

# Genesis and geochemistry of high fluoride bearing groundwater from a semi-arid terrain of NW India

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**Abstract** Occurrence of fluoride in natural water resources and the associated health hazards have been reported from many parts of India during the last decade. With the objective of organizing a systematic scientific programme to understand the geochemical behaviour of fluoride in natural water resources in relation to the local hydrogeological, climatic conditions and agricultural use, a typical semi-arid terrain in the northwestern part of India was chosen for detailed study. The present work is an attempt to study the fluoride contamination in groundwater in parts of Jaipur district, Rajasthan state, and to assess the origin and genesis of fluoride in groundwater. The area, falling under the semi-arid tract of central Rajasthan, is geologically occupied by alluvial formations and Precambrian rocks (gneisses and schists) where groundwater occurs under unconfined to semi-confined conditions. A total of 66 groundwater samples was collected during the pre-monsoon period and analysed, which gave a concentration of fluoride in water in the range of 0.35 to 9.3 mg/l with 62 % of the samples in excess of permissible limit of 1.5 mg/l. As compared to alluvial formations, fluoride enrichment in groundwater is higher in hard rock areas. The samples collected from the granite gneissic terrain show higher values when compared to those in the schist.

The groundwater of the shallow aquifers (soil–clay complex weathered zone) has a higher concentration of fluoride than the deep (fractured hard rock) aquifer does. The possible sources of fluoride are chemical weathering and leaching of fluorine-bearing minerals present in hard rocks and alluvial formations under the alkaline environment in arid to semi-arid conditions. High pH as well as alkalinity and low levels of Ca, Mg and total hardness suggest favourable chemical conditions for the fluoride dissolution process. A higher rate of evapotranspiration, intensive and long-term irrigation and heavy use of fertilizers are the supplementary factors that further increase the fluoride content in the groundwater. A groundwater management programme is suggested.

**Keywords** Groundwater · Fluoride · Jaipur district · Weathering · Fluorosis

## Introduction

Fluoride in drinking water is one of the most important geoenvironmental issues in the world and plays an important role in determining the suitability of water for potable purpose. Around 200 million people, from 25 nations the world over, are facing the threat of fluorosis. India is one among the nations, where health problems occur due to the consumption of fluoride-contaminated water. In India, 17 of its 32 states have been identified as endemic areas of fluoride ( $F^-$ ) contamination with an estimated 66 million people including 6 million children suffering from fluorosis (dental, skeletal and non-skeletal) because of consumption of fluoride-contaminated water (UNICEF 1999). The extent of fluoride contamination of water varies from 1 to 48 mg/l. (Susheela 1999). Studies

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indicate that 65 % of India's villages are exposed to fluoride risk (UNICEF 1999). The most seriously affected Indian states are Rajasthan, Andhra Pradesh, Punjab, Haryana, Gujarat, Tamil Nadu and Uttar Pradesh (Muralidharan et al. 2002).

The state of Rajasthan occupies a unique geographic position in NW India on account of variable and adverse climatic conditions (arid to semi-arid), low to scanty and erratic rainfall and lack of perennial water sources. Most of the fluoride related groundwater studies in Rajasthan have been focused on the western and southern parts of the state which are conventionally described as 'high fluoride' areas (Maithani et al. 1998; Choubisa 2001; Chaudhary et al. 2010; Singh et al. 2011). In Rajasthan, districts such as Jaipur, Jodhpur, Nagaur, Bikaner, Pali, Sirohi, Bhilwara, Ajmer, Udaipur and Barmer have soil and groundwater pockets with heavy fluoride concentrations. Excessive fluoride in the domestic water supply is reported in at least 10 % villages in Rajasthan (Jacks et al. 2005). Of 33,505 villages, 6,681 villages have wells or water sources, the fluoride concentration of which exceeds 1.5 ppm and in 48 villages it is approximately 10 ppm (Sinha 1997). Fluoride concentration in drinking water of northern Rajasthan was found to be in the range of 1.01 and 4.78 mg/l (Suthar et al. 2007), whereas, it varies from 0.6 to 4.74 mg/l in western Rajasthan (Singh et al. 2011), 0.5 to 8.5 mg/l in north-western Rajasthan (Chaudhary et al. 2010) and 8 to 22 mg/l in certain areas of eastern Rajasthan (Sinha 1997). Anomalously high concentrations of fluoride (up to 16 ppm) have been observed in groundwaters of Sirohi district (Maithani et al. 1998) and Ajmer district of Rajasthan (Vikas et al. 2009; Vikas 2009). Long-term use of groundwater for drinking has resulted in the onset of widespread fluorosis symptoms, from mild forms of dental fluorosis to crippling skeletal fluorosis (Susheela 1999; Kundu et al. 2001; Harrison Paul 2005). Chronic fluoride intoxication in the form of osteo-dental fluorosis was investigated in Dungarpur district of southern Rajasthan, where fluoride concentration in drinking water ranges from 1.2 to 8.9 ppm (Choubisa 2001). Dental and skeletal fluorosis was reported from Ajmer district where  $F^-$  concentration in groundwaters ranges between 0.12 and 16.9 mg/l with 66 % of the samples in excess of permissible limit of 1.5 mg/l (Vikas et al. 2009; Vikas 2009). This crippling disease is prevalent in most parts of Jaipur district in Rajasthan due to the excessive concentration of the toxic  $F^-$  in drinking water resources. In view of its significance, a baseline hydrochemical study has been carried out in parts of Jaipur district (Dudu, Phagi and Sambhar blocks) with a focus on fluoride occurrence and distribution in relation to hydrogeology and geological setting, fluorine geochemistry and management of  $F^-$  bearing groundwater.

## Study area

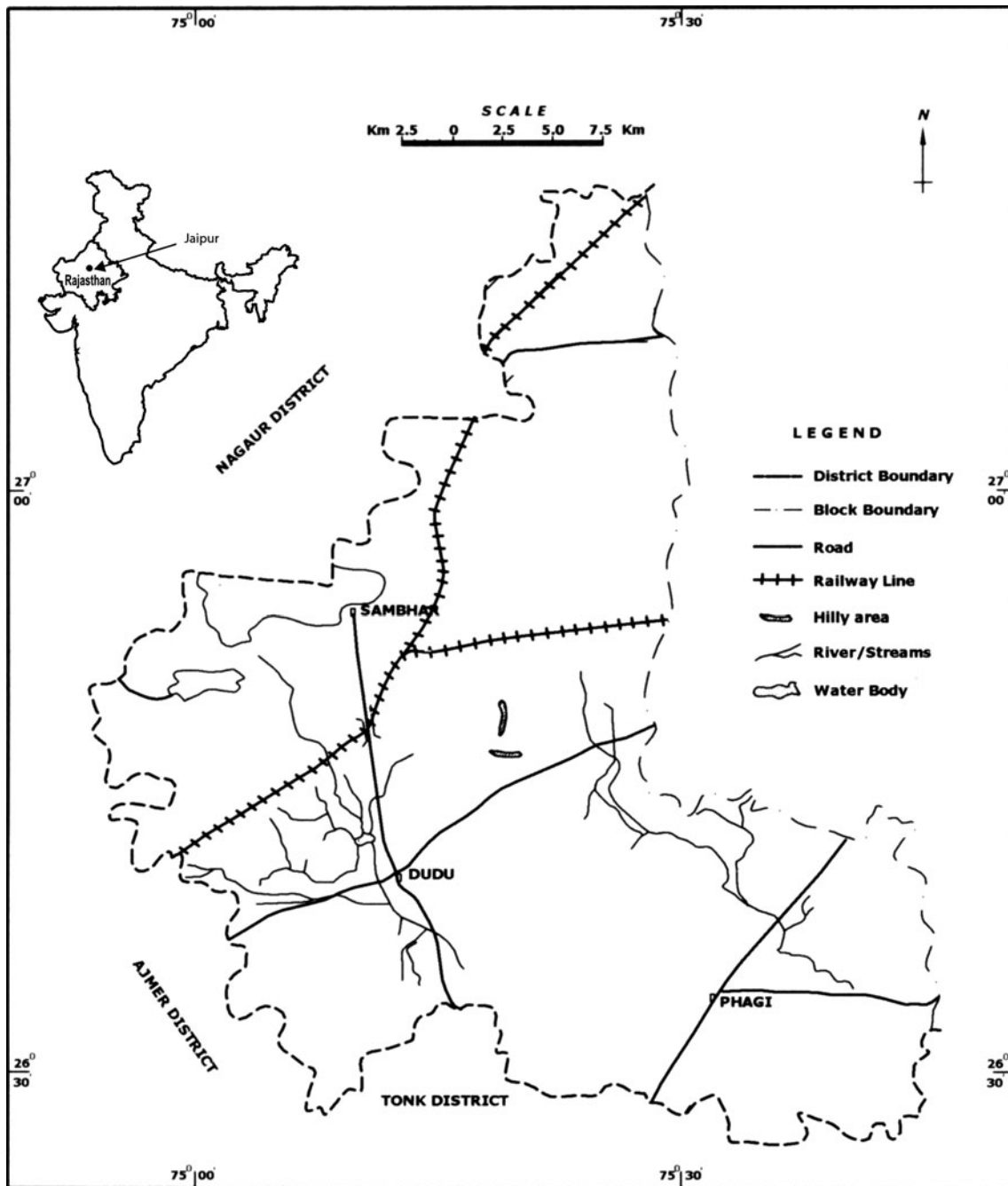
The largest Indian state, Rajasthan, covers an area of 34,271 million hectares, which is more than 10 % of the total geographical area of the country. It is one of the driest states of the country with a share of only about 1 % of the total surface water resources of India. The study area comprising Dudu, Phagi and Sambhar blocks falls in Jaipur district, occupies an area of 4,263 km<sup>2</sup>, and is located between latitudes 26°25'–27°30'N and longitudes 74°55'–75°45'E (Fig. 1). These blocks form the west and south-west portion of the Jaipur district.

## Climate

The study area belongs to the semi-arid region of NW India with minimum mean daily temperature of 27.3 °C and maximum temperature of 40.6 °C. The mean annual rainfall is 509 mm. The lowest normal monthly rainfall (2 mm) is received in the month of April and highest (170 mm) in the month of July. More than 90 % of the total annual rainfall is received during the southwest monsoon season. The total annual potential-evapotranspiration (PE) is 1,745 mm and is highest (257.4 mm) in the month of May and lowest (67.0 mm) in the month of December. It is observed that potential evapotranspiration is more than rainfall in all the months except in July and August. Therefore, ground recharge is possible only during the peak period of monsoon. The data on climatological parameters such as temperature, rainfall and PE of the study area have been collected from Indian Meteorological Department (IMD), Jaipur, Rajasthan (CGWB 2006).

## Physiography

A major portion of the study area is occupied by open undulating plains covered by Quaternary alluvial sand. Regional landform units of the area can be classified genetically as (a) units of fluvial origin, (b) units of denudational origin, and (c) units of alluvial origin. The main geomorphic features and landforms in the area are alluvial plains, pediments, buried pediments, sandy plain, aeolian plain, valley fill, ravines, etc. Pediments with thin to thick soil cover can be seen around Dudu and Phagi blocks forming flat gneissic outcrops. Aeolian sand dunes are found mainly in the northwestern part of the study area, particularly in the Sambhar block, which are few metres to 10 m in height. The main types of soil in the study area are sandy loam, sandy clay loam, sandy clay, clay, wind blown sand and river sand (CGWB 2007). Few ephemeral rivers like Bandi and Mendha and their tributaries drain through the study area. Sambhar salt lake, the largest playa within the Thar Desert, is situated in the



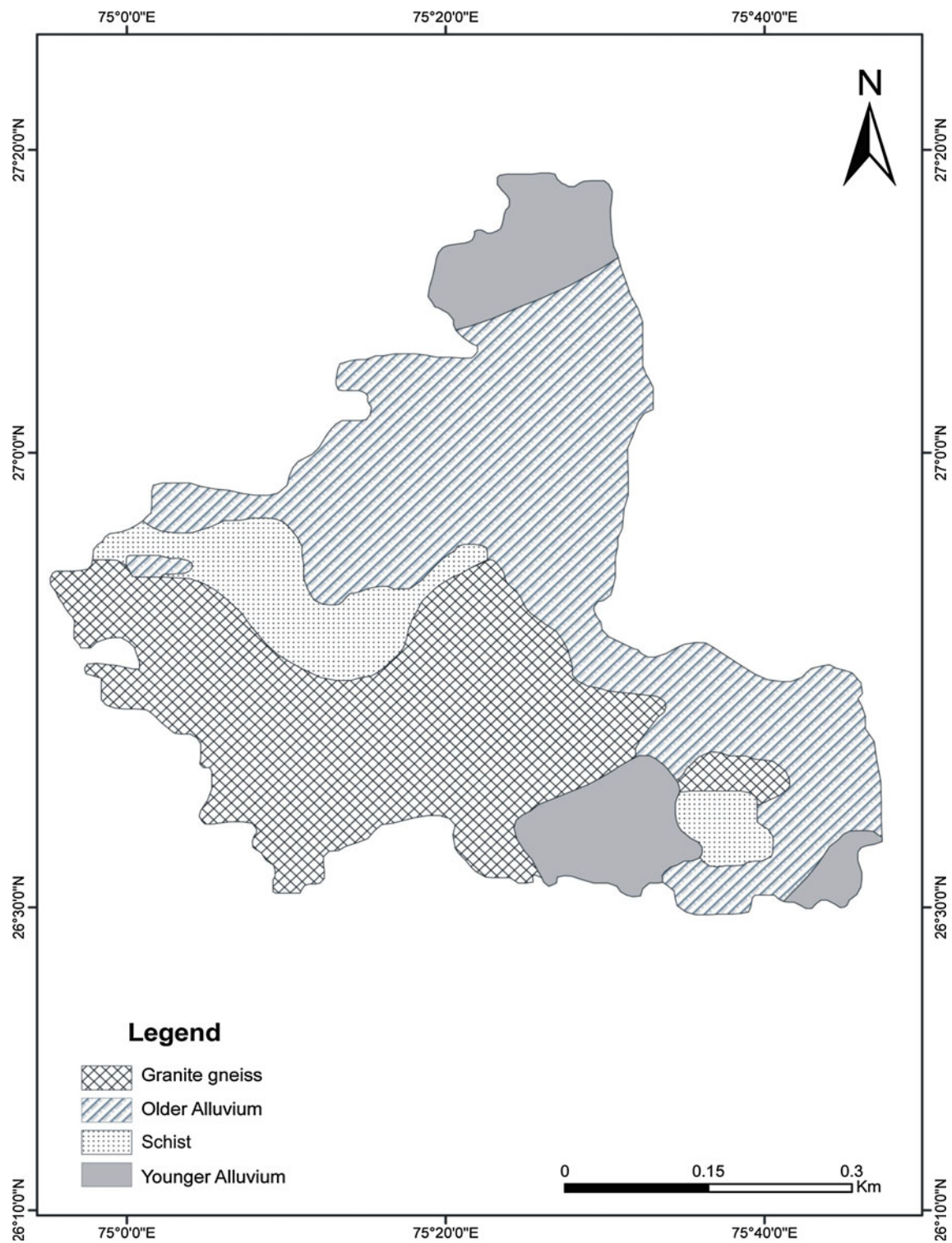
**Fig. 1** Location map of the study area showing Dudu, Phagi and Sambhar blocks of Jaipur district, Rajasthan, India

northwestern portion of the study area bordering Dudu and Sambhar blocks.

**Geology**

Archaean gneisses and schists of Bhilwara Super Group are the oldest rock types. It is overlain by schists, quartzites and conglomerates belonging to Proterozoic Delhi Super Group along with granite and pegmatite intrusives of

post-Delhi age (CGWB 2007). Hard rocks in major parts of the Jaipur district are covered by Quaternary fluvial and aeolian deposits. Older and Younger alluvium occupies major portions of Sambhar block and part of Phagi block of Jaipur district. Granite gneisses of Bhilwara Super Group occupy the south and southwestern part of the study area (Fig. 2). It covers major portions of the Dudu block and south of Sambhar block. The granite gneisses are light grey, medium to coarse grained, consisting of quartz,



**Fig. 2** Lithology map of the study area

plagioclase, orthoclase, garnet, hornblende and pyroxene as essential minerals, and apatite, biotite, fluorite and opaques as accessory minerals. Quartz-mica schist, quartzites and conglomerates belonging to Delhi Super Group of rocks occupy minimal portion of the study area particularly the

Dudu and Phagi block. Mineralogically, quartz-mica schist comprises quartz, feldspar (alkali feldspar and plagioclase) and various micaceous minerals (muscovite, biotite and sericite). The gneisses and quartzites are intruded by younger granites and pegmatites. Granite is pink-coloured



and medium-to-coarse grained, having k-feldspar (perthite and orthoclase), quartz, biotite, plagioclase, biotite and minor hornblende with magnetite, zircon, fluorite, rutile, tourmaline, sphene, and apatite as accessory minerals. The pegmatites are also coarse-grained and granitic in composition, composed of feldspars (orthoclase and albite) and quartz as the dominant constituents besides a variety of minerals like muscovite, biotite, tourmaline, fluorite, lithium mica, beryl, etc. Regional strike of the rocks in the area varies from NE-SW to NNW-SSE with steep dips in the eastern part and moderate dips in the west. Three phases of folds, differentiated as F<sub>1</sub>, F<sub>2</sub> and F<sub>3</sub> have NNW-SSE, NNE-SSW and ENE-WSW trends with characteristic fold style and geometry. The superposition of younger orogeny (Delhi) appears to have obliterated the pre-Aravalli folds. The Quaternary formations, occurring over the crystalline rocks include alluvium and aeolian sands. The alluvium (Older and Younger) consists mainly of sand, silt, clay and kankar. It occupies major portions of Sambhar block and north, south and eastern part of Phagi block of Jaipur district (Fig. 2). The alluvium is rich in illite, montmorillonite and mica group of minerals. The mineralogy of alluvium is inherited from the parent rocks and also from the tributaries of other river basins. Wind-blown sand is also a major component that often gets mixed with silt and, at some places, with clay. Kankar (CaCO<sub>3</sub> concretion) occurs as intercalation in the soil zone (CGWB 2007).

#### Hydrogeological setting

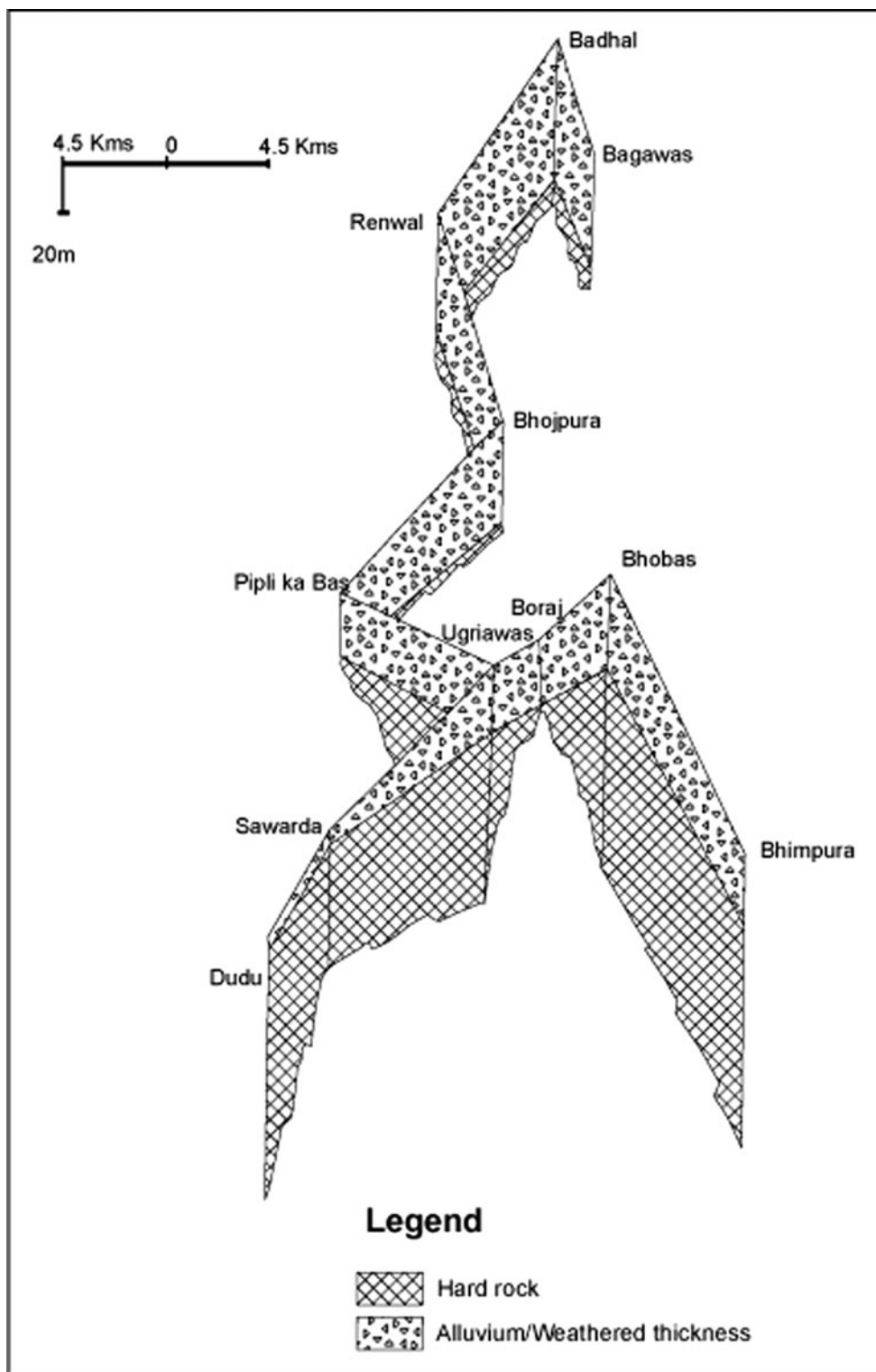
The main water-bearing formations of the study area are unconsolidated alluvial as well as aeolian formations and hard rocks. The general disposition of aquifers in and around the study area is shown in Fig. 3. A soil–clay complex weathered zone corresponds to the shallow aquifer (<40 mbgl, metres below ground level) and fracture zones make up the deep aquifers (>40 mbgl). Groundwater occurs under phreatic conditions in the low hydraulic conductivity weathered zone (shallow aquifer) and under semi-confined to confined conditions in the high hydraulic conductivity fractured zone (deep aquifer). Quaternary alluvium form good aquifers in parts of Jaipur district. The occurrence of clay beds intermixed with silt and kankar serve as aquitard. Alluvial thickness is less in southern and southwestern parts of the study area, i.e. in Dudu and Phagi blocks (Fig. 3). Maximum thickness of Quaternary sediments has been estimated to be up to 100 m. Gneisses and schists of Bhilwara Super Group, quartzites of Delhi Super Group and post-Delhi intrusives such as granite and pegmatite form major hard rock aquifers in the study area (Fig. 2). Movement of groundwater in these hard rocks is controlled by size, continuity and interconnectivity of weathered zone. The weathered mantle of hard rock yields

good discharge of water. Depth of wells generally varies from 11 to 66 m in alluvium and 6 to 49 m in consolidated formation areas. In the study area, the sub-surface lithological data show that the depth of top soil is from 2 to 4 m from the ground surface. The top soil is followed by clayey sand zone, sandy clay zone, weathered zone and fractured zone. The depth to water level during pre-monsoon period varies from less than 3.6 to 51.9 mbgl (metres below ground level), while during post-monsoon period, it ranges from less than 1.0 to 50.0 mbgl. The seasonal fluctuations in the water level during the pre-monsoon and post-monsoon seasons are 2.60–1.90 m. Specific capacity of wells varies from 58 to 500 lpm/m. Transmissivity value and storage coefficient vary from 10 to 850 m<sup>2</sup>/d and  $4.70 \times 10^{-5}$  to  $1.05 \times 10^{-3}$ , respectively (CGWB 2007). Groundwater development is through dug wells, hand pumps, dug cum bore wells and tube wells. In alluvium, the average yield of dug and dug cum bore wells varies from 50 to 1,200 m<sup>3</sup>/day whereas the average discharge of the tube wells varies from 10 to 85 m<sup>3</sup>/day. In hard rocks, the average yield of dug and dug cum bore wells varies from 0.5 to 200 m<sup>3</sup>/day. Rainfall is the direct recharge source and the usage of water for land use activities, domestic and agriculture purposes, is the indirect additional recharge source of groundwater. The water table varies from 290 m (amsl, above mean sea level) in the southeast to 400 m (amsl) in the north (Fig. 4). In its flow, groundwater mainly follows the topographic gradient. The flow direction, in general, is towards southeast and south of the study area. Dudu and Phagi blocks of the study area have been categorised as ‘Critical’ blocks, whereas the Sambhar block is categorised as ‘over-exploited’ block. The stage of groundwater development in the Sambhar block is estimated to be around 268 %, and thus, not recommended for further groundwater exploitation (CGWB 2007).

#### Materials and methods

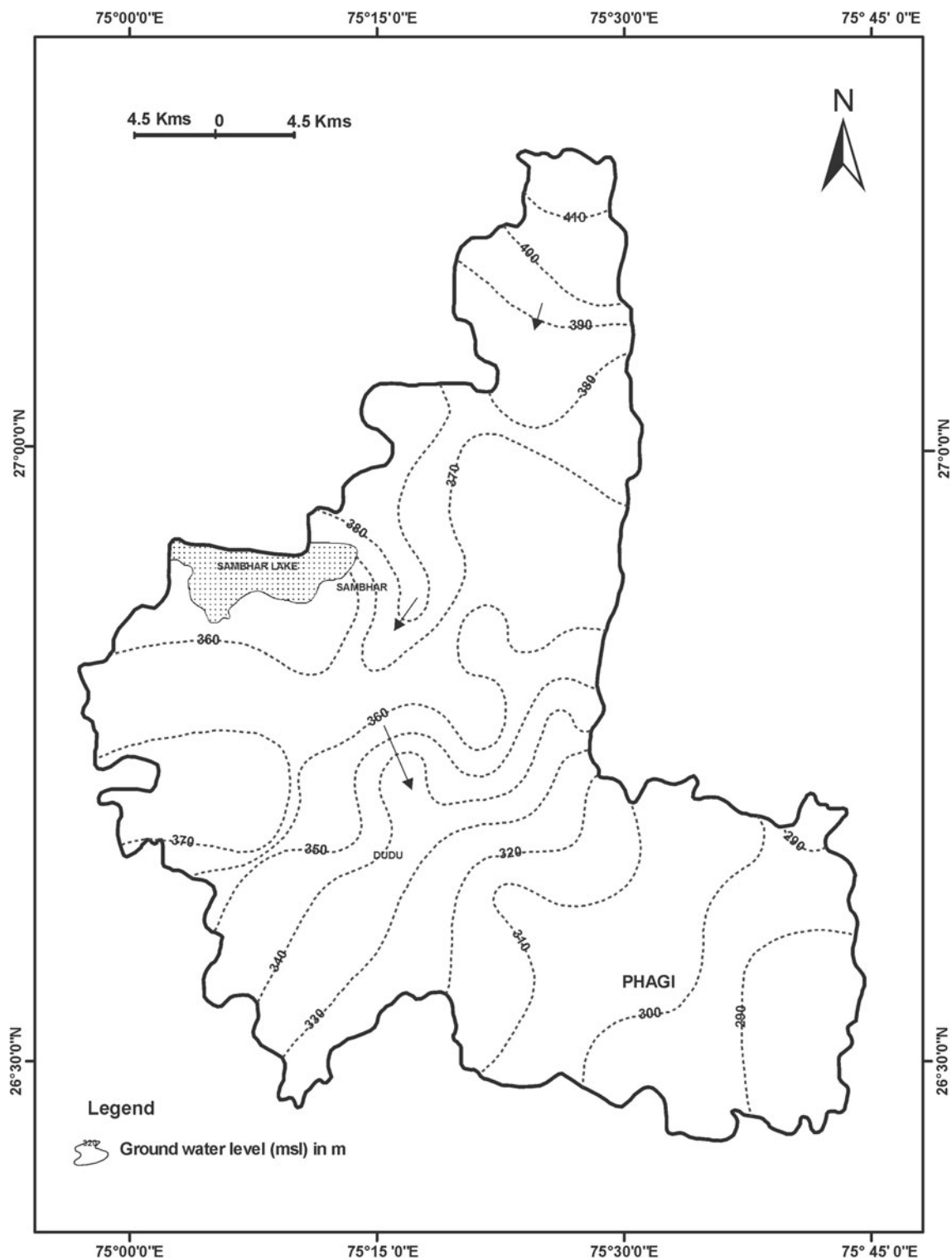
Sixty-six groundwater samples from shallow dug wells, dug cum bore wells, hand pumps, and deep tube wells were collected from various locations from the entire area during pre-monsoon period and were analysed at the chemical laboratory of the central ground water board (CGWB), Western region, Jaipur, Rajasthan for pH, electrical conductivity (EC), total hardness (TH), calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, sulphate, nitrate and fluoride as per the standard analytical procedures (APHA 1995) and the results are presented in Table 1. Hydrogen ion concentration (pH) and electrical conductivity (EC) were measured, using pH meter and EC meter. Total dissolved solids (TDS) were computed by multiplying the EC by a factor (0.55–0.75), depending on

**Fig. 3** Subsurface geological cross-section in and around the study area



the relative concentrations of ions. The cations like sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ) were measured by flame photometer. Total hardness (TH) as  $\text{CaCO}_3$ , calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ) were found out titrimetrically, using standard EDTA. Chloride ( $\text{Cl}^-$ ) was estimated by standard  $\text{AgNO}_3$  titration (Mohr method). Carbonate ( $\text{CO}_3^{2-}$ ) and

bicarbonate ( $\text{HCO}_3^{2-}$ ) were estimated by titrating with HCl. Fluoride ( $\text{F}^-$ ), nitrate ( $\text{NO}_3^-$ ) and sulphate ( $\text{SO}_4^{2-}$ ) concentrations were estimated using UV/VIS spectrophotometer. The ECR (Eriochrome Cyanine R) method was used for fluoride determination. The detection limit and analytical range of fluoride were 0.001 and 0–1.0 mg/l respectively. All



**Fig. 4** Spatial variation of water level (msl in m) in the study area

parameters are expressed in milligrams per litre (mg/l), except pH (units) and EC. The EC is expressed in microSiemens per centimetre ( $\mu\text{S}/\text{cm}$ ) at 25 °C. The analytical precision for the measurements of cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) to anions

( $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) is indicated by the ionic balance error, which is observed to be within the standard limit of  $\pm 5\%$ . The hydrochemical facies were determined using the hydrogeochemical software AQUACHEM.

## Results and discussion

The analytical results of chemical parameters of groundwater were compared with the standard guideline values as recommended by the Bureau of Indian Standards (BIS 2003) and World Health Organization (WHO 2004) for drinking and public health standards (Table 1). Comparison suggests that majority of the ionic and non-ionic constituents are falling above the maximum permissible limit for drinking purposes. There are remarkable differences in the water chemistry between shallow and deeper aquifers. The analytical results indicate that the groundwater is generally alkaline in nature with pH varying from 7.2 to 9.0 (mean = 8) in shallow aquifers and 7.5 to 9.0 (mean = 8.3) in deeper aquifers respectively (Table 2). The overall salinity of the area is high as indicated by higher EC values. The electrical conductivity (EC) varies from 400 to 19,150  $\mu\text{S}/\text{cm}$  at 25 °C (mean = 5,167  $\mu\text{S}/\text{cm}$ ) in shallow aquifer samples while deeper water samples are characterised by low EC values ranging from 790 to 17,300  $\mu\text{S}/\text{cm}$  (mean = 3,120  $\mu\text{S}/\text{cm}$ ). The saline groundwater condition is possibly attributed to low seasonal rainfall, evaporation and insignificant groundwater recharge. In the shallow groundwater samples, TDS ranges between 260 and 12,435 mg/l and the mean of 3,355 mg/l indicate the inorganic pollution load in the study area (Table 2). Whereas deeper water samples are characterised by low TDS ranging from 513 to 11,234 mg/l (mean = 2,026 mg/l). Hardness of water is due to calcium, magnesium and bicarbonate contents. The total hardness (TH) in the shallow and deeper groundwater ranges from 80–3,620 mg/l (mean = 899 mg/l) and 160–1,700 mg/l (mean = 462 mg/l) respectively and is due to the presence of alkaline earths such as calcium and magnesium. Sodium ( $\text{Na}^+$ ) is the most abundant cation in the groundwater of the study area and the concentration varies from 15 to 6,555 mg/l (mean = 1,037 mg/l) in the shallow aquifer samples while deeper aquifer samples are characterised by low sodium concentration ranging from 92 to 4,600 mg/l (mean = 603 mg/l). The higher concentration of sodium indicates the contribution from weathering process. In shallow aquifer samples, calcium ( $\text{Ca}^{2+}$ ) concentration varies from 12 to 560 mg/l (mean = 130 mg/l) and magnesium ( $\text{Mg}^{2+}$ ) concentration ranges from 5 to 698 mg/l (mean = 139 mg/l). Deeper aquifer samples possess comparatively low calcium (mean = 67 mg/l) and magnesium (mean = 72 mg/l) concentration in the study area (Table 2). Low concentration of calcium and magnesium are mainly due to carbonate/dolomite precipitation. Dissolved magnesium exceeds calcium in water once calcium precipitates after reaching supersaturation and accounts for higher magnesium concentrations than calcium (Hem 1991). Potassium ( $\text{K}^+$ ), the least abundant cation, ranges

from 1 to 439 mg/l (mean = 28 mg/l) and 1 to 30 mg/l (mean = 7.4 mg/l) in shallow and deep groundwater samples respectively. The resistance to weathering of  $\text{K}^+$  and its fixation in the clay minerals causes low concentrations of  $\text{K}^+$  in groundwater.

Chloride ( $\text{Cl}^-$ ) is the most abundant anion, with concentration ranging from 28 to 10,508 mg/l (mean = 1,502 mg/l) in the shallow groundwater whereas deeper water samples are characterised by low values ranging from 21 to 7,029 mg/l (mean = 753 mg/l). Being a semi-arid terrain, the high evaporation increases the  $\text{Cl}^-$  concentration of groundwater in relation to increase of TDS. Alkalinity (TA) of water is mainly due to the presence of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ . The TA in the shallow and deeper groundwater ranges from 130–1,141 mg/l (mean = 467 mg/l) and 140–1,091 mg/l (mean = 465 mg/l), respectively (Table 2). In the shallow and deep groundwater samples, the bicarbonate ( $\text{HCO}_3^-$ ) concentration was found to be high and it ranges from 159 to 1,391 mg/l (mean = 550 mg/l) and 159 to 1,135 mg/l (mean = 465 mg/l) respectively. Such higher concentration in pre-monsoon season can be attributed due to weathering of silicates in the area. The  $\text{CO}_3^{2-}$  ranges from trace to 120 mg/l (mean = 8.2 mg/l) in shallow groundwater samples while deeper water samples possess  $\text{CO}_3^{2-}$  values ranging from trace to 96 mg/l (mean = 24 mg/l). Sulphate ion ranges from 5 to 2,059 mg/l (mean = 401 mg/l) and 7 to 1,104 mg/l (mean = 172 mg/l) in shallow and deep groundwater samples, respectively (Table 2). Nitrate ( $\text{NO}_3^-$ ) content in shallow aquifer samples varies from 5 to 4,500 mg/l (mean = 235 mg/l) whereas deeper aquifer samples have lower  $\text{NO}_3^-$  values, ranging from 4 to 600 mg/l (mean = 102 mg/l). The high nitrate contamination in shallow aquifer samples implies the anthropogenic impact of pollution in the area (Vikas 2008). The ionic dominance (meq/l) pattern is in the order of  $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$  among cations and  $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{NO}_3^- > \text{F}^-$  among anions in premonsoon. Hydrochemical investigation reveals that groundwater in most parts of the study area is brackish, hard to very hard, alkaline and medium to high saline waters. Bicarbonate-chloride and Na–K type waters dominate the study area (Fig. 5). As compared to deep aquifer groundwater samples, shallow aquifer samples show high TDS, TH, Cl, EC,  $\text{SO}_4$ ,  $\text{NO}_3$  and F. High F, Cl and  $\text{NO}_3$  in shallow aquifer rendering it unsuitable for drinking purpose as per the standards prescribed by BIS (2003) and WHO (2004).

### Fluoride abundance and distribution in ground water

The concentration of fluoride in groundwater is not uniform in the study area. In the study area, it has been observed that the groundwater samples collected from the hard rock areas (mean F = 2.74 mg/l) show higher fluoride concentration as compared to those from alluvial



**Table 1** Analytical data for the groundwater samples from Jaipur district, Rajasthan, India

Sl. no.	Location	Block	Type of sample	Lithology	EC (uS/cm)	TDS (mg/l)	pH (units)	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	Cl (mg/l)	SO <sub>4</sub> (mg/l)	CO <sub>3</sub> (mg/l)	HCO <sub>3</sub> (mg/l)	NO <sub>3</sub> (mg/l)	F (mg/l)	TH (mg/l)	TA (mg/l)	Ionic balance error
1	Bagawas	Sambhar	Shallow	A	1,930	1,253	8.4	391	3	56	12	312	197	24	378	36	5.5	190	350	1.06
2	Junsiya	Sambhar	Shallow	A	1,880	1,221	8.2	345	2	68	22	249	91	0	634	22	9	260	520	1.03
3	Sanodiya	Sambhar	Shallow	A	11,700	7,597	8.1	2,530	16	272	379	3,798	2,059	0	305	6	0.9	2,240	250	1.0
4	Kajjipura	Sambhar	Shallow	A	1,600	1,039	9	308	4	40	44	128	166	84	537	21	2.4	280	581	1.0
5	Pratapura	Sambhar	Shallow	A	6,460	4,195	7.7	1,380	7	68	105	1,740	336	0	927	21	9.3	600	760	1.01
6	Dabari	Dudu	Shallow	A	16,830	10,929	8.7	4,899	41	52	124	4,331	422	48	1,257	4,500	1.2	640	1,111	1.01
7	Kojjewar	Dudu	Shallow	A	8,370	5,435	7.6	1,564	59	96	219	2,414	326	0	976	70	2.6	1,140	801	1.0
8	Bhobas	Dudu	Shallow	A	690	448	7.7	67	3	32	29	36	118	0	183	28	0.9	200	150	1.01
9	Kandadevli	Dudu	Shallow	A	19,150	12,435	7.7	6,555	16	300	698	10,508	1,382	0	308	1,700	6	3,620	253	1.0
10	Basri	Phagi	Shallow	A	2,300	1,494	8.9	506	3	20	36	284	43	120	781	5	1.3	200	841	1.01
11	Bhankrota	Phagi	Shallow	A	400	260	7.8	15	9	56	5	28	5	0	171	16	5.4	160	140	1.04
12	Bichi	Phagi	Shallow	A	1,080	701	8.7	87	16	60	48	85	35	24	427	13	1.8	350	390	1.0
13	Chandmakalan	Phagi	Shallow	A	3,270	2,123	8	655	1	56	56	490	374	0	769	95	1.8	370	631	1.01
14	Mandap	Phagi	Shallow	A	1,740	1,130	8.5	405	7	12	12	149	70	36	695	29	8	80	630	1.11
15	Bhagpura	Phagi	Shallow	A	2,195	1,425	7.8	391	3	36	44	256	153	0	683	45	2.3	270	560	1.01
16	Hirapura	Phagi	Shallow	A	5,800	3,766	8.2	1,035	12	80	126	1,122	144	0	1,391	120	5.2	720	1,141	1.01
17	Kuchhiawas	Phagi	Shallow	A	2,000	1,299	7.9	359	2	40	41	277	54	0	647	80	3.1	270	531	1.01
18	Jaisinghpura	Phagi	Shallow	A	3,200	2,078	8	408	4	60	122	817	44	0	366	50	1.2	650	300	1.0
19	Sitarampura	Dudu	Shallow	G	7,520	4,883	8.2	1,495	20	112	184	2,307	451	0	695	15	2	1,040	570	1.0
20	Girdani	Dudu	Shallow	G	2,610	1,695	8.1	552	3	36	27	319	202	0	842	35	6.6	200	691	1.02
21	Padasoli	Dudu	Shallow	G	3,840	2,494	7.9	713	1	52	75	979	101	0	586	8	6.1	440	481	1.01
22	Chaparwara	Dudu	Shallow	G	5,700	3,701	7.3	805	1	560	202	1,242	999	0	366	44	3.1	1,390	300	1.27
23	Mangalwara	Dudu	Shallow	G	11,800	7,662	7.4	2,254	117	432	272	4,473	499	0	427	70	4	2,200	350	1.0
24	Mandwara	Dudu	Shallow	G	1,280	831	7.7	115	5	80	56	220	12	0	403	38	1.8	430	331	1.0
25	Jhag	Dudu	Shallow	G	1,450	942	8.1	216	9	40	44	128	168	0	451	35	2.2	280	370	1.01
26	Gagotikhurd	Dudu	Shallow	G	8,200	5,325	7.2	1,081	100	376	282	1,740	1,402	0	464	350	2.3	2,100	381	1.0
27	Kankrala	Dudu	Shallow	G	2,490	1,617	7.9	345	4	116	54	504	106	0	488	50	2.4	510	400	1.01
28	Manpura	Phagi	Shallow	G	4,400	2,857	7.8	552	4	200	156	1,278	43	0	378	225	8	1,140	310	1.0
29	Pipla	Phagi	Shallow	G	4,750	3,084	7.7	690	7	196	114	1,420	86	0	378	44	1	960	310	1.01
30	Bisala	Phagi	Shallow	G	3,250	2,110	7.8	356	9	160	109	710	103	0	512	125	1.4	850	420	1.0
31	Bhojpura	Phagi	Shallow	G	3,370	2,188	7.7	646	2	32	63	596	70	0	964	38	4	340	791	1.01
32	Ghatiyali	Phagi	Shallow	G	890	578	7.7	69	10	60	36	64	57	0	342	40	1.1	300	281	1.0
33	Mendwas	Phagi	Shallow	G	12,000	7,792	7.4	2,162	7	440	404	4,118	1,104	0	537	64	3.1	2,760	440	1.0
34	Sawaimadhoshpura	Phagi	Shallow	G	1,450	942	7.9	267	3	48	10	142	36	0	573	40	7	160	470	1.01
35	Bhadoti	Dudu	Shallow	S	9,000	5,844	8.2	1,932	14	136	488	3,053	1,848	0	329	90	1.4	2,340	270	1.0
36	Jhapok	Dudu	Shallow	S	2,700	1,753	8.2	535	1	36	29	618	17	0	537	70	5.2	210	440	0.99
37	Gopalpura	Dudu	Shallow	S	5,250	3,409	8.2	920	9	160	141	1,775	109	0	366	90	0.9	980	300	1.0
38	Nangal	Dudu	Shallow	S	10,430	6,773	8.2	1,610	439	420	241	2,738	1,440	0	415	1,100	2.4	2,040	340	0.93
39	Udaypura	Dudu	Shallow	S	13,900	9,026	7.7	2,530	156	48	506	5,076	1,392	0	159	75	3.1	3,140	130	0.9

**Table 1** continued

Sl. no.	Location	Block	Type of sample	Lithology	EC (uS/cm)	TDS (mg/l)	pH (units)	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	Cl (mg/l)	SO <sub>4</sub> (mg/l)	CO <sub>3</sub> (mg/l)	HCO <sub>3</sub> (mg/l)	NO <sub>3</sub> (mg/l)	F (mg/l)	TH (mg/l)	TA (mg/l)	Ionic balance error
40	Kherabalaji	Phagi	Shallow	S	2,260	1,468	7.7	225	20	136	71	575	35	0	317	39	0.9	630	260	1.01
41	Phagi	Phagi	Shallow	S	2,700	1,753	8	552	4	40	19	469	137	0	586	105	5.2	180	481	1.01
42	Kudiyon ka bas	Sambhar	Deep	A	790	513	8.5	92	2	36	29	36	26	12	366	15	0.5	210	320	1.0
43	Bhatsawa	Sambhar	Deep	A	3,200	2,078	8.9	678	4	28	32	454	67	48	488	600	2.3	200	480	1.0
44	Karansar	Sambhar	Deep	A	1,480	961	8.4	308	2	20	27	128	28	84	561	28	2.4	160	600	1.0
45	Badidoongri kalan	Sambhar	Deep	A	2,000	1,299	8.5	405	2	20	34	298	182	24	476	34	1.8	190	430	1.01
46	Badhal	Sambhar	Deep	A	1,500	974	8.4	230	4	72	15	270	110	60	159	60	1.1	240	230	0.97
47	Sanodiya	Sambhar	Deep	A	2,930	1,903	8	449	4	68	78	497	18	0	671	300	1.8	540	550	0.97
48	Gumanpura	Sambhar	Deep	A	17,300	11,234	7.5	4,600	16	192	309	7,029	1,104	0	671	91	1.9	1,700	550	1.01
49	Bigawas	Sambhar	Deep	A	970	630	8.2	122	2	44	51	99	125	0	354	30	1	320	290	1.01
50	Dungri	Sambhar	Deep	A	1,350	877	8.8	267	1	28	41	78	122	36	610	25	0.7	240	560	1.08
51	Sundriawas	Sambhar	Deep	A	850	552	8.5	110	2	20	51	36	96	12	366	35	0.8	260	320	1.05
52	Karansar	Sambhar	Deep	A	2,330	1,513	8.5	460	5	28	32	426	187	48	366	34	1.7	200	380	1.02
53	Lalasar	Sambhar	Deep	A	3,700	2,403	8	610	1	64	126	951	192	0	537	29	1.4	680	440	1.0
54	Nawawas	Sambhar	Deep	A	910	591	8.6	124	2	32	46	114	105	24	207	75	1.4	270	210	1.0
55	Dhyodi	Sambhar	Deep	A	5,000	3,247	8.5	966	3	60	153	1,171	602	48	634	120	1.3	780	600	1.0
56	Asalpur	Dudu	Deep	A	4,750	3,084	7.7	736	3	176	107	1,093	107	0	634	252	0.7	880	520	1.05
57	Lorwara	Sambhar	Deep	G	840	545	8.8	400	2	16	32	21	195	96	781	6	0.9	170	801	1.01
58	Pigun	Dudu	Deep	G	3,940	2,558	8.6	690	27	60	80	852	96	12	744	90	2	480	630	1.02
59	Harsoli	Dudu	Deep	G	1,080	701	7.8	108	7	60	39	57	162	0	403	4	1.5	310	331	0.95
60	Rahlana	Dudu	Deep	G	1,050	682	7.6	113	12	56	34	107	26	0	415	25	1	280	340	1.01
61	Laporiya	Dudu	Deep	G	3,800	2,468	7.7	655	16	48	92	767	335	0	598	25	1.1	500	490	1.0
62	pahariya	Phagi	Deep	G	4,900	3,182	9	1,127	16	20	32	994	96	96	1,135	60	1.9	180	1,091	1.0
63	Dosra	Phagi	Deep	G	1,400	909	8.2	221	2	48	29	206	7	0	488	23	0.4	240	400	1.01
64	Sirohikhurd	Dudu	Deep	S	5,500	3,571	7.8	656	30	316	148	1,775	274	0	403	65	2	1,400	331	0.9
65	Akoda	Dudu	Deep	S	2,700	1,753	8	472	16	48	32	227	28	0	659	500	2.4	250	541	1.0
66	Pithawas	Dudu	Deep	S	3,740	2,429	7.7	483	3	112	146	1,136	22	0	342	34	1.9	880	281	1.0
	BIS DWS-MDL				750	500	8.5	NR	NR	75	30	250	200	NR	500	45	1	300	200	
	BIS DWS-MPL				3,000	2,000	NR	NR	NR	200	100	1,000	400	NR	1,000	45	1.5	600	600	
	% of samples with MPL				48	48	15	-	-	12	38	33	20	-	4	45	62	38	18	

EC Electrical conductivity, TDS total dissolved solids, TH total hardness, TA total alkalinity (as CaCO<sub>3</sub>), A alluvium, G granite gneiss, S schist, BIS DWS Bureau of Indian Standards Drinking Water Standards, NR not recommended, MDL maximum desirable limit, MPL maximum permissible limit

**Table 2** Statistical summary of chemical composition of groundwater in parts of Jaipur district, Rajasthan

Chemical parameter	Type of sample	Minimum	Maximum	Mean	Standard deviation
pH (units)	Shallow	7.2	9.0	8.0	0.4
	Deep	7.5	9.0	8.3	0.4
EC (uS/cm)	Shallow	400.0	19,150.0	5,167.0	4,625.0
	Deep	790.0	17,300.0	3,120.0	3,324.0
TDS (mg/l)	Shallow	260.0	12,435.0	3,355.0	3,003.0
	Deep	513.0	11,234.0	2,026.0	2,159.0
Na (mg/l)	Shallow	15.0	6,555.0	1,037.0	1,292.0
	Deep	92.0	4,600.0	603.0	878.0
K (mg/l)	Shallow	1.0	439.0	28.0	74.0
	Deep	1.0	30.0	7.4	8.2
Ca (mg/l)	Shallow	12.0	560.0	130.0	137.0
	Deep	16.0	316.0	67.0	68.0
Mg (mg/l)	Shallow	5.0	698.0	139.0	158.0
	Deep	15.0	309.0	72.0	65.0
SO <sub>4</sub> (mg/l)	Shallow	5.0	2,059.0	401.0	558.0
	Deep	7.0	1,104.0	172.0	232.0
CO <sub>3</sub> (mg/l)	Shallow	Traces	120.0	8.2	24.2
	Deep	Traces	96.0	24.0	32.0
HCO <sub>3</sub> (mg/l)	Shallow	159.0	1,391.0	550.0	271.0
	Deep	159.0	1,135.0	523.0	205.0
TH (mg/l)	Shallow	80.0	3,620.0	899.0	914.0
	Deep	160.0	1,700.0	462.0	398.0
TA (mg/l)	Shallow	130.0	1,141.0	467.0	225.0
	Deep	140.0	1,091.0	465.0	212.0
NO <sub>3</sub> (mg/l)	Shallow	5.0	4,500.0	235.0	748.0
	Deep	4.0	600.0	102.0	153.0
Cl (mg/l)	Shallow	28.0	10,508.0	1,502.0	2,013.0
	Deep	21.0	7,029.0	753.0	1,390.0
F (mg/l)	Shallow	0.9	9.3	3.49	2.45
	Deep	0.4	2.4	1.44	0.59

EC electrical conductivity, TDS total dissolved solids, TH total hardness, TA total alkalinity (as CaCO<sub>3</sub>)

formations (mean F = 2.69 mg/l). In the hard rock areas, groundwater samples collected from the gneissic terrain (mean F = 2.82 mg/l) show more F<sup>-</sup> enrichment as compared to those in schist (mean F = 2.54 mg/l) (Table 3). The comparison of fluoride in groundwater with respect to water table (shallow and deep aquifer) suggests that, in general, fluoride enrichment is more profound in shallow aquifers as compared to deeper aquifer irrespective of lithology. Fluoride concentration in shallow aquifer samples ranges between 0.9 to 9.3 mg/l with a mean value of 3.49 mg/l (Tables 2, 3). Deeper aquifer samples are characterised by low F<sup>-</sup> concentration values that ranges from 0.4 to 2.4 mg/l (mean = 1.44 mg/l). Dosra village in Phagi block recorded the lowest (i.e. 0.4 mg/l) F<sup>-</sup> concentration values whereas Pratapura in Sambhar block registered the

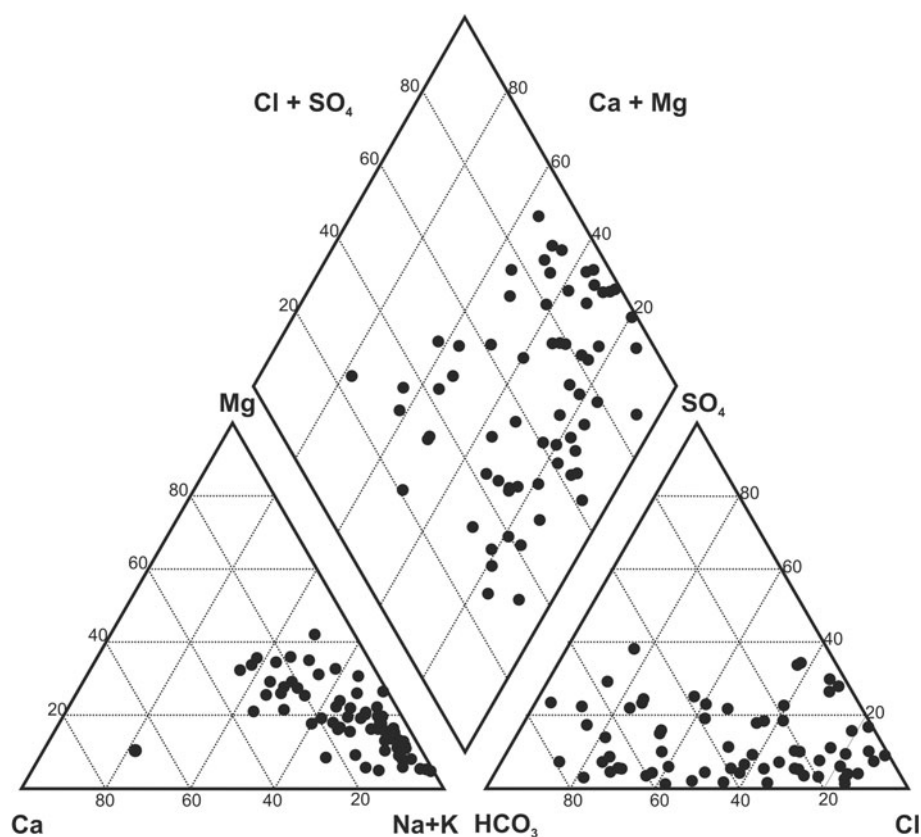
highest (i.e. 9.3 mg/l) F<sup>-</sup> value in the study area (Table 1). In the case of shallow aquifer, only 27 % of samples record F<sup>-</sup> concentration values within the maximum permissible limit of 1.5 mg/l (Fig. 6a; Table 3). On the other hand, in 56 % of deep well waters, the F<sup>-</sup> concentration values are within the maximum permissible limit (Fig. 6b). The mean fluoride concentration in different blocks of the study area reveals that Phagi block is seriously affected (Fig. 7). The spatial variation of the fluoride concentration is presented as a spatial distribution map (Fig. 8), which depicts its spatial behaviour and distribution. Occurrence of fluoride is very sporadic and marked differences in concentrations occur even at very short distances and hence the blocks show variable fluoride concentrations. F<sup>-</sup> concentration values lying above 3.0 mg/l cover a substantial portion of the study area.

### Origin and genesis of F<sup>-</sup> bearing groundwater

Occurrence of fluoride in groundwater is a natural phenomenon, influenced by local and regional geological setting and hydrogeological regime. Fluoride in waters can be derived from the weathering of fluorine-bearing minerals in rocks, from volcanic (Cuoco et al. 2010) and fumarolic activities (Aiuppa 2009), from precipitation in the form of rain (Aiuppa et al. 2001), snow, or dry fallout and from industrial emissions (Berner and Berner 1996). Its concentration in natural waters depends on several factors such as temperature, pH, presence or absence of ion complexes or precipitation of ions and colloids, solubility of fluorine-bearing minerals, anion exchange capacity of aquifer materials [(OH) for F], well depth, the size and type of geological formations through which the water flows and the time water is in contact with a particular formation (Apambire et al. 1997; Kim and Jeong 2005). Areas with semi-arid climate, crystalline igneous rocks and alkaline soils are more prone to the fluoride enrichment (Handa 1975; Sujatha 2003).

The study area lies in the semi-arid region of the Rajasthan state with an average mean annual rainfall of 481 mm. It is seen that these areas of less rainfall have higher content of fluoride as compared to other regions of the state (Deshkar et al. 1999; Vikas 2009). Physiographically, it is found that the plain regions of the study area have high fluoride content in groundwater and are concentrated mostly in the discharge areas (i.e. towards the southeast and south of study area, Fig. 8) than in the recharge areas with a trend of fluoride enrichment along the direction of flow. These observations are in agreement with the results obtained by Gaciri and Davis (1993), Qinghai et al. (2007) and Vikas et al. (2009). In general, fluoride derives mainly from the lithological sources (Hem 1991). It seems more appropriate that rocks rich in fluoride minerals have contributed to the fluoride enrichment in groundwater

**Fig. 5** Piper diagram showing hydrochemical facies of groundwater

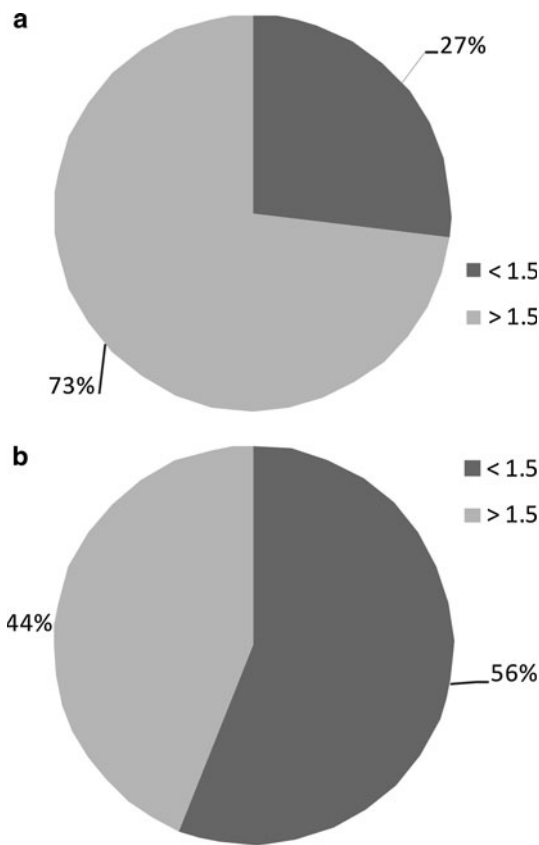


**Table 3** Spatial and depth-wise distribution of fluoride in mg/l

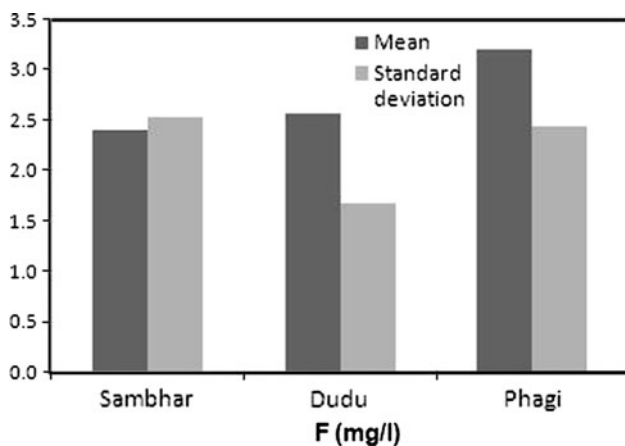
	Minimum	Maximum	Mean	Standard deviation	% of samples with F		
					<1	1–1.5	>1.5
Hard rock terrain	0.4	8.0	2.74	1.97	12	21	67
Gneiss	0.4	8.0	2.82	2.16	9	26	65
Schist	0.9	5.2	2.54	1.56	20	10	70
Alluvial terrain	0.5	9.3	2.69	2.43	18	24	58
Shallow aquifer	0.9	9.3	3.49	2.45	10	17	73
Deep aquifer	0.4	2.4	1.44	0.6	24	32	44

during weathering of rock types. Strunz (1970) reported about 150 fluorine-bearing minerals (63 silicates, 34 halides, 22 phosphates and 30 others), but many minerals may contain minor amounts of  $F^-$  replacing  $OH^-$ . High concentration of fluoride in water is common in pegmatite rich fractured hard rock terrains, which contain minerals like fluorite, topaz, fluor-apatite, villumite, cryolite, tourmaline and fluoride-replaceable hydroxyl ions in ferromagnesium silicates (Handa 1975; Ramesham and Rajagopalan 1985; Hem 1991; Jacks et al. 2005). Sedimentary horizons also have apatite as an accessory mineral and fluorite also often occurs as cement in some sandstones. In some cases, micas (muscovite and biotite) and amphiboles present in hard rock also contribute fluoride to water (Handa 1975).

Granitic gneisses, schists, quartzite, granite and pegmatite intrusives form the major hard rocks that occurs in the study area which has the presence of fluoride bearing minerals such as fluorite, apatite, biotite, hornblende, tourmaline and topaz. Among these minerals, fluorite ( $CaF_2$ ) and fluorapatite ( $Ca_3(PO_4)_2$ ) are most important. A minor occurrence of fluorspar deposit associated with granite gneiss and quartzite is noticed at Jaipur district in Rajasthan. Fluorite ( $CaF_2$ ) occurs in structurally weak planes like shear fracture zones, joints and host rock-vein quartz interface. Chemical weathering (hydrolysis) of minerals results in formation of Ca- and Mg-carbonates which serve as good sinks for fluoride ions (Jacks et al. 1993). In Rajasthan, sepiolite and palygorskite are the



**Fig. 6** Fluoride distribution in **a** shallow and **b** deeper aquifer groundwater samples of the study area



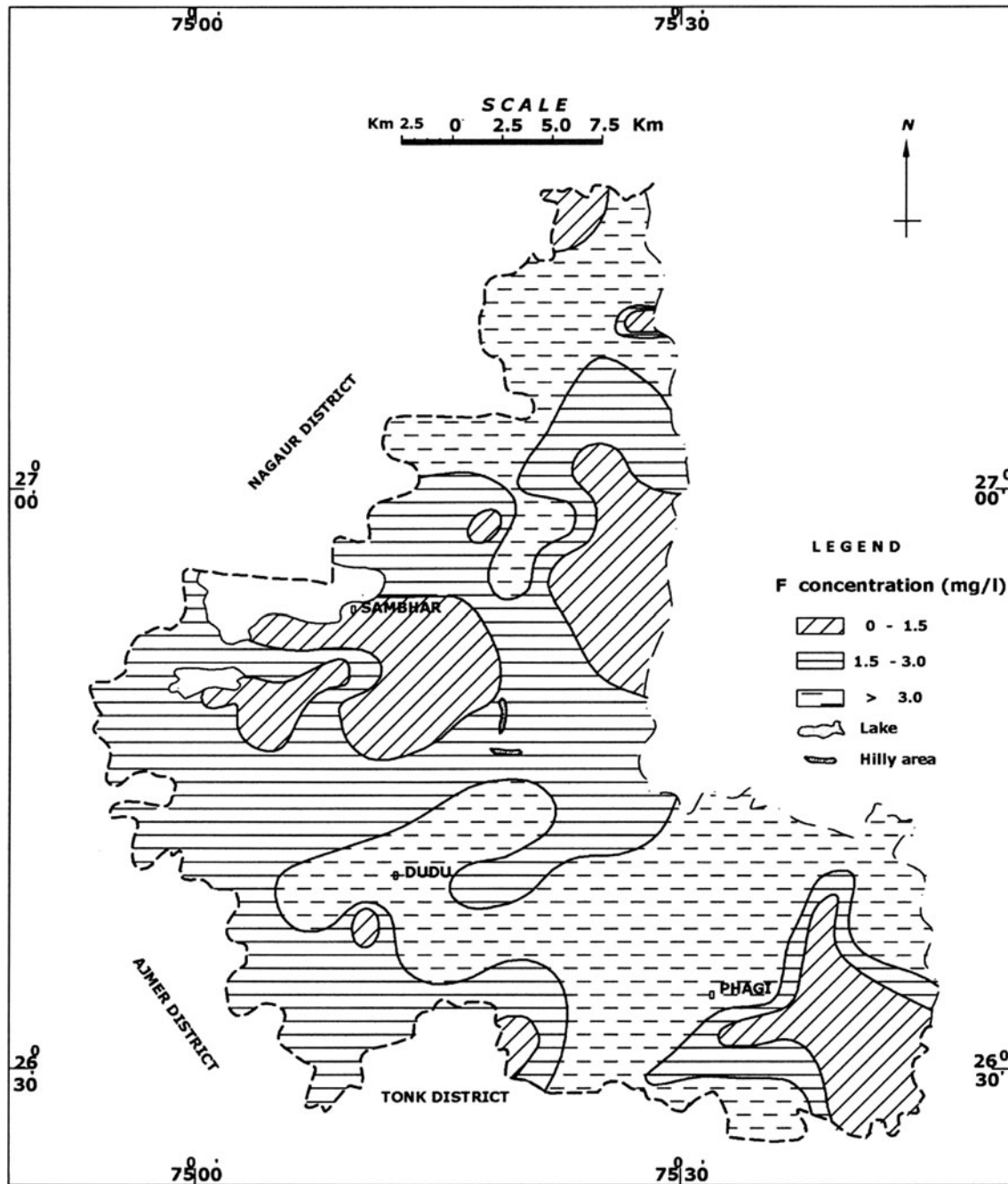
**Fig. 7** Fluoride concentration in different blocks of the study area

Mg-hydroxy-silicates that form the most important probable sources and sinks for  $F^-$  in the hydroxyl positions but at high pH values, sepiolite may turn into a source due to replacement of  $F^-$  by  $OH^-$  ions (Jacks et al. 2005). Fluoride ions from these fluorine bearing minerals present in hard rocks of the study area leach into the groundwater and contribute to high fluoride concentrations. Kundu et al. (2001); Saxena and Ahmed (2003); Tirumalesh et al.

(2007); Fantong et al. (2010) and Singh et al. (2011) also pointed out that high fluoride concentrations in water can be related to rocks containing fluoride like granites, granite gneisses, quartzite and pegmatite and fluoride is released into the soil and groundwater through weathering of the primary minerals in rocks. A positive relationship has been established between  $F^-$  content in the bulk rocks and in the associated groundwaters (Ramamohana Rao et al. 1993; Subba Rao et al. 1998; Saxena and Ahmed 2001; Subba Rao and John Devadas 2003; Fantong et al. 2010). Fluoride bearing minerals such as apophyllite, phlogophite, illite, hydromuscovite, biotite, chlorite, tourmaline and hornblende are generally found in clay dominated soil (Madhavan and Subramanian 2002; Kumar and Saxena 2011). Jacks et al. (2005) also found very high concentrations of fluoride in calcrete samples collected from arid areas of the Indian granitic terrain. The aquifers in the study area comprise alternate beds of sand, gravel and clay and hence some quantity of fluoride in groundwater is contributed from hydration of the above minerals present in the clay horizons. Fractions of soil in a high fluoride area neighbouring Jaipur district in Rajasthan have been found to contain about 10 (sand) to 130 (clay) mg/kg fluoride (Madhavan and Subramanian 2002). Apart from natural sources, a minor amount of fluoride may be contributed through anthropogenic activities. Modern agricultural practice, which involves the application of fertilizer and pesticides, also contributes fluoride to groundwater. A positive correlation of  $F^-$  with phosphate has been reported by Shukla et al. (1993), which can be attributed to contribution of phosphatic fertilizers, which are being used extensively in the study area. It has been reported elsewhere that phosphatic fertilizers can provide  $F^-$  as high as 25,670 mg/kg to the soils (Ravindra and Garg 2007).

The variation in fluoride content in the groundwater samples of shallow and deeper aquifer zones are believed to be the result of the interplay of several factors. The vertical geochemical zoning in the groundwater suggests that there is little hydraulic continuity between the shallow and deeper zones, which could be due to the presence of different recharge sources for both shallow and deeper aquifers. Otherwise both aquifers would have similar chemical quality. This is also in agreement with the observations of Subba Rao et al. (1998) for the high fluoride groundwater in Visakhapatnam region, Andhra Pradesh, India where shallow aquifers that supply water to dug wells have higher concentrations of fluoride than those of bore wells from deep aquifers. In the study area, it is observed that the potential evapotranspiration (PE) is more than rainfall for most part of the year and hence, groundwater recharge is possible only during the peak period of monsoon. Therefore, rainfall recharge was not sufficient to contribute much to the deeper zones and is confined mainly





**Fig. 8** Spatial distribution map of fluoride in the study area

to the shallow aquifer zones, leading to the leaching of fluoride from the soil-clay weathered zone. Moreover, the enrichment of fluoride in groundwater is also influenced by the groundwater flow rate. In alluvial areas comprising of sand, silt and clayey formations, there is stagnant groundwater flow in the horizontal direction and strong evaporation vertically. The low hydraulic conductivity in the weathered zone enables the waters to have a long residence time with the aquifer materials, promoting greater leaching of fluoride. In addition, the clay minerals present in the

weathered zone and alluvial formations also contain F ions in substitution of part of OH ions, may be an additional source to the circulating groundwater. During the weathering of parent rocks, F/OH exchange-adsorption reactions occur in the clay minerals (Hem 1991; Subba Rao 2003) which could be responsible for the higher concentration of fluoride in the groundwater samples of shallow aquifer zones. On the contrary, weathering is not so prominent in the deeper zones, particularly below the water table leading to lesser leaching of fluoride in this zone. Studies carried

out in the crystalline terrains from different parts of India and world have revealed that shallow well waters contain more fluoride than deep well waters (Subba Rao et al. 1998; Zhang et al. 2007; Vikas et al. 2009; Brindha et al. 2011) which is in conformity with the present study. However, the fluoride concentrations in groundwaters of the study area are not uniform due to the variations in the presence and accessibility of fluoride-bearing minerals to water as well as the associated hydrochemical processes evident in the area.

#### Management of groundwater

The present study shows that 73 % of shallow open wells and 44 % of deep bore wells of the study area have  $F^-$  concentration above the maximum permissible limit (1.5 mg/l) as per BIS (2003) and WHO (2004) and hence are unsuitable for drinking purposes. Dental and skeletal fluorosis is reported from the study area due to the usage of such high fluoride groundwater. Hence, the supply of high-quality groundwater with safe concentrations of  $F^-$  should be the goal for the sustainable management of groundwater in the area. The short-term solution to minimise the fluoride level in drinking water could be the use of domestic defluoridation filters. Villages that are suffering from fluoride problem above the permissible limits are provided with hand pumps attached with AA (activated alumina) filters under the 'Integrated Fluoride Mitigation programme' initiated by Government of Rajasthan. As a measure of fluoride mitigation in the study area, Public Health and Engineering department (PHED), Government of Rajasthan provides safe drinking water to those villages affected by fluoride contamination. The fluoride levels in groundwater can be lowered by the artificial recharge of groundwater through the rainwater harvesting and by digging deep bore wells as the deeper aquifer samples have less fluoride concentration in the study area. Bore well waters with low concentration (<0.5 mg/l) of fluoride can be mixed with water having higher concentration of fluoride (>1.5 mg/l) and supplied. Nalgonda (based on addition of lime and alum) and Prasanthi defluoridation techniques (based on adsorption using activated alumina) can be practiced (Bulusu and Nawlakhe 1990) on domestic and village basis. Efficient irrigation practices such as drip irrigation should be preferred to prevent weathering and leaching and to reduce evaporation and water consumption. As indicated by the relationship between soil pH and  $F^-$  in groundwater, lowering alkalinity may also decrease the mobility of  $F^-$ . Since gypsum is fairly abundant in Rajasthan, the gypsum treatment method of alleviating soil alkalinity may be feasible and cost effective in the study area. Environmental awareness of the health implications of  $F^-$  should be spread through education of the public and community participation.

#### Conclusions

The concentration of fluoride in groundwater is not uniform in the study area. The geochemistry of groundwater, relationship between physicochemical parameters, hydrogeology and geologic setting were correlated to define the origin and the geochemical mechanisms of fluorine enrichment in groundwater. Majority of the study area shows  $F^-$  concentration above the maximum permissible limit of 1.5 mg/l. As compared to alluvial formations, groundwater in the hard rock areas show higher fluoride concentration and more fluoride enrichment is noticed in samples collected from the granite gneissic terrain when compared to those in the schist. Fluoride enrichment is higher in shallow aquifers as compared to deeper aquifer irrespective of lithology. Chemical weathering under arid to semi-arid conditions with relatively high alkalinity favours high concentration of fluoride in groundwater. Rock–water interaction is the main process in which fluorine-bearing minerals are decomposed/dissociated from the source rock and fluoride is dissolved in the groundwater by dissolution. The relatively low concentrations of  $F^-$  in deeper aquifers can be attributed to the low vertical permeability of the shallow aquifer inhibiting easy entry of  $F^-$  to deeper groundwater. The better horizontal permeability of the shallow aquifers resulted in the lateral enrichment of  $F^-$  in the groundwater of shallow aquifers from the weathered formations of the study area. The clay layers in the alluvial formations act as an aquitard retarding the vertical percolation of the infiltrated water and hence increase the interaction/residence time in the aquifer system, thereby having longer contact time for dissolution of  $F^-$ -bearing minerals present. A higher rate of evapotranspiration, intensive and long term irrigation and heavy use of fertilizers are the supplementary factors that further increase the  $F^-$  content in the groundwater. Since dental and skeletal fluorosis are reported, dilution by blending, artificial recharge, efficient irrigation practices, well construction and use of Ca-enriched food supplements are the common groundwater management strategies that are to be adopted to combat the effect of fluoride pollution of groundwater.

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#### References

- Aiuppa A (2009) Degassing of halogens from basaltic volcanism: insights from volcanic gas observations. *Chem Geol* 263:99–109

- Aiuppa A, Bonfatti P, Brusca L, D'alessandro W, Federico C, Parello F (2001) Evaluation of the environmental impact of volcanic emissions from the chemistry of rainwater: Mount Etna (Sicily). *Appl Geochem* 16:985–1000
- Apambire WB, Boyle DR, Michel FA (1997) Geochemistry, genesis and health implications of fluoriferous groundwaters in the upper regions of Ghana. *Environ Geol* 33:13–24
- American Public Health Association (APHA) (1995) Standard methods for the examination of water and wastewater, 19th edn. APHA, Washington DC
- Berner EK, Berner Robert (1996) Global environment—water, rain and geochemical cycles. Prentice Hall, New Jersey
- BIS (2003) Drinking Water Standards (I.S 10500-91, Revised 2003)
- Brindha K, Rajesh R, Murugan R, Elango L (2011) Fluoride contamination in groundwater in parts of Nalgonda District, Andhra Pradesh, India. *Environ Monit Assess* 172:481–492
- Bulusu KR, Nawlakhe WG (1990) Defluoridation of water with activated alumina, batch operations. *Ind J Environ Health* 32:197–218
- CGWB (2006) Groundwater year book, Rajasthan. Central Ground Water Board, Ministry of Water Resources, Government of India, p 167
- CGWB (2007) Ground water scenario of Jaipur district, Rajasthan. District groundwater brochure, Central Ground Water Board, Ministry of Water Resources, Government of India, pp 1–25
- Chaudhary V, Kumar M, Sharma M, Yadav BS (2010) Fluoride, boron and nitrate toxicity in ground water of northwest Rajasthan, India. *Environ Monit Assess* 161:343–348
- Choubisa SL (2001) Endemic fluorosis in southern Rajasthan. *Fluoride* 34:61–70
- Cuoco E, Verrengia G, De Francesco S, Tedesco D (2010) Hydrogeochemistry of Roccamonfina volcano (Southern Italy). *Environ Earth Sci* 61:525–538
- Deshkar SM, Deshmukh AN, Vali SA (1999) Safe limit of fluoride content in drinking water in different climatic zones of India. *Ind J Environ Health* 2(1):17–20
- Fantong WY, Satake H, Ayonghe SN, Suh EC, Adelana SMA, Fantong EBS, Banseka HS, Gwanfogbe CD, Woincham LN, Uehara Y, Zhang J (2010) Geochemical provenance and spatial distribution of fluoride in groundwater of Mayo Tsanaga River Basin, Far North Region, Cameroon: implications for incidence of fluorosis and optimal consumption dose. *Environ Geochem Health* 32:147–163
- Gaciri SJ, Davis TC (1993) The occurrence and geochemistry of fluoride in some natural waters of Kenya. *J Hydrol* 143:395–412
- Handa BK (1975) Geochemistry and genesis of fluoride containing groundwater in India. *Groundwater* 13:275–281
- Harrison Paul TC (2005) Fluoride in water: A UK perspective. *J Fluor Chem* 126:1448–1456
- Hem JD (1991) Study and interpretation of the chemical characteristics of natural water. Book 2254, 3rd edn. Scientific Publishers, Jodhpur, India
- Jacks G, Rajagopalan K, Alveteg T, Jonsson M (1993) Genesis of high-F groundwaters, Southern India. *Appl Geochem (Suppl 2)*: 241–244
- Jacks G, Bhattacharya P, Chaudhary V, Singh KP (2005) Controls on the genesis of some high-fluoride groundwaters in India. *App Geochem* 20:221–228
- Kim K, Jeong GY (2005) Factors influencing natural occurrence of fluoride-rich groundwaters: a case study in the southeastern part of the Korean Peninsula. *Chemosphere* 58:1399–1408
- Kumar S, Saxena A (2011) Chemical weathering of the Indo-Gangetic Alluvium with special reference to release of fluoride in the groundwater, Unnao district, Uttar Pradesh. *J Geol Soc India* 77:459–477
- Kundu N, Panigrahi MK, Tripathy S, Munshi S, Powell MA, Hart BR (2001) Geochemical appraisal of fluoride contamination of groundwater in the Nayagarh district of Orissa. *India Environ Geol* 41:451–460
- Madhavan N, Subramanian V (2002) Fluoride in fractionated soil samples of Ajmer district, Rajasthan. *J Environ Monit* 4:821–822
- Maithani PB, Gurjar R, Banerjee R, Balaji BK, Ramachandran S, Singh R (1998) Anomalous fluoride in groundwater from western part of Sirohi district, Rajasthan and its crippling effects on human health. *Curr Sci* 74:773–777
- Muralidharan D, Nair AP, Sathyanarayana U (2002) Fluoride in shallow aquifers in Rajgarh tehsil of Churu district, Rajasthan—an arid environment. *Curr Sci* 83:699–702
- Qinghai G, Yanxin W, Teng M, Rui M (2007) Geochemical processes controlling the elevated fluoride concentrations in groundwaters of the Taiyuan Basin, Northern China. *J Geochem Explor* 93:1–12
- Ramamohana Rao NV, Suryaprakasa Rao K, Schuiling RD (1993) Fluorine distribution in waters of Nalgonda district, Andhra Pradesh, India. *Environ Geol* 21:84–89
- Ramesham V, Rajagopalan KJ (1985) Fluoride ingestion into the natural water of hard rock areas, Peninsular India. *J Geol Soc India* 26:125–132
- Ravindra K, Garg VK (2007) Hydro-chemical survey of groundwater of Hisar city and assessment of defluoridation methods used in India. *Environ Monit Assess* 132(1–3):33–43
- Saxena VK, Ahmed S (2001) Dissolution of fluoride in groundwater: a water-rock interaction study. *Environ Geol* 40:1084–1087
- Saxena VK, Ahmed S (2003) Inferring the chemical parameters for the dissolution of fluoride in groundwater. *Environ Geol* 43:731–736
- Shukla S, Singh P, Rajwansi P, Singh V, Gupta MK, Srivastava S, Dass S (1993) Fluoride content of commonly used chemical fertilizers. Proceedings of Indo-German conference on impact of modern agriculture on environment, Hisar Agriculture University, Hisar, India 111:59–62
- Singh CK, Rina K, Singh RP, Shashtri S, Kamal V, Mukherjee S (2011) Geochemical modeling of high fluoride concentration in groundwater of Pokhran area of Rajasthan, India. *Bull Environ Contam Toxicol* 86:152–158
- Sinha RK (1997) Fluorosis—a case study from the Sambhar Salt Lake region in Jaipur, Rajasthan, India. *Environ* 17:259–262
- Strunz H (1970) Mineralogische Tabellen, 5. Aufl. Geest und Portig, Leipzig, Germany
- Subba Rao N (2003) Groundwater quality: focus on fluoride concentration in rural parts of Guntur district, Andhra Pradesh, India. *Hydrol Sci* 48(5):835–847
- Subba Rao N, John Devadas D (2003) Fluoride incidence in groundwaters in a part of Peninsular India. *Environ Geol* 45:243–253
- Subba Rao N, Krishna Rao G, John Devadas D (1998) Variation of fluoride in groundwaters of crystalline terrain. *J Environ Hydrol* 6(3):1–5
- Sujatha D (2003) Fluoride levels in the groundwater of the south-eastern part of Ranga Reddy district, Andhra Pradesh, India. *Environ Geol* 44:587–591
- Susheela AK (1999) Fluorosis management programme in India. *Curr Sci* 77(10):1250–1256
- Suthar S, Garg VK, Jangir S, Kaur S, Goswami N, Singh S (2007) Fluoride contamination in drinking water in rural habitations of northern Rajasthan, India. *Environ Monit Assess* 145:1–6
- Tirumalesh K, Shivanna K, Jalihal AA (2007) Isotope hydrochemical approach to understand fluoride release into groundwaters of Ilkalarea, Bagalkot District, Karnataka, India. *Hydrogeol J* 15:589–598

- UNICEF (1999) State of the art report on the extent of fluoride in drinking water and the resulting endemicity in India. Report by Fluorosis and Rural Development Foundation for UNICEF, New Delhi
- Vikas C (2008) Geochemistry of groundwater—an overview of sporadic nitrate contamination in parts of Jaipur district, Rajasthan, India *J Appl Geochem* 10(2):166–172
- Vikas C (2009) Occurrence and distribution of fluoride in groundwaters of central Rajasthan and associated health hazards. *J Environ Sci Eng* 51(3):169–174
- Vikas C, Kushwaha RK, Pandit MK (2009) Hydrochemical status of groundwater in District Ajmer (NW India) with reference to fluoride distribution. *J Geol Soc India* 73:773–784
- World Health Organisation (WHO) (2004) Guidelines for drinking water quality recommendations, 3rd edn. World Health Organisation, Geneva
- Zhang B, Hong M, Zhang B, Zhang X, Zhao Y (2007) Fluorine distribution in aquatic environment and its health effect in the Western Region of the Songnen Plain, Northeast China. *Environ Monit Assess* 133:379–386