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Water quality and probabilistic non-carcinogenic health risk of groundwater: a half decadal scenario change in Vadodara

Haresh Z. Panseriya · Deepa J. Gavali · Jayendra J. Lakhmapurkar · Anuva Saha · Priyal Gandhi

Abstract Groundwater is essential to secure the safety of water supply in Vadodara, Gujarat. In this study, groundwater samples were collected from various part of the city which separated in 12 wards. The present study contains analyses of 720 groundwater samples gathered from various tube and open wells and analyzed for fluoride and other physicochemical parameters during 2014 and 2019. The results indicated that fluoride and TDS were high and the overall water quality was poor in the study area. Gastrointestinal and other health-related issues increased due to higher TDS in east, north and northeast regions. Likewise, hierarchical cluster analysis also indicated that TDS and chloride-rich water. Fluoride concentration was observed in the range of 0.66–1.61 mg/l (2014) and 0.86–1.77 mg/l (2019) which indicates that 62% samples are unfit for drinking purpose, which could cause dental and skeletal fluorosis. The water quality index (WQI) indicated lack of excellent water in the studied area in the last half-decade. As per WQI calculation suggest that 82.12% (2014) and 69.00% (2019) of groundwater samples represent poor, very poor and unsuitable categories, whereas remaining 17.85% (2014) and 31.00% (2019) of the samples represent good category for drinking purposes in entire Vadodara, Gujarat. Marginal improvement in the groundwater quality is reported due to good rainfall in 2019. Health risks associated with high fluoride drinking water were assessed for various age groups of inhabitants such as children, infants and adults. The non-carcinogenic hazard quotient estimated by oral intake was 1.38–3.36 (2014) and 1.79–3.70 (2019) for infants; 0.69–1.68 (2014) and 0.90–1.85 (2019) for children, whereas 0.07–0.18 (2014) and 0.10–0.20 (2019) for adults. Therefore, infant and children are relatively at higher health risk due to the intake of fluoride-rich drinking water than adult in the studied region. Both indices were indicated contaminated water or closer to contamination which induced non-carcinogenic health risk on citizens. Thus, the comprehensive results of present study can be used as a baseline data and valuable tool for government authorities for long-term monitoring, health monitoring and sustainable development of Vadodara, Gujarat.

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Introduction

Water, a primary component of all living organisms, plays significant role in their growth, survival, etc. About 71% earth's surface is covered by water, in which freshwater contributes to only 2.5% (Gleick, 1993). Out of 2.5%, nearly third quarter is frozen in glaciers. The remaining one third is available as the soil moisture, surface water and groundwater. Major sources of freshwater on earth were lakes, river, wetlands and groundwater aquifers (all of make < 1%), which regularly renewed by rainfall or snowfall and therefore available on a sustainable basis (MEA, 2005). The groundwater occurs in water bearing formations were referred as aquifers. Aquifers were water saturated geological formations that yields sufficient water for wells or springs (Lachassagne et al., 2001). Moreover, groundwater was remained a major source of water for many past civilizations. On the earth, total stored groundwater is believed to be of 8 million km^3 to 10 million km^3 region (Aureli et al., 2008). With the advent of electrification and modernization of technology, groundwater extraction was increased globally by more than 100%, i.e., from 312 km^3/year in the 1960s to 743 km^3/year in 2000 (Wada et al., 2010). Earlier studies in India (Shah, 2007) and Spain (Llamas & Garrido, 2007) indicated economic benefits of groundwater were more compared to surface water mainly due to water usage and suspected pollution. Moreover, it is available throughout the year, i.e., even in dry season.

India records the highest withdrawal of groundwater (251 km^3/year) among major countries of the world (Jac, 2012). Indian states such as Rajasthan, Gujarat, Punjab, Haryana and Delhi located in arid and semiarid climatic zone which experienced severe decline in groundwater resources along with quality degradation (Rodell et al., 2009; CGWB, 2013). Traditionally, agriculture has been a major cause of groundwater withdrawal in India. However, in fast developing state, i.e., Gujarat, groundwater is dominantly exploited due to suffice demand from the urban centers. Meeting the need of water for fast-growing cities especially commercial, domestic and industries was dependent on freshwater resources (Howard, 2007). This leads to lack of sufficient groundwater resources to satisfy the ever increasing water demand on sustainable basis (Taniguchi et al., 2009). Many cities have to go ever deeper groundwater due to depletion of water sources, at any costs that are ultimately unsustainable in both economic and environmental terms (Foster et al., 2013). In a recent study, groundwater exploitation and contamination were observed throughout the world because of urbanization (Howard, 2007; Taniguchi et al., 2009; Foster et al., 2013; Tirkey et al., 2017; Lapworth et al., 2021).

Several factors influenced groundwater, i.e., composition of the water bearing formations or geochemistry of aquifer, status of exploitation *vs* recharge, mixing of contaminated/polluted water into the aquifers and others. Therefore, WHO (World Health Organization) introduced international norms that were predicted water quality and their impact on human health. Similarly, India has also adopted the Bureau of Indian Standards (BIS) for sustainable environment. A BIS include influential biotic and abiotic parameters such as microbes, pH, dissolved organic/inorganic chemical, oxygen, hardness, and xenobiotic compounds. This chemical components majorly came from anthropogenic activities and increase load of TDS in groundwater. Fluoride is also known as xenobiotics and its impact on human health is through fluorosis (Zango et al., 2019). Moreover, other diseases observed due to fluoride includes ligaments calcification (Ozsvath, 2009; Yang et al., 2020), developmental disorder in children (Ding et al., 2011), liver and kidney dysfunction as well as a nervous weakness (Yadav et al., 2019). Apart from traditional water parameters, researchers have also evaluated health indicators and spatial–temporal variation with statistical analysis using geographic information system (GIS). Water quality indicators by groundwater exploring represent overall health of ecosystem such as water quality index (WQI) and health risk assessment/appraisal (HRA). Both indices were mathematical tool and evaluate data using multistep processes. The water quality assessment mainly needs the key parameters identification from standard guidelines. Moreover, without going into complications of reading individual parameter, WQI is a mathematical tool for addressing water quality status in simplified manner. Among that, an index is

reflecting the composite influence of different water quality parameters, which is considered and taken for calculation of water quality index. Therefore, WQI has been used to investigate large and complex dataset into single numerical score which encouraged to understand overall water quality of the studied area (Ott, 1978). Various researchers have made alteration in WQI with slight modifications in concepts (Tirkey et al., 2017). The recent studies indicated that many researcher applied WQI as a tool to evaluate the groundwater status from compound datasets. Moreover, water quality status has been carried out by WQI in India and other countries (Kannel et al., 2007; Nagels et al., 2001; Nasirian, 2007; Pesce & Wunderlin, 2000; Sargaonkar & Deshpande, 2003; Singh et al., 2008; Tirkey et al., 2017). Similarly, HRA follows multistep process and examines role of pollutants as a potential factor for the health risk model and determining hazard quotient (HQ) (Qiao et al., 2020; Zhang et al., 2017, 2020). In recent years, many studies have been carried out on groundwater and health risk (Qiao et al., 2020; Singh et al., 2020; Zhang et al., 2020). Yang et al. (2020) assessed health risk of groundwater and concluded that health risk is much higher through drinking water than dermal contact. Singh et al., (2020), He et al., (2021), Marghade et al., (2021) and Zhou et al., (2021) from India and other countries assessed the human health risk of pollutants including Fluoride in drinking water. Most of these health risk assessment studies were carried out using USEPA models which considered various factors such as gender, water consumption, body weight and pollutant concentration. The index gave brief detailed about pollutant exposure on human health and their impact on various age group of the entire population.

Therefore, extensive water demand by industries and domestic could affect the aquifer characteristics and natural composition of water quality of the studied area. The objectives of the present study were (1) to investigate groundwater characteristic by physico-chemical parameters and check its suitability for drinking purpose by comparing with recognized standard guidelines (2) to classify the sampling sites with the help of Hierarchical cluster analysis (HCA), (3) to evaluate suitable and unsuitable groundwater quality zones for drinking purpose using Water quality index (WQI), (4) to investigate health risk assessment (HRA) of groundwater for the study area and (5) to

represent the datasets using Geographic Information System (GIS) software.

Materials and methods

Study area description

The study area is 18th largest city in India, located 22.30°N 73.19°E at an elevation of $\sim$ 39 m on the banks of river Vishwamitri illustrated in Fig. 1. Climate of Vadodara is sub-tropical with moderate humidity and three main seasons: Summer, Monsoon and Winter. The temperature starts rising from March till it reaches maximum, as high as 41 °C. January is the coldest month of the year. Vadodara receives much of its rainfall from the south-west monsoon during the period between June and September; its maximum intensity being in the month of July and August. The average annual rainfall for last 20 years (1999 to 2019) for the city was 1000 mm, in this period low rainfall recorded in 1999, 2000, 2009 and 2015. Maximum rainfall was recorded in 2019, i.e., 1978 mm (GSDMA) (data mentioned in supplementary file). As per the 2011 census, the city population was $\sim$ 1.8 million spread over an area of 168 km^2. The population of the Vadodara has increased by 61.6% between 1991 and 2011 (Patel et al., 2019). Daily consumption of water for the City is around 510 MLD. Of which around 410 MLD was supplied by Ajwa Lake, Narmada Canal and Mahi River and remaining 100 MLD as groundwater.

Geologically large part of the city forms the alluvial plains with Quaternary formation forming the major aquifers, having both phreatic and confined aquifer conditions (Shah & Mistry, 2013). There were two exploitable aquifers exists, one at 80 feet and other at 120 feet depth. Being more extensive, yield of deeper aquifers is higher; therefore, most of the wells are being drilled to this level. Aquifer conditions of the Vadodara were very complicated, e.g., good aquifers and non-productive saline aquifers both present in the city (Gupte, 2010); therefore, the findings of this paper are important in deciding future scope of exploitation and recharge. The city was divided into 12 wards (W) for administration purpose by Vadodara Municipal Seva Sadan (VMSS (local governing body of the City); (Ward wise characteristic was given in supplementary file).
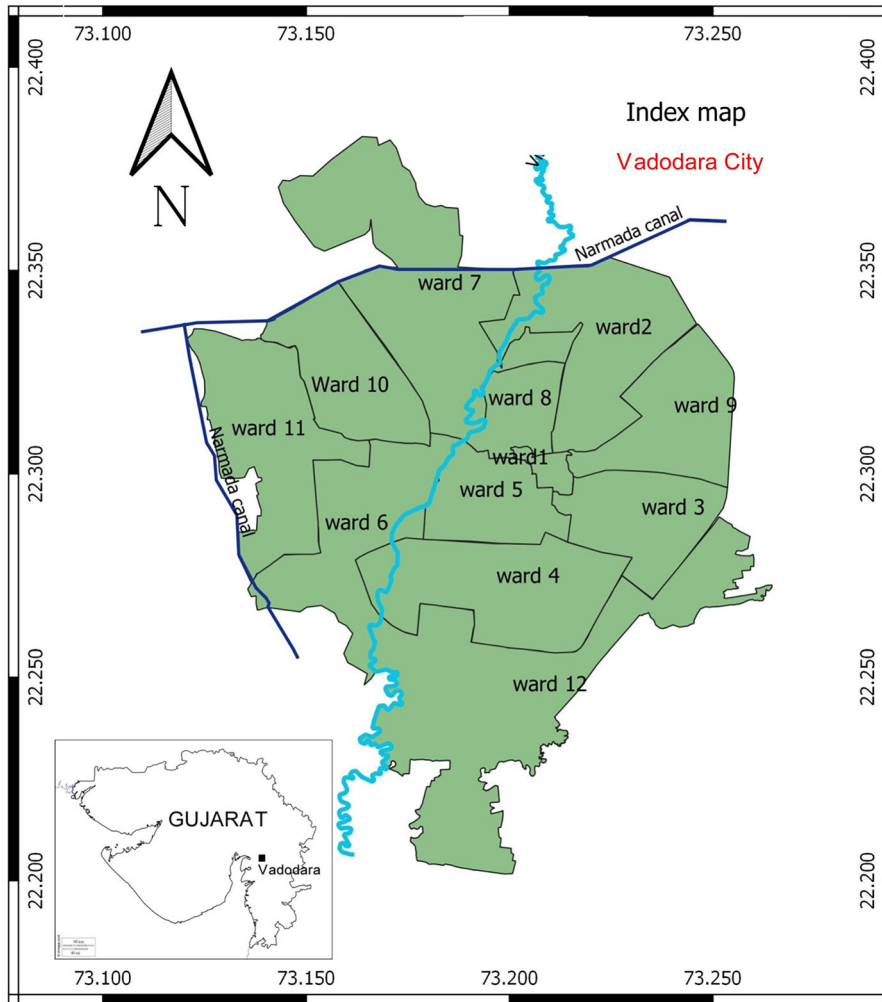
Fig. 1 Detailed study area and 12 sampling wards, Vadodara, Gujarat

Sampling strategy and water quality parameters assessment

Sampling strategy was designed in such way that covers wide area of city for accurate and unbiased representation of water quality trends. The detailed sampling area of Vadodara is mentioned in Fig. 1. Water samples were collected from tubes and open wells of the 12 wards in 2014 and 2019. So, the water quality trends and scenario were evaluated for past half-decade. Total 240 sampling points (720 samples) were covered in study area, 420 samples during 2014

and 300 samples during 2019. At each sampling point, samples were collected in triplicates in clean polyethylene terephthalate bottles. Samples were stored at 4 °C and transferred to the GES (Gujarat Ecology Society) laboratory, where samples were preserved at -20 °C until further analysis. For the water analysis, various physicochemical parameters are considered, i.e., depth of water, pH, electrical conductivity (EC), chlorinity (Cl), total dissolved solids (TDS), total hardness (TH), alkalinity, fluoride (F$^-$) and sulfate. The physicochemical analysis was followed by the standard methods as described by APHA, 1995.

Statistical analysis

Pearson's correlation analysis

Correlation coefficient (r) was statistical relationship between two variables to check significance of the model. It was considered to be more significant when the probability of significance (p) was less than 0.05 ($p < 0.05$). Generally correlation coefficient was followed by Ward's method which gave one and two tailed p values (Satheeshkumar & Khan, 2012).

Hierarchical cluster analysis (HCA)

The sampling locations were dispersed in 169 km^2 area. So, HCA was used for qualitative identification of water quality contamination (Gómez et al., 2020). The mean concentrations of each parameter were used for the similarities of the water quality along the various sampling stations in HCA analysis. The analysis was carried out using squared Euclidian distance by Ward's method (Egbueri, 2020; Panseriya et al., 2020, 2021).

Quality indicators of groundwater

Water quality index (WQI)

This index (WQI) is a mathematical tool, which used to investigate large and complex dataset into single numerical score and describe overall water quality status of the study area. The major aim of the index was to reflect environmental condition which used for the suitability for drinking purpose or decision-making.

WQI calculation, a weightage (wi), was assigned for the each parameter based on the overall importance, health effect and affecting in water quality. In a present paper, the weightage of each parameter was taken from various sources (Horton, 1965; Raj & Shaji, 2017; Ramakrishnaiah et al., 2009; Saha et al., 2018; Taloor et al., 2020; Varol & Davraz, 2015). The highest weight was assigned for the parameter due to their importance and major effect on water quality and harmful effect on public health whereas least weight mainly due to less harm than the highest weightage parameter (Table 1). The weight and the relative importance of parameters were calculated as:

$$Wi = wi / \sum_{i=1}^{n} wi$$

Here, Wi is the relative weight, wi is the weight of each parameter and n is the number of parameters.

$$qi = Ci \times Si$$

Here, qi is the quality rating, Ci is the concentration of each chemical parameter in each water sample in mg/l, Si is the drinking water standard for each chemical parameter in mg/l except for conductivity (μS/cm) and pH.

$$SIi = Wi \times qi$$

Here, SIi is the sub-index of ith parameter; qi is the rating based on concentration of ith parameter.

$$WQI = \sum SIi$$

The final water quality index value was calculated by sum of sub-index of quality parameters and their respective quality classification was excellent water quality to unfit for drinking, i.e., excellent (< 50), good (50–100), poor (100–200), very poor (200–300) and unfit for drinking (> 300) (Taloor et al., 2020).

Table 1 Relative weight of hydro-chemical parameters

Chemical parameter	Units	BIS-2012	Weight (wi)	Relative weight (Wi)
pH	–	7.5	3	0.16
TDS	mg/l	500	4	0.22
Fluoride	mg/l	1.5	5	0.27
Chlorine	mg/l	250	3	0.16
Total hardness	mg/l	300	3	0.16
			$\sum$wi = 18	$\sum$Wi = 1.0

Potential health risk appraisal (HRA) due to fluoride on Vadodara

Health risk appraisal/assessment (HRA) is a traditional model to evaluate the possible impact of toxic chemical or microbial agent over a specific time period (USEPA, 1989). The HRA index was used according to the Yadav et al., 2019 and Rahman et al., 2020, in which 3 categories of age group were selected to quantify probabilistic risk assessment in various environmental conditions. The total population was demarcated based on the physiological and social changes, i.e., infant age, child age and adults age (Yadav et al., 2019). The information observed by these age demarcation to know exposure and impact of toxic chemical on various population group of the city to estimate their potential non-carcinogenic health risk. People are mostly exposed to contaminants from oral intake, external exposure and inhalation absorption.

According to the Environmental Protection Agency (USEPA, 1993) standard, fluoride is scarcely absorbed through the respiration tract and external contact. Thus, in the present study, human health risks for fluoride existences were performed via only a single contact pathway: oral intake (USEPA, 1993). Generally, 3 age groups of resident population (Infants, children and adults) can exposed to fluoride content were computed by the estimated daily intake (EDI) in each drinking water sample. List of the input parameters for evaluate EDI and hazard quotient (HQ) is given in Table 2.

$$EDI = \frac{Fc \times IngD \times EF \times ED}{BW \times ET}$$

Here, EDI is for the estimated daily intake (mg/kg/d): Fc is fluoride concentration of the analyzed water sample, IngD is the intake dose of oral ingestion (L/d), EF is the exposed frequency (d/y), ED is the exposure duration, BW is the body weight taken and ET is the exposure time is computed as the byproduct of the number of years and number of estimated days.

The HQ fluoride (hazard quotient) was computed by the use of EDI and reference dose (RfD) of fluoride. For the oral ingestion, non-carcinogenic risk of the fluoride investigated.

$$HQ\,fluoride = \frac{EDI}{RfD}$$

Here, RfD is the reference dose for the long lasting fluoride exposure, i.e., 0.06 mg/kg/day according to the USEPA, 2009. HQ and EDI for fluoride were calculated by Yadav et al., 2019.

Geographic information system (GIS)

The GIS is widely used by environmental researchers in last decades. The GIS technology represents the data, in order that researchers were easily visualized spatio-temporal pattern of contamination or non-contamination zone for the interpretation from complicated datasets. In this study, QGIS software (Ver. 3.10) was used for effective, reliable and spatio-temporal mapping of pollutants present in the study area. Among that, the tool can visualize their impact on the bio-geological and health purpose.

Table 2 List of input parameters for health risk appraisal of fluoride through oral ingestion pathway

Parameters	Units	Infants	Children	Adults	Reference
Fluoride concentration (Fc)	mg/l	From present study			–
Ingestion rate (IngD)	L/day	0.75 ± 0.08	1.25 ± 0.57	1.95 ± 0.64	Zhang et al. (2017)
Exposure frequency (EF)	day/year	365	365	365	Rahman et al. (2020)
Exposure duration (ED)	year	6	6	6	Rahman et al. (2020)
Average time (AT)	days	2190	2190	9125	MEPRC (2014)
Body weight (BW)	kg	6 ± 0.60	20 ± 1.48	70 ± 1.10	Yadav et al. (2019)
Oral reference dose (RfD)	mg/kg/day	0.06	0.06	0.06	Yadav et al. (2019)

Result and discussion

Detailed hydro-geochemical exploration of groundwater

It is necessary to distinguish the quality of groundwater for drinking and domestic purposes because hydrogeochemistry of groundwater dependent on specific location. Various groundwater quality parameters and analytical results are mentioned in Table 3 for 2014 and 2019. The results were compared with the standard value (BIS, 2012) (Table 4). The mean concentration of each parameter was used for all the mathematical and statistical analysis.

In a present study, depth of groundwater was 64.38–196.67 feet during 2014 and 47.86–205.00 feet during 2019. A rainfall and floods (2019) leading to increased natural recharge and rise groundwater depth as compared to 2014 indicated recharge of aquifer.

There was no significant difference in the pH values on temporal scale. The pH of groundwater in 2014 ranged between 8.03 (W12)–8.49 (W1), whereas during 2019, pH was 8.01 (W4)–8.39 (W6). The pH of the study area was slightly basic at all the sampling points. Results of groundwater pH indicated that study stations were within a range of standard BIS maximum permissible limit during 2014 and 2019.

EC values indicate the presence of exchangeable ions in the groundwater, and in 2014, the EC values exceeded the permissible limits in the W2, 23, W9 and W12, situated towards E (East) and NE (Northeast) region of the city. The higher EC in the groundwater was due to lixiviation from soil or from the mixing of different sources of groundwater in the area (Yadav

Table 3 Mean groundwater quality parameters of Vadodara, Gujarat

Sampling year	Ward No	Depth	EC	Chloride	pH	TH	Fluoride	TDS	Calcium hardness	Sulfate	Alkalinity
2014	W1	64.38	1071.25	112.83	8.49	252.50	0.98	433.75	57.00	–	–
	W2	117.78	2258.89	1534.86	8.14	360.00	0.95	1191.11	141.33	–	–
	W3	76.67	3481.67	3789.75	8.03	490.67	1.20	743.33	209.67	–	–
	W4	81.07	1265.00	1027.78	8.11	438.86	1.26	784.29	116.86	–	–
	W5	69.67	1760.00	792.04	8.08	355.56	0.69	1137.78	91.56	–	–
	W6	83.33	1720.83	2067.97	8.09	442.00	0.70	1125.00	143.33	–	–
	W7	105.56	1847.78	1267.88	8.15	470.67	0.92	1305.56	148.67	–	–
	W8	116.67	1194.44	138.62	8.26	284.44	0.66	1148.89	93.33	–	–
	W9	196.67	3040.00	7303.39	8.39	404.00	1.61	1046.67	137.33	–	–
	W10	84.09	1576.36	859.01	8.32	533.09	1.01	912.73	149.45	–	–
	W11	92.63	1618.95	874.80	8.14	364.63	0.98	748.42	86.53	–	–
	W12	89.69	2041.88	2472.64	8.03	413.00	1.13	2577.50	105.50	–	–
2019	W1	47.86	1798.57	234.82	8.16	327.09	1.72	1162.86	–	30.22	431.43
	W2	87.86	3058.57	721.26	8.17	441.00	1.66	1748.57	–	64.69	331.43
	W3	73.33	1633.33	239.38	8.16	264.30	0.86	1180.00	–	72.64	403.33
	W4	59.44	1255.00	427.23	8.01	319.20	1.04	511.11	–	30.78	311.11
	W5	109.50	1264.00	407.88	8.13	278.28	1.75	744.00	–	33.3	318.00
	W6	113.75	1162.50	235.12	8.39	288.90	1.77	615.00	–	25.81	395.00
	W7	105.63	1617.50	536.28	8.13	349.43	1.77	1000.00	–	26.18	300.00
	W8	103.57	1105.71	214.96	8.31	212.66	1.14	1131.43	–	18.82	397.14
	W9	48.33	1446.67	398.69	8.22	244.20	1.40	906.67	–	73.79	360.00
	W10	205.00	1318.00	249.14	8.15	367.92	1.16	854.00	–	62.46	390.00
	W11	80.00	1020.83	217.54	8.13	292.20	1.71	658.33	–	24.22	435.00
	W12	69.00	1035.00	341.68	8.02	381.96	1.61	770.00	–	54.51	312.00

Table 4 Mean concentration of water quality in present study area and standard concentrations of water quality variables (WHO, 1984 and BIS, 2012) for drinking purpose

Parameters	Mean concentration in the study area	WHO (1984)		BIS (2012)		Reference
		Highest desirable limit	Maximum permissible limit	Highest desirable limit	Maximum permissible limit	
Depth	47–205	–	–	–	–	–
pH	7.67–8.57	7.0	8.5	6.5	8.5	–
EC	1010–3948.75	–	–	–	–	700–2000 (Prakash & Somashekar, 2006)
TH	212.66–529.00	100	500	300	600	–
Chloride	109.84–6065.06	200	600	250	1000	–
Fluoride	0.69–1.77	–	–	1.0	1.5	–
TDS	511.11–2487.50	500	1500	500	2000	–
Alkalinity	300.00–435.00	–	–	200	–	–
Sulfate	18.82–73.79	200	400	200	400	–

et al., 2019). However, in 2019, EC values recorded were within the standard limits except at station W2. The results indicated that W2 has presence of an impermeable clay layer at shallow depth (Gupte, 2010; Sabhaya et al., 2018) preventing recharge of groundwater and therefore no improvement was recorded in EC as compared to 2014. In case of other wards, good recharge of groundwater leads to improve the EC in 2019.

Chloride content was reported in the range of 112.83 mg/l (W1)–7303.09 (W9) mg/l during 2014, whereas during 2019 values differed from 214.96 (W8)–721.26 (W2) mg/l. In 2014, chloride values crossed the WHO guidelines in W2-W7, W9-W12 and BIS standards permissible limits in W2-W4, W6, W7, W9, and W12. The scenario of high Cl was indicated saline groundwater and overexploitation of fresh water. The improvement in chlorinity in 2019 was mainly due to the recharge of groundwater. The city needs a proper water recharging mechanism based on the geological profile of each ward.

Total hardness (TH) of groundwater ranged from 252.50 mg/l (W1)–533.09 mg/l (W10) during 2014 and 212.66 mg/l (W8)–441.00 mg/l (WW2) during 2019. The results indicated that slight decreases in TH were mainly due to the recharge of groundwater in 2019. The nature of the water, i.e., soft or hard was assessed through calcium hardness, water having soft when the Ca hardness was < 100 mg/l. In a present

study, 70% of the samples showed hard nature of groundwater mainly due to the presence of limestone, sedimentary rocks and calcium bearing minerals which was responsible for hardness of water.

The alkalinity of the groundwater ranged from 300.00 mg/l (W7)–435.00 (W11) mg/l and the values are above the desirable limit 250 mg/l (BIS, 2012). Presence of high alkalinity gives a bland taste of water and filtered through RO (Reverse Osmosis) system before being consumed, so excess salts removed. Sulfate content of the groundwater ranges from 18.82 (W8) mg/l–73.79 (W9) mg/l, and the values were within the permissible levels.

Spatial–temporal distribution of TDS in Vadodara

TDS content in groundwater of Vadodara during 2014 ranged from 433.77 mg/l (W1)–2577.50 mg/l (W12). Maximum permissible limit of TDS of drinking water was 2000 mg/l (BIS, 2012). The spatial–temporal results indicated that TDS are beyond the permissible limit in a studied region (Fig. 2). Depending on soil type and reactivity with groundwater, TDS was changed in an environment (Yadav et al., 2019). This scenario was changed in a half-decade; during 2019, TDS was observed from 511 mg/l (W4)–1748.57 mg/l (W2). The improvement was observed in W4-W7 and W9-W10, whereas W1-W3, W8 and W12 have higher TDS than 2014. Presence of high TDS in the
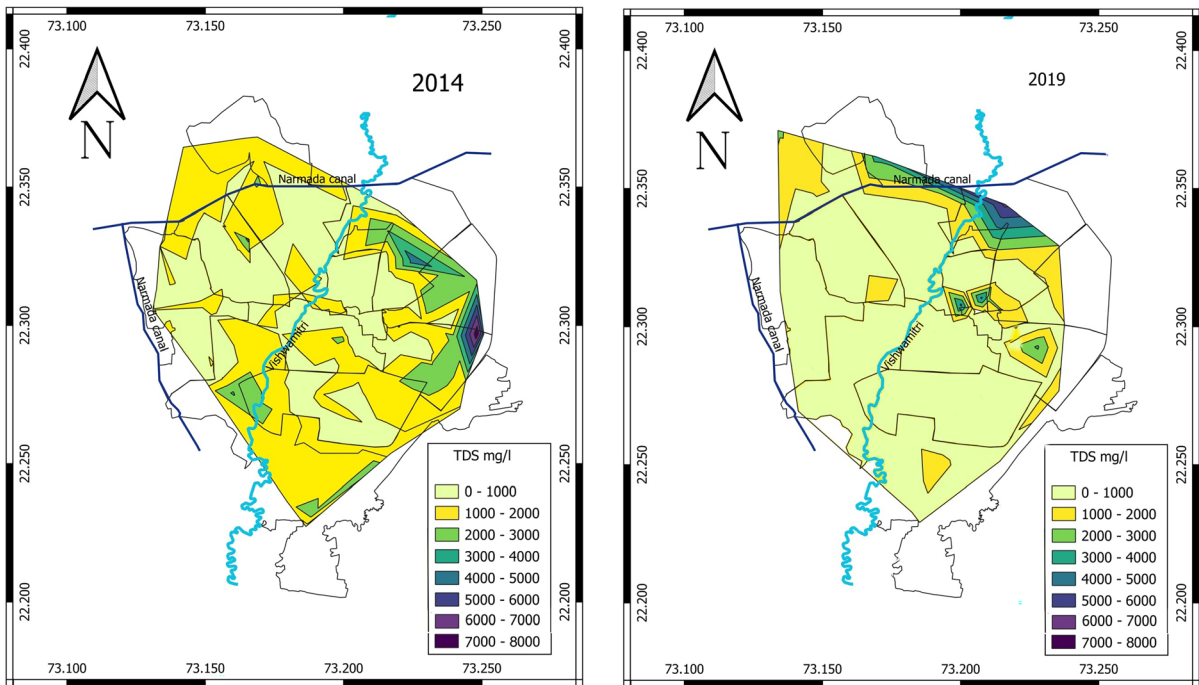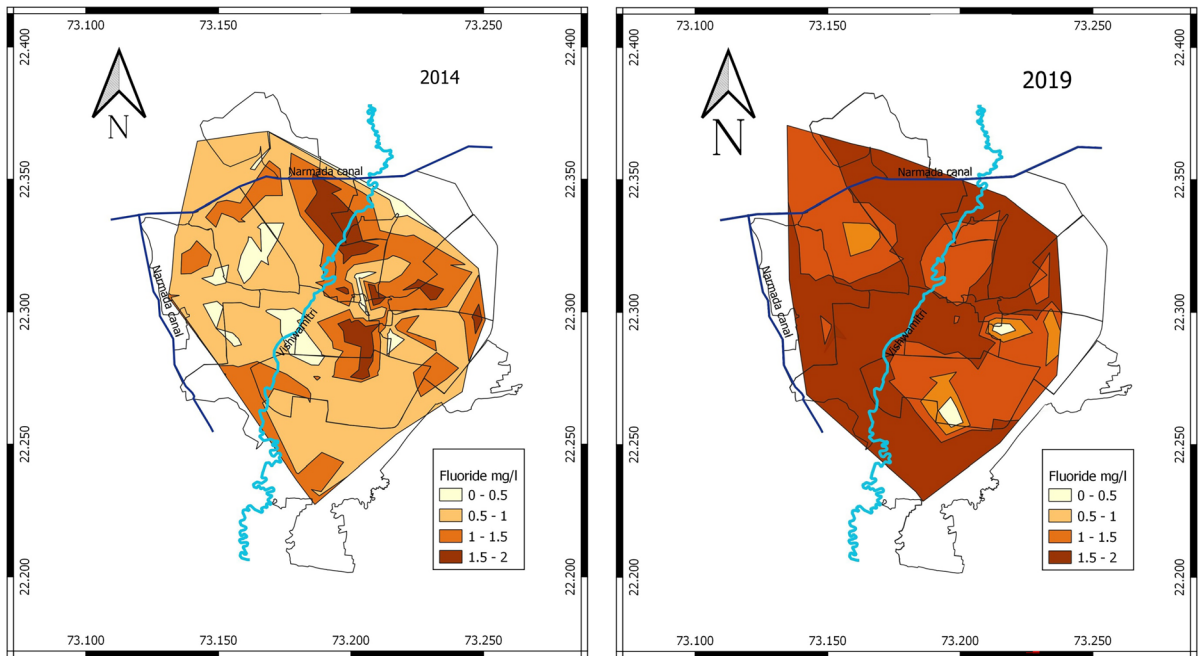
Fig. 2 TDS concentration which impacted groundwater of Vadodara, Gujarat

groundwater leads to gastrointestinal irrigation and other health-related issues (Taloor et al., 2020). The heavy rainfall, flood and water logging condition in the 2019 were resulted in groundwater recharge; therefore, TDS was changed in the study area. Moreover, GIS mapping (Fig. 2) showed shift of TDS in groundwater from east-northeast (E-NE) region to north-northeast (NNE) region. The TDS value was declined substantially in southwest-south-southeast (SW-S-SE) region of the city. The good recharge zone and low anthropogenic pressure in the southwest-south-southeast (SW-S-SE) attributed to improvement in TDS during 2019. The variation in TDS values during the event of low rainfall was a matter of concern like the situation in 2014. However, hydro-geological condition of north (N) and north-northeast (NNE) part of the city does not allow direct recharge of aquifer; therefore, surface water storage was better option in this region.

Spatial–temporal distribution of Fluoride in Vadodara

The results of fluoride changes indicate immense spatial temporal distribution pattern during 2014 and 2019 datasets (Fig. 3). The fluoride concentration was reported between 0.66 mg/l–1.61 mg/l during 2014 which increased in half-decade 0.86 mg/l–1.77 mg/l in 2019. The numbers of wards were increased during 2019 in context to environmental standard fluoride content, i.e., 1.5 mg/l (Banerjee, 2015) compared to 2014 (BIS, 2012). The GIS maps shows spatial pattern and indicates an eastern part of the city, i.e., W9 reported beyond fluoride standard, however by 2019 more wards (W1, W2, W5, W6, W7, W9 and W11) reported fluoride values above 1.5 mg/l. This includes center region, north to east and west to south of study area which was contaminated during past half of the decade. These suggest that fluoride contamination was increased in large scale and covered most of the study area. This phenomenon has taken place irrespective of heavy rainfall in 2019. These lead to deposition of anthropogenic fluoride into groundwater by a process where F^- can exchange with OH^- because fluoride and hydroxyl ions have similar ionic strength (Banerjee, 2015). The reaction is governed by the native hydro-geological conditions and mineral type. Among that, major sources of fluoride are (1) fluoride bearing minerals, (2) volcanic eruption and 3) natural source is marine aerosol (Lapworth et al., 2017; Thapa et al.,

Fig. 3 Fluoride concentration which impacted groundwater of Vadodara, Gujarat

2017). Additionally, potential sources of fluoride are geological, atmospheric and anthropogenic activities which enter fluoride in the environment (Mukherjee & Singh, 2018; Thapa et al., 2017). The higher concentration of fluoride in the groundwater increased health-related problems mainly fluorosis. As per WHO, 1996 and Rahman et al., 2020 fluoride concentration are divided into five classes based on their effect on human health. Based on this classification, the fluoride concentration in 2014 is distributed in following ways—12.86% of samples fall in class-I, and about 72.86% in class-II and 14.29% in class-III (Table 5). However, during 2019, 38% of samples fall in class II category and rest 62% in class III category. The results

of class II and Class III indicate that fluoride impact was on promoting development of strong bones/teeth and dental fluorosis (mottling of teeth), respectively. Moreover, the results also indicate that class has been switching into their upper class which will be creating future health-related problems for the population. The result interpreted as groundwater of class-III was increased 48.00% which was responsible for dental fluorosis on human. In a present study, overall fluoride content was increased in the groundwater which could lead to health issues in terms of fluorosis, ligaments calcification (Ozsvath, 2009), a developmental disorder in children (Ding et al., 2011), liver and kidney dysfunction as well as a nervous weakness (Xiong

Table 5 Fluoride in the study area

Classes	Fluoride (mg/L)	Effect on human health (Rahman et al., 2020; WHO, 1996)	% of sample	
			2014	2019
Class-I	< 0.50	Conducive to dental caries	12.86	0.00
Class-II	0.50–1.50	Promotes development of strong bones and teeth	72.86	38.00
Class-III	1.50–4.00	Dental fluorosis (mottling of teeth)	14.29	62.00
Class-IV	4.00–10.00	Dental and skeletal fluorosis (pain in the back and neck bones)	0.00	0.00
Class-V	> 10.00	Crippling fluorosis	0.00	0.00

et al., 2007). A quite similar fluoride distribution pattern was reported in India and Bangladesh (Redy & Rao, 2006; Raj & Shaji, 2017; Yadav et al., 2019; Rahman et al., 2020; Sahu et al., 2021). The reasons behind the fluoride distribution at the study area were 1) aquifer minerals, 2) transit time and 3) hydrogeochemical processes (Banerjee, 2015; Lapworth et al., 2017; Rahman et al., 2020).

Correlation of groundwater parameters

Correlation analysis is depicted in Table 6, and the level of significance between the parameters was reported high ($p < 0.01/0.05$). Fluoride is positively significant with pH ($p < 0.01$) and EC ($p < 0.01$). The reason behind this might be due to the exchange of ions between F^- and OH^- ion in groundwater (Yadav et al., 2019). TDS showed high significance level ($p < 0.01$) with all the parameters during 2014, and positive correlation was observed with TH ($p < 0.01$), Cl^- ($p < 0.01$), alkalinity ($p < 0.05$) and sulfate ($p < 0.01$) during 2019. Since TDS comprises of

carbonates, sulfates, chlorides and other substances, there is positive relation with all these parameters. TDS is used as an immediate marker to assess the groundwater quality; however, there is need to consider other parameters as well before a remedial measures can be undertaken. A close study of the geological conditions is important to relate the exact reason for elevated levels of TDS.

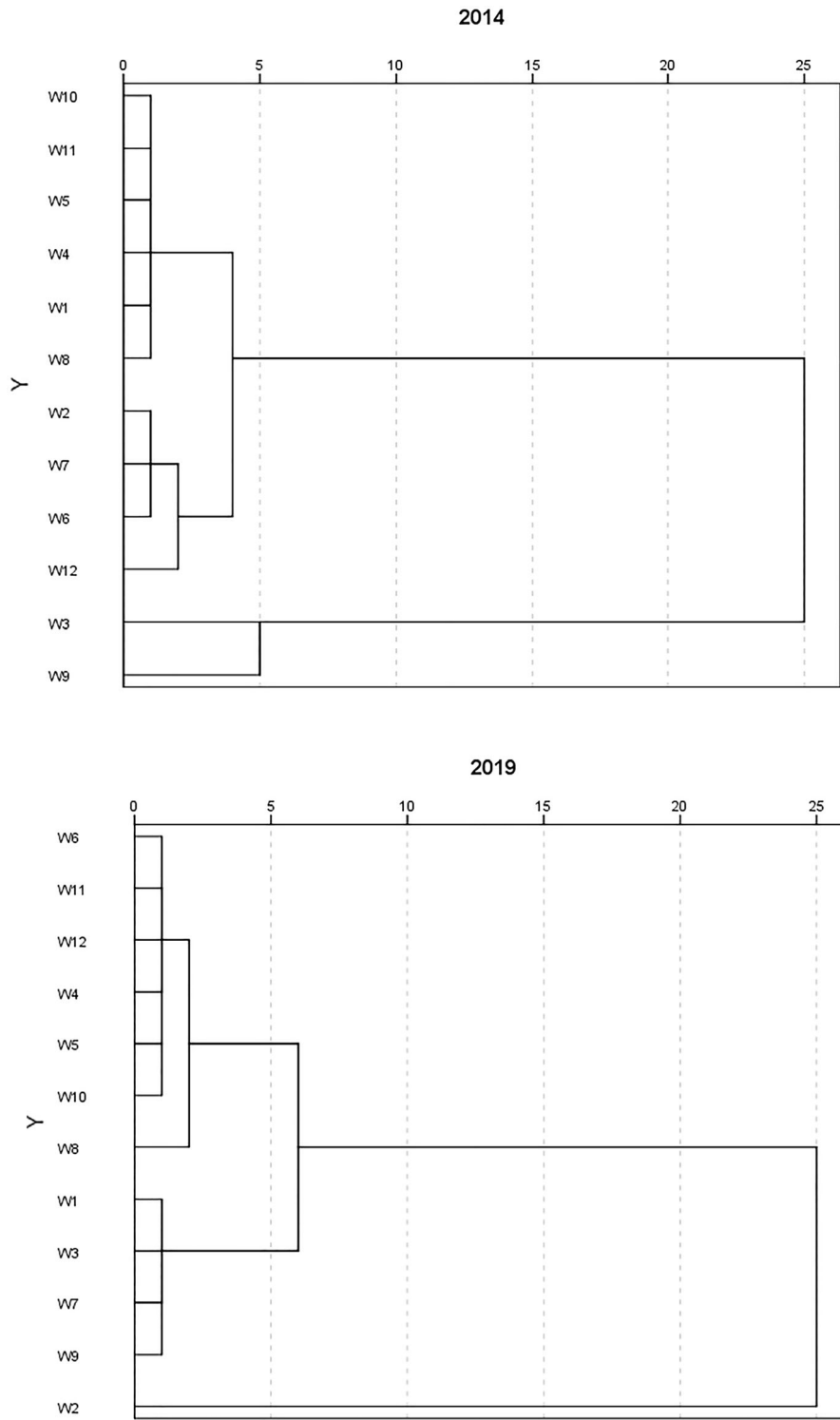Spatio-temporal pattern of groundwater of Vadodara

Hierarchical cluster analysis (HCA) is an expedient method to identify homogenous group of objects called cluster. Specific cluster share various characteristics of observation (Yadav et al., 2019). Ward's linkages method with squared euclidean distance was used to elucidate HCA similarity levels between groundwater parameters. In the present study, dendrograms were produced based on the year of sampling, parameters and sampling locations (Fig. 4).

Table 6 Pearson correlation of groundwater parameters of Vadodara, Gujarat

2014	Depth	pH	EC	TH	Ca hardness	Chloride	Fluoride	TDS
Depth	1.000							
pH	0.045	1.000						
EC	0.130	− **235****	1.000					
TH	0.110	− **.264****	**.480****	1.000				
Ca hardness	0.053	− **.223****	**.659****	**.745****	1.000			
Chloride	**.298****	− **.182***	**.799****	**.495****	**.672****	1.000		
Fluoride	0.130	**.212***	**.171***	− 0.125	− 0.024	0.102	1.000	
TDS	0.096	− **.242****	**.931****	**.565****	**.721****	**.799****	**.179***	1.000

2019	Depth	pH	EC	TDS	Hardness	Chloride	Fluoride	Alkalinity	Sulfate
Depth	1.000								
pH	− 0.023	1.000							
EC	− 0.071	0.163	1.000						
TDS	− 0.062	0.128	**.841****	1.000					
Hardness	− 0.019	− 0.116	**.617****	**.623****	1.000				
Chloride	− 0.081	− 0.059	**.634****	**.505****	**.618****	1.000			
Fluoride	− 0.083	0.174	0.142	0.057	0.181	0.168	1.000		
Alkalinity	0.089	**.200***	**.287****	**.223***	0.065	− 0.121	0.071	1.000	
Sulfate	− 0.028	0.044	**.390****	**.423****	**.475****	**.296****	− 0.019	0.150	1.000

Bold indicates the positive significance of the parameters whereas Italics with bold indicates the negative significance of the parameters

$^*p < 0.05$; $^{**}p < 0.01$

Fig. 4 Spatio-temporal patterns classifying the groundwater quality of Vadodara, Gujarat

In the year 2014, a total three clusters were observed: cluster I showed similarity in water quality of the following wards W10, W11, W5, W4, W1 and W8. Cluster II included W2, W7, W6, W12, and cluster III included W3 and W9. The extremity found in cluster III in HCA analysis mainly attributed due to higher levels of TDS and chlorides which limits were beyond the BIS level. The results of HCA 2019 also included three cluster viz., cluster I included (W6, W11, W12, W4, W5, W10, W8); Cluster II included (W1, W3, W7, W9) and Cluster III include W2. Overall HCA analysis showed that the water quality of W10, W11, W5, W4 and W8 is similar and these are located in the central and northwest area. The results indicated that water qualities in these zones were not altered between 2014 and 2019 and the city needs to rethink on usage of groundwater for various purposes in these wards. These zones need appropriate groundwater recharge techniques with minimal anthropogenic input which is the best suitable option for this zone. On the other area, W6 and W12 have shown improvement in terms of EC, TH, Cl and TDS during 2019. Incidentally the area lies within the river basin of Vishwamitri and considerable recharge has been taken place during the 2019 floods. Here, the recharge of deep aquifers can be considered best option and presence of recharge wells in the wetlands of these areas will reduce the water logging conditions. The overall results of HCA for 2014 were changed during 2019. The results of HCA indicate some of the study area have not affected by any local or natural activities whereas major areas of Vadodara were affected by the anthropogenic activities in the city.

Water quality trends according to the Water quality index (WQI) for Vadodara

Water quality index (WQI) is an important index for assessment of water quality for different geo-spatial locations. Major significance of the index is to check the water quality and make necessary changes of the area and justify our accountability towards the nature. The quality of groundwater based on WQI index is described below.

An individual station was computed for WQI and overall results gave spatio-temporal pattern in the study area, detailed result depicted in Table 7. Moreover, excellent groundwater quality was not observed in either 2014 or 2019. In 2014, about 47.85% of the sampling points include into poor water quality category, largely due to presence of high TDS. However in 2019, the poor water quality increased to 59% due to anthropogenic and developmental pressure in the study area. The results indicated good groundwater quality increased from 17.85% in 2014 to 31% in 2019. This could be due to good groundwater recharge in certain parts of the city which enabled to improvement water quality of the study area. The data clearly indicate that there is need to increase the recharge capacity of the city and techniques for implementation of the same should be promoted.

The WQI of 2014 and 2019 is represented in Fig. 5. WQI values of 2014 indicated that W9, W12 and W3 were highly polluted and water cannot be suitable for drinking purposes. Likewise W6, W2 and W7 were categorized as very poor water quality and W4, W5, W8, W10 and W11 have poor groundwater. The result of WQI indicated that W1 landscape has good groundwater quality from the entire study area. Overall water trends based on WQI of 2014 results concluded that there was over exploitation of

Table 7 Sampling point fall into the water quality grade in respective sampling years

Water quality value	2014		2019		Water Quality Grade
	Number of Sampling points	% sampling points fall into the grade	Number of Sampling points	% Sampling points fall into the grade	
< 50	0	0.00	0	0.00	Excellent
50–100	25	17.85	31	31.00	Good
100–200	67	47.85	59	59.00	Poor
200–300	25	17.85	8	8.00	Very poor
> 300	23	16.42	2	2.00	Unsuitable
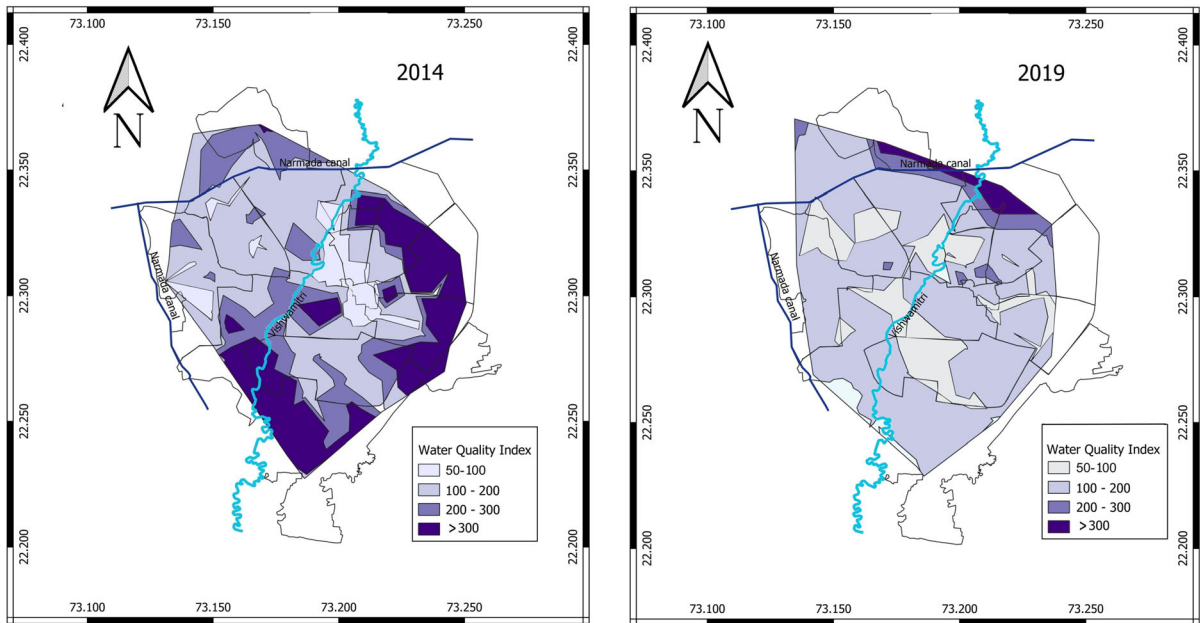
Fig. 5 Water quality index of the city ward, Vadodara, Gujarat

groundwater in Vadodara. In 2019, WQI showed that there was some improvement in the water quality mainly due to the results of good monsoons and all the wards include into the category of poor water quality.

Based on the WQI index, the wards were arranged in the order of water quality from drinkable water to worst. In 2014, the WQI order was in the following ways   W1 < W8 < W11 < W5 < W10 < W4 < W7 < W2 < W6 < W12 < W3 < W9.   Similarly, during 2019, WQI was obtained as W4 < W11 < W6 < W10 < W8 < W3 < W9 > W5 < W12 < W1 < W7 < W2. Due to the similar anthropogenic input, new techniques could be implemented for groundwater recharge for the sustainable use. Among that, Vadodara lies in the semiarid conditions with varied rainfall pattern. Moreover, different rainfall pattern and increased urbanization there is needed to keep a close watch on the groundwater quality.

Probabilistic health risk appraisal (HRA) due to the presence of fluoride in groundwater

The present paper has been calculated and evaluated to identify non-carcinogenic health risk in infants, children and adults due to groundwater fluoride consumption. For HRA, estimated daily intake (EDI) and hazard quotient (HQ) of fluoride were assessed for the

different age group of the city (Fig. 6). The results clearly indicated that EDI was high in infant and children. Similarly high HQ observed in infants and children from entire study region whereas adults observed less HQ. The obtained results indicated that the population of Vadodara is at high risk of dental and skeletal fluorosis.

Estimated daily intake (EDI)

The EDI of fluoride was calculated based on fluoride content in groundwater, intake of water and average body weight for infant, children and adults for Vadodara and depicted in Table 2 and Fig. 6. The results presented in the study indicated that average fluoride intake from groundwater in different age group were 0.08–0.22 mg/kg/day in infant, 0.04–0.11 mg/kg/day in children and 0.01 mg/kg/day in adults. The exposure dose in infant was increased from 0.08–0.20 mg/kg/day to 0.11–0.22 mg/kg/day during a half-decade. Similarly in children, EDI was increased from 0.04–0.10 mg/kg/day (2014) to 0.05–0.11 mg/kg/day (2019), whereas there was no impact observed in EDI of adult. Overall, high exposure of fluoride was observed at W1, W2, W5, W6, W7, W11, W12 in 2019 compared to 2014. The obtained data revealed that infants and children were

Fig. 6 EDI and HQ of infants, children and adults for Vadodara, Gujarat
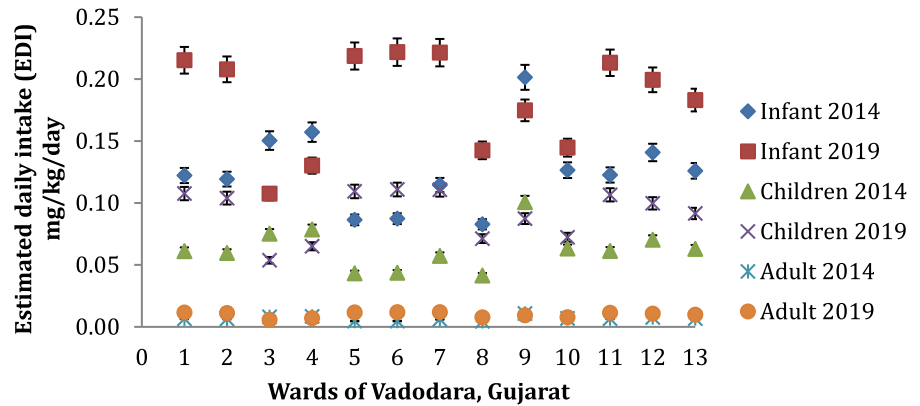
1 to 12 : Wards of Vadodara, Gujarat; 13 : Average EDI of Vadodara, Gujarat
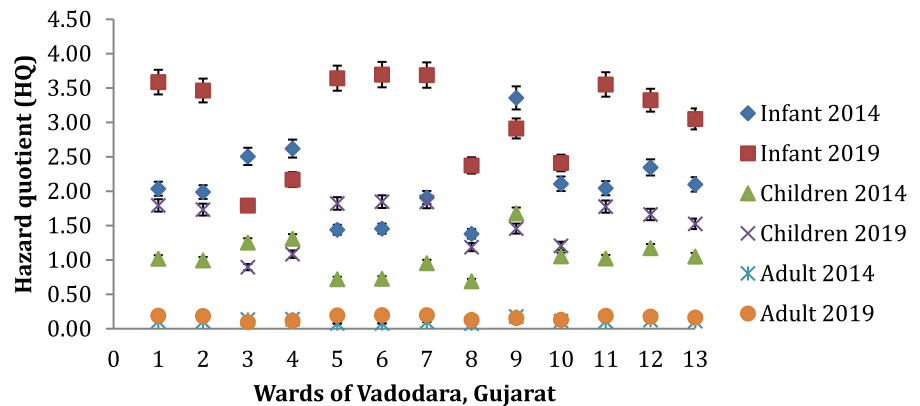
1 to 12 : Wards of Vadodara, Gujarat; 13 : Average HQ of Vadodara, Gujarat

most exposed towards fluoride risk when it compared with oral reference dose 0.06 mg/kg/day (Yadav et al., 2019). Previously, it has been reported that high fluoride exposure in children leads to dental problems during teeth development process by calcification process (Chouhan et al., 2010). Whereas in infants, fluorosis is not very common mainly due to limited intake of groundwater and depend on breast milk or consume cattle milk. Hence, fluoride exposure risk may not be as severe as expected.

Hazard quotient (HQ)

According to the USEPA (2009), HQ represents non-carcinogenicity of the population. The HQ > 1 is designated as potential for detrimental impact on human health hazard, whereas HQ < 1 designated as the tolerable range for non-carcinogenic risk of fluoride (USEPA, 2009). The result clearly indicated

that HQ > 1 in infant and children at all sites while in adults HQ < 1 from study area (Fig. 6). The obtained results indicated that the population of the Vadodara city is at higher risk of dental and skeletal fluorosis. The average HQ for adults was < 1 in 2014 and 2019 which indicated that adults were tolerable towards fluoride risk. The study stated that children and infants group were most exposed by fluoride, corroborates with the Yadav et al., (2019) and Rahman et al., (2020). Similar scenario was earlier reported in Punjab, India, where children were most vulnerable group towards fluoride hazard (Ahada & Suthar, 2019). Among that, Yadav et al., (2019) stated that infant and children were more prone to fluoride contamination. The mean HQ for infant was 2.10 which increased to 3.05, whereas HQ children were 1.05 and 1.53 during 2014 and 2019, respectively. According to the age group, non-carcinogenic health risk was observed as infants > children > adults.

Similar studies on fluoride impact on different age group were reported by Vishwanathan et al. (2009), Narsimha and Rajitha (2018) and Mukherjee et al., (2019). Moreover, various researcher supported this finding where infant and children were more venerable towards fluoride and reported three types of fluorosis, i.e., dental, bone and skeletal (Ali et al., 2019; Guissouma et al., 2017; Irigoyen-Camacho et al., 2016; Zango et al., 2019; Zhang et al., 2017). Among that, ward wise descending order of HQ in 2014 follow W9 > W4 > W3 > W12 > W10 > W11 > W1 > W2 > W7 > W6 > W5 > W8. However, in 2019, the scenario was totally changed and the trend remains W6 > W7 > W5 > W1 > W11 > W2 > W12 > W9 > 10 > W8 > W8 > W4 > W3. The results also indicated the shift of health risk by fluoride in various wards of Vadodara city.

As earlier mentioned, fluoride can lead either necessary element for the dental and skeletal structure or high amount can make health-related problems like severe fluorosis and other health-related issues such as kidney and nervous system failure (Mukherjee et al., 2019; Zango et al., 2019). These health problems could be make dental and skeletal fluorosis in children and infants (Yadav et al., 2019). The potential health risk and fluoride distribution indicated that the fluoride exposure has been increased in Vadodara. The half-decadal health risk appraisal analysis can be used to relate the health risk of the Vadodara citizens and long-term monitoring can be designed.

Conclusions

The present study is the comprehensive study of entire Vadodara city to assess the water quality and their impact on human health. In this investigation, 720 samples were analyzed for different physicochemical parameters (depth of water, pH, electrical conductivity, chlorinity, total dissolved solids, total hardness, alkalinity, fluoride and sulfate) to fitness and health risk. Positive correlation between the water quality parameters suggested that the local hydro-geological factors have a strong influence on water quality in the study area. Further consumption of groundwater with high TDS concentration (> 2000 mg/l) leads to gastrointestinal diseases and other health-related issues in east, north and northeast region of the city. Fluoride concentration in groundwater of the Vadodara

(0.66–1.61 mg/l during 2014 and 0.86–1.77 mg/l during 2019) indicates that 62% samples are unfit for drinking purpose, which could cause dental and skeletal fluorosis. Hierarchical cluster analysis suggested that anthropogenic impact of TDS and chloride was observed during 2014. The impact reduced marginally due to improvement in groundwater quality because of higher rainfall and increase recharge of aquifer during 2019. The WQI was indicated lack of excellent water in the study area in the last half-decade. As per WQI, 82.12% during 2014 and 69% during 2019 of groundwater samples represent poor, very poor and unsuitable categories whereas remaining 17.85% during 2014 and 31% during 2019 of the samples represent good category for drinking purposes in entire Vadodara, Gujarat. The non-carcinogenic risk evaluated based on hazard quotient (HQ) suggest that HQ score was 1.38–3.36 during 2014 and 1.79–3.70 during 2019 for infants; 0.69–1.68 during 2014 and 0.90–1.85 during 2019 for children, whereas 0.07–0.18 during 2014 and 0.10–0.20 during 2019 for adults. Therefore, infant and children were more prone for health risk by the consumption of fluoride-rich water than adult in the studied region. Thus, the results of this study recommend low dependency on ground-water for drinking purpose and rainwater harvesting to improve the ground water quality. Moreover, the study can be footprint for future research and develop policies and strategies for Vadodara, Gujarat, India.

Author contributions   HZP contributed to conceptualization, methodology, formal analysis, writing—original draft, review and editing. DJG contributed to conceptualization, methodology, formal analysis, supervision, and writing—review and editing. JJL contributed to conceptualization, methodology, supervision, formal analysis, and writing—review and editing. AS contributed to conceptualization, methodology, and formal analysis. PG contributed to conceptualization, methodology, and formal analysis.

Declarations

Conflict of interest   The authors declare that they have no conflict of interest.

References

Ahada, C. P. & Suthar, S. (2019). Assessment of human health risk associated with high groundwater fluoride intake in southern districts of Punjab, India. *Exposure and health, 11*(4), 267–275.

Ali, W., Aslam, M. W., Junaid, M., Ali, K., Guo, Y., Rasool, A., & Zhang, H. (2019). Elucidating various geochemical mechanisms drive fluoride contamination in unconfined aquifers along the major rivers in Sindh and Punjab, Pakistan. *Environmental Pollution, 249*, 535–549.

APHA. (1995). Standard methods for the examination of water and wastewater, *19*, 273–287.

Aureli, A., Ganoulis, J., & Margat, J. (2008). Groundwater resources in the Mediterranean region: importance, uses and sharing, *Water in the Mediterranean, 96*–105.

Banerjee, A. (2015). Groundwater fluoride contamination: A reappraisal. *Geoscience Frontiers, 6*(2), 277–284.

BIS. (2012). Indian standard specifications for drinking water. IS:10500, Bureau of Indian Standards, New Delhi, India.

CGWB (Central Ground Water Board). (2013). Ground water brochure: Adilabad District, Andhra Pradesh. Hyderabad, India.

Chouhan, S., Lomash, V., & Flora, S. J. S. (2010). Fluoride-induced changes in haem biosynthesis pathway, neurological variables and tissue histopathology of rats. *Journal of Applied Toxicology, 30*(1), 63–73.

Ding, Y., Gao, Y., Sun, H., Han, H., Wang, W., Ji, X., Liu, X., & Sun, D. (2011). The relationships between low levels of urine fluoride on children's intelligence, dental fluorosis in endemic fluorosis areas in Hulunbuir, Inner Mongolia, China. *Journal of Hazardous Materials, 186*, 1942–1946. https://doi.org/10.1016/j.jhazmat.2010.12.097

Egbueri, J.C., 2020. Groundwater quality assessment using pollution index of groundwater (PIG), ecological risk index (ERI) and hierarchical cluster analysis (HCA): a case study. Groundw. Sustain. Dev. 10, p.100292.

Foster, S., Chilton, J., Nijsten, G. J., & Richts, A. (2013). Groundwater—A global focus on the 'local resource.' *Current Opinion in Environment Sustainability, 5*(6), 685–695.

Gleick, P. H. (1993). Water and conflict: Fresh water resources and international security. *International Security, 18*(1), 79–112.

Gómez, K. R., Pasquali, C. L., González, G. P., Hernando, P. F., & Martínez, R. G. (2020). Statistical evaluation of fluoride contamination in groundwater resources of Santiago del Estero Province. *Argentina. Geosci. Front., 11*(6), 2197–2205.

Guissouma, W., Hakami, O., Al-Rajab, A. J., & Tarhouni, J. (2017). Risk assessment of fluoride exposure in drinking water of Tunisia. *Chemosphere, 177*, 102–108.

GUPTE, P.R. (2010). *West Central Region Ahmedabad, hydrogeological conditions, ground water resources & development potential of Vadodara dsitrict, Gujarat* (P. 144).

He, X., Li, P., Wu, J., Wei, M., Ren, X., & Wang, D. (2021). Poor groundwater quality and high potential health risks in the Datong Basin, northern China: Research from published data. *Environmental Geochemistry and Health, 43*(2), 791–812.

Horton, R. K. (1965). An index number system for rating water quality. *Journal of Water Pollution Control Federation, 37*(3), 300–306.

Howard, K. W.(Ed.). (2007). *Urban Groundwater, Meeting the Challenge: IAH Selected Papers on Hydrogeology* (Vol. 8). CRC Press.

Irigoyen-Camacho, M. E., Pérez, A. G., González, A. M., & Alvarez, R. H. (2016). Nutritional status and dental fluorosis among schoolchildren in communities with different drinking water fluoride concentrations in a central region in Mexico. *Science of the Total Environment, 541*, 512–519.

Jac, V. D. G. (2012). *Groundwater and global change: Trends, opportunities and challenges*. Technical report.

Kannel, P. R., Lee, S., Lee, Y. S., Kanel, S. R., & Khan, S. P. (2007). Application of water quality indices and dissolved oxygen as indicators for river water classification and urban impact assessment. *Environmental Monitoring and Assessment, 132*(1–3), 93–110.

Lachassagne, P., Wyns, R., Bérard, P., Bruel, T., Chéry, L., Coutand, T., Desprats, J. F., & Le Strat, P. (2001). Exploitation of high-yields in hard-rock aquifers: Downscaling methodology combining GIS and multicriteria analysis to delineate field prospecting zones. *Groundwater, 39*(4), 568–581.

Lapworth, D. J., Dochartaigh, B. Ó., Nair, T., O'Keeffe, J., Krishan, G., MacDonald, A. M., Khan, M., Kelkar, N., Choudhary, S., Krishnaswamy, J., & Jackson, C. R. (2021). Characterising groundwater-surface water connectivity in the lower Gandak catchment, a barrage regulated biodiversity hotspot in the mid-Gangetic basin. *Journal of Hydrology, 594*, 125923.

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

Llamas, M. R., & Garrido, A. (2007). *Lessons from intensive groundwater use in Spain: economic and social benefits and conflicts. The agricultural groundwater revolution: Opportunities and threats to development* (pp. 266–298).

Marghade, D., Malpe, D. B., & Subba Rao, N. (2021). Applications of geochemical and multivariate statistical approaches for the evaluation of groundwater quality and human health risks in a semi-arid region of eastern Maharashtra, India. *Environmental Geochemistry and Health, 43*(2), 683–703.

MEPRC (Ministry of Evironmetal Protection of the People's Republic of China. (2014). Technical guidelines for risk assessment of contaminated sites (HJ 253e2014).

Millennium Ecosystem Assessment, M.E.A. (2005). *Ecosystems and human well-being* (Vol. 5). Island Press.

Mukherjee, I., & Singh, U. K. (2018). Groundwater fluoride contamination, probable release, and containment mechanisms: A review on Indian context. *Environmental Geochemistry and Health, 40*(6), 2259–2301.

Mukherjee, I., Singh, U. K., & Patra, P. K. (2019). Exploring a multi-exposure-pathway approach to assess human health risk associated with groundwater fluoride exposure in the

semi-arid region of east India. *Chemosphere, 233*, 164–173.

Nagels, J. W., Davies-Colley, R. J., & Smith, D. G. (2001). A water quality index for contact recreation in New Zealand. *Water Science and Technology, 43*(5), 285–292.

Narsimha, A., & Rajitha, S. (2018). Spatial distribution and seasonal variation in fluoride enrichment in groundwater and its associated human health risk assessment in Telangana State, South India. *Human and Ecological Risk Assessment: an International Journal, 24*(8), 2119–2132.

Nasirian, M. (2007). A new water quality index for environmental contamination contributed by mineral processing: a case study of Amang (Tin Tailing) processing activity.

Ott, W. (1978). *Water quality indices: a survey of indices used in the United States* (Vol. 1). Environmental Protection Agency, Office of Research and Development, Office of Monitoring and Technical Support.

Ozsvath, D. L. (2009). Fluoride and environmental health: A review. *Reviews in Environmental Science & Biotechnology, 8*, 59–79. https://doi.org/10.1007/s11157-008-9136-9

Panseriya, H. Z., Gosai, H. B., Vala, A. K., Gavali, D. J., Dave, B. P. (2021). Assessment of surface water of Gulf of Kachchh, west coast of India: A chemometric approach. - *Marine Pollution Bulletin, 170*, 112589.

Panseriya, H. Z., Gosai, H. B., Sankhwal, A. O., Sachaniya, B. K., Gavali, D. J., & Dave, B. P. (2020). Distribution, speciation and risk assessment of heavy metals: Geochemical exploration of Gulf of Kachchh, Gujarat, India. *Environmental Earth Science, 79*, 1–10.

Patel, R., Bhatt B.V., & Shah J. (2019). Identification of Urban Void Spaces in an Area of Vadodara. *Global Research and Development Journal for Engineering*. e-ISSN: 2455-5703.

Pesce, S. F., & Wunderlin, D. A. (2000). Use of water quality indices to verify the impact of Córdoba City (Argentina) on Suquia River. *Water Research, 34*(11), 2915–2926.

Prakash, K. L., & Somashekar, R. K. (2006). Groundwater quality—Assessment on Anekal Taluk, Bangalore Urban district. *Indian Journal of Environmental Biology, 27*(4), 633–637.

Qiao, J., Zhu, Y., Jia, X., Niu, X., & Liu, J. (2020). Distributions of arsenic and other heavy metals, and health risk assessments for groundwater in the Guanzhong Plain region of China. *Environmental Research, 181*, 108957.

Rahman, M. M., Bodrud-Doza, M., Siddiqua, M. T., Zahid, A., & Islam, A. R. M. T. (2020). Spatiotemporal distribution of fluoride in drinking water and associated probabilistic human health risk appraisal in the coastal region, Bangladesh. *Science Total Environment, 724*, 138316.

Raj, D., & Shaji, E. (2017). Fluoride contamination in groundwater resources of Alleppey, southern India. *Geoscience Frontiers, 8*(1), 117–124.

Ramakrishnaiah, C. R., Sadashivaiah, C., & Ranganna, G. (2009). Assessment of water quality index for the groundwater in Tumkur Taluk, Karnataka State, India. *European Journal of Advanced Chemistry, 6*.

Reddy, A. G. S., & Rao, P. N. (2006). Occurrence, behaviour and genesis of fluoride in groundwater of Wailpalli Watershed in Nalgonda District, Andhra Pradesh. *Indian Journal of Applied Geochemistry, 8*(2A), 618–630.

Rodell, M., Velicogna, I., & Famiglietti, J. S. (2009). Satellite-based estimates of groundwater depletion in India. *Nature, 460*(7258), 999–1002.

Sabhaya, M., Solanki, P. M., Pancholi, V., & Singh, P. (2018). Geotechnical Characteristics of soils to identify substratification of Vadodara City, Gujarat, Western India.

Saha, R., Dey, N. C., Rahman, S., Galagedara, L., & Bhattacharya, P. (2018). Exploring suitable sites for installing safe drinking water wells in coastal Bangladesh. *Groundwater for Sustainable Development, 7*, 91–100.

Sahu, S., Gogoi, U., & Nayak, N. C. (2021). Groundwater solute chemistry, hydrogeochemical processes and fluoride contamination in phreatic aquifer of Odisha, India. *Geoscience Frontier, 12*(3), 101093.

Sargaonkar, A., & Deshpande, V. (2003). Development of an overall index of pollution for surface water based on a general classification scheme in Indian context. *Environmental Monitoring and Assessment, 89*(1), 43–67.

Satheeshkumar, P., & Khan, A. B. (2012). Identification of mangrove water quality by multivariate statistical analysis methods in Pondicherry coast, India. *Environmental Monitoring Assessment, 184*(6), 3761–3774.

Shah, T. (2007). *The groundwater economy of South Asia: an assessment of size, significance and socio-ecological impacts. The agricultural groundwater revolution: Opportunities and threats to development* (pp.7–36).

Shah, S. M., & Mistry, N. J. (2013). Groundwater quality assessment for irrigation use in Vadodara District, Gujarat, India. *International Journal of Agricultural Biology, 7*(7), 719–724.

Singh, A. K., Mondal, G. C., Kumar, S., Singh, T. B., Tewary, B. K., & Sinha, A. (2008). Major ion chemistry, weathering processes and water quality assessment in upper catchment of Damodar River basin, India. *Environmental Geoscience, 54*(4), 745–758.

Singh, G., Rishi, M. S., Herojeet, R., Kaur, L., & Sharma, K. (2020). Evaluation of groundwater quality and human health risks from fluoride and nitrate in semi-arid region of northern India. *Environmental Geochemistry and Health, 42*(7), 1833–1862.

Taloor, A. K., Pir, R. A., Adimalla, N., Ali, S., Manhas, D. S., Roy, S., & Singh, A. K. (2020). Spring water quality and discharge assessment in the Basantar watershed of Jammu Himalaya using geographic information system (GIS) and water quality Index (WQI). *Groundwater Sustainability Development*, 100364.

Taniguchi, M., Shimada, J., Fukuda, Y., Yamano, M., Onodera, S. I., Kaneko, S., & Yoshikoshi, A. (2009). Anthropogenic effects on the subsurface thermal and groundwater environments in Osaka, Japan and Bangkok, Thailand. *Science of the Total Environment, 407*(9), 3153–3164.

Thapa, R., Gupta, S., & Reddy, D. V. (2017). Application of geospatial modelling technique in delineation of fluoride contamination zones within Dwarka Basin, Birbhum, India. *Geosciene Frontiers, 8*(5), 1105–1114.

Tirkey, P., Bhattacharya, T., Chakraborty, S., & Baraik, S. (2017). Assessment of groundwater quality and associated health risks: A case study of Ranchi city, Jharkhand, India. *Groundwater for Sustainable Devlopment, 5*, 85–100.

USEPA. (1989). Risk assessment guidance for superfund volume I: Human health evaluation manual (part A). EPA/

540/1e89/002. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response.

USEPA. (1993). Risk assessment guidance for superfund volume I: Human health evaluation manual (part E). Retrieved September 10, 2016 from http://www.epa.gov/oswer/riskassessment/ragse/pdf/introduction.pdf,

USEPA. (2009). National primary drinking water regulations. U.S. Environmental Protection Agency. U.S. Environmental Protection Agency.

Varol, S., & Davraz, A. (2015). Evaluation of the groundwater quality with WQI (Water Quality Index) and multivariate analysis: A case study of the Tefenni plain (Burdur/Turkey). *Environment and Earth Science, 73*(4), 1725–1744.

Viswanathan, G., Jaswanth, A., Gopalakrishnan, S., & Aditya, G. (2009). Determining the optimal fluoride concentration in drinking water for fluoride endemic regions in South India. *Science of the Total Environment, 407*(20), 5298–5307.

Wada, Y., Van Beek, L.P., Van Kempen, C.M., Reckman, J.W., Vasak, S., & Bierkens, M. F. (2010). Global depletion of groundwater resources. *Geophysics Research Letters, 37*(20).

WHO. (1984). *Health promotion: A discussion document on the concept and principles: summary report of the Working Group on Concept and Principles of Health Promotion, Copenhagen, 9–13 July 1984* (No. ICP/HSR 602 (m01)). WHO Regional Office for Europe.

WHO. (1996). Guidelines for drinking-water quality. In: Health criteria and other supporting information (2nd edn). 2. World Health Organization, Geneva.

Xiong, X. Z., Liu, J. L., Hea, W. H., Xia, T., He, P., Chen, X. M., Yang, K. D., & Wanga, A. G. (2007). Dose–effect relationship between drinking water fluoride levels and damage to liver and kidney functions in children. *Environmental Research, 103*, 112–116.

Yadav, K. K., Kumar, V., Gupta, N., Kumar, S., Rezania, S., & Singh, N. (2019). Human health risk assessment: Study of a population exposed to fluoride through groundwater of Agra city, India. *Regulatory Toxicology and Pharmacology, 106*, 68–80.

Yang, J. Y., Wang, M., Lu, J., Yang, K., Wang, K. P., Liu, M., Luo, H. Q., Pang, L. N., & Wang, B. (2020). Fluorine in the environment in an endemic fluorosis area in Southwest, China. *Environmental Research, 184*, 109300.

Zango, M. S., Sunkari, E. D., Abu, M., & Lermi, A. (2019). Hydrogeochemical controls and human health risk assessment of groundwater fluoride and boron in the semi-arid North East region of Ghana. *Journal of Geochemical Exploration, 207*, 106363.

Zhang, Q., Xu, P., Qian, H., & Yang, F. (2020). Hydrogeochemistry and fluoride contamination in Jiaokou Irrigation District, Central China: Assessment based on multivariate statistical approach and human health risk. *Science Total Environment, 741*, 140460.

Zhang, L. E., Huang, D., Yang, J., Wei, X., Qin, J., Ou, S., Zhang, Z., & Zou, Y. (2017). Probabilistic risk assessment of Chinese residents' exposure to fluoride in improved drinking water in endemic fluorosis areas. *Environmental Pollution, 222*, 118–125.

Zhou, Y., Li, P., Chen, M., Dong, Z., & Lu, C. (2021). Groundwater quality for potable and irrigation uses and associated health risk in southern part of Gu'an County, North China Plain. *Environmental Geochemistry and Health, 43*(2), 813–835.