RSC Advances

ROYAL SOCIETY OF CHEMISTRY

PAPER

Check for updates

Cite this: *RSC Adv.*, 2024, **14**, 30272

Appraising groundwater quality and probabilistic human health risks from fluoride-enriched groundwater using the pollution index of groundwater (PIG) and GIS: a case study of adama town and its vicinities in the central main Ethiopian rift valley

Hassen Shube, [a] Shankar Karuppannan, *[ab] Muhammed Haji, [a] Balamurugan Paneerselvam, [c] Nafyad Kawo, [d] Abraham Mechal [ef] and Ashu Fekadu [a]

Received 18th April 2024
Accepted 3rd September 2024

DOI: 10.1039/d4ra02890b

rsc.li/rsc-advances

This research's main objective is to identify the level of contamination in drinking water in Adama town and its environs by employing PIG, GIS and HHRA. The physical–chemical parameters of groundwater were determined, and the results were compared to regional and global drinking water quality guidelines. The pH of groundwater is alkaline, and the contents of Ca^{2+}, Na^{+}, HCO_3^{-}, and F^{-} in the majority of samples surpassed the permissible drinking limit. The hydrochemical facies were identified in the following order: Ca–Mg–HCO_3, Na–Ca–HCO_3, and Na–HCO_3. Cation exchange and Rock–water interaction are the major dominant natural mechanisms controlling groundwater chemistry. Using IDW interpolation methods with Arc GIS 10.8, spatial analysis of the physico-geochemical content of water divulged that TDS, pH, TH, EC, Mg^{2+}, Ca^{2+}, K^{+}, Na^{+}, Cl^{-}, HCO_3^{-}, F^{-}, and SO_4^{2-} all exhibit a positive trend in the direction of groundwater flow from the upland to the lowland (rift floor). As per PIG, the results show that 57%, 33%, 7% and 3% of the samples were found in the insignificant, low, moderate and high, correspondingly. The total hazard index (THI) is calculated from hazard quotients (HQIntake and HQDermal) results showing 83%, 73%, and 57% of the samples exceed the non-carcinogenic health threat of fluoride THI >1 in drinking water for children, women and men. Children are more susceptible to danger than either males or women, according to the THI data, based on body weights and consumption rates. Similarly, females are also more vulnerable to health risks than men.

1. Introduction

Over the last two decades, groundwater has become an increasingly important source of water supply in different locations all over the globe. The main source of water for many nations is groundwater. Groundwater is an important aspect of our system, and it is largely used for drinking and agriculture. Groundwater is a primary supply of domestic water in many African cities.[1,2] Rapid population growth, irrigation development, and an expanding tendency of industrialization have all contributed to increased demand for groundwater. Natural processes degrade groundwater quality, but anthropogenic pollution, which comes from sources such as agricultural fertilizers, industrial effluents, municipal wastewater, landfills, and animal wastes, is also a major driver of water quality degradation.[3–5] However, one of the concerns of the twenty-first century is the degradation of water quality.[6] Groundwater quality is declining worldwide as a result of anthropogenic activities like increasing urbanisation, industrial expansion, and agrarian intensification.[7–11] Polluted groundwater is less obvious than pollution in rivers and lakes, but it is more difficult to clean up. Groundwater quality has a significant impact on plant development and human health. A slight change in

[a]Department of Applied Geology, School of Applied Natural Science, Adama Science and Technology University, Adama, P.O. Box 1888, Ethiopia. E-mail: geoshankar1984@gmail.com

[b]Department of Research Analytics, Saveetha Dental College and Hospitals, Saveetha Institute of Medical and Technical Sciences (SIMATS), Saveetha University, Chennai 600077, Tamil Nadu, India

[c]Center of Excellence in Interdisciplinary Research for Sustainable Development, Chulalongkorn University, Bangkok, 10330, Thailand

[d]School of Natural Resources, University of Nebraska-Lincoln, 244.1 Hardin Hall, 3310 Holdrege Street, Lincoln, NE, 68583-0996, USA

[e]Geology Department, Addis Ababa Science and Technology University (AASTU), P.O. BOX 16417, Addis Ababa, Ethiopia

[f]Mineral Exploration, Extraction, and Processing Center of Excellence, AASTU, Ethiopia

water quality indicates that the aquatic ecosystem is not working properly. Because of weathering from source rocks, anthropogenic activities, and local environmental and ecological circumstances, the quality of groundwater is greatly influenced by physical and chemical soluble factors.[12] Precipitation, the geological structure as well as the mineralogy of aquifers and watersheds, as well as the geological procedures occurring inside the aquifer, are only a few of the variables that affect the chemical composition of groundwater.[13] In order to improve water resources over the long term, it is essential to comprehend the geochemical evolution of groundwater. The physical and chemical characteristics that impact groundwater quality in a given location are substantially influenced by geogenic and anthropogenic activity.

Inadequate surface water supplies, as well as uncertain and frequent monsoon failures, have prompted planners to look to a more reliable water source, groundwater. Overexploitation of this critical water source, on the other hand, has led to a rapid drop in groundwater levels, which is a problem in many regions of the world, particularly in developing and underdeveloped countries. The implications of such overexploitation have led to the establishment of plans for the long-term development of groundwater resources at all levels: local, regional, and global. Inputs from the evaluation of groundwater resources are critical for such planning, and the current work incorporates a rigorous scientific investigation of several groundwater parameters. Although the notion of groundwater quality appears to be straightforward, determining how to study and evaluate it remains a challenge. It is vital to consider the quality and quantity of groundwater resources to meet the growing demand for water caused by population growth, urbanization, and industrialization, particularly in developing countries. Because of groundwater pollution and aquifer vulnerability, urbanization is a difficult issue in developing countries like Ethiopia.[14–17] The quality of water sources is significantly influenced by human activity in the natural system.[18]

Contamination of groundwater by geogenic and anthropogenic causes can have serious health and social repercussions.[19–21] The primary cause of waterborne infections, specifically in rural regions of developing nations like India, South Africa, and Ethiopia, is the use of very contaminated drinking water.[22–24] High priority is given in evaluations of the safety of drinking water to the protection of aquatic ecosystem services, the reduction of the possibility of adverse health effects, and the assurance that uncontaminated water sources will be accessible over the course of many years.[25–27] Inverse Distance Weighting (IDW) and Geographic Information system (GIS) interpolation methods are crucial tools for evaluating and monitoring groundwater properties.[28–32] IDW (deterministic process) is a spatial interpolation algorithm that estimates values between measurements. Spline and kriging techniques are less efficient than IDW because they require more computing and modelling time, whereas kriging requires more user input.[19,33–37] Furthermore, this interpolation method fits well with real-world parameters. Researchers have widely used the IDW interpolation method to study the spatial distribution of physicochemical parameters.[15,38]

GIS is an effective method for determining the spatial distribution of contaminants plumes and water resources.[39] In order to track the distribution, trends, and physicochemical characteristics of water resources, it is a cost-effective approach to transform data into geographical forecasts.

Many dry and semi-arid parts of Ethiopia depend on groundwater supplies for residential uses, irrigation needs, or agricultural output. Ethiopia presently gets more than 80% of its drinking water from subsurface water.[40,41] Groundwater dependence will become even more reliant in the future as demand rises due to population growth and climate change. In addition, the industry's water requirements have increased overall. The groundwater table is being driven down by intense rivalry among consumers in the agriculture, industry, and household sectors. The quality of groundwater is quickly declining as a result of extensive surface water contamination. Furthermore, untreated wastewater discharged through bores and leachate from non-scientific solid waste disposal contaminates groundwater, lowering the quality of freshwater supplies. In both urban and rural regions of Adama Woreda, groundwater serves as the main source of drinking water. Furthermore, despite increased access to water, the amount, quality, and long-term viability of urban water services are major concerns.

In the MER (Main Ethiopian Rift), groundwater is intensively utilised for the provision of drinking water.[42] The aquifers throughout the RV (Rift Valley) and the highlands have diverse hydrochemistry. Several researchers have observed high F-levels in RV groundwater,[43,44] and it is the primary geological problem for the supply of drinking water. Due to the presence of mica aquifers, amphiboles, and pyroxene, fluoride may be discovered in the groundwater of the research area.[45] Furthermore, anthropogenic activities like urban sewage, industrial, as well as agricultural intensification are affecting the quality of surface and groundwater in Adama Woreda, (MER). In spite of the fact that millions of people living along the MER depend on groundwater supplies for their survival, there was no groundwater quality monitoring system in place, nor were there any aquifer or well-head protection zones. For the purpose of efficiently developing new groundwater schemes and managing groundwater resources in the area under investigation, it is required to have a regional variation map of the principal cations and anions. The study's goals are to analyze groundwater quality for drinking applications.

The groundwater is in close touch with a variety of minerals, all of which are soluble in water in different ways. Water's utility for various purposes is determined by dissolved minerals. A rift with igneous structures runs through the research area. Groundwater is the principal source of water in this area, serving not only household but also agricultural and industrial needs. With these considerations in mind, the current research sought to better understand the nature of groundwater, its seasonal hydrogeochemical fluctuations, and its suitability for various uses such as irrigation and residential activities. To determine the best way to develop solutions for the water resource challenge, a powerful tool GIS application, the PIG is utilized to determine the quality of water. Using pollution index of groundwater (PIG), Human health risk assessment (HHRA), and GIS methodologies, the primary aim of this research is to examine the safety of using groundwater for drinking reasons, in addition to the dangers that fluoride pollution may cause to human health.

2. Materials and methods

2.1. Portrayal of research site

2.1.1. Location and climate. Adama Woreda is positioned inside the north-central part of the Main Ethiopian Rift (CMER), within the East Showa area of the Oromia. The geographical location of the town ranges from 8027.5′N–8035.7′N and 39 013.5′E–39019′E with an altitude that generally ranges from 1360–2338 m above sea level (Fig. 1). It's located in the East African Rift Valley (EARV), about 99.5 km southeast of the Ethiopian capital city of Finfinnee (Addis Ababa). It's nestled between two mountain ridges in the Great Rift Valley on generally flat lowland, which is located in the Awash River basin. Adama is the fourth largest city in Ethiopia and one of the most important cities in the Oromiya region. This country's second-most populous city has seen tremendous growth. It is the most populous and rapidly urbanising city in the Oromia Region, which is centrally located on the express highway connecting Addis Ababa and Djibouti and has a plethora of industries and manufacturing enterprises, making it a major commercial and transportation hub. In the Adama woreda, the annual rainfall ranges from 1200 mm to 800 mm. It has bimodal rainfall patterns, with the main rainy season, the summer monsoon, extending from June to September, and the dry period extending between October and February. There is a short rainy season between February and May, with an average rainfall of 800 mm. The mean annual temperature ranges between 8 and 28 °C. The month of May has the highest recorded temperature. The mean relative humidity is 61.3% (National meteorological service agency).

2.1.2. Geological and hydrological context. Various lithological units, starting from the tertiary to the quaternary age, are outcropped within the study area. The realm is principally lined by volcanic and substance rocks. The sedimentary rock comprises a deposit cowl and a body of water sequences. The geology of the research area is dominated by geological formations associated with volcanism and alluvial deposits. Volcanic rocks and materials include basalts, trachyte, rhyolitic lava flows and domes, pumice fall, tuffs, ignimbrites, scoria, obsidian, and ash flow deposits (Fig. 2).

Ignimbrite is exposed in the northern and central part of the investigation area and forms the major part of the volcanic rock. It is made of welded tuff (ignimbrite) and a non-welded pyroclastic case (ash and tuff). It is heavily welded, and characterized by developed vertical joints and breaks that offer high to

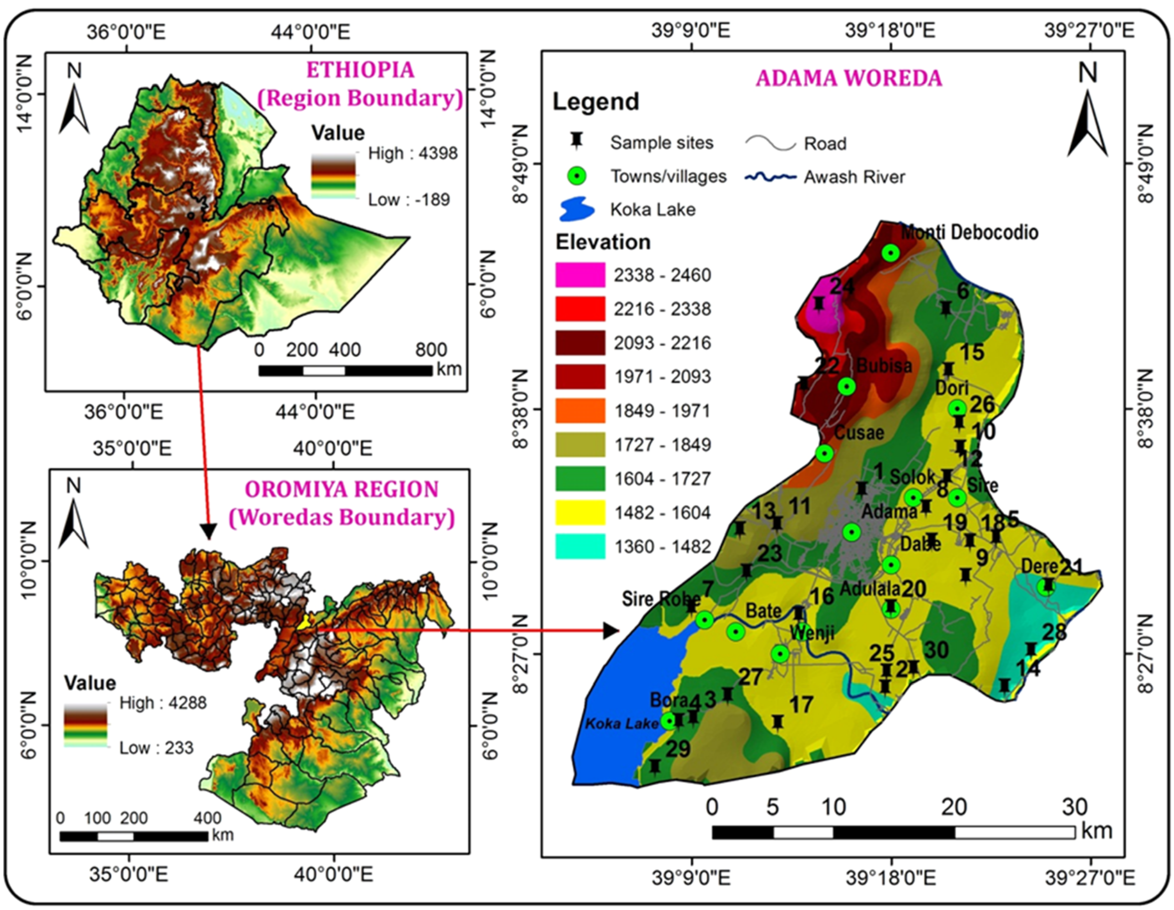

Fig. 1 Location of the research site.

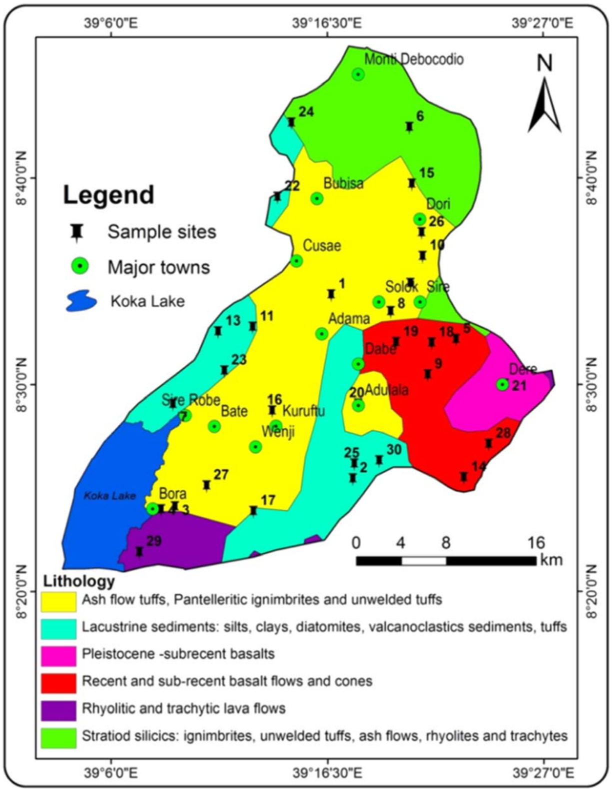

Fig. 2 Geological map of the study area.

moderate permeability. Basalts are vesicular basalts that have been filled with carbonate minerals. The Adama unit (Nazareth group) is made up of a dense sequence of welded ignimbrites with fiamme pumice ash and acidic lava flows, as well as domes with basaltic units. Between lava domes and ignimbrites, one is interlayered. Rhyolites, light-coloured trachyte, and dark obsidian layers comprise these rock units. They have distinct flow structures and are characterised by columnar joints in some places. In general, these rocks are porphyritic, with a felsic to glassy groundmass containing plagioclase, quartz, pyroxene, and alkali feldspar phenocrysts. The soil profile in the area has largely been influenced by pedogenic processes associated with volcanism. The lacustrine sediments were deposited in this great ancestral lake[43,46] and are found in the lakes and on the shoulders of the Pliocene-Pleistocene ignimbrite that pervades the rift in general and Adama and the environs in particular. These fine-grained deposits are typically yellowish-brown in colour, have fine stratification, and frequently contain a high proportion of volcanic matrix. The hydrogeology of Adama woreda is blanketed with volcanic rocks of various and variable hydraulic characteristics. The primary aquifers in this area are relatively permeable quaternary scoriaceous basalts with high number one hydraulic conductivity; deep wells may contain ignimbrites and sloppily fractured basalts.[47] Apart from weathered and fractured zones, the Nazaret unit (welded ignimbrites) has poor hydraulic conductivity. Along with weathered and fractured zones, the locally acidic volcanic gadgets of the quaternary bede gebaba volcanic unit exhibit low permeability. These are much less fractured and faulted formations.[48]

2.2. Sample collection and analysis

Water analyses have been executed *via* way of means of the use of general procedures "American Public Health Association".[49] For the purpose of characterising and mapping the appropriateness of the groundwater throughout the study site, a total of thirty wells were selected from a wide variety of sites. A global positioning system (GPS device) was used to record the sample sites and altitude. During water samples collection, handling, protection, and analysis, general strategies endorsed with the aid of using the[49] had been observed to make sure facts were quality and consistent. The parameters together with pH and electric conductivity (EC) have been measured within side the discipline even as the attention of chemical constituents together with Mg^{2+}, Ca^{2+}, K^+, Cl^-, Na^+, NO_3^-, SO_4^{2-} and F^- in groundwater samples turned into decided with inside the laboratory. The sampling maintenance and evaluation have been executed according to the standard methods (Table 1) prescribed *via* way of means of the.[49] In the current study, duplicates have been used for QC (Quality Control) and QA (Quality Assurance). To check the accuracy of the analytical findings, IBE ("Ionic Balance Error") turned into calculated (eqn (1)). All major anions and cations have been taken in milliequivalents according to a litre (meq L^{-1}) and the IBE values have to now no longer surpass the secure restriction of ±5%.

$$\text{IBE}\ (\%) = \left(\sum\text{Cations} - \sum\text{Anions}\right)/\left(\sum\text{Cations} + \sum\text{Anions}\right) \times 100 \quad (1)$$

2.3. Pollution index of groundwater (PIG)

It is widely accepted and used by researchers around the world to appraise the water quality index,[51–53] which was initially formulated and proposed by ref. 54. It is a numerical representation of the extent of contaminants in groundwater based on the relative influence of physicochemical (pH, TDS, major cations, and anions) parameters.[26] On the basis of the WHO drinking standards, PIG was calculated using the method suggested by ref. 54.

PIG enables quantifying the relative effect of each chemical variable, such as pH, TDS, Cl^-, Mg^{2+}, SO_4^{2-} *etc.*, individually on the overall groundwater quality. For the present study, the estimation of PIG was done in 5 steps. In the 1st step, relative weight (from 1–5) was apportioned to every chemical variable (Table 2). The highest weight ($R_w = 5$) was assigned to the parameter having the highest significance and its relative effect on public health. Similarly, the lowest weight ($R_w = 1$) was assigned to the parameter having the lowest effect on human health.[54] In "the next step, the Wp (weight parameter) was estimated for each chemical variable to evaluate its relative impact on groundwater quality (eqn (2)):

$$\text{Wp} = R_w/\sum R_w \quad (2)$$

Table 1 Analytical techniques adopted to analyze physicochemical parameters[50]

Parameters	Units	Analytical techniques
Hydrogen ion (pH)	Range	Field kit (IONIX portable water quality meter) *in situ*
Electrical conductivity (EC)	(μS cm^{-1})	
Total dissolved solids (TDS)	(mg L^{-1})	
Sodium (Na^+) & potassium (K^+)		Flame photometric
Calcium (Ca^{2+}) & magnesium (Mg^{2+})		EDTA titrimetric
Chloride (Cl^-)		$AgNO_3$ titrimetric
Bi-carbonate (HCO_3^{2-})		H_2SO_4 titrimetric
Sulphate (SO_4^{2-})		Turbidity (UV-Visible spectrophotometer)
Fluoride (F^-)		Ion chromatography

Table 2 Relative weight of chemical parameters (after ref. 54)[a]

Chemical parameters	Drinking standard, D_s	Relative weight (R_w)	Weight parameter (Wp)
pH	7.5	5	0.1316
TDS	500	5	0.1316
F^-	1.5	5	0.1316
Cl^-	250	3	0.0789
SO_4^{2-}	150	2	0.0526
NO_3^-	45	4	0.1053
HCO_3^{2-}	300	5	0.1316
Na^+	200	4	0.1053
K^+	10	1	0.0263
Mg^{2+}	30	2	0.0526
Ca^{2+}	75	2	0.0526
		$\sum R_w = 38$	$\sum W_i = 1.000$

[a] Note: All parameters in mg L^{-1} except pH.

In the 3rd step, the status of content, denoted by Sc, was estimated for individual parameters (eqn (3)):

$$Sc = C/D_s \tag{3}$$

where C is: the concentration of a specific quality variable for a particular spot, and D_s is the threshold limit of that specific variable with respect to drinking quality.[54]

In the next step, overall water quality (Ow) was evaluated by multiplying the Wp and Sc (eqn (4)):

$$Ow = Wp \times Sc \tag{4}$$

In the fifth and final step, the PIG was computed through summation of all the Ow values (eqn (5)):

$$PIG = \sum Ow \tag{5}$$

Table 3 Classification of groundwater quality as per PIG values

PIG values	Classification of groundwater quality
<1.0	Insignificant pollution
1.0–1.50	Low pollution
1.50–2.0	Moderate pollution
2.0–2.50	High pollution
>2.50	Very high pollution

During the PIG appraisal, the relative influence of an individual chemical parameter from each sampling location is taken into consideration. The individual impact of a particular pollutant on the overall groundwater quality becomes clear through the values of Ow for a particular contaminant. When a specific contaminant's Ow value exceeds 0.1, it contributes 10% to the PIG value of 1.0.[51,54] The categorization of PIG based on its values is given in Table 3.

2.4. Human health risk assessment (HHRA)

Health risk is the severe toxic effects on the human that results from pollution.[55] Fluoride in drinking water interacts population in three different pathways such as intake, dermal and inhalation.[56] However, inhalation way of health risk is not considered in this study because of the absence of toxicological information like fluoride reference dose and transfer percentage from water to air. US EPA ("U.S. Environmental Protection Agency") suggested that health risk assessment mainly made from four methods like exposure assessment, risk characterization, dose–response assessment, and hazard identification[1,57] was followed in the current study. Based on the two pathways discussed above, DAD and CDI (mg kg^{-1} day^{-1}) were computed to estimate the receiving doses *via* individual pathways. CDI stands for chronic daily intake and DAD stands for dermally absorbed dose. Calculating the non-carcinogenic risk linked with the drinking of water *via* the CDI pathway requires the use of eqn (6):[58]

$$CDI = C \times IR \times ED \times EF/BW \times AT \tag{6}$$

here the term 'CDI' stands for 'chronic daily intake' (mg kg^{-1} day^{-1}); C stands for the fluoride content in groundwater (mg L^{-1}); IR stands for ingestion rate (L day^{-1}: 0.90 L day^{-1} for infants and 1.5 L day^{-1} for men and women); The exposure duration is ED (years: 30 for men and women, and 12 for children, correspondingly); EF stands for exposure frequency (365 days per years for children, males, and females); BW is the average body weight (in kilogrammes; for men, women, and children, correspondingly: 70, 55, and 15); AT stands for the average time (days: 10 950 for men and women, 4380 for children, correspondingly). Dermal contact pathway was computed with eqn (7):

$$DAD = TC \times K_i \times EV \times ED \times EF \times SSA \times CF/BW \times AT \tag{7}$$

DAD stands for dermally absorbed dose (mg kg^{-1} day^{-1}); TC; contact duration (h day^{-1}) 0.4 for children, men and women. K_i; dermal adsorption parameters (cm h^{-1}: 0.001 cm h^{-1}); EV; bathing frequency (times per day) 1 considered as time in a day). SSA; skin surface area (cm^2) 12 000 and 16 600 cm^2 for children and female, male correspondingly); CF; conversion factors (0.001). ED stands for exposure duration (years: 30 and 12 for male, female and children, correspondingly). EF stands for exposure frequency (days per year) 365 days for children, male and female); BW indicate body weight (kg: 55, 70, and 15 for female, male, and children correspondingly), and AT stands for average time (days: 10 950 for female and male, 4380 children, correspondingly). HQ_{oral} and HQ_{dermal} hazard quotient for the fluoride health risk evaluation is calculated using eqn (8) and (9).

$$HQ_{oral}\frac{CDI}{RfD} \tag{8}$$

$$HQ_{dermal}\frac{DAD}{RfD} \tag{9}$$

RfD indicates the reference dosage of a particular contaminant. The RfD of fluoride (0.04 mg kg^{-1} day^{-1}). The total hazard index (THI) which indicates the non-carcinogenic risk is evaluated by *s* hazard quotients (HQ_{oral} + HQ_{Dermal}) and are computed by eqn (10):

$$THI_i = HQ_{oral} + HQ_{dermal} \tag{10}$$

Based on the THI values, <1 value indicates no major risk of non-carcinogenic" effects. Although, in the case of THI value that surpasses THI > 1 are risks to inhabitants.[58]

2.5. Software used

The places of every well have been taken into the GIS surroundings and the consequences of every parameter analysis have been introduced to the involved wells. Spatial analyst, a prolonged module of ArcGIS 10.8 became used to discover the spatial conduct of the groundwater pleasant parameters. GIS application software An IDW (Inverse Distance Weighting) spatial distribution map for water quality indicators was made using ArcGIS 10.8.[18,19] The concentration of geochemical parameters and the approximate groundwater quality index for the preparation of spatial maps are very convenient and efficient decision-makers in the field of water resources. The geochemical characterization became performed *via* way of means of the usage of AqQA software.

3. Results and discussion

3.1. Variation of physico–chemical ions

Physico–chemical ionic concentrations and statistical metrics such as minimum, maximum, and average as well as consuming water quality standards[59,60] are given in Table 4.

3.2. Physical characteristics of ground water

The pH of the groundwater in the area under investigation ranged from 6.5 to 8.2, with an average value of 7.5; this suggests that all samples were of a nature that was moderately acidic to alkaline, which is in conformity with the guidelines made by the WHO for normal groundwater quality (6.5 to 8.5). Fig. 3a depicts an interpolated spatial variation map of groundwater pH. The pH level is highest in the north-eastern and southern parts of the research area. High pH values are found in RV aquifers, where Na-rich igneous rock serves as a major aquifer.[1,47] The high pH values found in the investigation area's northern parts were caused by underground water moving through faults in the deep ground.

The EC varied between 110.7-3040 µS cm^{-1}, with mean values of 794.4 µS cm^{-1} (Table 4). According to WHO guidelines, the prescribed limit for EC is 1500 s cm^{-1}; however, with the exception of sampling site number 25, the limit was surpassed (Fig. 3b). In the research region, high EC values may be induced by agricultural practices that add certain salts to the ground as well as wastewater discharge from industrial and urban areas (Amanial, 2015).[61] The TDS values varied between 55.4 and 1814 mg L^{-1} with an average of 483.6 mg L^{-1} and most of the samples illustrated TDS values within the desirable limit of

Table 4 Statistical overview of the various physicochemical ions in groundwater

Ions	Minimum	Maximum	Mean	Std. dev.	CES, 2013	WHO, 2017		% of the samples exceeding the limit
						Most desirable	Not permissible	
pH	6.5	8.2	7.5	0.5	6.5–8.5	6.5 to 8.5	<6.5 and >8.5	0
EC (µS cm^{-1})	110.7	3040.0	794.4	646.7	—	<1500	>1500	13
TDS (mg L^{-1})	55.4	1814.0	483.6	406.8	1000	<500	>1500	3
TH (mg L^{-1})	5.9	717.3	122.4	127.7	—	<100	>500	—
Ca^{2+} (mg L^{-1})	2.2	224.0	34.7	41.4	75	<75	>200	3
Mg^{2+} (mg L^{-1})	0.1	38.4	8.7	8.5	50	<50	>150	0
Na^+ (mg L^{-1})	9.5	562.3	178.6	157.0	200	<200	>200	50
K^+ (mg L^{-1})	1.5	52.0	19.1	12.2	1.5	<10	>10	80
Cl^- (mg L^{-1})	5.8	192.0	42.8	51.7	250	<200	>600	0
SO_4^{2-} (mg L^{-1})	4.3	243.2	40.8	50.6	250	<400	>400	0
HCO_3^{2-} (mg L^{-1})	143.0	1171.0	458.0	245.9	—	<300	>600	20
F^- (mg L^{-1})	1.0	10.5	4.2	3.3	1.0	<1.5	>1.5	83

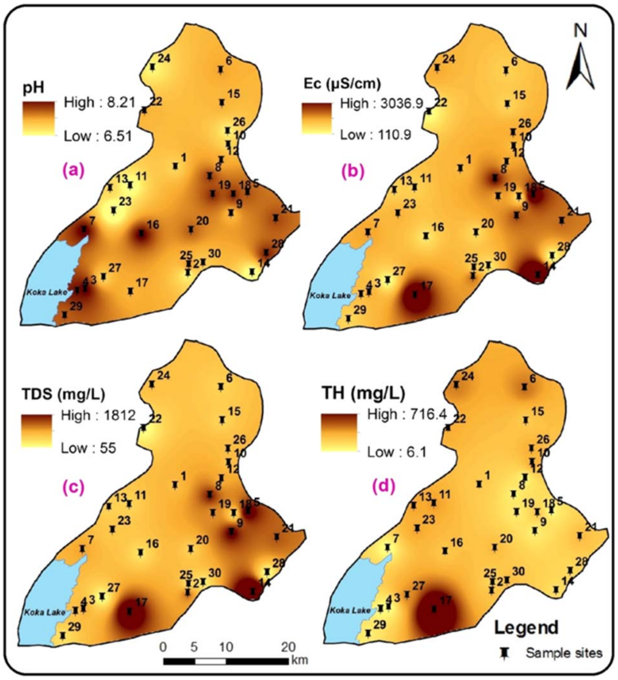

Fig. 3 Spatial variation maps of pH (a), EC (b), TDS (c), and TH (d).

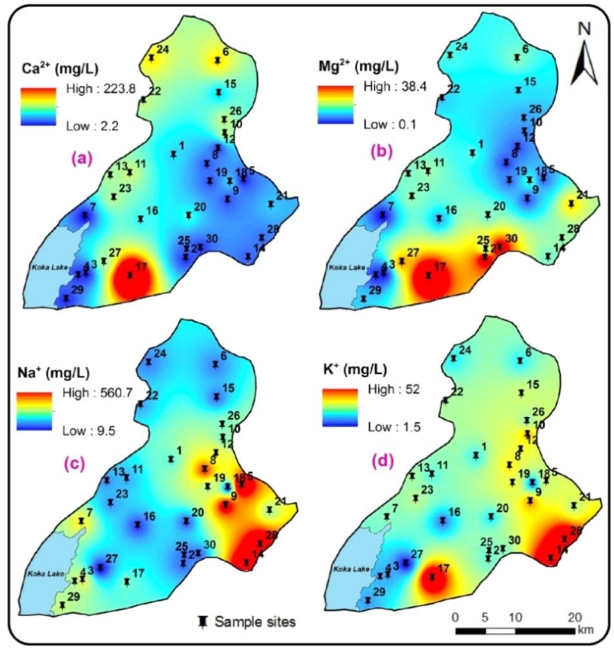

Fig. 4 Spatial variation map of Ca (a), Mg (b), Na (c) and K (d).

1000 mg L^{-1} as per[59,60] standards (Table 4). Samples 5, 9, 14, and 17 surpassed the limit (Fig. 3c) of 1000 mg L^{-1} and were unsuitable for drinking. Higher TDS content is owing to salts from thick soil and weathered rock, as well as longer groundwater residence times in contact with aquifers.

3.3. Chemical characteristics of groundwater

3.3.1. Major cations. Calcium levels in the Adama woreda range between 2.2 and 224 mg L^{-1}, with a mean of 34.7 mg L^{-1}. Analogously, the Mg^{2+} content varies considerably and is ranging between 0.1 and 38.4 mg L^{-1}, with an average of 8.4 mg L^{-1} in the commended area. As per WHO drinking water norms, almost all samples of groundwater are safe to drink for Mg^{2+} and Ca^{2+}, except for one sample.[17] Ca^{2+} and Mg^{2+} concentrations were found to be elevated in the central as well as south-eastern regions of the investigation area (Fig. 4a and b) as a consequence of the weathering of basic volcanic rocks comprising mafic minerals (pyroxene and olivine), which comprises a wider portion of the study site. Sodium is the most abundant cation in the region, particularly in groundwater samples from the rift floor. The Na^{+} content varies between 9.5 and 562.3 mg L^{-1}, with a mean of 178.6 mg L^{-1}. The values reflect the rising trend of aquifers from the highlands to the rift floor (Fig. 4c). As per the WHO's drinking water norms, more than half of the samples of the groundwater in the research region are under the permitted range. The high rock–water interactions with the abundant acidic volcanic rocks found along the flow path from highland to lowland (rift floor) in the Woreda stimulate the discharge of Na^{+} into groundwater. K^{+} content in the area groundwater samples displays a similar pattern with Na^{+} and varies from 1.5 to 52 mg L^{-1}. K^{+} content is typically greater in the research region, with nearly 80% of samples exceeding the permissible level for potable water. The major sources of elevated sodium concentrations in groundwater are weathering, natural underground salt deposits, and the disintegration of sodium-bearing minerals and rocks *via* cation exchange. The positive trend rift ward (Fig. 4d) might be attributed to weathering of K^{+}-bearing minerals (K-feldspars/orthoclase) in the host rock in the direction of groundwater flow. K^{+} levels in groundwater samples from the Woreda act similarly to Na^{+} and range from 1.5 to 52 mg L^{-1}, with 80% of samples surpassing the permitted limit for drinking water. The propensity of a positive trend rift ward (Fig. 4d) might be attributed to weathering of K^{+} bearing minerals (K-feldspars/orthoclase) from host rocks in the direction of groundwater flow.

3.3.2. Major anions. The concentration of HCO_3^{-} the dominant anion in the Woreda ranged between 143 to 1171 mg L^{-1} "with a mean value of 458 mg L^{-1}. The spatial variation map of HCO_3^{-} in the research region reveals that the western, northwest, and southwest portions (Fig. 5c) are noticeably higher due to carbonate rock formation and silicate hydrolysis. Additionally, the chemical process between underground water and silicate minerals resulted in an elevated level of HCO_3^{-} in the groundwater.[62] In the mer and research area, the interaction of dissolved CO_2 with acidic volcanic rocks resulted in elevated levels of HCO_3^{-} in groundwater.[63] The levels of Cl^{-} and SO_4^{2-} in the woreda ranged from 5.8 to 192 mg L^{-1} with a mean value of 257.8 mg L^{-1} and 4.3 to 243.2 mg L^{-1} with a mean value of 40.8 mg L^{-1}, correspondingly (Table 4). In the region, the concentrations of both parameters in groundwater are typically low. All water samples in the research area are safe to consume as per who drinking water quality criteria. The high content of Cl^{-} and SO_4^{2-} was noticed

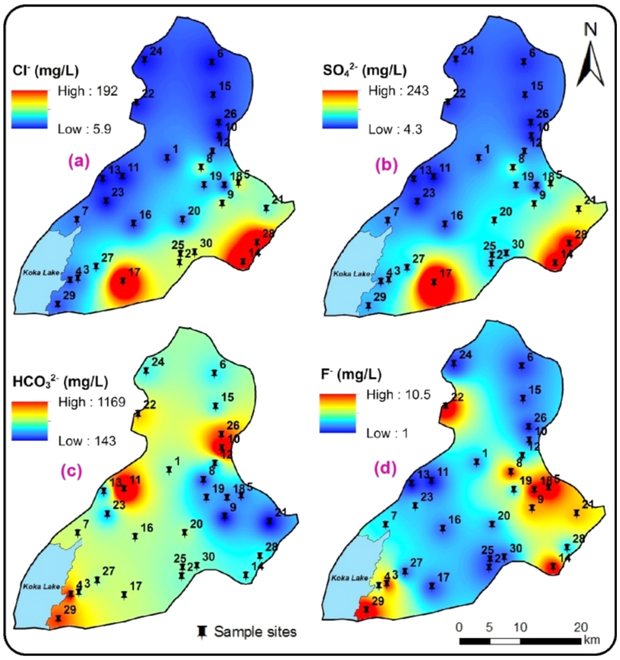

Fig. 5 Spatial variation map of Cl^- (a), SO_4^{2-} (b), HCO_3^- (c), and F^- (d).

in the south and southwest of the research area (Fig. 5a and b) owing to interaction with the lithosphere and the impacts of evaporation, which can be attributed to anthropogenic influences such as agricultural activity, exaggerated usage of inorganic fertilizers, city municipal waste disposal, agricultural runoff, landfill leachate, household sewage, industrial effluent release, and power generation.

The F^- content in the study site varies from 1 to 10.5 mg L^{-1}, with a mean of 4.2 mg L^{-1} (Table 4). Most water samples were found to be unsuitable for humans to consume, as per WHO norms. Unfit samples are most widely found in the southern and southeastern parts of the research area (Fig. 5d). When the level of F^- in natural water is between 0.5 and 1.5 mg L^{-1}, the enamel of the teeth is strengthened. F^- Concentrations in natural drinking water above 4 mg L^{-1}, above 1.5 mg L^{-1}, and above 10 mg L^{-1} are associated with skeletal fluorosis, dental fluorosis, and crippling skeletal fluorosis, correspondingly.[64,65] Fluoride levels in groundwater may be elevated as a result of fluoridated water salts percolating through acidic volcanic rocks (unwelded tuffs, lacustrine sediments, pyroclastic deposits, rhyolitic lava flows and ignimbrite) and geothermal water in this investigated region.[44,66–68] The content of groundwater is overhauled as it moves down from the highlands to the lowlands of the rift valley. In highland aquifers, F^- content is typically low, but it increases along the groundwater flow line in rift floor aquifers.

3.4. Hydrochemical facies (piper plot)

The Piper tri-linear plot, which was developed by ref. 69, has been utilised in order to determine the various hydrochemical facies and the geochemical development of groundwater chemistry in accordance with their dominating ions. In the current research area, the Piper tri-linear plot (Fig. 6) shows that

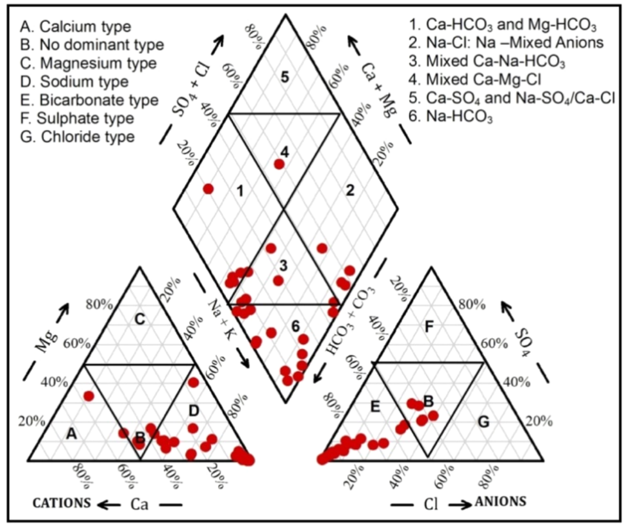

Fig. 6 Hill piper plot for the groundwater.

Na^+ and Ca^{2+} are the dominant cations relative to Mg^{2+}. Although, Cl^-, and HCO_3^- are the more prominent anions when compared with SO_4^{2-}. The major hydrochemical facies are of the order of Ca–Mg–HCO_3, Na–Ca–HCO_3, and Na–HCO_3. The mixed Ca–Na–HCO_3 facies illustrated that the groundwater primarily reacts with basic volcanic aquifers and Na–HCO_3 in the acidic volcanic aquifers that are widespread in the study area.

3.5. Pollution index of groundwater (PIG)

The assessment and quantification of groundwater contamination shall be carried out considering all the relative

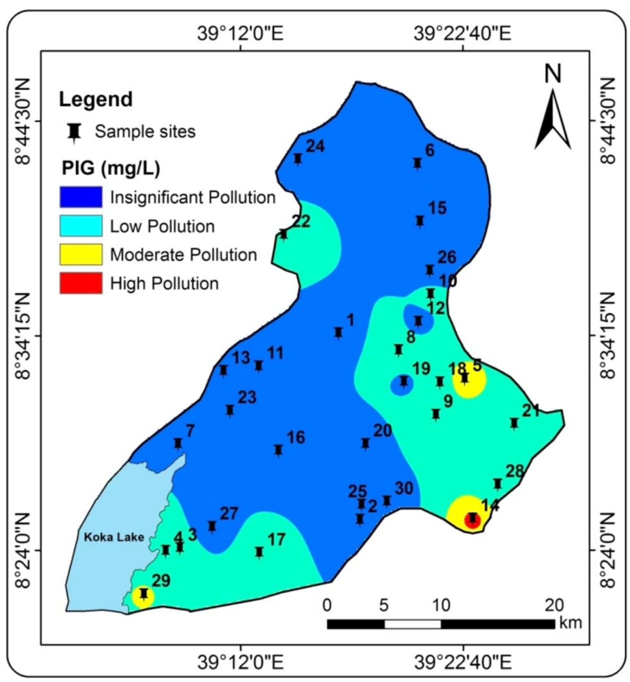

Fig. 7 Spatial distribution of PIG.

Table 5 Results of pollution index of groundwater

S. no.	PIG values	Classification of GWQ	No. wells	Percentage (%) of wells
1	<1.0	Insignificant pollution	1, 2, 6, 7, 11, 12, 13, 15, 16, 19, 20, 23, 24, 25, 26, 27, 30	57
2	1.0–1.5	Low pollution	3, 4, 8, 10, 17, 18, 21, 22, 28	33
3	1.5–2.0	Moderate pollution	5, 29	7
4	2.0–2.5	High pollution	14	3
5	>2.5	Very high pollution	—	0

contributions of the physicochemical parameters. If the total groundwater quality parameter, *i.e.*, Ow, exceeds 0.1, is 10% of the total PIG value of 1.0, values less than 1.0 are classified as insignificant pollution.[54,70] Exceeding Ow values provides ample information on the extent of pollution in the aquifer system.[53] In this basin, PIG values range from 0.56 to 2.56 with a mean value of 1.04. It can be said that these parameters had the most adverse impact on the quality of groundwater. The site-wise spatial variation map of PIG is displayed in Fig. 7. The majority of the study area is occupied by insignificant pollution, moderate pollution occupied 3 wells, and a small portion of the southeast, south of the basin is occupied by low pollution. However, the PIG values show that only 33%, 57% of the samples (1–1.5, <1) were found in the 'low pollution zone' and 'insignificant pollution zone,' while 3%, 7% of the samples were found in the high and moderate pollution, correspondingly (Table 5).

3.6. Human health risk assessment (HHRA)

The presence of a substantial level of fluoride in human drinking water may provide a number of health risks. The THI was used in this study to show the overall non-carcinogenic health risk of fluoride in drinking water. Table 5 depicts the

Table 6 For children, women, and men, the health hazards associated with drinking water ingestion and skin contact were estimated

	HQ oral			HQ dermal			THQ total		
S. no	Children	Women	Men	Children	Women	Men	Children	Women	Men
1	1.74	1.53	1.24	9.38×10^{-5}	1.46×10^{-4}	1.37×10^{-4}	1.74	1.53	1.24
2	1.12	0.98	0.79	6.00×10^{-5}	9.36×10^{-5}	8.74×10^{-5}	1.12	0.98	0.79
3	5.92	5.21	4.22	3.19×10^{-4}	4.97×10^{-4}	4.64×10^{-4}	5.92	5.21	4.22
4	3.07	2.70	2.19	1.65×10^{-4}	2.57×10^{-4}	2.40×10^{-4}	3.07	2.70	2.19
5	7.32	6.43	5.22	3.94×10^{-4}	6.14×10^{-4}	5.73×10^{-4}	7.32	6.44	5.22
6	1.05	0.92	0.75	5.63×10^{-5}	8.78×10^{-5}	8.19×10^{-5}	1.05	0.92	0.75
7	2.30	2.02	1.64	1.24×10^{-4}	1.93×10^{-4}	1.80×10^{-4}	2.30	2.02	1.64
8	5.85	5.15	4.17	3.15×10^{-4}	4.91×10^{-4}	4.59×10^{-4}	5.86	5.15	4.17
9	4.88	4.29	3.48	2.63×10^{-4}	4.10×10^{-4}	3.82×10^{-4}	4.88	4.29	3.48
10	1.39	1.23	0.99	7.50×10^{-5}	1.17×10^{-4}	1.09×10^{-4}	1.39	1.23	0.99
11	0.70	0.61	0.50	3.75×10^{-5}	5.85×10^{-5}	5.46×10^{-5}	0.70	0.61	0.50
12	2.23	1.96	1.59	1.20×10^{-4}	1.87×10^{-4}	1.75×10^{-4}	2.23	1.96	1.59
13	0.70	0.61	0.50	3.75×10^{-5}	5.85×10^{-5}	5.46×10^{-5}	0.70	0.61	0.50
14	6.34	5.58	4.52	3.41×10^{-4}	5.32×10^{-4}	4.97×10^{-4}	6.34	5.58	4.52
15	1.25	1.10	0.89	6.75×10^{-5}	1.05×10^{-4}	9.83×10^{-5}	1.25	1.10	0.89
16	1.39	1.23	0.99	7.50×10^{-5}	1.17×10^{-4}	1.09×10^{-4}	1.39	1.23	0.99
17	1.12	0.98	0.79	6.00×10^{-5}	9.36×10^{-5}	8.74×10^{-5}	1.12	0.98	0.79
18	6.69	5.88	4.77	3.60×10^{-4}	5.62×10^{-4}	5.24×10^{-4}	6.69	5.88	4.77
19	2.26	1.99	1.61	1.22×10^{-4}	1.90×10^{-4}	1.77×10^{-4}	2.26	1.99	1.61
20	1.74	1.53	1.24	9.38×10^{-5}	1.46×10^{-4}	1.37×10^{-4}	1.74	1.53	1.24
21	4.74	4.17	3.38	2.55×10^{-4}	3.98×10^{-4}	3.71×10^{-4}	4.74	4.17	3.38
22	6.97	6.13	4.97	3.75×10^{-4}	5.85×10^{-4}	5.46×10^{-4}	6.97	6.13	4.97
23	2.09	1.84	1.49	1.13×10^{-4}	1.76×10^{-4}	1.64×10^{-4}	2.09	1.84	1.49
24	0.91	0.80	0.65	4.88×10^{-5}	7.61×10^{-5}	7.10×10^{-5}	0.91	0.80	0.65
25	0.98	0.86	0.70	5.25×10^{-5}	8.19×10^{-5}	7.65×10^{-5}	0.98	0.86	0.70
26	0.84	0.74	0.60	4.50×10^{-5}	7.02×10^{-5}	6.55×10^{-5}	0.84	0.74	0.60
27	1.39	1.23	0.99	7.50×10^{-5}	1.17×10^{-4}	1.09×10^{-4}	1.39	1.23	0.99
28	2.23	1.96	1.59	1.20×10^{-4}	1.87×10^{-4}	1.75×10^{-4}	2.23	1.96	1.59
29	6.97	6.13	4.97	3.75×10^{-4}	5.85×10^{-4}	5.46×10^{-4}	6.97	6.13	4.97
30	1.25	1.10	0.89	6.75×10^{-5}	1.05×10^{-4}	9.83×10^{-5}	1.25	1.10	0.89
Min	0.70	0.61	0.50	3.75×10^{-5}	5.85×10^{-5}	5.46×10^{-5}	0.70	0.61	0.50
Max	7.32	6.43	5.22	3.94×10^{-4}	6.14×10^{-4}	5.73×10^{-4}	7.32	6.44	5.22
Mean	2.91	2.56	2.08	1.57×10^{-4}	2.45×10^{-4}	2.28×10^{-4}	2.91	2.56	2.08

HQ results for children, women, as well as men on the basis of the intake and dermal pathway. The observed HQ_{oral} values ranged from 0.61 to 6.43 for women, 0.50 to 5.22 for men, and 0.70 to 7.32 for children The HQ_{dermal} values for men ranged from 5.46×10^{-5} to 5.73×10^{-4}, for women 5.85×10^{-5} to 6.14×10^{-4}, and for children ranged 3.75×10^{-5} to 3.94×10^{-4}. The THI ranges from 0.70 to 7.32 for children, 0.61 to 6.44 for women, and 0.50 to 5.22 for men. The result revealed that 83% for children, 73% for women, and 57% for men of the samples surpassed the THI > 1 (Table 6 & Fig. 8). Based on body weights and ingestion rates, children are at a greater risk than men and women, according to THI results. Comparative studies conducted in various parts of the world have been identified. For example, in South India,[71] China,[72] and Iran,[73] children and women face a greater risk than males due to their lower body weights. Individual body weight is a primary indicator of health effects, as men's heavier weight protects them from health risks when compared to women and infants. The highest fluoride content in groundwater contributes to health issues like skeletal and dental fluorosis, which predominantly affect infants.[33] Regular consumption of fluoride-contaminated water raises the risk of developing fluorosis, skeletal and tooth decay, and spinal disorders.

3.7. Recommendations for future management of groundwater quality

A detailed hydrogeochemical study in the research area noticed that most people are in the need of groundwater for their day to day primary activities and it is quite important to monitor the assessment of the health threat due to the presence of high level of concentration of fluoride in certain areas. Finally, the research study proposed the following remedial measures to be taken as follows.

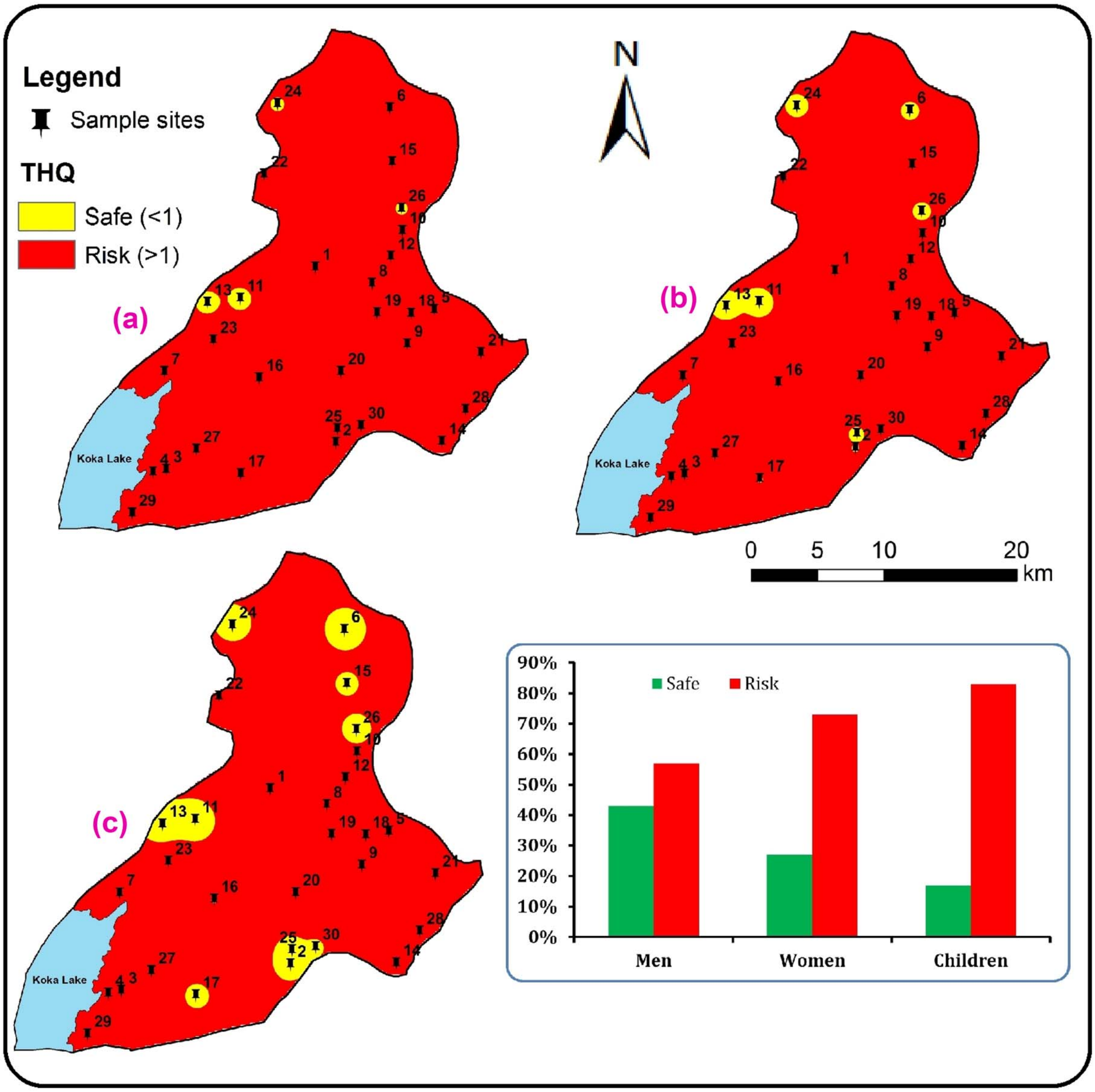

Fig. 8 Calculated THI for all woreda groundwater samples to evaluate health risks for children (a), women (b), and men (c).

• The study results are either to treat fluoride-rich groundwater as reverse osmosis (RO) treatment to provide community people with safe drinking water supplies and avoid major health risks of fluorosis.

• Suggest effective remedial measures of large and small scale rainwater harvesting and the construction of artificial recharge structures in the basin which will be an effective way to recharge the groundwater so that it will dilute the concentration of fluoride.

4. Conclusion

This research investigation delineates the aptness of groundwater quality using various criteria such as PIG, HHRA, GIS, and the human health risks linked with fluoride in ingestion water. This research aimed to provide valuable hydrogeochemical information that is vital for the efficient and well-planned use of available groundwater resources which is non-harmful to human beings. The following concise description of this study's main findings:

• The groundwater is found slightly acidic to nearly alkaline in the research area. Na^+ followed by Ca^{2+} resulted as dominant cations while HCO_3^-, followed by Cl^- and SO_4^{2-} also resulted as dominant anions in the basin. Ca–Mg–HCO_3, Na–Ca–HCO_3, as well as Na–HCO_3 are dominant water types.

• As per PIG, the results show that 57%, 33%, 7% and 3% of the samples were found in the insignificant, low, moderate and high, correspondingly.

• The THI is calculated from hazard quotients (HQ_{Intake} and HQ_{Dermal}) results showing 83%, 73%, and 57% of the samples exceed the non-carcinogenic health threat of fluoride THI > 1 in drinking water for children, females and males. Children are more susceptible to danger than either males or women, according to the THI data, based on body weights and consumption rates. Similarly, females are also more vulnerable to health risks than men.

The final outcome of this research tried to provide valuable information to decision-makers on potential groundwater management practices and to lay the foundations for groundwater monitoring stations for the assessment of groundwater quality in central Ethiopia.

Data availability

Data will be made available on request.

Author contributions

Hassen Shube and Shankar Karupannan: conceptualization, methodology, investigation, supervision, writing- original draft preparation, validation, writing- reviewing and editing; Nafyad Serre Kawo: assist in manuscript writing and interpretation of data; Mohammed Haji and Abraham Mechal: data curation, writing- reviewing and editing; Balamurugan Panneerselvam: data curation, visualization, writing- reviewing and editing; Ashu Fekadu: helps in the interpretation of data – writing-reviewing and editing.

Conflicts of interest

The authors confirm no conflict of interest.

References

1 M. Haji, S. Karuppannan, D. Qin, H. Shube and N. S. Kawo, Potential Human Health Risks Due to Groundwater Fluoride Contamination: A Case Study Using Multi-techniques Approaches (GWQI, FPI, GIS, HHRA) in Bilate River Basin of Southern Main Ethiopian Rift, Ethiopia, *Arch. Environ. Contam. Toxicol.*, 2021, **80**(1), 277–293.

2 D. J. Lapworth, G. Krishan, A. M. MacDonald and M. S. Rao, Groundwater quality in the alluvial aquifer system of northwest India: New evidence of the extent of anthropogenic and geogenic contamination, *Sci. Total Environ.*, 2017, **599–600**, 1433–1444.

3 Ş. Şener, E. Şener and A. Davraz, Evaluation of water quality using water quality index (WQI) method and GIS in Aksu River (SW-Turkey), *Sci. Total Environ.*, 2017, **584–585**, 131–144.

4 T. Mohanakavitha, R. Divahar, T. Meenambal, K. Shankar, V. S. Rawat, T. D. Haile, *et al.*, Dataset on the assessment of water quality of surface water in Kalingarayan Canal for heavy metal pollution, Tamil Nadu, *Data Brief*, 2019, **22**, 878–884.

5 T. Mohanakavitha, K. Shankar, R. Divahar, T. Meenambal and R. Saravanan, Impact of industrial wastewater disposal on surface water bodies in Kalingarayan canal, Erode district, Tamil Nadu, India, *Arch. Agric. Environ. Sci.*, 2019, **4**(4), 379–387.

6 A. O. Oki and T. S. Akana, Quality Assessment of Groundwater in Yenagoa, *Geosciences*, 2016, **6**(1), 1–12.

7 E. D. Sunkari, M. Abu, P. S. Bayowobie and U. E. Dokuz, Hydrogeochemical appraisal of groundwater quality in the Ga west municipality, Ghana: Implication for domestic and irrigation purposes, *Groundwater for Sustainable Development*, 2019, **8**, 501–511.

8 R. Ravi, S. Aravindan, K. Shankar and P. Balamurugan, Suitability of groundwater quality for irrigation in and around the main Gadilam river basin on the east coast of southern India, *Arch. Agric. Environ. Sci.*, 2020, **5**(4), 554–562.

9 B. Panneerselvam, S. Karuppannan and K. Muniraj, Evaluation of drinking and irrigation suitability of groundwater with special emphasizing the health risk posed by nitrate contamination using nitrate pollution index (NPI) and human health risk assessment (HHRA), *Hum. Ecol. Risk Assess.: Int. J.*, 2020, **27**(5), 1324–1348.

10 B. Panneerselvam, S. K. Paramasivam, S. Karuppannan, N. Ravichandran and P. Selvaraj, A GIS-based evaluation of hydrochemical characterisation of groundwater in hard rock region, South Tamil Nadu, India, *Arabian J. Geosci.*, 2020, **13**(17), 1–22.

11 S. Subbarayan, S. Thiyagarajan, S. Karuppannan and B. Panneerselvam, Enhancing groundwater vulnerability assessment: Comparative study of three machine learning models and five classification schemes for Cuddalore district, *Environ. Res.*, 2024, **242**, 117769.

12 P. Aravinthasamy, D. Karunanidhi, K. Shankar, T. Subramani, R. Setia, P. Bhattacharya, *et al.*, COVID-19 lockdown impacts on heavy metals and microbes in shallow groundwater and expected health risks in an industrial city of South India, *Environ. Nanotechnol., Monit. Manage.*, 2021, **16**, 100472.

13 M. Haji, D. Qin, Y. Guo, L. Li, D. Wang, S. Karuppannan, *et al.*, Origin and geochemical evolution of groundwater in the Abaya Chamo basin of the Main Ethiopian Rift: application of multi-tracer approaches, *Hydrogeol. J.*, 2021, **29**(3), 1219–1238.

14 A. Mechal, H. Shube, T. R. Godebo, K. Walraevens and S. Birk, Application of multi-hydrochemical indices for spatial groundwater quality assessment: Ziway Lake Basin of the Ethiopian Rift Valley, *Environ. Earth Sci.*, 2022, **81**(1), 25.

15 A. Fentahun, A. Mechal and S. Karuppannan, Hydrochemistry and quality appraisal of groundwater in Birr River Catchment, Central Blue Nile River Basin, using multivariate techniques and water quality indices, *Environmental Monitoring and Assessment*, Springer International Publishing, 2023, vol. 195, DOI: 10.1007/s10661-023-11198-6.

16 W. Yadeta, S. Karuppannan, D. Diriba and H. Shube, Identification of groundwater potential zones for sustainable groundwater resource management using an integrated approach in Sirkole watershed, Western Ethiopia, *Groundwater for Sustainable Development*, 2024, **27**, 101328. https://www.sciencedirect.com/science/article/pii/S2352801X24002510.

17 D. Diriba, S. Karuppannan, T. Takele and M. Husein, Delineation of groundwater potential zonation using geoinformatics and AHP techniques with remote sensing data, *Heliyon*, 2024, **10**(3), e25532.

18 S. Karuppannan and N. Serre Kawo, Groundwater Quality Assessment Using Geospatial Techniques and WQI in North East of Adama Town, Oromia Region, Ethiopia, *Hydrospatial Anal.*, 2020, **3**(1), 22–36.

19 K. B. Soujanya, P. R. Saxena, R. M. Kurakalva and K. Shankar, Evaluation of seasonal and temporal variations of groundwater quality around Jawaharnagar municipal solid waste dumpsite of Hyderabad city, India, *SN Appl. Sci.*, 2020, **2**(3), 1–22.

20 A. Kadam, V. Wagh, B. Umrikar and R. Sankhua, An implication of boron and fluoride contamination and its exposure risk in groundwater resources in semi-arid region, Western India, *Environ. Dev. Sustain.*, 2020, **22**(7), 7033–7056.

21 H. Mousazadeh, M. H. Mahmudy-Gharaie, A. Mosaedi and H. R. Moussavi, Hydrochemical assessment of surface and ground waters used for drinking and irrigation in Kardeh Dam Basin (NE Iran), *Environ. Geochem. Health*, 2019, **41**(3), 1235–1250.

22 World Health Organization, *Hardness in Drinking-Water: Background Document for Development of WHO Guidelines for Drinking-Water Quality*, World Heal Organ, 2011, pp. 1–19.

23 S. Sellamuthu, S. Joseph, S. Gopalakrishnan, S. Sekar, R. Khan and S. Shukla, Appraisal of groundwater quality for drinking and irrigation suitability using multivariate statistical approach in a rapidly developing urban area, Tirunelveli, India, *Environ. Sci. Pollut. Res.*, 2022, 1–17.

24 M. Saleem, A. Hussain, G. Mahmood and M. Waseem, Hydrogeochemical assessment of groundwater in shallow aquifer of greater Noida region, Uttar Pradesh (U.P), India, *Appl. Water Sci.*, 2018, **8**(6), 186.

25 P. Balamurugan, P. S. Kumar and K. Shankar, Dataset on the suitability of groundwater for drinking and irrigation purposes in the Sarabanga River region, Tamil Nadu, India, *Data Brief*, 2020, **29**, 105255.

26 V. M. Wagh, D. B. Panaskar, J. A. Jacobs, S. V. Mukate, A. A. Muley and A. K. Kadam, Influence of hydrogeochemical processes on groundwater quality through geostatistical techniques in Kadava River basin, Western India, *Arabian J. Geosci.*, 2019, **12**(1), 1–25.

27 K. Shankar, S. Aravindan and S. Rajendran, Hydrogeochemistry of the paravanar river sub-basin, cuddalore district, Tamilnadu, India, *E-Journal Chem.*, 2011, **8**(2), 835–845.

28 B. Panneerselvam, N. Ravichandran, S. P. Kaliyappan, S. Karuppannan and B. Bidorn, Quality and Health Risk Assessment of Groundwater for Drinking and Irrigation Purpose in Semi-Arid Region of India Using Entropy Water Quality and Statistical Techniques, *Water*, 2023, **15**(3), 601.

29 N. S. Kawo and S. Karuppannan, Groundwater quality assessment using water quality index and GIS technique in Modjo River Basin, central Ethiopia, *J. Afr. Earth Sci.*, 2018, **147**, 300–311.

30 A. K. Sarfo and S. Karuppannan, Application of Geospatial Technologies in the COVID-19 Fight of Ghana, *Trans. Indian Natl. Acad. Eng.*, 2020, **5**(2), 193–204.

31 N. S. Magesh, N. Chandrasekar and L. Elango, Occurrence and distribution of fluoride in the groundwater of the Tamiraparani River basin, South India: a geostatistical modeling approach, *Environ. Earth Sci.*, 2016, **75**(23), 1483.

32 S. S. K. Aravindan, Ground Water Quality Maps of Paravanar River Sub Basin, Cuddalore District, Tamil Nadu, India, *J. Indian Soc. Remote Sens.*, 2011, **39**(4), 565–581.

33 P. Balamurugan, P. S. Kumar, K. Shankar, R. Nagavinothini and K. Vijayasurya, Non-carcinogenic risk assessment of groundwater in southern part of Salem district in Tamilnadu, India, *J. Chil. Chem. Soc.*, 2020, **65**(1), 4697–4707.

34 S. Rajendran, Study of Trace Element abundance in Paravanar River Sub-Basin, Cuddalore District, Tamil Nadu Using GIS Technique, In *Applied Chemistry in Marine Sciences: Current and Future Trends and Annual Genral Body Meeting*, Indian Society of Applied Geochemists (ISAG), Hyderabad, 2010.

35 K. Shankar, G. Elangovan, P. Balamurugan and R. Saravanan, Spatial distribution of Groundwater quality assessment using Water Quality Index and GIS techniques in Thanjavur Taluk, Thanjavur District, Tamil Nadu, India, *Int. J. Civ. Environ. Agric. Eng.*, 2022, 32–58.

36 A. Yenehun, K. Walraevens and O. Batelaan, Spatial and temporal variability of groundwater recharge in Geba basin, Northern Ethiopia, *J. Afr. Earth Sci.*, 2017, **134**, 198–212.

37 N. S. Kawo and S. Karuppannan, Groundwater quality assessment using water quality index and GIS technique in Modjo River Basin, central Ethiopia, *J. African Earth Sci.*, 2018, **147**, 300–311.

38 N. A. Mohamed, A. C. Wachemo, S. Karuppannan and K. Duraisamy, Spatio-temporal variation of groundwater hydrochemistry and suitability for drinking and irrigation in Arba Minch Town, Ethiopia: An integrated approach using water quality index, multivariate statistics, and GIS, *Urban Clim.*, 2022, **46**, 101338.

39 A. M. Al-Rawabdeh, N. A. Al-Ansari, A. A. Al-Taani, F. L. Al-Khateeb and S. Knutsson, Modeling the risk of groundwater contamination using modified DRASTIC and GIS in Amman-Zerqa Basin, Jordan, *Cent. Eur. J. Eng.*, 2014, **4**(3), 264–280.

40 S. B. Awulachew, Irrigation potential in Ethiopia: Constraints and opportunities for enhancing the system, *Gates Open Res.*, 2019, **3**(22), 22.

41 S. B. Awulachew, A. D. Yilma, M. Loulseged, W. Loiskandl, M. Ayana and A. Tena, *Water Resources and Irrigation Development in Ethiopia*, Iwmi, Working Pa, 2007, pp. 1–32.

42 C. Reimann, K. Bjorvatn, B. Frengstad, Z. Melaku, R. Tekle-Haimanot and U. Siewers, Drinking water quality in the Ethiopian section of the East African Rift Valley I - Data and health aspects, *Sci. Total Environ.*, 2003, **311**(1–3), 65–80.

43 W. Furi, M. Razack, T. A. Abiye, T. Ayenew and D. Legesse, Fluoride enrichment mechanism and geospatial distribution in the volcanic aquifers of the Middle Awash basin, Northern Main Ethiopian Rift, *J. Afr. Earth Sci.*, 2011, **60**(5), 315–327.

44 T. Rango, G. Bianchini, L. Beccaluva and R. Tassinari, Geochemistry and water quality assessment of central Main Ethiopian Rift natural waters with emphasis on source and occurrence of fluoride and arsenic, *J. Afr. Earth Sci.*, 2010, **57**(5), 479–491.

45 W. Furi, M. Razack, T. A. Abiye, S. Kebede and D. Legesse, Hydrochemical characterization of complex volcanic aquifers in a continental rifted zone: The Middle Awash basin, Ethiopia, *Hydrogeol. J.*, 2012, **20**(2), 385–400.

46 S. Karuppannan, V. Shreedhara, K. Shankar and M. Haji, A Morphometric Analysis of Wonji Drainage Basins around Central Rift Valley, Ethiopia, using Geospatial Tools Article in, *Int. J. Adv. Sci. Res.*, 2020, **9**(8), 787–794. https://www.researchgate.net/publication/345763840.

47 N. S. Kawo and S. Karuppannan, Groundwater quality assessment using water quality index and GIS technique in Modjo River Basin, central Ethiopia, *J. Afr. Earth Sci.*, 2018, **147**(June), 300–311.

48 W. Furi, M. Razack, T. Haile, T. A. Abiye and D. Legesse, The hydrogeology of Adama-Wonji basin and assessment of groundwater level changes in Wonji wetland, Main Ethiopian Rift: Results from 2D tomography and electrical sounding methods, *Environ. Earth Sci.*, 2011, **62**(6), 1323–1335.

49 APHA, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association/American Water Works Association/Water Environment Federation, Washington, 22nd edn, 2012.

50 APHA, *Standard Methods for the Examination of Water and Wastewater*, 2012, vol. 1496.

51 J. C. Egbueri, Groundwater quality assessment using pollution index of groundwater (PIG), ecological risk index (ERI) and hierarchical cluster analysis (HCA): A case study, *Groundwater for Sustainable Development*, 2020, **10**, 100292.

52 S. Tenodi, D. Krčmar, J. Agbaba, K. Zrnić, M. Radenović, D. Ubavin, *et al.*, Assessment of the environmental impact of sanitary and unsanitary parts of a municipal solid waste landfill, *J. Environ. Manage.*, 2020, **258**, 110019.

53 N. S. Rao, B. Sunitha, R. Rambabu, P. V. N. Rao, P. S. Rao, B. D. Spandana, *et al.*, Quality and degree of pollution of groundwater, using PIG from a rural part of Telangana State, India, *Appl. Water Sci.*, 2018, **8**(8), 227.

54 N. Subba Rao, PIG : a numerical index for dissemination of groundwater contamination zones, *Hydrol. Process*, 2012, **26**(22), 3344–3350.

55 A. Çelebi, B. Şengörür and B. Kløve, Human health risk assessment of dissolved metals in groundwater and surface waters in the Melen watershed, Turkey, *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.*, 2014, **49**(2), 153–161.

56 K. Usuda, T. Ueno, Y. Ito, T. Dote, H. Yokoyama, K. Kono, *et al.*, Risk Assessment Study of Fluoride Salts: Probability-Impact Matrix of Renal and Hepatic Toxicity Markers, *Biol. Trace Elem. Res.*, 2016, **173**(1), 154–160.

57 N. Adimalla, P. Li and S. Venkatayogi, Hydrogeochemical Evaluation of Groundwater Quality for Drinking and Irrigation Purposes and Integrated Interpretation with Water Quality Index Studies, *Environ. Process*, 2018, **5**(2), 363–383.

58 US Environmental Protection Agency (USEPA) *Baseline human health risk assessment Vasquez Boulevard and I-70 superfund site*, Denver CO, 2001, https://www.epa.gov/region8/superfund/sites/VB-170-Risk.pdf. Accessed 20 Jan 2011.

59 CES-58, *Compulsory Ethiopian Standard: Drinking Water Specifications*, ESA, 2013.

60 WHO, *Guidelines for drinking water quality, Library Cataloguing-in-Publication Data. NLM Classification: WA 675*, World Health Organization, Geneva, 4th edn, 2017.

61 H. R. Amanial, Assessment of physicochemical quality of spring water in Arbaminch, Ethiopia, *J. Environ Anal. Chem.*, 2015, **2**(157), 2380–2391.

62 A. Tesema, M. Jothimani, A. Abebe, J. Gunalan, E. Getahun and S. Karuppannan, Hydrochemical Characterization and Water Quality Assessment for Drinking and Irrigation Purposes Using WQI and GIS Techniques in the Upper Omo River Basin, Southern Ethiopia, *J. Chem.*, 2023, **2023**, 3246851.

63 A. Fetene, D. Alem and Y. Mamo, Effects of Land use and Land cover changes on extent and distribution of Afroalpine vegetation of northern Western Ethiopia: The case of Choke mountains, *Res. J. Environ. Sci.*, 2014, **8**, 17–28.

64 C. B. Dissanayake, The fluoride problem in the groundwater of sri lanka-environmental management and health, *Int. J. Environ. Stud.*, 1991, **38**(2–3), 137–155.

65 K. Brindha, G. Jagadeshan, L. Kalpana and L. Elango, Fluoride in weathered rock aquifers of southern India: Managed Aquifer Recharge for mitigation, *Environ. Sci. Pollut. Res.*, 2016, **23**(9), 8302–8316.

66 J. J. Carrillo-Rivera, A. Cardona and W. M. Edmunds, Use of abstraction regime and knowledge of hydrogeological conditions to control high-fluoride concentration in abstracted groundwater: San Luis Potosí Basin, Mexico, *J. Hydrol.*, 2002, **261**(1–4), 24–47.

67 T. Rango, J. Kravchenko, B. Atlaw, P. G. McCornick, M. Jeuland, B. Merola, *et al.*, Groundwater quality and its health impact: An assessment of dental fluorosis in rural inhabitants of the Main Ethiopian Rift, *Environ. Int.*, 2012, **43**(1), 37–47.

68 L. A. Olaka, F. D. H. Wilke, D. O. Olago, E. O. Odada, A. Mulch and A. Musolff, Groundwater fluoride enrichment in an active rift setting: Central Kenya Rift case study, *Sci. Total Environ.*, 2016, **545–546**, 641–653.

69 A. M. Piper, A graphic procedure in the geochemical interpretation of water-analyses, *Trans., Am. Geophys. Union*, 1944, **25**(6), 914–928.

70 J. C. Egbueri, Assessment of the quality of groundwaters proximal to dumpsites in Awka and Nnewi metropolises: a comparative approach, *Int. J. Energy Water Resour.*, 2018, **2**(1–4), 33–48.

71 D. Karunanidhi, P. Aravinthasamy, M. Deepali, T. Subramani and K. Shankar, Groundwater Pollution and Human Health Risks in an Industrialized Region of Southern India: Impacts of the COVID-19 Lockdown and the Monsoon Seasonal Cycles, *Arch. Environ. Contam. Toxicol.*, 2021, **80**(1), 259–276.

72 Y. Zhai, X. Zhao, Y. Teng, X. Li, J. Zhang, J. Wu, *et al.*, Groundwater nitrate pollution and human health risk assessment by using HHRA model in an agricultural area, NE China, *Ecotoxicol. Environ. Saf.*, 2017, **137**, 130–142.

73 F. S. Hourieh, M. Bakaeian, H. Parsian, A. Amouei, H. Asgharnia, M. Ghanbarian, *et al.*, Potentially harmful heavy metal contamination in Babolrood river: evaluation for risk assessment in the Mazandaran province, Iran, *Int. J. Environ. Anal. Chem.*, 2022, **102**(18), 7209–7223.