 12.17$	1.021	0.321	$4.90 \pm 1.15$	$5.08 \pm 1.04$	- 0.226	0.829
Phosphate (PO <sub>4</sub> <sup>3<sup>–</sup>) (mg/L)</sup>	DS vs RS	$0.380 \pm 0.180$	$0.305 \pm 0.152$	1.017	0.323	$0.772 \pm 0.300$	$1.18 \pm 0.30$	- 1.943	0.100
Lead (Pb) (mg/L)	DS vs RS	ND	DN	ND	ND	ND	ND	ND	ND
Iron (Fe) (mg/L)	DS vs RS	DN	DN	DN	ND	$0.024 \pm 0.049$	3.77±2.94	- 2.546	0.044*
Cadmium (Cd) (mg/L)	DS vs RS	$0.073 \pm 0.082$	QN	2.812	0.020*	$0.064 \pm 0.057$	ND	2.267	0.064 <sup>ns</sup>
Chromium (Cr) (mg/L)	DS vs RS	ND	DN	ND	ND	ND	ND	ND	ND
Manganese (Mn) (mg/L)	DS vs RS	ND	$0.201 \pm 0.092$	- 6.928	0.001*	$0.053 \pm 0.044$	$0.476 \pm 0.149$	- 5.424	0.002*
Copper (Cu) (mg/L)	DS vs RS	DN	$0.372 \pm 0.073$	- 16.171	0.001*	ND	$0.336 \pm 0.065$	- 10.274	0.001*
Zinc (Zn) (mg/L)	DS vs RS	$0.234 \pm 0.212$	$0.091 \pm 0.051$	2.078	0.052	$0.275 \pm 0.213$	$0.134 \pm 0.063$	1.267	0.252
Total coliform (CFU/100 mL)	DS vs RS	$148\pm407$	$136 \pm 93$	0.093	0.927	$18,000 \pm 4690$	$23,750 \pm 9535$	- 1.082	0.321
Feacal coliform (CFU/100 mL)	DS vs RS	30±91	25±41	0.164	0.871	$2550 \pm 933$	$4775 \pm 2339$	- 1.767	0.128
BOD <sub>5</sub> (mg/L)	DS vs RS	I	I	I	I	$9.54 \pm 0.88$	$4.69 \pm 0.51$	9.542	0.001*
COD (mg/L)	DS vs RS	$22.47 \pm 9.00$	$20.66 \pm 9.44$	0.439	0.666	$57.23 \pm 9.81$	$28.80 \pm 9.90$	4.078	0.007*

Table 3 Two-sample t-test for seasonal comparison of physicochemical and biological parameters of GW and GW

Table 4Two-sample t-test forcomparison between GW andSW samples

		DRY SEASO	NC	RAINY SEA	SON
Parameter	Statistical com- parison	t. test	Sig	t. test	Sig
Temperature (°C)	GW vs SW	- 2.318	0.039*	1.513	0.156 <sup>ns</sup>
рН	GW vs SW	- 4.474	0.001*	- 5.120	0.001*
Turbidity (NTU)	GW vs SW	- 2.552	0.084*	- 8.539	0.003*
Electric conductivity (µS/cm)	GW vs SW	- 3.121	0.009*	1.770	0.102 <sup>ns</sup>
TDS (mg/L)	GW vs SW	- 3.117	0.009*	1.708	0.113 <sup>ns</sup>
Total hardness (as CaCO <sub>3</sub> , mg/L)	GW vs SW	0.493	0.631 <sup>ns</sup>	3.849	0.003*
Calcium (Ca) (mg/L)	GW vs SW	1.045	0.317 <sup>ns</sup>	4.134	0.002*
Magnesium (Mg) (mg/L)	GW vs SW	- 0.281	0.784 <sup>ns</sup>	3.382	0.006*
Sodium (Na) (mg/L)	GW vs SW	2.419	0.032*	1.656	0.126 <sup>ns</sup>
Potassium (K) (mg/L)	GW vs SW	- 1.578	0.213 <sup>ns</sup>	- 1.334	0.274 <sup>ns</sup>
Bicarbonate (HCO <sub>3</sub> <sup></sup> ) (mg/L)	GW vs SW	- 1.519	0.155 <sup>ns</sup>	2.804	- 0.019*
Chloride (Cl <sup>—</sup> ) (mg/L)	GW vs SW	- 2.131	0.055 <sup>ns</sup>	0.398	0.698
Nitrate (NO <sub>3</sub> <sup>-</sup> ) (mg/L)	GW vs SW	5.177	0.001*	2.440	0.031*
Phosphate (PO <sub>4</sub> <sup>3—</sup> ) (mg/L)	GW vs SW	- 3.060	0.010*	- 7.475	0.001*
Lead (Pb) (mg/L)	GW vs SW	ND	ND	ND	ND
lron (Fe) (mg/L)	GW vs SW	- 1.000	0.391 <sup>ns</sup>	- 2.562	0.083 <sup>ns</sup>
Cadmium (Cd) (mg/L)	GW vs SW	0.193	0.850 <sup>ns</sup>	ND	ND
Chromium (Cr) (mg/L)	GW vs SW	ND	ND	ND	ND
Manganese (Mn) (mg/L)	GW vs SW	- 2.437	0.093 <sup>ns</sup>	- 4.257	0.001*
Copper (Cu) (mg/L)	GW vs SW	ND	ND	0.858	0.408 <sup>ns</sup>
Zinc (Zn) (mg/L)	GW vs SW	- 0.326	0.750 <sup>ns</sup>	- 1.366	0.197 <sup>ns</sup>
Total coliform (CFU/100 mL)	GW vs SW	- 7.601	0.005*	- 4.953	0.016*
Feacal coliform (CFU/100 mL)	GW vs SW	- 5.393	0.012*	- 4.062	0.027*
COD (mg/L)	GW vs SW	- 6.380	0.001*	- 1.439	0.176 <sup>ns</sup>

GW means groundwater while SW means surface water. "—" means not detected or not determined, and ns indicates no significance while \* indicates significance at the 0.05 probability level of confidence

anthropogenic interference [47]. In 70% of the samples (n = 20), NO<sub>3</sub><sup>--</sup> was above 13 mg/L suggesting anthropogenic contribution of nitrate into the aquifer. This may be due to agriculture which is a dominant activity in the area. On the other hand,  $PO_4^{3-}$  was of concern to ecological integrity only [13], mostly exceeding the USEPA limit of 0.1 mg/L set for environmental protection of SW bodies [48]. The present results are similar to those reported in other local GW studies [49–51]. Groundwater can contribute phosphate to SW through base flow, with potential of enhancing eutrophication [10]. Sources of nitrogen and phosphorus in the area include human and animal wastes, manure and fertilizers.

Except for once at BH02 (where Cl<sup>-</sup> exceeded the WHO limit), concentrations in GW of all major constituents (Na, K, Mg, Ca, Cl<sup>-</sup> and HCO<sub>3</sub>) either fell below the WHO criteria (Tables 8) or were considered common and normal. While K, Mn and Cu were significantly higher (p < 0.05) in concentration during the rainy season (Table 3), Cd was significantly higher during the dry season, being below detection during the rainy season. Except for Mn during the rainy season, the trace metals (Pb, Cr, Cu, Fe, and Zn) invariably occurred below concentrations of health significance (Tables 8). However, virtually all samples in the dry season manifested Mn levels that could affect taste, laundry and plumbing fixtures. Similarly, while Cd was consistently below detection limit in the rainy season samples, a few dry season samples (BH01, BH02, BH03 and BH4) representing 20% (n = 20) registered concentrations exceeding the WHO threshold limits (Table 8). Continuous and prolonged (or lifetime) exposure to Cd concentration in the range 0.010–0.020 mg/L is a health risk, and above 0.020 mg/L, kidney damage may result [14]. Otherwise, GW was largely of satisfactory chemical quality. The lower Cd and Mn concentrations in the rainy season are attributable to dilution. Sources of manganese in the area include solid wastes while cadmium might have originated from historical use of phosphatic fertilizers. A comparison of GW and SW (Tables 4 and 3) shows that during the rainy season, Ca, Mg and HCO<sub>3</sub><sup>-</sup> were in both seasons significantly higher (p < 0.05) in SW. Similarly, NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> were in both seasons significantly higher (p < 0.05) in GW and SW, respectively.



(2024) 2:62

lable 5	Physical
charact	eristics of GW and SW
samples	s in Chileka

Site/Sample ID	Temp (°C)	рН	EC (μS/cm)	TDS (mg/L)	TH (as CaCO3, mg/L)	Turb (NTU)
BH01	26.6 (26.1)	<b>5.86</b> (6.91)	366 (423)	240 (248)	499 (319)	0.527 (0.230)
BH02	27.6 (26.5)	6.91 (6.75)	1117 (858)	762 (582)	859 (641)	0.393 (0.157)
BH03	26.2 (27.7)	6.49 (6.92)	329 (330)	214 (211)	192 (242)	0.570 (0.353)
BH04	26.7 (26.6)	7.02 (7.05)	522 (505)	347 (339)	419 (424)	0.363 (0.170)
BH05	26.3 (26.4)	7.37 (7.86)	483 (478)	319 (309)	<b>551</b> (484)	0.343 (0.333)
BH06	27.2 (28.0)	6.82 (6.65)	327 (341)	212 (222)	119 (132)	0.357 (0.443)
BH07	27.2 (27.2)	6.64 (7.13)	267 (258)	172 (162)	153 (176)	0.480 (1.76)
BH08	26.4 (28.2)	7.30 (6.76)	632 (667)	425 (446)	351 <b>(562)</b>	0.503 (1.25)
BH09	28.6 (27.6)	6.72 (6.74)	417 (410)	274 (264)	190 (235)	0.473 (0.587)
BH10	27.3 (27.4)	7.22 (7.31)	442 (492)	291 (330)	373 (335)	0.337 (0.440)
LK01	28.2 (24.5)	7.60 (8.24)	<b>853</b> (350)	579 (225)	294 (165)	240 (366)
LK02	27.8 (26.1)	7.81 (8.06)	<b>879</b> (303)	596 (193)	265 (152)	135 (634)
LK03	28.5 (26.5)	8.18 (7.88)	<b>883</b> (308)	597 (195)	236 (107)	59.7 (580)
LK04	27.3 (28.1)	8.10 (7.82)	<b>915</b> (305)	620 (196)	451 (151)	35.9 (646)
WHO	30	6.5–8.5	1500	600	500	5
IWS	-	6.5–8.4	3000	2000	-	-
LDWS	-	-	-	1000	-	-

BH denotes a GW site

LK denotes Likhubula River site

Temp, denotes "temperature", EC donotes "electrical conductivity, TDS denotes "total dissolved solids", TH denotes "total hardness", and Turb denotes "turbidity."

Bracketed values are for the rainy season and unbracketed values for the dry season.

For each parameter in each season, n = 10 for each GW and n = 4 for SW.

WHO means World Health Organization prescribed standards for human drinking water [4], IWS means irrigation water standards by FAO [43], and LDWS means livestock drinking water standards [43, 44]. Most parameters complied with the WHO limits [4], except for the values in bold type.



Fig. 2 Canonical correspondence analysis (CCA) biplot between trace elements and ions (a), trace elements and physicochemical parameters (b)

In similarity with GW, all SW samples (n = 8) in the two seasons met the WHO limit for  $NO_3^-$  in drinking water (Table 8), and ranged from excellent to acceptable (Table 9). The  $PO_4^{3-}$  concentrations exceeded the USEPA limit of 0.03 mg/L set for environmental protection of SW bodies [48]. Therefore,  $PO_4^{3-}$  is a threat to the ecological integrity of the river. The  $PO_4^{3-}$  levels found in this study are within the ranges reported in SW in some studies [45, 52] and were slightly higher in the rainy season probably due to input from agriculture. All major constituents (Na, K, Mg, Ca, Cl<sup>-</sup> and HCO<sub>3</sub>) were either



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Table 6       Classification of water         based on TDS and FC values	Class	TDS range (mg/L)	EC range (µS/cm)
(Source: [41, 42])	Freshwater	Less than 1000	Less than 1400
	Slightly saline	1000–3000	1400-4000
	Moderately saline	3000-10,000	4000-14000
	Very saline	10,000-35,000	14,000–50,000
	Briny	More than 35,000	More than 50,000
Table 7Classification of waterhardness (Source: [41])	Category		Concentra- tion of CaCO <sub>3</sub> (mg/L)
	Soft water		0–60
	Moderately hard water		61–120
	Hard water		121–180
	Very hard water		≥180

within the WHO thresholds (Tables 8) or considered common and normal. The trace metals (Pb, Cr, Cu and Zn) consistently occurred below concentrations of health significance (Tables 8). Concentrations of Fe and Mn were such as would be of both health and aesthetic concern particularly in the rainy season [4]. Table 4 shows that  $HCO_3^-$ , Cl<sup>-</sup>, BOD<sub>5</sub> and COD were significantly higher (p < 0.05) during the dry season while Fe, Mn and Cu were lower. The higher Cu, Fe and Mn concentrations in the rainy season (Table 3) were likely consequent to erosion into the river of solid wastes containing copper and manganese, and of the relatively iron-rich soils (Table 10). Cadmium (Cd) exceeded the WHO limit at 3 out of 4 sites but later underwent dilution by rainfall recharge to below the detection limit. Sources of Cd contamination in SW include pesticides and solid wastes. However, the water was mostly of fair chemical quality.

Biochemical oxygen demand ( $BOD_5$ ) and Chemical oxygen demand (COD) are among the key indicators of pollution in a water body. While  $BOD_5$  is a surrogate of organic matter content in water, COD measures both organic matter and chemical contents. Based on the  $BOD_5$  and COD concentrations measured in this study (Table 11), the river in the study area may be said to range from slightly polluted to polluted (Table 9) [53], with the pollution slightly increasing in the dry season. Both  $BOD_5$  and COD were significantly higher (Table 3) in the dry season than in the rainy season due to dilution due to rainfall recharge [6, 50]. The area being dominated by agricultural activities including rearing of cattle, the increased pollution in the dry season may be attributed to concentration of animal and plant wastes in the river water that was much lower in volume and slower in flow-speed at the time.

#### 3.4 Suitability of water for human and agricultural use

#### 3.4.1 Human health risk assessment for nitrate and cadmium exposure

According to USEPA, no convincing data exists to suggest nitrate in drinking water is associated with any adverse effect other than methemoglobinemia [54]. The HHR assessment was performed by calculating the hazard index (HI) (Eq. 3) for NO<sub>3</sub><sup>--</sup> and Cd, and the carcinogenic risk (CR) (Eq. 4) for Cd. The risk assessment data is summarised in Table 12. The results showed that HI > 1 for adults, children and infants, for at least 30% (6 out of 20) of the GW samples and for 60% (3 out 8) SW samples. Habineza et al. [55] reported HI values of 6.13E+01 mg/kg/day and 1.71E+02 mg/ kg-day for adults and children, respectively, which are significantly greater than 1 for both age groups. Similar findings are also reported in this study, raising a concern for non-carcinogenic adverse health effects associated with water usage. Similarly, CR > 0.001 for adults, children, and infants, for at least 15% (3 out 20) of the GW samples and for 18% (1 out of 8) of the SW samples. Habineza et al. [55] reported the CR of 0.013951 for Cd which is higher than the value reported in this study. However, USEPA recommended range for CR is  $10^{-4}$  and  $10^{-6}$  [55]. This suggests that the values reported in this study fall outside the range  $(10^{-4}-10^{-6})$ . Thus, there is a risk of developing cancer during a lifetime due to Cd exposure. Though both GW and SW are generally of good chemical quality, some chronic exposure to nitrate and cadmium is a health risk in the area.



Site/Sample ID	NO <sub>3</sub> -	PO4 <sup>3-</sup>	HCO <sub>3</sub> -	cr	Ca	Cd	J	Cu	Fe	×	Mg	MM	Na	Pb	Zn
BH01	36.1 (25.9)	0.362 (0.312)	10.3 (15.8)	28.0 (18.0)	106 (59.6)	<b>0.217</b> (nd)	(pu) pu	nd (0.426)	(pu) pu	0.145 (12.0)	56.8 (41.3)	nd ( <b>0.207</b> )	16.0 (10.6)	(pu) pu	0.226 (0.128)
BH02	40.9 (26.7)	0.765 (0.611)	17.9 (15.0)	<b>263</b> (161)	208 (141)	<b>0.086</b> (nd)	(pu) pu	nd (0.321)	(pu) pu	0.495 (8.79)	82.7 (70.5)	nd ( <b>0.232</b> )	43.0 (31.7)	(pu) pu	0.310 (0.142)
BH03	21.5 (9.96)	0.386 (0.269)	15.3 (17.4)	24.5 (9.46)	40.2 (50.0)	<b>0.056</b> (nd)	(pu) pu	nd (0.445)	(pu) pu	0.135 (8.56)	22.2 (28.4)	nd ( <b>0.061</b> )	15.5 (10.8)	(pu) pu	0.250 (0.131)
BH04	14.1 (5.11)	0.117 (0.057)	22.8 (30.1)	38.2 (20.4)	84.6 (86.0)	<b>0.142</b> (nd)	(pu) pu	nd (0.361)	(pu) pu	0.163 (11.6)	50.4 (50.9)	nd ( <b>0.314</b> )	26.9 (19.2)	(pu) pu	0.301 (0.078)
BH05	9.71 (12.4)	0.204 (0.131)	29.5 (25.9)	28.1 (13.1)	117 (99.6)	(pu) pu	(pu) pu	nd (0.354)	(pu) pu	0.239 (10.5)	62.8 (57.2)	nd ( <b>0.286</b> )	13.5 (10.9)	(pu) pu	0.290 (0.045)
BH06	23.8 (19.6)	0.263 (0.251)	16.6 (15.0)	17.1 (9.03)	27.0 (30.9)	(pu) pu	(pu) pu	nd (0.500)	(pu) pu	0.066 (11.3)	12.6 (13.3)	nd ( <b>0.075</b> )	27.1 (24.0)	(pu) pu	nd (0.055)
BH07	28.5 (19.4)	0.359 (0.311)	9.53 (9.54)	29.7 (14.2)	33.6 (39.2)	(pu) pu	(pu) pu	nd (0.405)	(pu) pu	0.109 (9.24)	16.7 (19.0)	nd ( <b>0.140</b> )	13.3 (5.13)	(pu) pu	nd (0.181)
BH08	40.4 <b>(47.8)</b>	0.516 (0.414)	25.3 (31.1)	38.4 (25.5)	64.6 (110)	<b>0.185</b> (nd)	(pu) pu	nd (0.359)	(pu) pu	0.386 (7.54)	46.0 (70.1)	nd ( <b>0.163</b> )	29.3 (23.6)	(pu) pu	0.732 (0.045)
BH09	37.8 (24.9)	0.479 (0.385)	9.38 (12.5)	33.8 (16.5)	42.5 (45.0)	(pu) pu	(pu) pu	nd (0.263)	(pu) pu	0.231 (6.28)	20.3 (29.9)	nd ( <b>0.212</b> )	22.5 (15.6)	(pu) pu	0.162 (0.064)
BH10	7.15 (11.3)	0.352 (0.304)	21.6 (26.5)	31.0 (17.1)	69.4 (58.7)	<b>0.044</b> (nd)	(pu) pu	nd (0.289)	(pu) pu	nd (6.72)	48.5 (45.8)	nd ( <b>0.319</b> )	23.6 (13.6)	(pu) pu	0.067 (0.037)
LK01	6.09 (4.88)	0.991 (1.24)	29.9 (12.0)	142 (22.7)	49.6 (26.1)	nd (nd)	(pu) pu	nd (0.332)	nd (0.341)	42.2 (22.8)	41.3 (24.1)	0.036 ( <b>0.410</b> )	11.0 (14.3)	(pu) pu	0.254 (0.155)
LK02	4.81 (5.84)	0.401 (0.852)	21.9 (13.3)	118 (22.4)	37.3 (29.1)	0.063 (nd)	(pu) pu	nd (0.430)	nd ( <b>5.38</b> )	3.11 (22.8)	41.8 (19.3)	0.081 ( <b>0.640</b> )	13.3 (12.0)	(pu) pu	0.333 (0.110)
LK03	3.37 (3.69)	0.657 (1.08)	23.8 (14.1)	102 (21.0)	43.5 (19.8)	0.138 (nd)	(pu) pu	nd (0.296)	0.097 ( <b>2.45</b> )	8.29 (20.0)	30.9 (13.9)	nd ( <b>0.302</b> )	9.38 (12.1)	(pu) pu	0.512 (0.062)
LK04	5.34 (5.90)	1.04 (1.56)	18.9 (12.0)	187 (18.0)	68.8 (23.5)	0.056 (nd)	(pu) pu	nd (0.287)	nd ( <b>6.92</b> )	5.35 (17.5)	67.9 (22.4)	0.096 ( <b>0.550</b> )	12.7 (9.68)	(pu) pu	nd (0.210)
онм	50	Ι	Ι	250	Ι	0.003	0.05	2	0.3	Ι	Ι	0.08	200	0.01	4
IWS	I	I	I	I	I	0.01	0.1	0.2	5	I	I	0.2		5	2
LDWS	100	Ι	Ι	1500	1000	0.01	-	0.5	10	Ι	500	10	Ι	0.1	20
BH denotes	s a GW site														
LK denotes	a Likhubula	River site													
Productod .	ind are solded	- the value of	in pac actor	w hotodotod	- Hor for the	den concon									
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nd means "not detected". The limits of detection were 0.003 mg/L for cadmium, 0.025 mg/L for Cu, 0.001 mg/L for Pb, 0.005 mg/L for Zn, 0.002 mg/L for Mn, 0.003 mg/L for Cr, and 0.005 mg/L for Fe

For each parameter in each season, n = 10 for GW and n = 4 for SW

WHO means World Health Organization prescribed standards for human being drinking water[4], IWS means irrigation water standards by FAO [43], and LDWS means livestock drinking water standards [43, 44].

Most parameters complied with the WHO limits [4], except for the values in bold type

Table 8 Chemical characteristics of GW and SW samples from Chileka

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Table 9Classification ofsurface water quality (Source:[53])

Class			Parameter		
	$NO_3^{-}$ (mg/L)	BOD <sub>5</sub> (mg/L)	COD (mg/L)	Fe (mg/L)	Mn (mg/L)
l (Excellent)	0–4	0–1.5	0–10	0–0.1	0–0.05
ll (Acceptable)	4–12	1.5–3.0	10–20	0.1–0.3	0.05-0.17
III (Slightly polluted)	12–36	3.0–6.0	20–40	0.3–0.9	0.17-0.5
IV (Polluted)	36–108	6.0-12.0	40-80	0.9–2.7	0.5–10
V (Heavily polluted)	>108	12.0->12.0	>80	2.7->2.7	1.0->1.0

#### 3.4.2 Suitability for irrigation and livestock watering

The pH values of both GW and SW generally measured within the range of 6.5–8.4 prescribed by FAO (1985) [43] for irrigation water. Further, TDS values recorded in this study (Table 5) suggest that while both GW and SW exclusively exceeded the 100 mg/L threshold set for livestock watering [44], both GW and SW were according to FAO guidelines [43] suitable for use in irrigation either with no restriction (< 450 mg/L), or with slight to moderate restrictions (450–2000 mg/L). On



Table 10 T	he values of	physicochen	nical parame	ters of topsoil a	nd subsoi	in the dry ar	nd rainy seas	uo						
Q	Hď	NO <sup>3-</sup>	3- PO4	Ca	Cd	J	G	Fe	×	Mg	Mn	Na	Pb	Zn
BH01	5.62 (6.59) <b>5.33 (5.49)</b>	20.6 (50.2) <b>34.4 (6.84)</b>	258 (81.2) <b>50.3 (123)</b>	1888 (1579) <b>1412 (1298)</b>	(pu) pu ( <b>pu</b> )	(pu) pu	48.9 (43.3) <b>49.6 (48.2)</b>	6118 (5951) <b>6187 (6176</b> )	557 (1087) <b>1230 (596)</b>	1639 (1405) <b>2327 (1732)</b>	645 (386) <b>447 (799)</b>	544 (249) <b>494 (304)</b>	(pu) pu <b>nd (nd)</b>	50.8 (42.7) <b>37.0 (24.0</b> )
BH02	5.40 (5.88)	17.1 (6.84)	311 (150)	3361 (2564)	(pu) pu	(pu) pu	47.1 (46.0)	6277 (6143)	598 (913)	3126 (2139)	597 (796)	466 (265)	(pu) pu	69.1 (54.0)
	4.99 (5.52)	53.1 (4.52)	38.6 (101)	2861 (2168)	(pu) pu	(pu) pu	44.3 (48.4)	6356 (6267)	1222 (530)	2669 (2378)	601 (905)	503 (318)	(pu) pu	46.2 (27.7)
BH03	5.35 (5.85) <b>5.15(5.56)</b>	31.0 (20.0) <b>25.2 (14.3)</b>	116 (84.1) <b>87.8 (67.2)</b>	874 (3012) <b>1192 (1644)</b>	<b>(pu) pu</b>	(pu) pu <b>nd (nd)</b>	49.0 (47.7) <b>46.6 (50.2)</b>	6264 (6186) <b>6309 (6315)</b>	590 (1076) <b>1096 (517)</b>	635 (2809) <b>2478 (1441)</b>	1061 (970) <b>807 (896)</b>	303 (207) <b>111 (56.4)</b>	(pu) pu (pd)	26.7 (45.5) <b>26.3 (25.4)</b>
BH04	5.16 (5.43) <b>4.77 (5.54)</b>	16.9 (7.01) <b>20.5 (7.01)</b>	97.4 (65.0) <b>51.1 (54.7)</b>	924 (1283) <b>966 (1074)</b>	(pu) pu (pu) pu	(pu) pu (pu) pu	54.0 (48.9) <b>50.5 (47.6)</b>	6140 (6182) <b>6236 (6241)</b>	766 (1186) <b>1214 (606)</b>	776 (1149) <b>1258 (1372)</b>	580 (381) <b>661 (372)</b>	235 (164) <b>85.7 (58.5)</b>	(pu) pu (pu) pu	65.4 (51.0) <b>41.4 ( 25.4)</b>
BH05	5.22 (5.39) <b>4.48 (5.41)</b>	21.0 (9.34) <b>35.5 (8.84)</b>	61.4 (156) <b>60.3 (92.6)</b>	1248 (1125) <b>1480 (1334)</b>	(pu) pu (pu) pu	(pu) pu (pu) pu	58.2 (53.1) <b>60.4 (47.2)</b>	6220 (6303) <b>6340 (6284)</b>	586 (953) <b>1237 (516)</b>	1 003 (1645) <b>1 2 46 (1 1 2 0)</b>	529 (488) <b>317 (412)</b>	104 (235) <b>269 (138)</b>	(pu) pu (pu) pu	47.4 (44.2) <b>39.9 (27.5)</b>
BH06	5.42 (5.87) <b>5.13 (5.57)</b>	39.9 (22.3) <b>50.2 (6.93)</b>	275 (506) <b>50.7 (435)</b>	9604 (8808) <b>11608 (8309)</b>	<b>(pu) pu</b> (pu) pu	26.6 (27.7) <b>26.4 (23.9)</b>	57.9 (55.7) <b>58.4 (44.0)</b>	6019 (6250) <b>6081 (6200)</b>	2345 (3435) <b>3103 (2758)</b>	9200 (8860) <b>9581 (7722)</b>	870 (1210) <b>1015 (1175</b> )	91.2 (241) <b>345 (87.7)</b>	(pu) pu ( <b>pu)</b>	173 (94.2) <b>122 (59.0)</b>
BH07	5.41 (5.77) <b>4.55 (5.40)</b>	8.38 (33.5) <b>30.5 (13.8)</b>	148 (145) <b>84.8 (117)</b>	3751 (2444) <b>2301 (2089)</b>	<b>(pu) pu</b> (pu) pu	2.75 (3.82) <b>2.59 (2.80)</b>	51.5 (52.0) <b>60.4 (45.8)</b>	6332 (6484) <b>6500 (6552)</b>	395 (630) <b>565 (445)</b>	3331 (2348) <b>2103 (2027)</b>	809 (636) <b>709 (632)</b>	61.7 (15.4) <b>63.1 (5.33)</b>	(pu) pu <b>nd (nd)</b>	52.5 (45.4) <b>43.9 (33.2)</b>
BH08	5.55 (6.03) <b>5.32 (5.53)</b>	2.60 (15.3) <b>13.5 (17.3)</b>	160 (88.8) <b>102 (61.5)</b>	3083 (1736) <b>1949 (1977)</b>	<b>(pu) pu</b> (pu) pu	4.54 (16.3) <b>nd (nd)</b>	42.8 (37.8) <b>41.3 (33.8)</b>	6301 (6310) <b>6332 (6280)</b>	443 (743) <b>632 (393)</b>	2928 (2440) <b>1583 (2892)</b>	1307 (917) <b>779 (1124)</b>	71.6 (18.9) <b>28.5 (3.58)</b>	(pu) pu <b>nd (nd)</b>	90.0 (42.2) <b>68.4 (34.1)</b>
BH09	5.42 (5.56) <b>4.98 (5.56)</b>	9.56 (58.9) <b>16.2 (16.5)</b>	215 (128) <b>98.6 (93.6)</b>	1754 (1531) <b>1282 (1118</b> <u>)</u>	<b>(pu) pu</b>	(pu) pu <b>nd (nd)</b>	40.4 (37.1) <b>35.6 (38.8)</b>	6225 (6294) <b>6289 (6247)</b>	622 (739) <b>919 (576)</b>	1572 (1881) <b>1787 (912)</b>	666 (562) <b>780 (660)</b>	143 (30.7) <b>179 (13.6)</b>	(pu) pu (pu) pu	83.5 (47.0) <b>49.9 (28.5)</b>
BH10	5.32 (4.47) <b>4.74 (5.55)</b>	10.7 (8.26) <b>22.4 (13.3)</b>	364 (123) <b>82.9 (94.3)</b>	964 (1835) <b>1 269 (932)</b>	<b>(pu) pu</b> (pu) pu	(pu) pu <b>nd (nd)</b>	43.2 (43.4) <b>40.7 (42.7)</b>	6316 (6328) <b>6378 (6406)</b>	389 (572) <b>519 (319)</b>	695 (1718) <b>1334 (1415)</b>	592 (397) <b>399 (730)</b>	186 (96.8) <b>136 (33.9)</b>	(pu) pu (pu) pu	58.2 (46.1) <b>40.7 (26.2)</b>
LK01	4.58 (5.08) <b>4.42 (4.94)</b>	2.98 (34.0) <b>17.5 (22.1)</b>	136 (291) <b>127 (125)</b>	10359 (12382) <b>8750 (8281)</b>	<b>(pu) pu</b>	3.20 (4.41) <b>5.08 (8.65)</b>	25.3 (24.1) <b>25.0 (36.7)</b>	5738 (5821) <b>5951 (6164)</b>	1116 (1860) <b>1598 (1981)</b>	10493 (8655) <b>8428 (9143)</b>	661 (886) <b>496 (1104)</b>	152 (89.2) <b>80.1 (227)</b>	(pu) pu (pu) pu	106 (74.0) <b>75.0 (67.3)</b>
LK02	4.74 (5.42) <b>4.85 (5.58)</b>	0.681 (14.4) <b>4.61 (15.0)</b>	250 (164) <b>91.1 (230)</b>	13309 (15571) <b>11287 (16074)</b>	( <b>pu) pu</b> (pu) pu	3.62 (4.33) <b>4.90 (5.88)</b>	31.4 (25.3) <b>25.6 (33.8)</b>	5718 (5746) <b>5828 (5923)</b>	2069 (3523) <b>3166 (3890)</b>	12960 (14204) <b>11248 (14263)</b>	1001 (644) <b>1192 (580)</b>	287 (202) <b>251 (240)</b>	(pu) pu (pu) pu	190 (131) <b>124 (160)</b>
LK03	4.81 (5.57) <b>4.62 (5.39)</b>	1.64 (29.5) <b>6.09 (2.43)</b>	395 (210) <b>28.2 (388)</b>	11353 (13060) <b>12172 (21592)</b>	<b>(pu) pu</b>	(pu) pu <b>nd (nd)</b>	23.5 (17.8) <b>22.4 (23.1)</b>	5307 (5333) <b>5321 (5431)</b>	1149 (2325) <b>1326 (1749)</b>	9549 (8218) <b>8253 (6770)</b>	701 (533) <b>700 (562)</b>	302 (24.5) <b>220 (108)</b>	(pu) pu (pu) pu	121 (50.0) <b>60.3 (38.7)</b>
LK04	4.97 5.71) <b>4.76 (5.66)</b>	0.755 (4.85) <b>1.13 (16.9)</b>	234 (215) <b>101 (77.5)</b>	15294 (18765) <b>6642 (22334)</b>	<b>(pu) pu</b> (pu) pu	(pu) pu <b>nd (nd)</b>	30.7 (24.9) <b>25.0 (32.5)</b>	5483 (5561) <b>5862 (6222)</b>	1381 (3368) <b>3240 (5758)</b>	1 2483 (10646) <b>9640 (20523)</b>	588 (269) <b>471 (634)</b>	231 (156) <b>132 (257)</b>	(pu) pu (pu) pu	105 (83.4) <b>79.3 (157)</b>
EMR (2007)			I	I	-	100*	200	I	I	I	1800	I	200	150

Bracketed values are for the rainy season while unbracketed values are for the dry season. Values in regular type are for topsoil while the values in bold type are for subsoil

nd means not detected

Except pH all values are in milligrams per kilogram (mg/kg)

For each parameter, n = 14

EMR (2007) is the Environmental Management (Soil Quality Standards) Regulations of 2007of The United Republic of Tanzania [60]

\*Limit is for hexavalent chromium

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Research

## Table 11Chemicalcharacteristics of LikhubulaRiver water samples

Site/ Sample ID	BOD <sub>5</sub> (mg/L)	COD (mg/L)
LK01	8.60 (4.43)	59.1 (19.8)
LK02	10.7 (5.13)	69.2 (38.8)
LK03	9.60 (5.11)	55.1 (35.8)
LK04	9.26 (4.10)	45.5 (20.8)

LK denotes a Likhubula River site

Bracketed values are for the rainy season and unbracketed values for the dry season

For each parameter, n=4 for each season

Table 12HHR assessmentresults for Chileka BW and SWsamples

HHR Assess- ment Parameter	GW			SW		
	Adults	Children	Infants	Adults	Children	Infants
HI range	0.091–13.0	0.240-34.2	0.486–36.5	0.066 to 7.95	0.229–20.9	0.185–22.2
CR range	0-0002	0-0.005	0-0.0066	0-0.0015	0–0.0039	0-0.0042

HI means hazard index and CR means carcinogenic risk

 $HI \leq 1$  denotes no health risk to humans

HI > 1 denotes higher level of hazard

 $CR < 1 \times 10^{-6}$  denotes very low risk of developing cancer in a lifetime

 $CR > 1 \times 10^{-3}$  denotes very high risk of developing cancer in a lifetime

the other hand, the chemical data and the standards in Table 8 show that Cd, Fe and Mn concentrations exceeded the prescribed limits for water intended for irrigation, and for livestock watering in a few samples. Otherwise, Pb, Cr, Cu, and Zn concentrations fell within the stipulated quality criteria. Similarly,  $NO_3^-$ ,  $CI^-$ , Na, Mg, and Ca concentrations complied with both standards (Table 8). Therefore, both GW and SW in the area is mostly suitable for both irrigation and livestock watering [43, 44] at least with respect to the parameters investigated in this study.

### 3.5 Canonical correspondence analysis (CCA) biplot, and hierarchical agglomerative cluster analysis (HCA) of water samples

The canonical correspondence analysis (CCA) biplot between trace elements and ions, and between trace elements and physicochemical parameters is given in Fig. 2. The arrow length indicates the significance of the variable and shows positive or negative correlations with the axis. Manganese (Mn), Cu, Cd, Pb, and Cr indicated strong association and are positively correlated with Na. Iron (Fe) showed a strong positive correlation with HCO<sub>3</sub>, Mg, Ca, K, and Cl, and a negative correlation with Cr. In Fig. 3b, Cr and Cd positively correlated with temperature, NO<sub>3</sub><sup>--</sup>, COD and BOD<sub>5</sub> but not with pH that instead showed negative correlation. Similarly, while Zn negatively correlated with EC, TDS and TH, it is positively correlated with temperature, COD and NO<sub>3</sub><sup>--</sup>, and positively correlated with pH.

Sampling sites in the same cluster in Fig. 3 have similar characteristics and natural background. This suggests that they could be affected by similar factors. This also applies to the parameters in the same cluster. According to Edet [56], correlation between chemical species in GW may indicate derivation from a common source. The dissolution of minerals such as halite, calcite, dolomite and gypsum could explain at least part of the contained Na, Ca, Mg and Cl<sup>-</sup>.

#### 3.6 Pearson correlation analysis for selected GW, SW and topsoil physicochemical parameters

To establish comparative relationships between samples from the topsoil, GW and SW matrices across the different sites, we invoked the Pearson correlation analysis. The results, demonstrating the strength and direction of linear relationships between different variables, are presented in Tables 13 and 14. The correlation tables indicate the extent of association between species within and across matrices at a significance level of either  $p \ge 0.05$  or  $p \ge 0.01$ . The values of the Pearson coefficient (*r*) show both positive and negative correlations between the parameters of soil, GW and SW, where r < |0.600|



Table 13	Pearson correlation	between g	roundwater	and topsoi	l physicochemic	al parameter
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		GW										
		pН	Ca	Mg	Na	К	$NO_3^{-}$	PO <sub>4</sub> <sup>3-</sup>	Cd	Mn	Cu	Zn
GW	рН	1										
	Ca	0.084	1									
	Mg	0.204	0.927**	1								
	Na	- 0.115	0.550*	0.424	1							
	К	0.244	- 0.089	- 0.026	- 0.366	1						
	$NO_3^{-}$	- <b>0.464</b> *	0.253	0.171	0.440	- 0.317	1					
	PO4 <sup>3-</sup>	- 0.296	0.441	0.288	0.584**	- 0.317	0.720**	1				
	Cd	- 0.302	0.258	0.281	0.332	- 0.516*	0.339	0.203	1			
	Mn	0.358	0.054	0.209	- 0.308	0.807**	- 0.291	- 0.265	- 0.471*	1		
	Cu	0.179	- 0.235	- 0.067	- 0.377	0.963**	- 0.241	- 0.271	- <b>0.534</b> *	0.730**	1	
	Zn	0.091	0.249	0.254	- 0.326	- 0.384	0.315	0.330	0.709**	- 0.414	- 0.410	1
TS	рН	- 0.291	- 0.016	- 0.038	- 0.071	0.447*	0.345	0.147	- 0.119	0.049	0.479*	- 0.031
	Ca	- 0.198	- 0.288	- <b>0.462*</b>	0.286	0.027	0.122	0.033	- 0.148	- 0.243	0.079	- 0.190
	Mg	- 0.169	- 0.286	- <b>0.446</b> *	0.269	0.076	0.144	0.010	- 0.175	- 0.190	0.140	- 0.219
	Na	- 0.421	0.518*	0.377	0.309	- 0.116	0.117	0.246	0.519*	- 0.215	- 0.188	0.157
	К	- 0.118	- 0.299	- 0.401	0.131	0.395	- 0.145	- 0.284	- 0.284	0.049	0.414	- 0.329
	Fe	0.301	- 0.045	- 0.050	- 0.162	- 0.035	- 0.002	0.141	- 0.103	0.058	0.047	0.058
	$NO_3^{-}$	- 0.252	- 0.316	- 0.366	- 0.299	0.159	0.005	- 0.080	- 0.200	0.027	0.179	- 0.214
	PO4 <sup>3-</sup>	- 0.230	- 0.027	- 0.188	0.431	- 0.131	0.126	0.245	0.134	- 0.358	- 0.107	- 0.111
	Cr	- 0.165	- 0.305	- 0.367	0.228	0.081	0.193	- 0.100	- 0.190	- 0.147	0.184	- 0.252
	Mn	- 0.272	- 0.270	- 0.332	0.269	- 0.194	0.375	0.281	0.219	- 0.471*	- 0.064	0.364
	Cu	0.121	- 0.054	- 0.200	- 0.097	- 0.061	- 0.436	- 0.475*	- 0.009	- 0.268	- 0.114	- 0.046
	Zn	- 0.048	- 0.218	- 0.334	0.467*	- 0.276	0.166	0.040	0.052	- 0.357	- 0.278	0.021

GW means groundwater, TS means topsoil. Bold values indicate statistical significance where by \* and \*\* indicates significance at the 0.05 and 0.01 probability levels of confidence, respectively

and r > |0.600| denote weak and strong associations, respectively. In GW (Table 13), weak negative correlations show for the pairs pH-NO<sub>3</sub><sup>--</sup>, K-Cd, Cd-Mn and Cd-Cu, a weak positive association for Ca-Mg, and strong positive associations for Na-PO<sub>4</sub><sup>3--</sup>, K-Mn, K-Cu and Cd-Zn. Similarly, there exists in SW (Table 14) strong negative associations between the pairs Ca-Cu and Mg-Cu, and strong positive correlations between the pairs Ca-Mg, K-Fe, K-PO<sub>4</sub><sup>3--</sup>, Fe-Mn, Fe-Cu and Mn-Cu. Between the parameters of each GW sample and those of its corresponding topsoil sample (Table 13), weak negative correlations manifest for Mg-Ca, Mg-Mg, Cu- PO<sub>4</sub><sup>3-</sup> and Mn-Mn, and weak positive correlations for Ca-Na, Na-Zn, K-pH, Cd-Na and Cu-pH. According to Table 14, while between the SW and topsoil parameters strong negative associations exist for the pairs NO<sub>3</sub><sup>--</sup>PO<sub>4</sub><sup>3-</sup>, Mn-PO<sub>4</sub><sup>3-</sup>, Zn- PO<sub>4</sub><sup>3-</sup>, Mn-K, Mn-Fe, and Cu-Fe, strong positive correlations show for the pairs Ca-Fe, Mg-Fe, Mg-Cu, Fe-pH, Fe-Ca, Fe-K, Cd-Na, Cd- PO<sub>4</sub><sup>3-</sup>, Cu-pH, Cu-K, Cu-NO<sub>3</sub><sup>--</sup>. Within the topsoil (Table 14), Ca correlates positively with Mg, K, PO<sub>4</sub><sup>3-</sup> and Zn, and negatively with Cu. Further, Mg correlates positively with K, PO<sub>4</sub><sup>3-</sup>, Cr, and Zn, and negatively with Cu. Similarly, K correlates positively with Cr and Zn, and negatively with Cu. Other positive correlations exist between the pairs Cu-NO<sub>3</sub><sup>--</sup>, Cr-, PO<sub>4</sub><sup>3--</sup>, Zn-PO<sub>4</sub><sup>3--</sup>, Cr-Mn and Cr-Zn.

#### 3.7 Soil physicochemical parameters

The physico-chemical data for soil in Chileka are presented in Table 10. The soil pH fell in the acidic ranges 4.42–5.62, and 4.47–6.59 in the dry and rainy seasons, respectively. These results compare well with those reported by Lakudzala and Khonje [57] in another study conducted in Blantyre. Soil pH affects the sorption and mobility of trace elements within the soil matrix. According to Rieuwerts [58], lower pH tends to decrease sorption thereby enhancing mobility and bio-availability of most forms of trace metals. Therefore, acidic soils would support movement of trace metals between the soil and water matrices. However, the current trace metal concentrations in GW suggest little or no interference from the surface. Soil quality standards have not been developed for Malawi, but for all the samples (n = 14 in each season),

Table 1₄	Pearson co	rrelation b	oetwee	n ground	dwater	and tops	oil physic	ochemical	paramete	r									
	SW										TS								
	pH Ca	Mg	Na	¥	Fe	$NO_{3}^{-}$	PO4 <sup>3-</sup>	Cd Mn	Cu	Zn	Ħ	Са	Mg	Na K	Fe	NO <sub>3</sub> <sup>-</sup> PO <sub>4</sub> <sup>3-</sup> C	r	D C L	Zn
SW pH	-																		
G	0.029 1																		
Mg	- 0.028 0.94	6** 1																	
Na	0.248 – 0.0	11 0.168	-																
¥	- 0.354 - 0.3	74 – 0.305	5 - 0.5	141															
Fe	- 0.124 - 0.5	79 - 0.569	9 - 0.3	72 <b>0.741</b> *	-														
NO <sup>3-</sup>	- 0.415 0.16	3 0.224	0.054	1 0.454	0.378	-													
$PO_4^3$	0.017 - 0.2	87 - 0.253	3 - 0.1	46 <b>0.735</b> *	0.533	0.366	-												
Cd	0.367 0.457	7 0.374	- 0.3	16-0.396	- 0.48	2 - 0.598	- 0.617	-											
Mn	0.167 – 0.6	73 – 0.632	2 0.081	0.499	0.853	** 0.377	0.552	- 0.656 1											
G	0.249 – <b>0.</b> 7	169* - 0.76	<b>3</b> * 0.175	5 0.314	0.719	* 0.156	0.505	- 0.661 <b>0.94</b>	6** 1										
Zn	- 0.043 - 0.0	10 - 0.093	3 - 0.4	97-0.019	0.25	3 – 0.363	- 0.488	0.675 - 0.4	52 – 0.4	62 1									
TS pH	0.099 – 0.6	62 - 0.618	3 - 0.1	370.569	0.859	* 0.046	0.629	- 0.496 0.82	7* 0.80	7* - 0	.4811								
G	0.031 - 0.2	10 - 0.079	9 - 0.1	45 0.666	0.801	* 0.414	0.502	- 0.289 0.669	9 0.445	- 0	0.408-0.1	111							
Mg	- 0.088 0.34;	7 0.391	0.113	3 - 0.103	0.205	0.541	- 0.395	0.042 0.148	3 – 0.0	70 – 0	0.129-0.1	58 <b>0.917</b> **	-						
Na	0.142 0.54	3 0.516	- 0.2	51-0.226	- 0.24	6 - 0.031	- 0.657	<b>0.783</b> * – 0.4	35 – 0.6	04 0.5	88 – 0.1	190.079	0.127	1					
¥	- 0.050 - 0.6	63 - 0.586	5 - 0.0	480.537	0.924	* 0.347	0.339	- 0.523 - <b>0.5</b>	908** 0.79	<b>7</b> * - 0	0.323-0.0	25 <b>0.792</b> **	0.869**	0.161 1					
Fe	- 0.290- <b>0.80</b>	3* 0.753*	* - 0.2	09-0.377	- 0.579	9 0.007	- 0.653	0.627 – <b>0.8</b>	328* - 0.9	22** 0.4	26 0.118	3 – 0.164	- 0.108	-0.102 - 0.080	-				
NO3-	0.343 - 0.6	48 - 0.628	3 0.501	I - 0.118	0.100	- 0.256	0.362	- 0.530 0.489	9 0.72	<b>4</b> * – C	.4280.186	5 - 0.193	- 0.176	0.133 0.006	0.104	1			
$PO_4^3$	- 0.668 0.04	5 0.011	- 0.1	32-0.242	- 0.370	0 - 0.743	* – 0.262	<b>0.794</b> * – 0.3	42 – 0.2	67 0.5	88 – 0.1	11 0.401 **	0.312*	0.090 0.243	- 0.053	- 0.2141			
ბ	- 0,014 - 0.1	83 – 0.138	3 0.579	9 - 0.281	- 0.11:	5 0.403	- 0.274	- 0.363 0.23	9 0.260	0 - 0	0.002 0.1 14	t 0.233	0.321*	- 0.102 <b>0.407**</b>	0.068	0.214 0.395** 1			
Mn	0.218 0.12;	7 0.193	0.641	I – 0.735	<b>3</b> * – 0.70.	2 -0.242	– 0.719*	0.294 - 0.3	93 – 0.2	87 0.3	06 0.077	7 0.051	0.156	- 0.031 0.092	0.101	- 0.061 0.212 <b>0</b> .	.509** 1		
Ū	- 0.036 0.63	3 0.779*	* 0.274	4 – 0.139	- 0.27	5 0.435	- 0.371	0.278 - 0.2	87 – 0.5	14 0.0	52 0.204	t – 0.635**	- 0.581**	0.132 – <b>0.364</b> **	* 0.121	<b>0.340*</b> – 0.188 0.	.216 0.0	047 1	
Zn	-0.128 0.31	1 0.374	0.085	3 - 0.315	- 0.23	3 0.123	- 0.799*	0.461 - 0.3	14 – 0.4	57 0.4	68 - 0.1	57 <b>0.688</b> **	0.822**	0.191 <b>0.688**</b>	- 0.159	- 0.112 <b>0.346** 0</b> .	<b>.401</b> ** 0.	211 - 0.3	:13* 1
SW mei tively	ans surface w	ater, TS m <sub>t</sub>	eans tc	psoil. Bc	uld valu	es indica <sup>.</sup>	te statisti	cal significa	ince wher	e by * a	nd ** in	dicates sig	nificance	at the 0.05 and	d 0.01 pr	obability levels	s of conf	idence,	respec-

Discover Environment (2024) 2:62

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the concentrations of Pb, Cd, Cr, Mn, Cu, Fe and Zn reported in the present study were generally low and comparable to values considered ambient elsewhere (Table 15). Further, the current trace metal profile of the soils at Chileka fall within the limits prescribed in some standards in the region (Table 15), and may essentially be of no environmental concern. Sources of trace metals in Chileka include fertilizers, animal manure, pesticides, welding, burning of tyres during baking of bricks, and solid waste disposal. These sources might require close monitoring and control to prevent long-term cumulative effects. The minerals K, Na, Mg, and Ca occurred in abundance in the soils, and are known to naturally constitute 99% of the elemental composition of the earth's crust [59]. Soil mineral abundance may vary with geographical region due to lithological differences. GW mineral content is influenced by dissolution from practically all solids and rocks, but especially from limestone, dolomite, and gypsum.

Nitrate (NO<sub>3</sub><sup>--</sup>) occurred in the ranges 0.681–39.9 mg/kg and 4.85–58.9 mg/kg, and phosphate (PO<sub>4</sub><sup>3--</sup>) in the ranges 61.4–395 mg/kg and 65.0–506 mg/kg in the dry and rainy seasons, respectively. These nutrient levels in soil agree with those reported in a study done by Chidya [45] in Zomba, Malawi. Sources of nitrogen and phosphorus in the study area include fertilizers and animal manure. Although phosphorous manifests reduced mobility due to adsorption to soil particles, it may be more readily transported by erosion and runoff into SW bodies, where it is a limiting nutrient for eutrophication, than into GW by percolation [13]. In contrast, NO<sub>3</sub><sup>--</sup> is highly mobile in soil and can be transported into both environmental compartments, with its excessive presence in GW intended for drinking being of public health significance [4, 14]. The results of this study suggest that NO<sub>3</sub><sup>--</sup> and PO<sub>4</sub><sup>3--</sup> from the soil might constitute a threat to the quality of GW and SW, respectively, in the study area.

#### 3.8 Seasonality of soil chemistry and impact on water quality

The seasonal variation of physicochemical parameters in soil is shown by box-and-whisker plots in Fig. 4a and b, and assessed by the Two-Sample Independent t-Test.

In both the topsoil and the subsoil, pH (Fig. 4a and Table 16) was higher (p < 0.05) in the rainy season than in the dry season probably due to the prevalent use of animal manures for agricultural purposes in the area. However, the abundance of  $NO_3^{-1}$  in subsoil was significantly higher (p < 0.05) during the dry season. Similarly, a comparison of topsoil and subsoil shows that pH and PO<sub>4</sub><sup>3-</sup> were significantly higher (p < 0.05) in topsoil than in subsoil during the dry season. Similarly, NO<sub>3</sub><sup>-</sup> was significantly higher (p < 0.05) in subsoil than in topsoil during the rainy season. Otherwise, the variation of Ca, Mg, Na, K, Cr, Cu, Fe, and Mn both between the seasons and between the topsoil and subsoil was not significant. This suggests limited mobility of the minerals in the soil matrix due to pH changes. But due to high mobility, nitrate leached from the surface resulting in the higher concentrations in the dry season than in the rainy season in subsoil. In contrast, the seasonal variation of topsoil  $NO_3^-$  was not significant probably due to compensation on the surface, through contribution from agriculture, of leached nitrate. Similarly, seasonal variation of  $PO_4^{3-}$  concentration in the topsoil was not significant likely consequent to low mobility due to sorption. Again, the higher PO<sub>4</sub>-P concentration in topsoil during the dry season is attributable to solid waste disposal and use of manures. Phosphorus is one of the major chemical constituents that constitute over 99% of the total elemental composition of the earth's crust [59]. Thus, phosphate in soil derives from the rock parent material, and from possible anthropogenic addition especially to agricultural soils through application of fertilizers and manures. Therefore, while contamination of GW by nitrate and SW by phosphate may occur in Chileka during the rainy season through transfer from the soil, the phenomenon is limited and unlikely for trace metals.

#### 4 Conclusions and recommendations

The purpose of this research was to assess the extent of contamination with trace metals, nutrients, and microbes (total coliforms and faecal coliforms) of water and associated soils in Chileka Township, Blantyre. The results show that both raw GW and SW in Likhubula River are not safe for drinking mainly due to bacterial contamination. The river is also rated as ranging from slightly polluted to polluted. On the other hand, GW is largely of satisfactory chemical quality but with a possibility of Cd exposure to the communities in excess of WHO thresholds especially in the dry season. Further, the communities are exposed to Mn beyond WHO limits. Nitrate, being mobile in soil, threatens GW quality whereas phosphate may, due to adsorption, potentially affect SW quality only. The trace metal levels in soil do not yet constitute an environmental problem. It is recommended that responsible authorities should continue to promote good sanitation, and include  $NO_3^-$  and Cd under surveillance studies in the area. The transfer of nitrate and phosphate from soil into SW may be minimized through proper solid waste disposal, and securing riverbanks against cultivation. Although the study



Element	Values compiled from	the present study	Reported max	ima and range	s from other stuc	lies	Common range for	Soil Quality Standards of the
			Malawi			Sub-Saharan Africa	soils worldwide	United Kepublic of Lanzania
	Dry Season (range)	Rainy Season (range)	[45]	[ <mark>5</mark> ]	[61]	[62]	[63]	[60]
Na, mg/kg	61.7-544	15.4–265	10.67–3169	I	I	. 1		
K, mg/kg	389-2345	572-3523	9.40-305	I	I	291–77,898		
Mg, mg/kg	635-12,960	1,149–14,204	3.41-112	I	I	I		
Ca, mg/kg	874-15,294	1,125–18,765	0.740-892	I	I	82-426,431		
Cd, mg/kg	nd	pu	I	nd-0.18	11, max	I	0.01-0.70	1
Cr, mg/kg	nd-26.6	nd-27.7	I	nd-8.19	8.19, max	0.7-598	1-000	100*
Cu, mg/kg	23.5-58.2	17.8–55.7	I	0.12-10.1	69, max	0.3-114	2-100	200
Fe, mg/kg	5307-6332	5333-6484	I	I	17,600, max	20-181,691	7000-550,000	I
Mn, mg/kg	529-1307	269-1210	I	9.00–31.4	I	1.6-6,575	20-3000	1800
Pb, mg/kg	nd	nd	I	0.03–3.49	231, max	0.3–639	2-200	200
Zn, mg/kg	26.7–190	42.2–131	I	0.26-17.5	210, max	0.3–138	10–300	150
nd denotes "n	ot detected"							
max denotes '	"maximum value"							
For each para	meter, n = 14							
*The limit for o	chromium is for the hexa	avalent form						

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Table 15 Summarized data for chemical analysis of soil samples from Chileka as compared to literature values

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a Box and whisker plot of seasonal variation of soil quality parameters.

Fig. 4 a Box and whisker plot of seasonal variation of soil quality parameters. b Box and whisker plot of seasonal variation of soil quality parameters

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#### Fig. 4 (continued)

has reached its aims, other equally important contaminants such as fluoride and arsenic were not included in this study due to financial and time constraints. The purposive sampling strategy employed and the limited number of samples taken probably did not adequately capture spatial and temporal variation in the characteristics of GW and SW. Therefore, a study including more boreholes and shallow wells, and more sampling sites along the Likhubula river is recommended. There is also a need to investigate whether or not on-site sanitation systems (pit-latrines and septic tanks) in the area might be contributing to nitrate, phosphate and chloride in groundwater.



(2024) 2:62

#### Table 16 Two-sample t-test for comparison between topsoil and subsoil samples and between seasons

		TOPSOIL		SUBSOIL			DRY SEA	SON	RAINY SE	ASON
Parameter	Statistical comparison	t. test	Sig	t. test	Sig	Statistical comparison	t. test	Sig	t. test	Sig
pН	DS vs RS	- 2.496	0.019*	- 6.703	0.001*	TS vs SS	2.997	0.006*	1.353	0.197 <sup>ns</sup>
Nitrate (NO <sub>3</sub> <sup></sup> ) (mg/L)	DS vs RS	- 1.686	0.104 <sup>ns</sup>	2.620	0.018*	TS vs SS	- 1.976	0.059 <sup>ns</sup>	2.234	0.040*
Phosphate (PO <sub>4</sub> <sup>3-</sup> ) (mg/L)	DS vs RS	1.078	0.291 <sup>ns</sup>	- 2.177	0.047 <sup>ns</sup>	TS vs SS	5.018	0.001*	0.559	0.581 <sup>ns</sup>
Calcium (Ca) (mg/L)	DS vs RS	- 0.260	0.797 <sup>ns</sup>	- 0.743	0.464 <sup>ns</sup>	TS vs SS	0.492	0.627 <sup>ns</sup>	- 0.121	0.905 <sup>ns</sup>
Magnesium (Mg) (mg/L)	DS vs RS	0.095	0.925 <sup>ns</sup>	- 0.370	0.714 <sup>ns</sup>	TS vs SS	0.282	0.780 <sup>ns</sup>	- 0.204	0.840 <sup>ns</sup>
Sodium (Na) (mg/L)	DS vs RS	1.831	0.079 <sup>ns</sup>	1.472	0.153 <sup>ns</sup>	TS vs SS	0.357	0.724 <sup>ns</sup>	0.259	0.798 <sup>ns</sup>
Potassium (K) (mg/L)	DS vs RS	- 1.984	0.058 <sup>ns</sup>	0.061	0.952 <sup>ns</sup>	TS vs SS	- 1.895	0.069 <sup>ns</sup>	0.240	0.812 <sup>ns</sup>
Lead (Pb) (mg/L)	DS vs RS	ND	ND	ND	ND	TS vs SS	ND	ND	ND	ND
lron (Fe) (mg/L)	DS vs RS	- 1.047	0.305 <sup>ns</sup>	0.488	0.630 <sup>ns</sup>	TS vs SS	- 1.224	0.232 <sup>ns</sup>	- 1.149	0.261 <sup>ns</sup>
Cadmium (Cd) (mg/L)	DS vs RS	ND	ND	ND	ND	TS vs SS	ND	ND	ND	ND
Chromium (Cr) (mg/L)	DS vs RS	- 0.395	0.696 <sup>ns</sup>	- 0.063	0.951 <sup>ns</sup>	TS vs SS	0.047	0.963 <sup>ns</sup>	0.391	0.699 <sup>ns</sup>
Manganese (Mn) (mg/L)	DS vs RS	1.156	0.258 <sup>ns</sup>	0.649	0.366 <sup>ns</sup>	TS vs SS	0.995	0.329 <sup>ns</sup>	- 1.080	0.290 <sup>ns</sup>
Copper (Cu) (mg/L)	DS vs RS	0.743	0.464 <sup>ns</sup>	0.057	0.827 <sup>ns</sup>	TS vs SS	0.273	0.787 <sup>ns</sup>	- 0.286	0.777 <sup>ns</sup>
Zinc (Zn) (mg/L)	DS vs RS	1.918	0.066 <sup>ns</sup>	0.312	0.569 <sup>ns</sup>	TS vs SS	1.827	0.079 <sup>ns</sup>	0.583	0.565 <sup>ns</sup>

DS means dry season, RS means rainy season, TS means topsoil, SS means subsoil, ND means not detected, and ns indicates no significance while \* indicates significance at the 0.05 probability level of confidence

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**Data availability** All the data for the study has been provided in this manuscript. The authors are also available to provide any data that may be needed by the journal.

#### Declarations

Competing interests The authors declare no competing interests.

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