

Potential health concerns due to elevated nitrate concentrations in groundwater of villages of Vadodara and Chhota Udaipur districts of Gujarat, India

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ABSTRACT

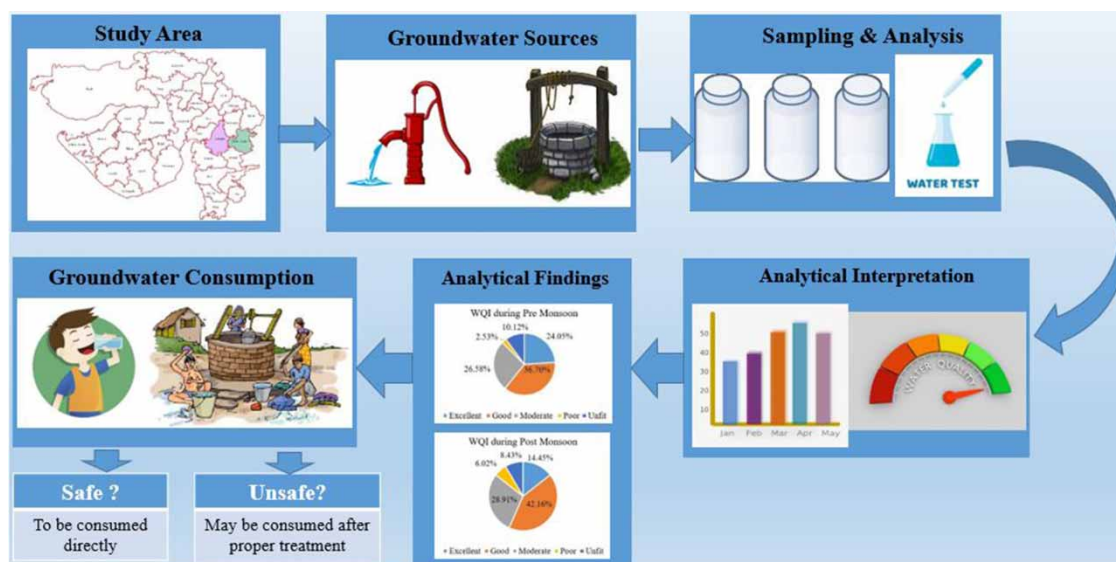
In an attempt to assess the groundwater quality of Vadodara and Chhota Udaipur districts and check its suitability for drinking purposes, a total of 162 samples (50 samples during pre-monsoon season and 54 samples during post-monsoon season from Vadodara district and 29 samples during both pre- and post-monsoon seasons from Chhota Udaipur district) were collected from 63 villages of both the districts for pre-monsoon and post-monsoon seasons during 2016–17. The analysis was carried out for physicochemical characteristics and the analytical results have been interpreted by graphical representation, correlation and regression analysis and water quality index so that the quality of groundwater can be easily understood. The analytical results were then compared with the Indian Standards Drinking Water-Specification (Second Revision). From this study, it is concluded that the overall groundwater quality of the region is comparatively good; however, elevated nitrate levels resulted in many of the samples having raised concern and the necessity to make all possible efforts to improve the quality of groundwater wherever deteriorated.

Key words: correlation and regression analysis, groundwater, high nitrate levels, total dissolved solids, Vadodara and Chhota Udaipur, water quality index

HIGHLIGHTS

- Elevated nitrate and fluoride concentration observed in the samples collected has raised concern about the quality of groundwater.
- Physico-chemical analysis of groundwater quality of samples collected were compared with Indian Drinking Water Quality Standard.
- Correlation and regression as well as water quality index was used to determine overall quality of water.

GRAPHICAL ABSTRACT



INTRODUCTION

One of the essential and natural resource for life on Earth is water. The human population has sustained itself for thousands of years because of water's complex interactions with the rest of the natural environment (Khatri *et al.* 2016). Also, the sustainable socioeconomic development of every community is dependent on the availability of freshwater resources (Sharma *et al.* 2016). Around 99.97% of the total freshwater available is groundwater, while the remaining is available as streams, lakes and rivers (Khatri *et al.* 2020b). Hence, out of other sources of fresh water like rivers, ponds and lakes, groundwater is the broadly used resource for drinking as well as irrigation and industrial purpose due to its quality and quantity considerations (Dohare *et al.* 2014). A significant fraction of the total supply for domestic, industrial and agricultural sectors is provided by groundwater in many countries. The groundwater is believed to be comparatively much cleaner and free from pollution than surface water; however, it is generally affected by anthropogenic activities. Pollution of groundwater is aggravated due to municipal, industrial, agricultural and other miscellaneous sources and causes. Also, the ever-increasing demand for groundwater due to rapid industrialization and urbanization results in overexploitation of groundwater resources causing depletion of water levels and also the degradation of groundwater (Chourasia 2018). Groundwater contamination results in poor drinking water quality, loss of water supply, high clean-up costs, high costs for alternative water supplies and/or potential health problems. Owing to poor drinking water quality, the world is affected with 80% of diseases, as per the WHO, 1984 (Kalaivanan *et al.* 2017).

Water quality, measured by assessing the physicochemical and biological properties of water against a set of standards, is used to determine whether water is suitable for consumption or safe for the environment (Khatri & Tyagi 2014). Hence, assessment of groundwater quality and quantity becomes necessary to be acquainted with the sustainability of groundwater resources (Shah & Mistry 2013). In the present study, we have selected Vadodara and Chhota Udaipur districts of Gujarat state as our study area. Vadodara is a well-known district in Gujarat, India and is located on the banks of the Vishwamitri river. It was the capital of Gaekwad state until 1947 and is prominent for Laxmi Vilas Palace, which served as the residence of the Maratha royal Gaekwad dynasty, that ruled over Baroda state (History of Vadodara district 2021). Chhota Udaipur, carved out of the Vadodara district, is a tribal district in the state of Gujarat with a rich indigenous history and culture. Chhota Udaipur district has a rich forest area that forms a part of Jambughoda and Ratanmahal wildlife sanctuaries. The district is also known for the Rathwa tribal community and is home to a large dairy industry (History of Chhota Udaipur district 2021). Both the districts selected for the study has enriched tourist sites explored by numerous visitors across the year amplifying the need for groundwater quality assessment. Groundwater collected from Vadodara and Chhota Udaipur districts was checked by analysing a total of 162 samples during the pre-monsoon (April–May) and post-monsoon (October–November) seasons.

Objective of the study

The primary objectives of this study are as follows: to assess the current status of groundwater quality of Vadodara and Chhota Udaipur districts by examining and evaluating the physicochemical characteristics of groundwater; to assess the overall quality of monitored sources by comparing the analytical results with the Indian Standards Drinking Water-Specification (Second Revision) (IS 10500:2012); to provide the current database with aid in decision-making for policy level change at different levels with respect to the current status of groundwater; to carry out statistical analysis using various data interpretation techniques, namely, seasonal comparison, water quality index and correlation and regression analysis methods.

Study area

Vadodara and Chhota Udaipur districts are located in the central part of mainland Gujarat. Chhota Udaipur district was carved out of the Vadodara district on August 15, 2013 with its headquarters at Chhota Udaipur town (Shah 2016–17). The districts are bounded to the north and northeast by Anand, Panchmahals and Dahod districts, to the east and southeast by Madhya Pradesh and Maharashtra state, to the southeast by Narmada district and to the south and west by Bharuch district (District Groundwater Brochure: Vadodara 2011). A brief district profile of both the districts is presented in Table 1.

Groundwater availability

The taluka-wise details of available groundwater recharge per year, existing gross groundwater draft per year and level of groundwater development along with categorization for future groundwater development for both the districts is given in Table 2. The data were used as a primary source for selection of sampling locations at large.

METHODOLOGY

The hydro-geochemistry study of Vadodara and Chhota Udaipur districts was carried out by monitoring and analysing the groundwater samples from randomly selected villages. The methodology adopted includes site selection, sample collection, analysis, results, discussion and conclusion, followed by correlation and regression analysis and water quality index which were also found for both districts.

Table 1 | Brief profile of Vadodara and Chhota Udaipur districts

Particulars	Vadodara district	Chhota Udaipur district
Geographical area	7,548.50 sq. km	3,087 sq. km
Latitudes	21°49'19" to 22°48'37"	20.49' to 22.49'
Longitudes	72°51'05" to 74°16'55"	72.51' to 74.17'
Number of villages	657	888
Name of talukas	Dabhoi, Karjan, Padra, Savli, Shinor, Vadodara and Vaghodiya	Chhota Udaipur, Pavi Jetpur, Kawant, Naswadi, Sankheda and Bodeli
Maximum temperature	41 °C	45 °C
Minimum temperature	12 °C	8 °C
Average annual rainfall	965 mm	1,083 mm
Soil type	Black soil, alluvial soil and hilly soil	Hard black soil, medium black soil, sandy loam soil and saline soil
Hydrogeology	Groundwater occurs both as unconfined and confined conditions. Saturated zones of unconsolidated shallow alluvium and weathered zones, shallow depth jointed and fractured rocks form unconfined aquifers, whereas multilayered aquifer below impervious clay horizons in alluvium formation and interflow zones of basalts, inter-trappean beds, deep seated fracture zones, shear zones in basalts, granites and gneisses give rise to semi-confined to confined conditions	

Table 2 | Details of groundwater availability

Sr. No.	Talukas	Available groundwater recharge in MCM/year	Existing gross groundwater draft for all uses in MCM/year	Level of groundwater development (%)	Category
Vadodara district					
1.	Dabhoi	123.52	84.91	68.74	Safe
2.	Karjan	161.31	137.71	85.37	Semi-critical
3.	Padra	113.01	77.73	68.78	Safe
4.	Savli	71.35	37.56	52.65	Safe
5.	Shinor	80.99	64.76	79.96	Semi-critical
6.	Vadodara	100.99	104.12	103.10	Over-exploited
7.	Vaghodiya	63.84	14.69	23.01	Safe
Chhota Udaipur district					
8.	Chhota Udaipur	55.61	26.93	48.42	Safe
9.	Pavi Jetpur	99.96	60.45	60.47	Safe
10.	Kawant	29.36	19.14	65.20	Safe
11.	Naswadi	34.19	12.17	35.59	Safe
12.	Sankheda	66.26	35.96	54.27	Safe
13.	Bodeli	–	–	–	–

MCM, million cubic meter.

(Source: District Groundwater Brochure: Vadodara 2011).

Site selection

About 50 sampling locations during the pre-monsoon season and 54 sampling locations during the post-monsoon season of Vadodara district were selected; whereas for Chhota Udaipur district, 29 samples were selected based on the stratified random sampling method and their respective geographical locations for sampling and monitoring. The selected villages represent the groundwater quality of the districts. The taluka-wise list of villages selected for sampling is given in Table 3, also the location map of the villages selected is shown in Figure 1.

Sampling and monitoring

A total of 162 groundwater samples were collected from the identified villages during pre- and post-monsoon seasons, respectively, and the collection method used was 'grab sampling' method. The samples were collected in polyethylene carboys as per Gujarat Environment Management Institute (GEMI)'s sampling protocol for water and wastewater, and samples requiring preservation were preserved on-site using preservatives as prescribed in *Standard Methods for the Examination of Water and Waste Water (2012)*.

The primary information collected by GEMI's sampling team during sampling includes allotment of unique sample IDs that are further used for representation of analytical data in graphical form for each sample collected from a distinct location along with its latitude and longitude, source type and depth of source and are summarized in Tables 4 and 5. The use of the groundwater sources from where the samples were collected was mostly drinking and domestic use followed by irrigation at a few locations. This implies direct dependency of the resident population in the study area on groundwater.

Analysis of groundwater

The samples collected were submitted to GEMI's laboratory with due procedure where analysis was carried out as per *Standard Methods for the Examination of Water and Waste Water* for the drinking water parameters. GEMI's laboratory is recognized as a 'State Water Lab', 'Environmental Laboratory', 'National Accreditation Board for Testing and Calibration Laboratory (NABL)', and as a 'Scientific and Industrial Research Organization (SIRO)'. All the groundwater samples were analysed for the selected relevant physicochemical parameters. The physical parameters include pH and turbidity. The

Table 3 | Taluka-wise details of villages selected for sampling in Vadodara and Chhota Udaipur districts

Sr. No.	Taluka	Villages
Vadodara district		
1.	Waghodia	Asoj, Jarod ^a , Waghodia, Sangadol, Timbi
2.	Savli	Manjusar, Savli, Shihora, Vejpur, Mevli, Ghantiyal
3.	Nandod	Poicha
4.	Becharaji	Kanoda
5.	Sankheda	Kasumbia
6.	Dabhoi	Mohammadpura, Tentlav, Chandod, Shirola, Koyavarohan, Meghakui ^a , Borbar ^a
7.	Sinor	Awakhal, Sinor
8.	Vadodara	Ranoli, Alkapuri, Por, Por Kayavarohan Road, Wadsala ^a
9.	Karjan	Choranda, Alampura, Motikoral, Samri, Divi, Sayar ^a
10.	Padra	Mobha, Muval, Ranu, Sarasvani, Padra
Chhota Udaipur district		
11.	Chhota Udaipur	Puniyavant, Kasara, Kachhel, Gabadiya, Ganthiya, Oliamba
12.	Naswadi	Naswadi, Nannupura, Akona, Rampuri, Kukavati, Kandva, Rayansingpura, Piplej, Anandpuri
13.	Sankheda	Sankheda, Malu, Gajipur, Talakpur, Akakheda, Handod, Khandupura, Ratanpur, Bahadurpur

^aVillages monitored in the post-monsoon season only.

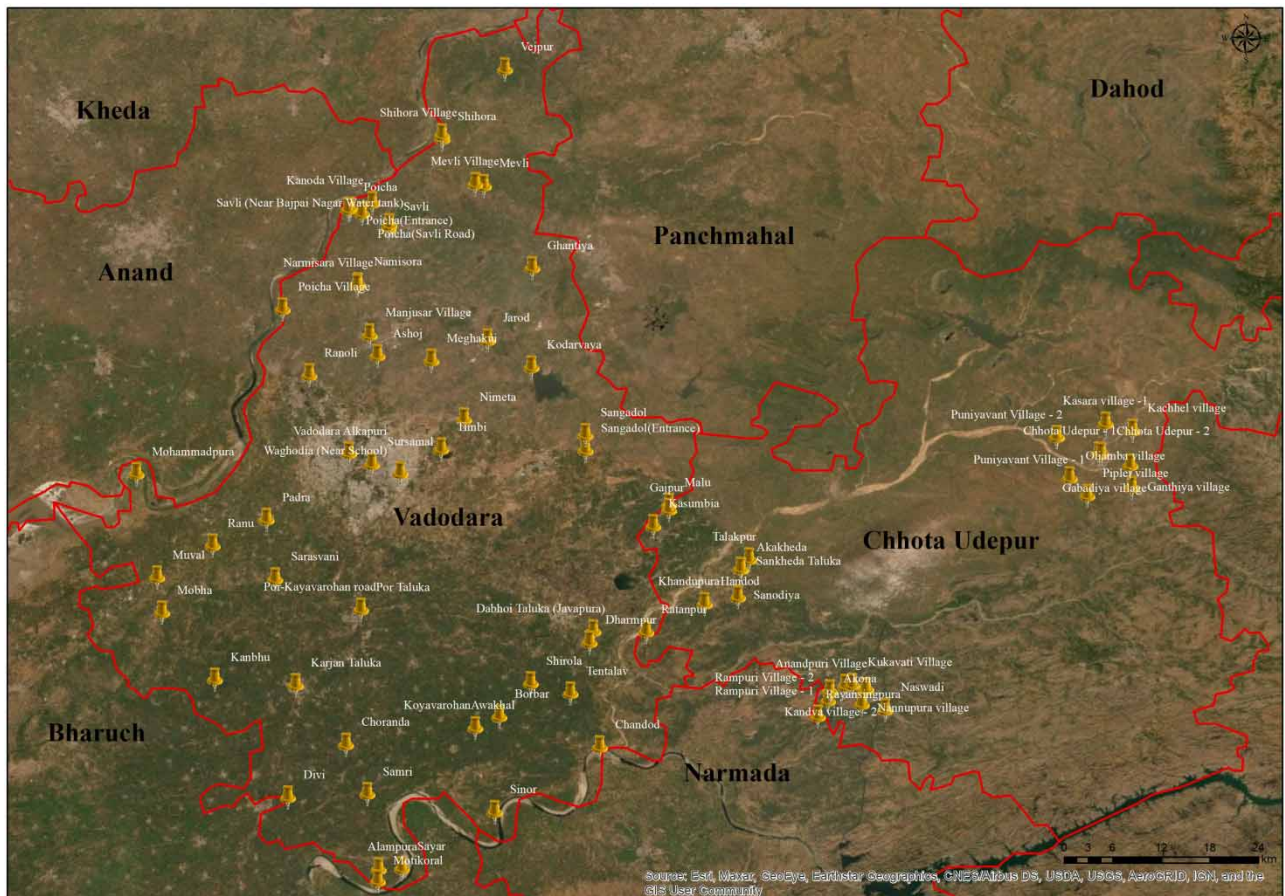


Figure 1 | Sampling locations for Vadodara and Chhota Udaipur districts.

Table 4 | Details collected during sampling and monitoring of Vadodara district

Sample ID	Village	Latitude	Longitude	Source type	Depth of source (ft)
1.	Ashoj	22.422051	73.208271	Borewell	160
2.	Manjusar	22.445154	73.19986	Borewell	150
3.	Savli_1	22.56367	73.22036	Borewell	160
4.	Savli_2	22.56797	73.22164	Borewell	160
5.	Poicha_1	22.58644	73.17814	Borewell	150
6.	Kanoda	22.59275	73.20281	Borewell	160
7.	Namisora	22.501895	73.186956	Borewell	170
8.	Poicha_2	22.58536	73.17581	Borewell	180
9.	Poicha_3	22.58097	73.19147	Hand pump	180
10.	Shihora	22.663892	73.280364	Borewell	150
11.	Vejpur	22.741369	73.350238	Hand pump	160
12.	Mevli	22.61174	73.326656	Hand pump	150
13.	Ghantiya	22.519921	73.380448	Hand pump	160
14.	Jarod	22.43925	73.33111	Borewell	170
15.	Kodarvaya	22.409305	73.37971	Hand pump	160
16.	Nimeta	22.351219	73.304914	Hand pump	180
17.	Waghodia (near school)	22.291346	73.233778	Borewell	170
18.	Sangadol_1	22.31664	73.43969	Borewell	160
19.	Sangadol_2	22.33378	73.43969	Hand pump	150
20.	Kasumbia	22.232665	73.515238	Hand pump	150
21.	Mohammadpura	22.290323	72.940151	Borewell	70
22.	Timbi	22.31784	73.279485	Borewell	40
23.	Dabhoi (Javapura)	22.11542	73.44839	Borewell	100
24.	Dharpur	22.102905	73.444539	Borewell	80
25.	Tentalav	22.046044	73.423178	Borewell	70
26.	Chandod	21.985793	73.455587	Borewell	80
27.	Shirola	22.057356	73.378975	Borewell	180
28.	Awakhal	22.00757	73.317075	Borewell	120
29.	Koyavarohan	22.00757	73.317075	Borewell	160
30.	Ranoli	22.400377	73.13201	Borewell	170
31.	Alkapuri	22.313295	73.176588	Borewell	180
32.	Por Taluka	22.139507	73.189985	Borewell	120
33.	Por-Kayavarohan road	22.139567	73.189995	Borewell	230
34.	Karjan	22.05521	73.117257	Borewell	250
35.	Choranda	21.988927	73.173313	Borewell	250
36.	Sinor	21.9137	73.338729	Borewell	180
37.	Sursamal	22.30136	73.202022	Borewell	170
38.	Alampura	21.849902	73.209683	Borewell	80
39.	Motikoral	21.836598	73.208932	Borewell	110
40.	Samri	21.933566	73.197066	Borewell	150
41.	Divi	21.930128	73.108405	Borewell	90
42.	Kanbhu	22.061559	73.027245	Borewell	160

(Continued.)

Table 4 | Continued

Sample ID	Village	Latitude	Longitude	Source type	Depth of source (ft)
43.	Mobha	22.136074	72.9682	Borewell	170
44.	Muval	22.175358	72.963048	Borewell	170
45.	Ranu	22.210704	73.024524	Hand pump	190
46.	Sarasvani	22.173335	73.094389	Borewell	110
47.	Padra	22.239437	73.084798	Borewell	90
48.	Sayar	21.850664	73.235472	Borewell	160
49.	Meghakui	22.41667	73.268499	Borewell	150
50.	Borbar	22.02056	73.34389	Borewell	80
51.	Shihora	22.65777778	73.27194444	Borewell	80
52.	Narmisara	22.50305556	73.18500000	Borewell	200
53.	Poicha	22.58638889	73.17805556	Borewell	80
54.	Mevli	22.61194444	73.31972222	Borewell	85

chemical parameters include electrical conductivity, total dissolved solids, chloride, total hardness, calcium hardness, magnesium hardness, alkalinity, fluoride, sulfate and nitrate concentration. Further analysis for heavy metals was also performed in a few selected groundwater samples. The parameters analysed were compared with Indian Standards Drinking Water-Specification (Second Revision) (IS 10500: 2012) since the groundwater of the study area is used for drinking and domestic purposes (Khatri *et al.* 2021).

ANALYTICAL RESULT AND INTERPRETATION

The analytical details pertaining to the monitored parameters for both Vadodara and Chhota Udaipur districts including their acceptable and permissible limits, result range of pre-monsoon and post-monsoon seasons, sample IDs exceeding permissible limit and relevant inferences drawn for respective parameters are discussed further along with the graphical representation of the analytical results reported.

pH of solution is taken as the negative logarithm of hydrogen ion concentration for many practical purposes. The value range of pH from 7 to 14 is alkaline, from 0 to 7 is acidic and 7 is neutral. The pH of drinking water lies between 6.5 and 8.5. The overall pH of the pre-monsoon samples ranged between 6.65 and 8.74, whereas post-monsoon samples ranged from 6.72 to 8.22. Overall, the pH of the samples was found to be within the permissible limits of Indian Standards Drinking Water-Specification (Second Revision) except for a few samples. The graphical representation of the analytical results for all the monitored sources is illustrated in Figure 2.

Electrical conductivity is the capacity of water to carry an electrical current and varies both with number and types of ions the solution contains. In contrast, the conductivity of distilled water is less than 1 $\mu\text{mhos/cm}$. This conductivity depends on the presence of ions, their total concentration, mobility, valence and relative concentration and on the temperature of the liquid. Solutions of most inorganic acids, bases and salts are relatively good conductors. The overall conductivity of the pre-monsoon samples ranged between 406 $\mu\text{S/cm}$ and 3,370 $\mu\text{S/cm}$ and for post-monsoon samples ranged between 294 $\mu\text{S/cm}$ and 6,160 $\mu\text{S/cm}$.

Total dissolved solids (TDS) is generally not considered as a primary pollutant, but it is rather used as an indication of aesthetic characteristics of drinking water and as an aggregate indicator of the presence of a broad array of chemical contaminants. It indicates the general nature of water quality or salinity. The acceptable and permissible limit of TDS is 500 mg/L to 2,000 mg/L, respectively, according to the specifications of Indian Standards. The overall concentration of TDS was reported between 140 mg/L and 1,956 mg/L in the pre-monsoon samples. Post-monsoon samples showed a TDS range of about 136 mg/L to 3,604 mg/L. Only two samples from Vadodara district and collected during the post-monsoon season exceeded the permissible limit. The high TDS might be due to leaching of various pollutants into the groundwater, industrial effluents, agricultural runoff, etc. The graphical representation of the analytical results for all the monitored sources is shown in Figure 3.

Table 5 | Details collected during sampling and monitoring of Chhota Udaipur district

Sample ID	Village	Latitude	Longitude	Source type	Depth of source (ft)
55.	Malu	22.25621755	73.53268845	Borewell	100
56.	Gajpur	22.25036972	73.53278056	Hand pump	80
57.	Talakpur	22.19552059	73.62199615	Hand pump	90
58.	Akakheda	22.18400463	73.61262878	Borewell	110
59.	Sankheda	22.18518144	73.61233771	Borewell	120
60.	Handod	22.14591587	73.5723729	Hand pump	100
61.	Khandupura	22.14591587	73.5723729	Borewell	80
62.	Sanodiya	22.15318448	73.60934488	Borewell	130
63.	Ratanpur	22.11464018	73.50716918	Hand pump	100
64.	Akona	22.03775000	73.70936111	Hand pump	40–50
65.	Rampuri_1	22.04875000	73.71150000	Hand pump	50
66.	Rampuri_2	22.04841667	73.71144444	Hand pump	50
67.	Anandpuri	22.05444444	73.72875000	Borewell	70–80
68.	Kukavati	22.05586111	73.73641667	Borewell	70–80
69.	Kandva_1	22.05116667	73.75180556	Borewell	70–80
70.	Kandva_2	22.05027778	73.75158333	Hand pump	50
71.	Naswadi	22.02808333	73.77308333	Canal	100
72.	Nannupura	22.03430556	73.74675000	Hand pump	50
73.	Rayansingpura	22.02022222	73.69836111	Hand pump	50
74.	Puniyavant_1	22.33172222	73.96441667	Borewell	100
75.	Puniyavant_2	22.33161111	73.96408333	Hand pump	50
76.	Chhota Udaipur_1	22.31358333	74.01122222	Hand pump	40
77.	Chhota Udaipur_2	22.31291667	74.01347222	Borewell	180
78.	Kasara -1	22.34672222	74.01866667	Hand pump	50
79.	Kachhel	22.33877778	74.04855556	Hand pump	40
80.	Gabadiya	22.30000000	74.04636111	Hand pump	50
81.	Ganthiya	22.27536111	74.04769444	Hand pump	30
82.	Piplej	22.26650000	73.99819444	Hand pump	50
83.	Oliamba	22.28569444	73.97883333	Hand pump	30

Chloride in excess quantity is usually taken as an index of pollution and considered as a tracer for groundwater contamination. All types of natural and raw water contain chlorides. It comes from activities carried out in agricultural areas, industrial activities and from chloride stones. As per IS 10500: 2012, the desirable limit for chloride is 250 mg/L and the permissible limit is 1,000 mg/L. The concentration of chloride ranged between 21 mg/L and 615 mg/L in the pre-monsoon samples. Post-monsoon samples showed a concentration of 0 mg/L to 1,154 mg/L. The higher concentration of chloride found in one sample of groundwater may be due to pollution sources such as domestic effluents, fertilizers, septic tanks, human waste, livestock waste and due to natural resources. Continuous consumption of higher chloride concentration may cause cardiac and kidney disease. The graphical representation of the analytical results for all the monitored sources is illustrated in [Figure 4](#).

The desirable and permissible limit for total hardness as per IS 10500: 2012 lies between 200 mg/L and 600 mg/L, respectively. The effect of hardness is demonstrated as scaling in utensils, hot water systems in boilers, etc. Soap scum sources are dissolved calcium and magnesium from soil and aquifer minerals containing limestone or dolomite. In the study, pre-monsoon samples showed a hardness range of 100 mg/L to 1,150 mg/L and post-monsoon samples a hardness range of about

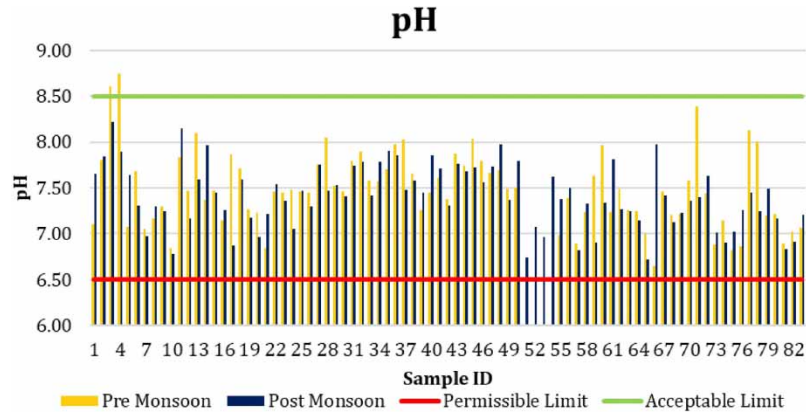


Figure 2 | Seasonal variations of pH in Vadodara and Chhota Udaipur districts.

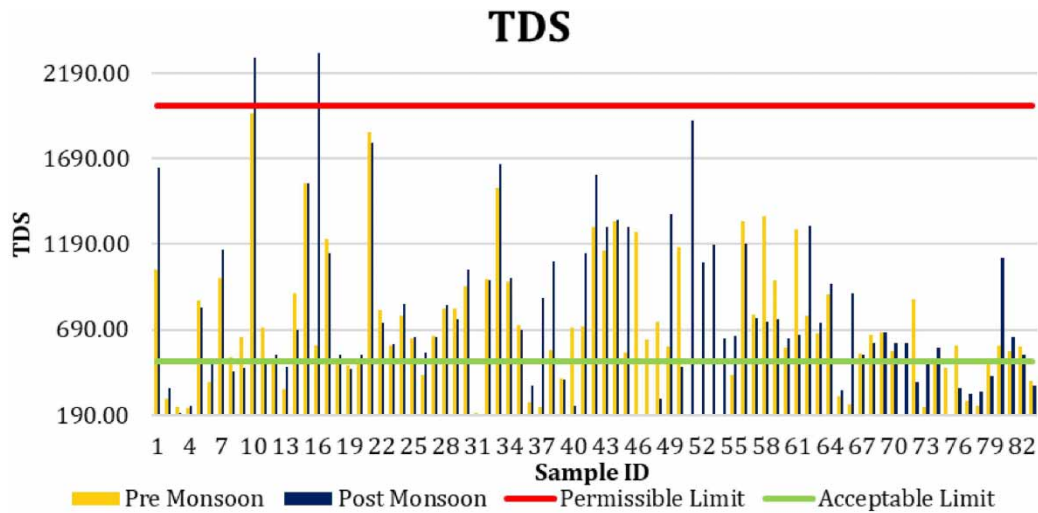


Figure 3 | Seasonal variations of TDS in Vadodara and Chhota Udaipur districts.

120 mg/L to 1,290 mg/L. [Figure 5](#) indicates the concentration of total hardness for different samples with respect to seasonal variations.

Alkalinity is the sum total of components in the water that tend to elevate the pH to the alkaline side of neutrality. It is measured by titration with standardized acid to a pH value of 4.5 and is expressed commonly as milligrams per litre as calcium carbonate (mg/L as CaCO_3). Commonly occurring materials in water that increase alkalinity are carbonate, phosphates and hydroxides. Pre-monsoon samples showed an alkalinity range of about 124 mg/L to 1,004 mg/L and post-monsoon samples alkalinity ranges of about 116 mg/L to 959 mg/L. [Figure 6](#) indicates the value of alkalinity for different samples with respect to seasonal variations.

Fluoride is more commonly found in groundwater than in surface water. Among factors which control the concentration of fluoride are the climate of the area and the presence of accessory minerals in the rock minerals' assemblage through which the groundwater is circulating. Pre-monsoon and post-monsoon samples showed fluoride ranges of about 0–7.23 mg/L and 0–2.16 mg/L, respectively. The fluoride concentration of approximately less than or equal to 1 mg/L in drinking water is beneficial to human health, but if the fluoride concentration is more than the permissible limit, i.e., more than 1.5 mg/L, then it may cause dental fluorosis (tooth decay), bone fractures and, more seriously, skeletal fluorosis. The graphical representation of the analytical results for all the monitored sources is illustrated in [Figure 7](#).

Sulfate: Natural water contains sulfate ions and most of these ions are also soluble in water. Sulfate ion is one of the major anions occurring in natural water. Sulfate concentration was reported to be in the range of 0–203 mg/L in the pre-monsoon

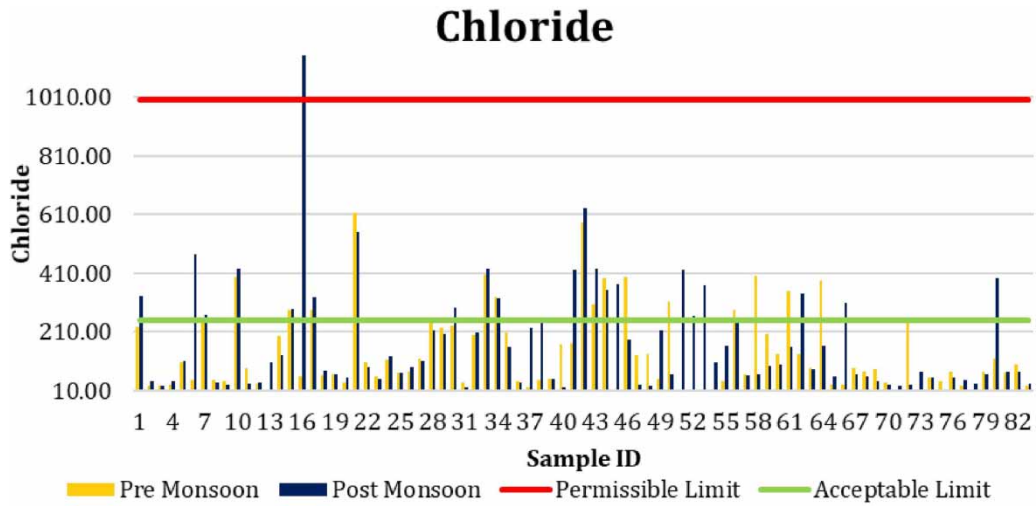


Figure 4 | Seasonal variations of chloride in Vadodara and Chhota Udaipur districts.

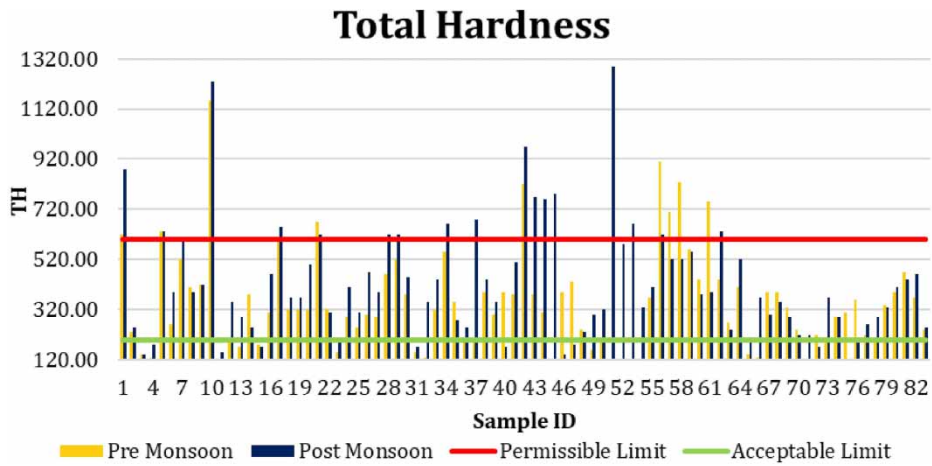


Figure 5 | Seasonal variations of total hardness in Vadodara and Chhota Udaipur districts.

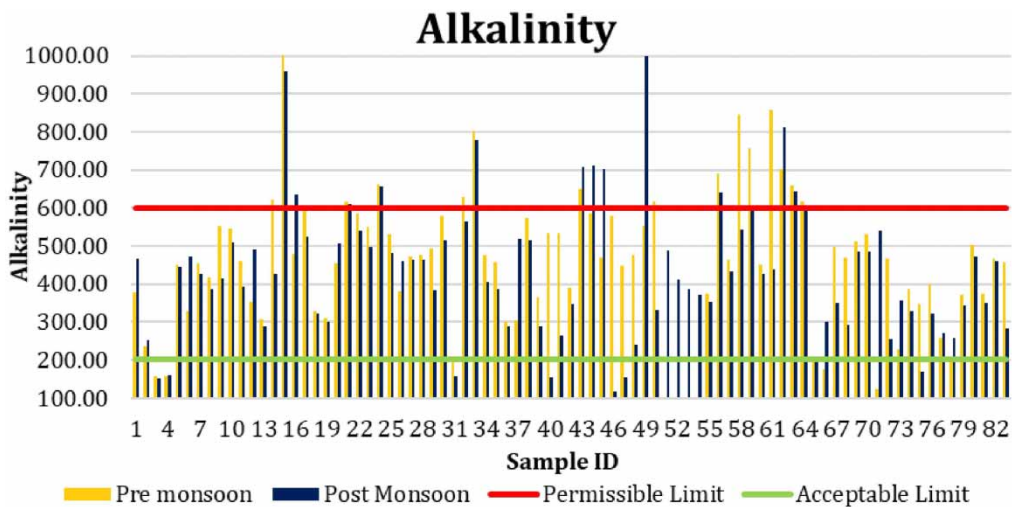


Figure 6 | Seasonal variations of alkalinity in Vadodara and Chhota Udaipur districts.

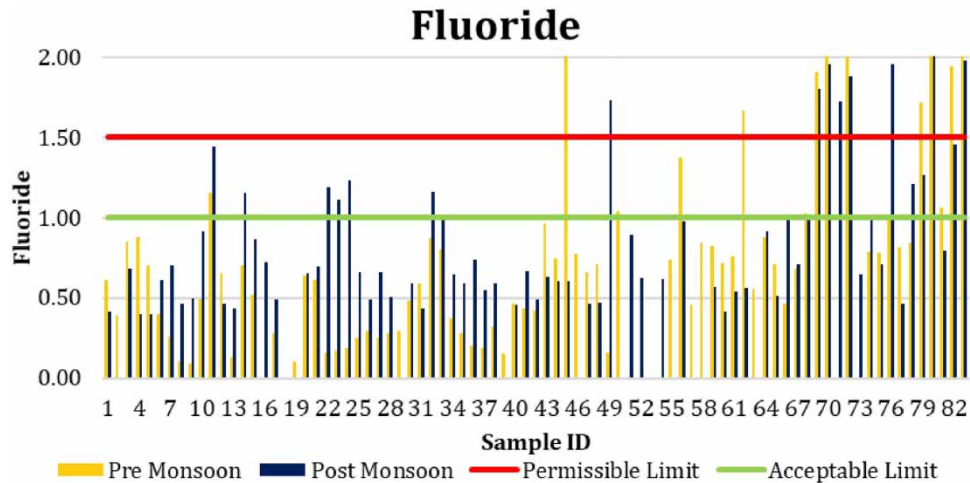


Figure 7 | Seasonal variations of fluorides in Vadodara and Chhota Udaipur districts.

samples. Post-monsoon samples showed a sulfate concentration of about 0 mg/L–283 mg/L. Water with about 300 mg/L–400 mg/L sulfate concentration causes a bitter taste and if the concentration rises up to 1,000 mg/L or more it can cause intestinal disorders. Water containing appreciable amounts of sulfate can cause hard scale in boilers. The graphical representation of the analytical results for all the monitored sources is illustrated in [Figure 8](#).

Nitrate concentration is present in raw water and, mainly, it is a form of N_2 compound (of its oxidizing state). Nitrate is produced by chemical and fertilizer factories, animal matter, decaying vegetables, domestic and industrial discharge. The method to measure quantity of nitrate is by UV spectrophotometer. As per IS 10500:2012, the desirable limit for nitrate is a maximum of 45 mg/L and there is no relaxation in permissible limit. Pre-monsoon samples showed a nitrate range of about 0–489.5 mg/L and post-monsoon samples a nitrate limit of 0–569 mg/L. A total of 12 and 21 samples of Vadodara district and 10 and 8 samples of Chhota Udaipur district analysed during pre-monsoon and post-monsoon seasons, respectively, exceeded the desirable limit. Elevated levels of nitrate found in many of the samples analysed raised concerns and have also influenced the overall groundwater quality of the region. The graphical representation of the analytical results for all the monitored sources is illustrated in [Figure 9](#).

Heavy metal analysis in groundwater

Heavy metals such as lead, cadmium, iron, nickel, chromium, zinc, arsenic were analysed to detect the heavy metal pollution of groundwater. The analytical results showed that the heavy metals were within the permissible limits except for iron and

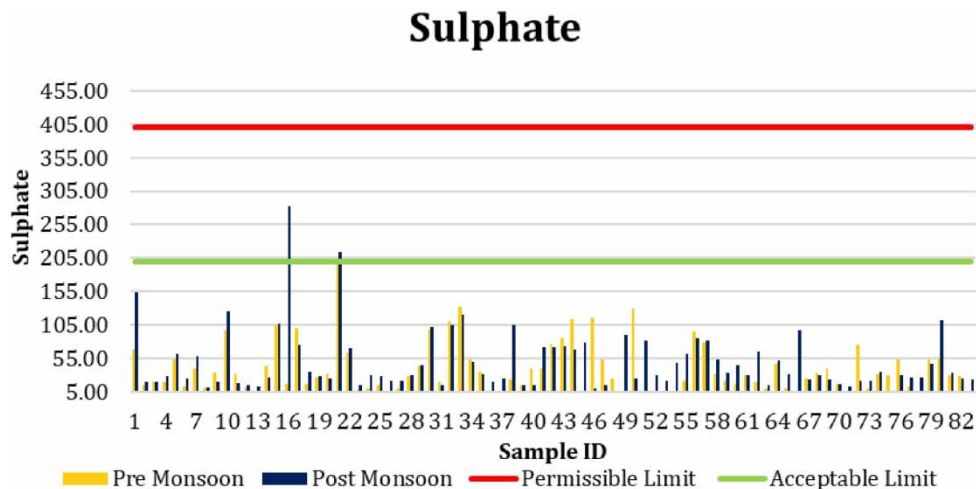


Figure 8 | Seasonal variations of sulfates in Vadodara and Chhota Udaipur districts.

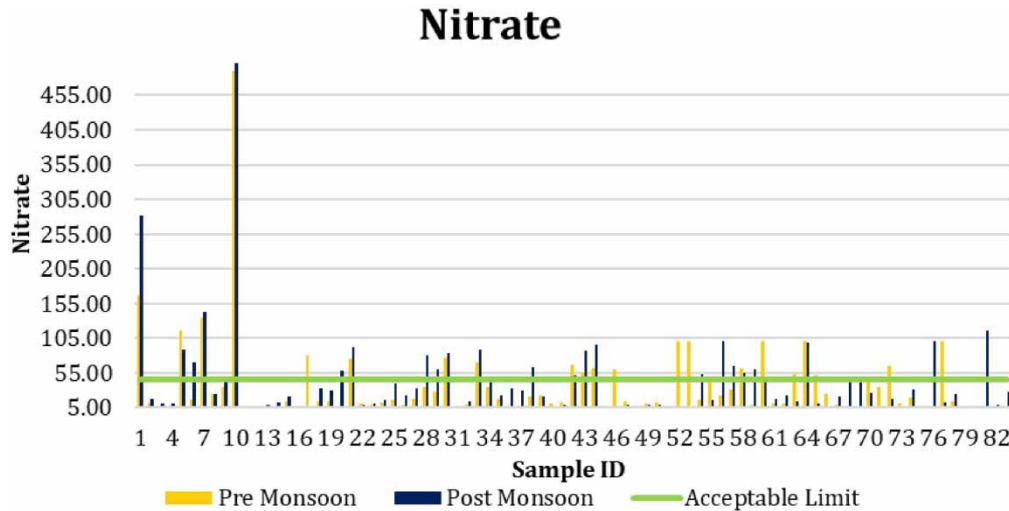


Figure 9 | Seasonal variations of nitrates in Vadodara and Chhota Udaipur districts.

lead, where their concentration exceeded the permissible limit of 0.3 mg/L and 0.01 mg/L, respectively, as per Indian Standards of drinking water. The maximum concentration of iron detected was 9.9 mg/L and of lead was 0.057 mg/L. However, the iron concentration exceeded mainly in the range of 0.3 mg/L–0.8 mg/L. Heavy metals more than the permissible limits can be fatal and can cause even death after prolonged exposure.

Correlation and regression

Correlation is the mutual relationship between two variables. Correlation coefficient (r) measures the degree of association that exists between two variables, one taken as the dependent variable (Chaubey & Patil 2015). It determines the relationship of water quality parameters with each other of the water samples analysed (Dutta & Sarma 2018). It can be calculated by the equation given below. Here, x and y are any two variables (water quality parameters) and n the total number of observations (samples analysed). Now, between the selected variables x and y , the correlation coefficient (r) can be calculated as:

$$r = \frac{n \sum (x * y) - \sum x * \sum y}{\sqrt{f(x) * f(y)}}$$

where, $f(x) = n \sum (x^2) - (\sum x)^2$, $f(y) = n \sum (y^2) - (\sum y)^2$, and all the summations are to be taken from 1 to n .

Now, if the value of the correlation coefficient between two variables x and y is legitimately large, then it indicates that these two variables are highly correlated. In that case, it is likely to try a linear relation of the form

$$y = Ax + B$$

The constant A and B are to be determined in order to correlate the variables x and y . According to the well-known method of least squares, the value of constants A and B are given by the relations

$$B = y_{\text{mean}} - Ax_{\text{mean}}$$

and

$$A = \frac{n \sum (x * y) - \sum x * \sum y}{n \sum (x - x_{\text{mean}})^2}$$

where,

$$x_{\text{mean}} = \frac{\sum x}{n}$$

$$y_{\text{mean}} = \frac{\sum y}{n}$$

The linear equation we get from this is also known as regression equation. The regression equation is used as a mathematical tool to calculate different dependent characteristics of water quality by substituting the values for the independent parameters in the equations. The regression analysis is usually carried out when the water quality parameters have a better and higher level of significance in their correlation coefficient.

Result of correlation and regression

For the present study a total of nine parameters are taken for correlation and regression analysis and the resulting correlation coefficients (r) are specified in Tables 6 and 7 for pre- and post-monsoon, respectively. As stated before, a regression equation needs to be found if the value of the correlation coefficient is fairly large; however, in this case, there is no need to find the linear regression equation as the value of correlation coefficients are not too large (>1).

The method of linear correlation has been found to be a significant approach to get an idea of quality of the groundwater by determining a few parameters experimentally. From the result of pre-monsoon, it can be stated that alkalinity, conductivity, chloride and sulfate have strong correlation with TDS. Also, conductivity and alkalinity, chloride and conductivity, sulfate and conductivity and sulfate and chloride are strongly correlated as all these have the value of correlation coefficient >0.7 . Alkalinity, conductivity, chloride, sulfate and nitrate have moderate correlation with TH. Also TH and TDS, nitrate and TDS, chloride and alkalinity, sulfate and alkalinity, nitrate and conductivity, nitrate and chloride and nitrate and sulfate are moderately correlated as the value of correlation coefficient varies between 0.3 and 0.7. Parameters other than these have a weak or negative correlation with each other.

While discussing the post-monsoon season, from the correlation analysis, it can be stated that conductivity, chloride and sulfate have strong correlation with TDS. Also, conductivity has strong correlation with chloride and sulfate and chloride has strong correlation with sulfate. These all have a value of correlation coefficient (r) >0.7 . TH, alkalinity and nitrate have moderate correlation with TDS. Alkalinity, conductivity, chloride, sulfate and nitrate have moderate correlation with TH. Conductivity, chloride and sulfate have moderate correlation with alkalinity. Also, nitrate has moderate correlation with conductivity, chloride and sulfate. These can also be seen in the Table 7 as these all have correlation coefficient values between 0.3 and 0.7. Parameters other than these have a weak or negative correlation with each other.

Water quality index (WQI)

The Weighted Arithmetic Water Quality Index (WAWQI) was first proposed by Horton (Horton 1965), in which a weight is assigned to each parameter such that this weight influences the importance of the parameter in determining the water quality (Khatri *et al.* 2020a). However, WQI indicates the quality of water in terms of index number which represents the overall quality of water for any intended use (Falowo *et al.* 2019). It is defined as a rating reflecting the comprehensive influence of different water quality parameters taken into consideration for the calculation of WQI (Chaurasia *et al.* 2018). The indices are among the most effective ways to communicate the information on water quality status to the general public or to policy-makers. In calculation of the WQI, the relative importance of various parameters depends on the intended use of the water (Hariharan 2007).

The calculation of WQI was made using the weighed arithmetic index method in the following steps.

Table 6 | Correlation coefficient (r) among various water quality parameters for pre-monsoon season

Parameters	pH	TDS	TH	Alkalinity	Conductivity	Chloride	Fluoride	Sulfate	Nitrate
pH	1								
TDS	-0.23	1							
TH	-0.39	0.67	1						
Alkalinity	-0.19	0.76	0.41	1					
Conductivity	-0.37	0.98	0.63	0.72	1				
Chloride	-0.12	0.9	0.62	0.59	0.95	1			
Fluoride	-0.1	-0	-0.08	0.06	0.18	0	1		
Sulfate	-0.16	0.81	0.42	0.49	0.82	0.78	0.06	1	
Nitrate	-0.33	0.56	0.69	0.17	0.52	0.41	-0.08	0.39	1

Table 7 | Correlation coefficient (r) among various water quality parameters for post-monsoon season

Parameters	pH	TDS	TH	Alkalinity	Conductivity	Chloride	Fluoride	Sulfate	Nitrate
pH	1								
TDS	-0.22	1							
TH	-0.33	0.66	1						
Alkalinity	-0.19	0.62	0.37	1					
Conductivity	-0.44	0.99	0.61	0.63	1				
Chloride	-0.1	0.89	0.58	0.43	0.91	1			
Fluoride	-0.05	-0.02	-0.2	0.1	0.19	-0.1	1		
Sulfate	-0.07	0.87	0.44	0.48	0.88	0.81	-0.03	1	
Nitrate	-0.28	0.54	0.66	0.22	0.47	0.37	-0.08	0.44	1

Let there be n water quality parameters and quality rating (q_n) corresponding to n^{th} parameter is a number reflecting relative value of this parameter in the polluted water with respect to its standard permissible value. q_n values are given by the relationship.

Calculation of quality rating (q_n)

For calculation, the ideal value is taken as v_i and the permissible value is v_s . Similarly, the ideal value is zero for other parameters and the permissible value is taken from standards. Therefore, the quality rating is calculated from the following relation:

$$q_n = 100 (v_o - v_i) / (v_s - v_i)$$

where,

v_o = observed value

v_i = ideal value

v_s = standard permissible value.

In most cases $v_i = 0$ except in certain parameters like pH, dissolved oxygen, etc.

Calculation of unit weight (W_n)

The unit weight (W_n) to various water quality parameters is inversely proportional to the recommended standards for the corresponding parameters.

$$W_n = k / s_n$$

where,

W_n = unit weight for n^{th} parameter

s_n = standard permissible value for n^{th} parameter

k = proportionality constant

$k = 1 / (1/v_{s1} + 1/v_{s2} + 1/v_{s3} + 1/v_{s4} + \dots + 1/v_{sn})$

s_n = 'n' number of standard values.

Calculation of water quality index (WQI)

WQI is calculated by the following equation:

$$WQI = \frac{\sum_{n=1}^n q_n W_n}{\sum_{n=1}^n W_n}$$

Assessment of water quality based on WQI

Application of WQI is a useful method in assessing the suitability of water for various beneficial uses, hence, WQI has been classified into five categories as shown in Table 8. The suitability of WQI values for human consumption according to Mishra & Patel (2001) is shown below.

Results of water quality index

For calculation, the WQI of nine parameters, namely, pH, TDS, TH, Ca H, Mg H, fluorides, chlorides, sulfates and nitrates were taken into consideration. WQI thus calculated for the sampling points of pre-monsoon and post-monsoon seasons is listed in Table 8. Similarly, the chart representation for both seasons is given in Figure 10.

DISCUSSION

A total of 162 samples was collected from the villages of Vadodara and Chhota Udaipur districts during pre-monsoon and post-monsoon seasons to assess the overall groundwater quality of the districts. The sampling was conducted as per the GEMI's Sampling Protocol for Water and Wastewater and the analysis of the samples was carried out in the GEMI's

Table 8 | Water quality index of Vadodara and Chhota Udaipur districts during pre- and post-monsoon seasons

Water quality index (WQI)	Status	Sample ID
Pre-monsoon season		
0–25	Excellent	8, 9, 13, 16, 18, 19, 22, 23, 24, 25, 26, 27, 36, 37, 39, 49, 62, 67, 69
26–50	Good	1, 2, 6, 7, 12, 14, 15, 17, 20, 21, 28, 29, 30, 31, 34, 35, 38, 40, 41, 42, 47, 48, 51, 53, 59, 61, 63, 70, 71
51–75	Moderate	3, 4, 5, 10, 11, 32, 33, 43, 44, 46, 50, 54, 55, 56, 57, 60, 64, 72, 73, 74, 77
76–100	Poor	52, 75
100 and above	Unfit for drinking	45, 58, 65, 66, 68, 76, 78, 79
Post-monsoon season		
0–25	Excellent	2, 18, 19, 29, 39, 46, 50, 53, 55, 57, 58, 63
26–50	Good	3, 4, 5, 6, 8, 9, 12, 13, 17, 20, 25, 26, 27, 28, 30, 31, 35, 37, 38, 40, 41, 42, 47, 48, 52, 54, 59, 60, 61, 62, 65, 67, 73, 75, 77
51–75	Moderate	1, 7, 14, 15, 16, 21, 22, 23, 24, 32, 33, 34, 36, 43, 44, 45, 51, 56, 64, 66, 68, 74, 78, 81
76–100	Poor	10, 11, 71, 79, 82
100 and above	Unfit for drinking	49, 69, 70, 72, 76, 80, 83

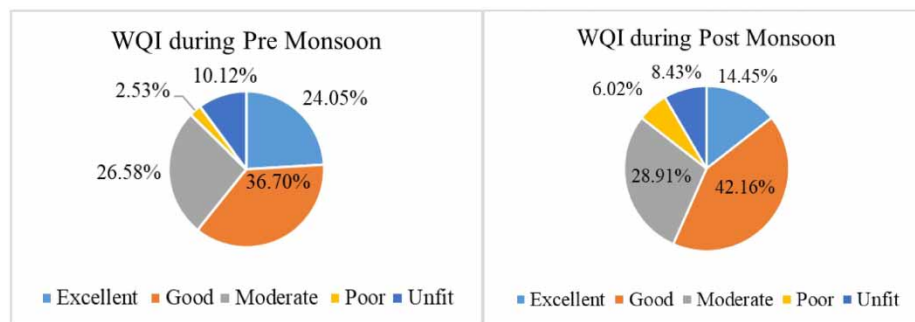


Figure 10 | Water quality index of Vadodara and Chhota Udaipur districts during pre- and post-monsoon seasons.

laboratory recognised as a 'State Water Lab' for different physicochemical parameters. The analytical findings were compared with Indian Standards Drinking Water-Specification (Second Revision) (IS 10500: 2012) to produce a view of overall groundwater quality of both the districts. The overall evaluation of the analytical results with standards is given in Table 9.

The limits are as per Indian Standards Drinking Water-Specification (Second Revision) (IS 10500: 2012).

Based on the analysis of results, the following inferences are drawn:

1. Overall, the pH of all the samples were found to be within the permissible limits according to Indian Standards (IS 10500: 2012) except that two samples showed a little higher pH.
2. High variations are observed in the concentration of conductivity, TDS, chloride, total hardness, alkalinity, fluoride, sulfate parameters. The concentrations of the parameters were found to be within the permissible limits as prescribed by the Indian Standards almost for all the samples for the respective parameters. Moreover, slight variation was observed in the sulfate concentration.
3. Nitrate concentrations, at places, were found to be higher than the permissible limits. High nitrate concentrations such as 569 mg/L was observed at Shihora village of Vadodara district. Moreover, many other villages have shown higher nitrate concentrations than the limits prescribed which is a matter of concern.
4. Heavy metals were analysed in a few groundwater samples to detect whether the groundwater was contaminated with heavy metals. The analytical results of heavy metals for groundwater samples were found to be within the acceptable limits except for a few samples for iron and lead. In particular, iron was found to be high, in the range of 0.2 mg/L to 9.9 mg/L, whereas the permissible limit is only 0.3 mg/L.

Table 9 | Results of the parameters analysed

S. No.	Parameters	Requirement (acceptable limit)	Permissible limit in the absence of alternate source	Vadodara district		Chhota Udaipur district	
				Range of present study (pre-monsoon)	Range of present study (post-monsoon)	Range of present study (pre-monsoon)	Range of present study (post-monsoon)
1	pH	6.5–8.5	No relaxation	6.84–8.74	6.74–8.22	6.65–8.39	6.72–7.98
2	EC ($\mu\text{S}/\text{cm}$)	–	–	406–3,370	294–6,160	743–2,470	–
3	TDS (mg/L)	500	2,000	204–1,956	200–3,604	140–1,352	136–1,298
4	Cl^- (mg/L)	250	1,000	21–615	21–1,154	24–399	0–394
5	TH (mg/L)	200	600	100–1,150	140–1,290	120–910	120–630
6	Ca^{++} (mg/L)	75	200	20–850	70–860	70–380	60–330
7	Mg^{++} (mg/L)	30	100	20–850	70–860	30–690	10–530
8	Alkalinity (mg/L)	200	600	156–1,004	116–959	124–858	168–812
9	Turbidity (NTU)	1	5	1.10–76.9	0.1–90	–	–
10	F^- (mg/L)	1.0	1.5	0–2.25	0.4–1.73	0–7.23	0–2.16
11	SO_4 (mg/L)	200	400	2–203	10–283	0–95.32	0–111.52
12	NO_3^- (mg/L)	45	No relaxation	0–489.5	0–569	0–100	0–115
13	Pb (mg/L)	0.01	No relaxation	0–0.006	0.057	0–5.447	0–14.06
14	Cd (mg/L)	0.003	No relaxation	BDL	BDL	BDL	BDL
15	Fe (mg/L)	0.3	No relaxation	0–0.364	0.1–9.98	0–2.045	0–3.248
16	Ni (mg/L)	0.02	No relaxation	0.001	0–0.01	BDL	BDL
17	Cr (mg/L)	0.05	No relaxation	0–0.004	0	BDL	BDL
18	Zn (mg/L)	5	15	0–0.0003	0–2.45	0–0.117	BDL
19	As (mg/L)	0.01	0.05	0–0.003	0–0.005	BDL	BDL

BDL, below detection limit.

Table 10 | Sources and health effects of drinking water characteristics

Sr. No.	Characteristic	Source	Health impact
1.	pH	Carbonate-rich rocks, effluent discharge, chemical dumping	pH < 6.5 causes aesthetic problems, metallic taste
2.	EC	Dissolved matter of inorganic salts, acids and bases	High concentrations affect taste, damage crops, degrade drinking water
3.	TDS	Landfill leachate, sewage	Gastrointestinal irritation, corrosive, salty and brackish taste
4.	Chloride	Domestic effluents, fertilizers, septic tanks, human waste, livestock waste	Affects heart, kidney patients
5.	TH	Weathering of limestone, sedimentary rocks, calcium bearing minerals, industrial effluents, application of lime to soil in agricultural areas	Urolithosis, cardiovascular disorder, kidney problems, cancer
6.	Alkalinity	Naturally occurring alkalis like CO_3^{2-} , HCO_3^- , OH^- , salts of Mg, Ca, K and Na, acid rain	Bitter taste, slippery feel, dry skin
7.	Turbidity	Inorganic sources like Fe, Mn from natural sources, geology and suspended matter	Waterborne diseases
8.	Fluoride	Weathering of rocks, fertilizers, liquid waste, volcanic ash, fly ash, industrial effluents	Dental fluorosis, effects on skeletal tissues
9.	Sulfate	Occurs naturally in soils, rocks, minerals, gypsum, decomposition of organic matter, fertilizers	Diarrhoea, dehydration, sulfate >250 mg/L creates medicinal taste
10.	Nitrate	Excessive use of inorganic nitrogenous fertilizers and manures	Methaemoglobin. Long-term exposure causes pregnancy and neural tube defects, colorectal cancer, bladder, birth defects, thyroid disease
11.	Lead	Carbonates and hydroxide complex in soil, erosion of natural deposits	Poor muscle coordination, blood pressure, reproductive problems, damage nervous system, anaemia, liver and kidney damage
12.	Cadmium	Erosion of natural deposits, discharge from metal refineries, runoff from waste batteries and paints	Kidney damage
13.	Iron	Naturally occurring, industrial effluents, sewage and landfill leachate	Haemorrhagic necrosis, genetic disorder (haemochromatosis)
14.	Nickel	Leakage from metals, dissolution from nickel ore-bearing rocks	Long-term exposure causes decreased body weight, heart and liver damage
15.	Chromium	Improper disposal of mining tools and industrial waste	Skin rashes, nose irritations and nose bleeds, ulcers, weakened immune system, kidney and liver damage
16.	Zinc	Occurs in small amounts in almost all igneous rocks	Fever, nausea, vomiting, stomach cramps, and diarrhoea
17.	Arsenic	By-products of agricultural and industrial activities	Cancer of bladder, lungs, skin, kidney, nasal passages

Source: WHO (1996); Patel (2015); Ward *et al.* (2018).

- From the comparison study of pre- and post-monsoon groundwater quality it was concluded that EC, TDS, total hardness, alkalinity, fluoride, sulfate, nitrate concentrations, etc. were found to be a little higher in post-monsoon samples than the pre-monsoon samples.
- Results of the WQI of Vadodara and Chhota Udaipur districts for pre-monsoon season showed that 24.05% of the water samples fell in the excellent category, 36.70% the good category, 26.53% were found to be of moderate quality, 2.53% of poor quality and 10.12% were found to be unfit for drinking purposes.
- The results of the WQI of Vadodara and Chhota Udaipur districts for post-monsoon season showed that 14.45% of the water samples fell in the excellent category, 42.16% the good category, 28.91% were found to be of moderate quality, 6.02% of poor quality and 8.43% were found to be unfit for drinking purposes.

Human health concerns

The present study shows elevated nitrate and fluoride concentrations in many sources. Availability of both the elements in the human body may be essential; although long-term consumption with excessive concentration may cause serious disease and sometimes even be life-threatening. Thus, it is important to understand the threat to human health due to elevated concentration of each parameter, as described in Table 10.

CONCLUSION

From the present study, it can be concluded that most of the groundwater sources analysed have satisfactory water quality and are suitable for human consumption as they meet the drinking water quality standards, except for the sources having elevated nitrate or fluoride concentrations. The water of the sources with elevated levels and not meeting the standards shall be consumed after receiving appropriate treatment, either at individual or village level, so as to minimize the health risk associated with consumption of such water. This study can be used to further collaborate with advanced hydrogeological and GIS studies to assess the sources and causes of such high nitrate and fluoride concentrations in the districts and ensure the safe quality of water with the application of suitable mitigation measures.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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