

Impact of urbanization coupled with drought situations on groundwater quality in shallow (basalt) and deeper (granite) aquifers with special reference to fluoride in Nanded-Waghala Municipal Corporation, Nanded District, Maharashtra (India)

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Abstract Rapid expansion in urbanization and industrialization coupled with recent drought conditions has triggered unplanned groundwater development leading to severe stress on groundwater resources in many urban cities of India, particularly cities like Nanded, Maharashtra. In the quest of tapping drinking water requirement, due to recent drought conditions, people from the city are piercing through entire thickness of shallow basalt aquifers to reach productive deeper granite aquifers. Earlier reports from Nanded and surrounding districts suggest that

deeper granite aquifer is contaminated with fluoride (geogenic). The study aimed to find out variations in fluoride concentration in shallow basalt (10–167 m) and deeper granite aquifers (below 167 m) and to find out the relationship between fluoride and other ions. Study suggests that concentration of fluoride in shallow basalt aquifer is within maximum permissible limits of Bureau of Indian Standards and deeper granite aquifer contains as high as 4.9 mg/l of fluoride and all samples from granite aquifers are unfit for human consumption. The groundwater from basalt aquifer is mainly Ca-HCO₃-Cl type, and from granite aquifer, it is Ca-Na-Cl type. The correlation plot between F⁻ vs. pH, Na⁺ and HCO₃⁻ shows a positive correlation and an inverse relationship with Ca²⁺ in both aquifers. As recommendations, it is suggested that granite aquifers should not be tapped for drinking purposes; however, in drought situations, water from this aquifer should be blended with treated surface water before supplying for drinking purposes. Efforts may be made to utilize 1.35 MCM of rainwater from available rooftop, which is sufficient to cater for the needs of ~40,800 people annually. Most effective defluoridation techniques like electrolytic de-fluoridation (EDF), ion exchange and reverse osmosis may be adopted along with integrated fluorosis mitigation measures.

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Introduction

Urbanization is increasing worldwide, as in 1900, only 10% lived in cities and for the year their number is estimated to be at 50% (UN 1991). In Maharashtra, ~45% of the population lives in urban areas as compared to all India with an average of ~31%. This rapid expansion in urbanization and industrialization has triggered unplanned groundwater development leading to severe stress on groundwater resources in many urban cities of India. With depleting resources from shallow basalt aquifers (100 m), coupled with drought conditions, the users are tapping deeper granite aquifers (below 167 m), which have proved to be counterproductive economically and ecologically as it is geogenically contaminated with fluoride.

Some elements are essential in trace amount for human beings, while their higher concentration can cause toxic effects, and fluoride (F^-) is one of them (CGWB 1999), and it is a conclusive fact that the concentration of F^- between 0.6 and 1.0 mg/l is essential in potable water to protect tooth decay and enhance bone development, while their higher concentration may lead to fluorosis (Apambire et al. 1997; Kundu et al. 2001; BIS 2012). About 30 nations with 67 million people around the globe are facing one or another type of fluorosis, and India is one of them. In India, more than 20 states with 66 million people, of which 6 million are children (below the ages of 14 years), are suffering from fluorosis (Madhnure et al. 2007). The granite rocks contain an average of 810 $\mu\text{g/g}$ of fluoride in mineral form whereas basalt rock (shallow aquifer) contains 360 $\mu\text{g/g}$ (Wedepohl 1969).

The main sources of fluoride in groundwater are F^- -bearing minerals present in rocks, like fluorite, fluorapatite, cryolite and apophyllite as well as F replacing OH in ferromagnesium silicates (amphiboles and micas) and soil consisting of clay minerals (Ramesam and Rajagopalan 1985; Madhnure et al. 2007). Degree of weathering and leachable F present in the rocks of an area plays an important role in deciding F content in water rather than the mere presence of F-bearing minerals in bulk soils/rocks (Ramesam and Rajagopalan 1985). The alkaline nature of groundwater with high HCO_3^- and moderate EC is a favourable condition for dissolution of F-bearing minerals (Saxena and Ahmed 2001; Madhnure et al. 2007).

High concentrations of fluoride in groundwater have been reported from many parts of the world, particularly

India, China and Sri Lanka' (Ayoob and Gupta 2006), and many of the world's high-fluoride areas are underlain by crystalline igneous and metamorphic rocks (i.e., parts of India, Sri Lanka, Senegal, Ghana, Cameroon, Tanzania, South Africa, the Pampean Ranges in southern South America and Scandinavia (Ayoob and Gupta 2006)). Variations in concentration of fluoride in shallow and deeper aquifers have been reported from many parts of India (Subba Rao 2006; Prem Babu et al. 2004; Madhnure et al. 2007; Madhnure et al. 2016; Reddy et al. 2010; Reddy 2014). Sayeed Juned et al. (2015) reported the occurrence of 'F' in the range 0.73–2.69 mg/l from southern parts of Nanded city.

The study area, Nanded, is covered by basalt rock, the thickness of which varies from ~167 to 196 m, below which granites occurs. The study area, Nanded, is facing severe drought situations in the last few years. In quest of tapping drinking water, bore wells are drilled deeper and the entire thickness of basalt is pierced through and thus groundwater from deeper granitic aquifer is tapped, and generally, granite is the source of F in groundwater. Keeping this very aspect in mind, the present study is carried out to compare groundwater quality from shallow and deeper aquifer with special reference to "fluoride".

Study area

Nanded-Waghala Municipal Corporation (NWMC) is located on banks of river Godavari, falling in Survey of India toposheet 56E/8. The Municipal Corporation is spread over an area of ~44 km^2 and bounded by north latitude $19^\circ 10.015'$ – $19^\circ 12.445'$ and east longitude $77^\circ 16.621'$ – $77^\circ 20.693'$ at topographic elevations from 360 to 380 m above mean sea level (m amsl) (Fig. 1). The area receives ~900 mm normal annual rainfall, whereas during the years 2014 and 2015, it received only 50 and 72% rainfall to normal rainfall. As per 2011 census, the population of the town is 5.5 lakh and the total water requirement for the year 2026 is estimated to be at 118.64 million litres/day (MLD) whereas, presently, ~110 MLD of water is supplied (Rode 2009).

Hydro geological setup

Geologically, the study area is covered by basalt which is underlain by granites. Granites occur at different

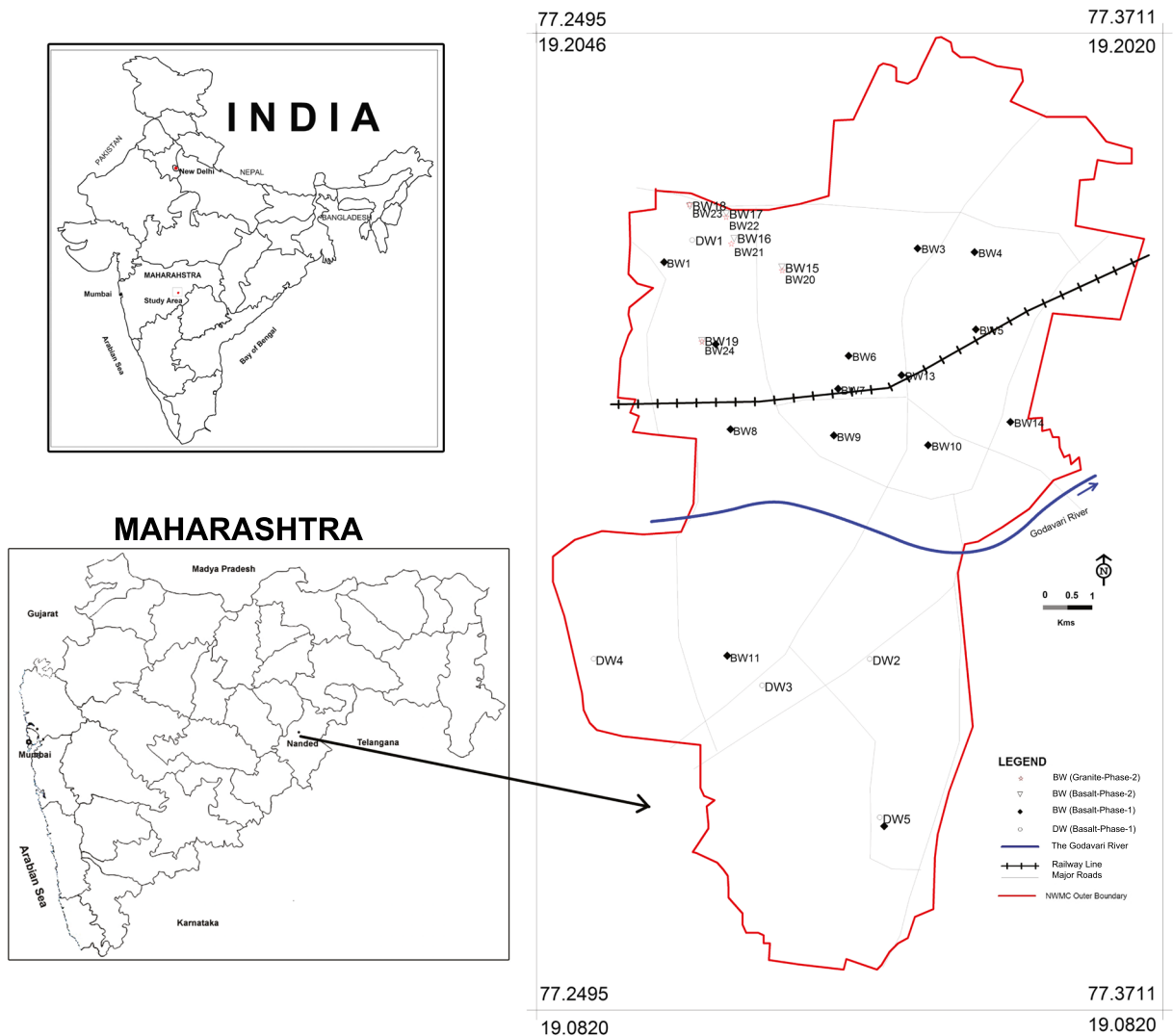


Fig. 1 Location of the study area

depths depending on the elevation in the area i.e. at 196 m on the right bank of the river at Vishnupuri and at 167 m on the left bank at Kabra Nagar (Madhnure 2014). Basalt is massive, fine grained and bluish grey to brown in colour, and each flow is separated by clay beds (intertrappean) with 0.25–3.25 m thickness and the average thickness of each flow is 24 m. The colour of the granite depends upon the colour of feldspar in it. Grey granite consisting of fluoride-bearing dark-coloured minerals occur at the upper level at deeper aquifers such as amphiboles and biotite (Fig. 2a) and pink-coloured hybrid granites from the lower level of deeper aquifers with dark-coloured amphiboles and mica (Fig. 2b). The lithological sequence from the Vishnupuri Exploratory

well confirms the existence of eight flows (Fig. 3) (Madhnure 2003). Groundwater occurs under unconfined to semi-confined/confined conditions, and water levels are at shallower levels (2.3–10.4 m below ground level (m bgl)) on the right bank of river Godavari and at deeper levels (5.3–22.8 m bgl) on the left bank during the month of February 2012 (Madhnure 2004). In recent past, the water levels have still gone below this level due to more extraction coupled with droughts. Yield from basalt aquifer ranges from 10 to 325 m³/day, and from granites it ranges from 10 to 250 m³/day. Transmissivity in basalt aquifer ranges from 14 to 86 m²/day having storativity of 0.002–0.0095 (Madhnure 2004).

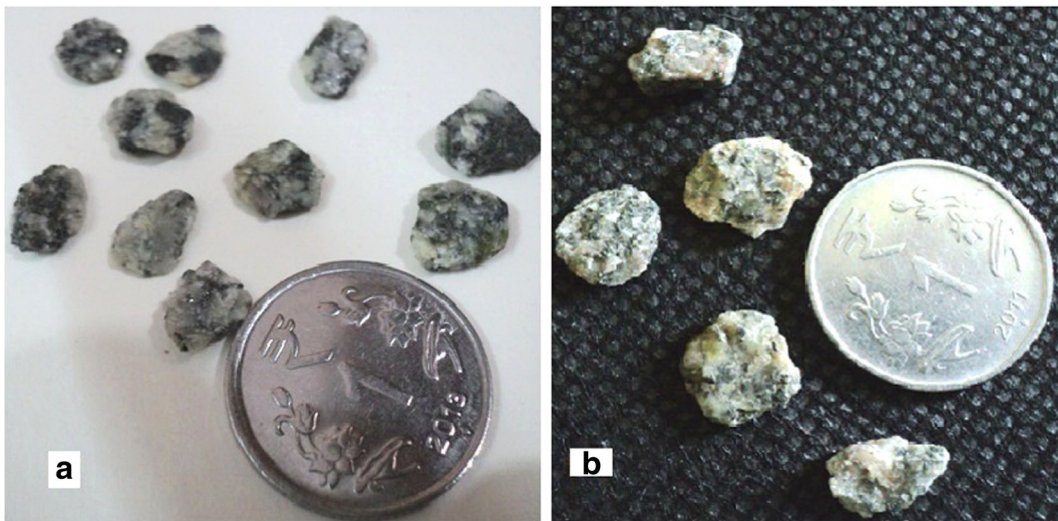


Fig. 2 a, b Granite rock cutting from shallow and deeper levels from deeper aquifers

Analytical techniques and presentation of data

To assess the aquifer-wise variations in fluoride concentrations, samples were collected in two phases (Fig. 1).

Phase 1: Nineteen groundwater samples from shallow basalt aquifers (dug wells and shallow bore wells) and one surface water sample from river Godavari at Langar house Gurudwara were collected during February 2002 for normal analysis and two (shallow bore wells) from basalt aquifers for heavy metal analysis (Fe, Cu, Zn and Pb) (Fig. 1 and Table 1).

Phase 2: Ten groundwater samples (all bore wells) tapping shallow and deeper aquifers from five locations (with proximity with each other) were collected during the pre-monsoon season of 2015 (May) (Fig. 1 and Table 1).

Samples during phase 2 were collected immediately after encountering a fractured zone in each aquifer as per procedure suggested by Handa (1974). For preservation, storage and analysis of samples, guidelines suggested by APHA (1998) were followed. Total 12 parameters (viz., pH, TDS, TH, Ca, Na, Mg, K, HCO_3^- , Cl^- , SO_4^- , NO_3^- and F^-) are analysed by using standard methods (APHA 1998).

pH and EC are measured in the field by using a portable pH metre (Hanna Instruments). The value of EC is used to calculate total dissolved solids (TDS) (HEM 1991). The sum of calcium and magnesium concentrations is normally defined as total hardness (expressed as CaCO_3) (APHA 1998). Ca is determined by titration method using a standard

ethylenediaminetetraacetic acid (EDTA) solution. Magnesium is estimated by the difference between total hardness and calcium (APHA 1998). Sodium and potassium are determined by a SYSTRONICS flame photometre at 589- and 766.5-nm wavelengths (APHA 1998). Chloride is determined by argentometric titration method, sulphate and nitrate by spectrophotometric method at 420 and 275 nm. Fluoride is determined by SPADNS colorimetric method (APHA 1998) and iron, copper, zinc and lead by spectrophotometric method. The ionic balance between total cation and total anion is within an acceptable range of $\pm 5\%$ (APHA 1998). Suitability of groundwater for drinking purposes is assessed based on the Bureau of Indian Standards (BIS 2012). Characteristics of groundwater are identified by using a Piper diagram (Hill 1940; Piper 1944), and correlation of regression between F^- vs. other ions is studied by a scatter plot.

Results and discussions

In the present study, the results of phase 2 samples are considered for knowing the suitability for drinking purposes, and for fluoride distributions, phase 1 and phase 2 samples are considered.

Hydrogen ion concentration (pH)

In most natural waters, pH value is dependent on the carbon dioxide-carbonate-bicarbonate equilibrium

LITHOLOGY, DEPTH Vs. PENETRATION RATE AT VISHNUPURI VILLAGE, NANDED DISTRICT

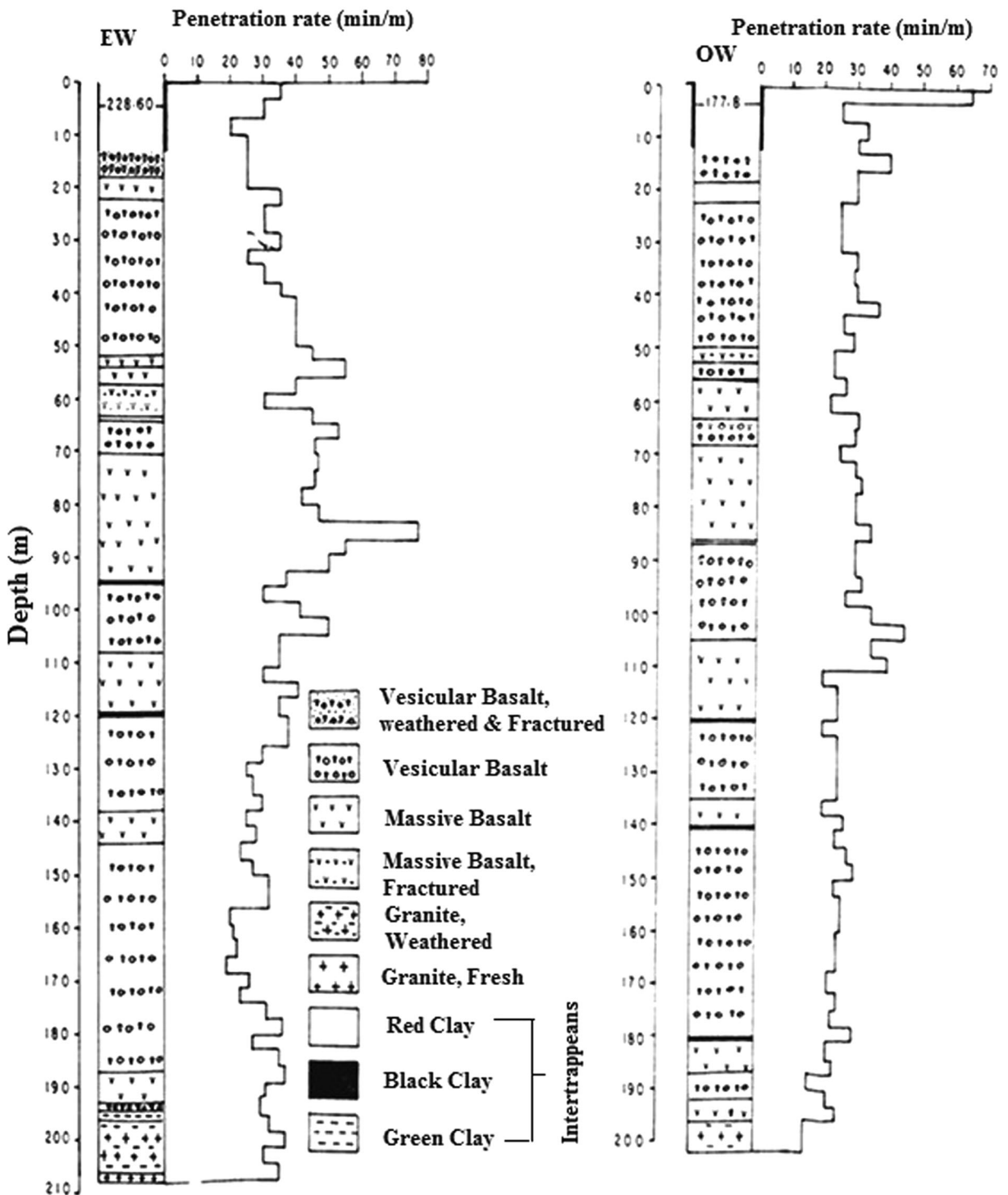


Fig. 3 Lithological section, depth vs. penetration rate at a Vishnupuri Exploratory well

Table 1 Results of groundwater quality tapping shallow basalt aquifer (phases 1 and 2)

S. no.	Sample ID	X	Y	Aquifer	Depth (m)	pH	TDS (mg/l)	TH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	F ⁻	Phase
1	DW ¹	77.2813	19.1786	Basalt	10.6	7.94	675	475	62	78	63	1.2	354	152	76	68	0.8	1
2	DW ²	77.3188	19.1264	Basalt	10.9	7.63	640	455	52	79	44	1.2	275	131	86	111	0.7	1
3	DW ³	77.2981	19.1236	Basalt	18.95	7.83	1642	430	30	86	425	2	519	117	700	26	1.2	1
4	DW ⁴	77.2652	19.1276	Basalt	11.1	7.86	860	300	38	50	218	1.6	506	124	128	52	0.8	1
5	DW ⁵	77.3219	19.1069	Basalt	8.7	7.59	653	400	46	69	52	52	421	113	76	37	0.7	1
6	BW1	77.276	19.176	Basalt	60	7.98	708	455	46	83	84	1.6	415	142	68	80	0.9	1
7	BW2	77.2866	19.1657	Basalt	60	7.81	757	485	80	69	77	1.7	366	131	142	76	0.8	1
8	BW3	77.3251	19.1766	Basalt	60	7.55	841	600	124	70	49	1.2	299	188	126	135	0.5	1
9	BW4	77.3362	19.1759	Basalt	60	7.75	459	330	70	38	34	0.4	256	96	24	71	1.1	1
10	BW5 ^a	77.337	19.1664	Basalt	60	7.72	928	355	32	67	216	1.5	421	167	214	24	0.9	1
11	BW6	77.3125	19.1637	Basalt	60	7.74	773	535	124	55	55	1.8	336	145	114	113	0.7	1
12	BW7	77.3107	19.1597	Basalt	60	7.55	1329	740	90	125	204	2	403	418	143	148	0.9	1
13	BW8	77.2901	19.1552	Basalt	60	7.4	938	680	88	112	65	1.6	470	184	146	110	0.7	1
14	BW9	77.3102	19.154	Basalt	60	7.67	746	475	96	57	96	1.6	366	121	120	75	0.6	1
15	BW10 ^b	77.3286	19.1524	Basalt	60	7.8	1255	425	34	83	300	0.8	549	220	200	148	0.9	1
16	BW11	77.2911	19.1274	Basalt	60	7.84	1164	370	20	78	328	1.2	775	124	212	20	0.9	1
17	BW12	77.3228	19.1058	Basalt	60	7.76	591	415	79	53	53	1.2	348	106	64	64	0.7	1
18	BW13	77.3229	19.1611	Basalt	60	7.91	700	320	34	57	142	2.5	354	156	105	25	1.2	1
19	BW14	77.3444	19.1549	Basalt	60	7.34	1360	535	180	21	312	1.5	244	468	79	236	0.6	1
20	BW15	77.2989	19.1749	Basalt	30	8.2	670	384	58	58	79	1	236	150	32	82	1.21	2
21	BW16	77.2894	19.1786	Basalt	29	8.2	1515	868	45	184	148	2	408	446	106	50	1.2	2
22	BW17	77.2877	19.1817	Basalt	106	8.3	1222	632	58	119	146	2	272	338	52	172	1.4	2
23	BW18	77.2806	19.1828	Basalt	106	8.4	670	388	37	72	60	2	248	90	40	57	1.31	2
24	BW19	77.2839	19.1662	Basalt	137	8.5	962	384	104	30	172	1	236	240	134	22	1.35	2
25	BW20	77.299	19.1745	Granite	228.6	7.8	939	196	48	18	210	0	96	290	115	6	2.85	2
26	BW21	77.2889	19.178	Granite	204	9	884	148	37	202	14	1	185	272	123	7	4.9	2
27	BW22	77.2877	19.1813	Granite	207	8.4	975	320	80	194	29	1	174	280	93	61	3.95	2
28	BW23	77.2805	19.183	Granite	167	8.6	780	208	64	177	12	1	92	240	95	47	3.7	2
29	BW24	77.2839	19.1661	Granite	243	8	702	180	26	167	28	2	140	216	67	41	4.8	2
30	Surface water	77.6161	19.1466			7.8	318	185	36	54	23	4.4	226	35	52	2	0.48	

^a Fe, 0.16; Cu, 0.051; Zn, below detectable limits

^b Fe, Cu, Zn and Pb are below detectable limits (mg/l)

(Karanth 1987). The pH value is less than 7 if the H^+ ions exceed the OH^- ions, and it is more than 7 when OH^- ions exceed H^+ ions (Karanth 1987).

In the groundwater from the study area, pH in basalt aquifer ranges from 8.2 to 8.5 and from 7.8 to 9 in granite aquifer. It is noticed that the average pH from shallow basalt aquifer is lower than that from deeper granite aquifer, and this may be due to recharge and flushing of shallow aquifers during the rainy season (Gupta and Sharma 1995; Gupta and Deshpande 2003; Jacks et al. 2005) and longer residence time in deeper aquifers (Handa 1975; Ramamohana Rao et al. 1993; Wodeyar and Sreenivasan 1996; Subba Rao et al. 1998; Saxena and Ahmed 2001; Subba Rao and Rao 2003; Madhnure et al. 2007; Madhnure et al. 2016).

Total dissolved solids

The concentration of TDS in groundwater depends upon the nature of rock formations, porosity and permeability, depth through which water is passing, climate and geomorphology of the area. Contamination of water by human and animal activities including septic tanks disposal and agricultural practices and mixing of different types of water also affects TDS (Handa 1975; CGWB 1998). In general, the TDS value in basaltic shallow aquifers of the Maharashtra state varies between 35 and 4200 mg/l (CGWB 1998).

In the study area, the concentration of TDS from shallow basalt aquifer ranges from 670 to 1515 mg/l (average 1008) and from deeper granite aquifers 702 to 975 mg/l (average 856). As compared to deeper granite aquifers, shallow basalt aquifers have high TDS, and this may be due to more dissolution of minerals in shallow aquifers.

Total hardness

Total hardness is the capacity of water to neutralize soap and is the sum of Ca^{2+} and Mg^{2+} (Handa 1975; APHA 1998). Total hardness in groundwater from basaltic shallow aquifers of the Maharashtra state varies between 15 and 2295 mg/l (CGWB 1998). In the study area, total hardness in shallow aquifers ranges from 384 to 868 mg/l (avg 531) and in deeper aquifer it ranges from 148 to 320 mg/l (avg 210).

Calcium

The average abundance of Ca^{2+} in the earth's crust is 4.9%, and in groundwater, it varies from 1 to more than 500 mg/l (APHA 1998). In most of the naturally occurring groundwater, calcium is the main cation due to its abundance in the earth's crust and high mobility (Hem 1991). The most common forms of Ca are $CaCO_3$ and $CaMgCO_3$. The principal sources of calcium in groundwater are minerals present in igneous rock, especially silicates, like plagioclase and pyroxenes (Handa 1975; Hem 1991; APHA 1998). It is also present in the form of adsorbed ions on negatively charged mineral surfaces in soils and rocks. Calcium in groundwater from shallow basaltic rock formations of the Maharashtra state varies between 4 and 329 mg/l (CGWB 1998). In the study area, Ca in shallow aquifers ranges between 37 and 104 mg/l (avg 60) and in deeper aquifer it ranges from 26 to 80 mg/l (avg 51).

Magnesium

Magnesium is the 8th most abundant mineral in the solar system (Handa 1974). The average abundance of Mg in the earth's crust is 2.1%, and in groundwater, it is more than 5 mg/l (APHA 1998). Weathering of basic igneous rocks such as dunites and pyroxenites; volcanic rocks such as basalts; metamorphic rocks like amphibolites, talc and tremolite schist; and sedimentary rocks such as dolomite is the main source of Mg^{2+} in the groundwater (Karanth 1987). Use of surface water for irrigation is another source of Mg^{2+} in groundwater (Kakkar et al. 1987; Hem 1991). In the groundwater from basaltic shallow aquifers of Maharashtra, the concentration of Mg^{2+} varies between 1 and 428 mg/l (CGWB 1998).

In the study area, Mg in shallow basalt aquifers ranges between 30 and 184 mg/l (avg 93) and in deeper granite aquifers it ranges from 12 to 29 mg/l (avg 20). As in most natural waters, in the study area also, the concentration of Mg is lower than Ca concentration, and this is an agreement with Hem (1991).

Sodium

The average abundance of Na^+ in the earth's crust is 2.5%; in soil, it is 0.02 to 0.62% and in groundwater it is generally 5 mg/l (APHA 1998). Silicate minerals such as labradorite ((Ca,Na)Al₁₋₂Si₃₋₂O₈ with 30–50% Na) and augite ((Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)₂O₆) in basalt

are the main sources of Na^+ in groundwater. The other sources are rainwater, dissolution of evaporite minerals and sodium disposal through septic tanks and industrial wastes (Handa 1975). Certain clay minerals and zeolite can increase the sodium concentration in groundwater by base exchange reaction (Karanth 1987). Sodium concentration in shallow basaltic aquifers of the Maharashtra state ranges between 3 and 644 mg/l (CGWB 1998).

In the study area, Na^+ concentration in shallow aquifers ranges between 60 and 172 mg/l (avg 121) and in deeper aquifers it ranges from 167 to 210 mg/l (avg 184). Deeper granite aquifers have higher concentrations of Na than shallow basalt aquifers.

Chloride

Chloride in the form of Cl^- is one of the major inorganic anions in groundwater and wastewater (APHA 1998). Hydrolysis of halite and related minerals, rainwater, irrigation and industrial effluents are the main sources of Cl^- in groundwater (Handa 1975; Karanth 1987; Kakkar et al. 1987; Hem 1991; CGWB 1998). Minerals like sodalite, mica, chloro-apatite and hornblende are the other minor sources of chloride in groundwater (Karanth 1987). Abnormal concentration of Cl^- in groundwater may result due to pollution of sewage wastes and planting of coconut trees (Karanth 1987). Chloride concentration in groundwater from basaltic aquifers of Maharashtra ranges between 7 and 1184 mg/l (CGWB 1998).

In the study area, concentrations of Cl^- in shallow basalt aquifers vary from 90 to 446 mg/l (avg 253) and in deeper granite aquifers it varies from 216 to 290 mg/l (avg 260). The source of chloride in groundwater is mainly due to its anthropogenic nature, and the occurrence of high Cl^- in deeper aquifer suggests interconnectivity between two aquifers.

Nitrate

Nitrogen present in the atmosphere reacts with rainwater and forms nitrate and ammonium ions. The incidence of high nitrate in groundwater has been observed due to pollution from anthropogenic sources, specially leaching from sewage/septic tanks (Walker 1973; Dudley 1990; Faillat and Rambaud 1991; Barnes et al. 1992; Wetselar et al. 1993; Alcocer et al. 1998; Agrawal et al. 1997). In Maharashtra, high nitrate concentration

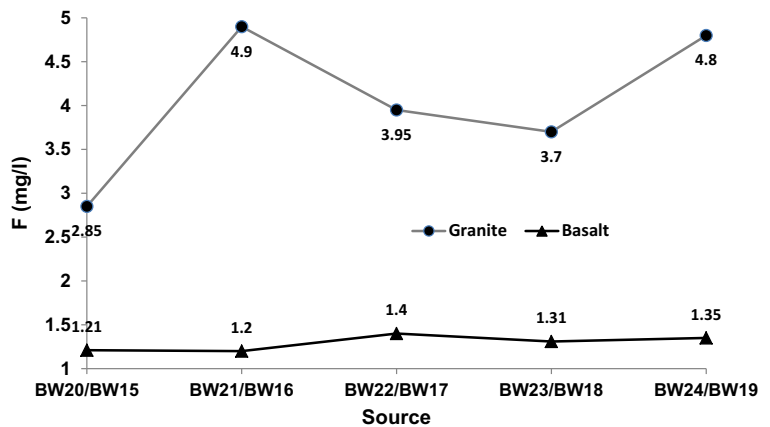
in groundwater from basaltic aquifer is highly erratic and anthropogenic activities might be responsible for their concentration (CGWB 1998).

In the study area, nitrate concentration in shallow basalt aquifers varies from 22 to 172 mg/l (avg 77) and from deeper granite aquifers it varies from 6 to 61 mg/l (avg 32). In some cases, high nitrate-bearing groundwater is associated with high concentration of chloride, which may be due to contamination of groundwater from domestic and urban wastes (Piskin 1973; Ritter and Chirnside 1984; Barnes et al. 1992; Kross et al. 1993; Madhnure 2004). Groundwater from shallow basalt aquifers contains comparatively higher concentration of nitrate than from deeper aquifer waters. However, in some cases, the concentration of nitrate in groundwater from deeper aquifers is also high, and this may be due to the hydraulic connectivity between two aquifers.

Fluoride

In the study area, F^- concentration in shallow basalt aquifers varies from 0.5 to 1.2 mg/l (avg 0.8) from phase 1 samples and from phase 2 samples it varies from 1.2–1.4 mg/l (avg 1.3) in shallow basalt aquifers. In deeper granite aquifers, it ranges from 2.85 to 4.9 mg/l (avg 4.04). The comparison of F^- concentration of groundwater from the shallow and deeper aquifers from the same location has indicated that deeper granite aquifers have higher concentration of F^- than shallow basalt aquifers (Fig. 4), and this is in agreement with the observations made by Wodeyar and Sreenivasan (1996), Madhnure et al. (2007), and Madhnure et al. (2016). In India and other parts of the world, higher concentrations of F^- have been reported from deeper aquifers (Back 1966; Apambire et al. 1997; Kruse and Ainchil 2003; Prem Babu et al. 2004; Madhnure et al. 2007; Madhnure et al. 2016). In the present study, a moderate degree of positive correlation is observed between depth vs. F^- in samples collected during phase 2 ($R^2 = 0.70$) (Fig. 5). However, in some areas of the country, shallow aquifers also contain higher concentration of F^- than deeper aquifers (Ramesam and Rajagopalan 1985; Subba Rao et al. 1998; Subba Rao and Rao 2003; Subba Rao 2006). Higher concentration of F^- in shallow as well as deeper aquifers has also been reported from the Palghat district of Kerala state (Shaji et al. 2007).

Fig. 4 Variation of 'F' in granite (deeper) and basalt (shallow) aquifers—phase 2



Occurrences of heavy metals

Concentration of heavy metals (from phase 1) like iron (Fe 0.16), copper (Cu 0.051), zinc (Zn, below detectable limit) and lead (Pb 0.017) is detected in one sample (HP⁵), and in another sample (HP¹⁰), all parameters are below detectable limits.

Iron concentrations in shallow aquifers from basalt (phase 2) vary from 0.5 to 0.9 mg/l (avg 0.64), and from deeper granite aquifers, it varies from 0.3 to 0.9 mg/l (avg 0.57) and is beyond the permissible limits of drinking water standards i.e. 0.3 mg/l (BIS 2012).

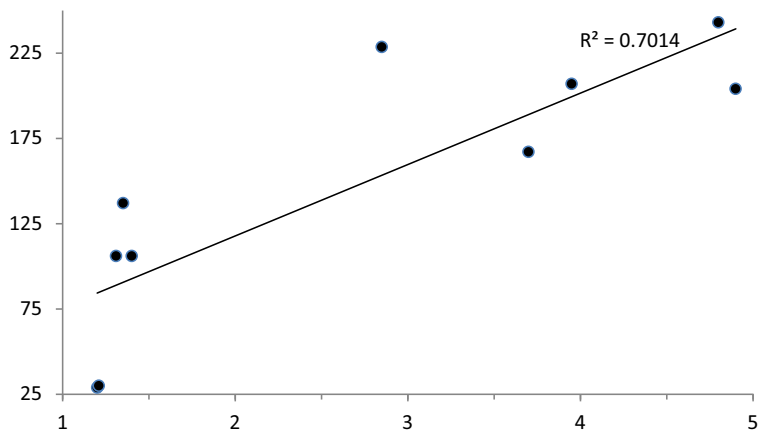
Source of fluoride in groundwater

Fluorine is a lithophile element (those that show an affinity for silicate phases and are concentrated in silicate portion of the earth's crust and mantle), and the

average concentration of fluoride in the earth's crust is 611 ppm (Varcia and Borgnino 2015) and in granite 810 ppm (Wedepohl 1969). A large number of minerals contain F⁻ in their chemical formulas as a primary constituent or include it as an impurity, and among the primary minerals in igneous rocks are biotite and muscovite which may contain about 1 wt% of F⁻. Granite consists of minerals like K-feldspar, quartz, amphibole, biotite and muscovite of which amphibole, biotite and muscovite contain F⁻.

As fluoride ions have the same charge and nearly the same radius as hydroxyl ions, they may replace each other in the octahedral sheet of mineral structures (Brigatti and Guggenheim 2002). This kind of substitution is common in mica lattices, where the halogen is found at the same level as the apical oxygen of the tetrahedral sheets where they are bonded to octahedral

Fig. 5 Depth-wise variation in fluoride concentration (phase 2 samples)



cations, and thus, fluoride is released into groundwater. In addition to the minerals described above, granite also contains accessory minerals like fluorite and apatite with a chemical composition as CaF_2 for fluorite and $\text{Ca}_5(\text{Cl}, \text{F}, \text{OH})(\text{PO}_4)_3$ for apatite. The apatite-group minerals include three accepted species: fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$), chlorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$) and hydroxyl apatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$). Fluorapatite, in particular, is a ubiquitous accessory phase in igneous rocks (Pan and Fleet 2002). It may be noted that, prior to deep drilling by CGWB (Madhnure 2003) down to 200 m, there were no reports of tapping granite aquifers from the town.

Basalts, in addition to plagioclase feldspar (labradorite) ($\text{Ca}, \text{Na})\text{Al}_1\text{-}2\text{Si}_3\text{-}2\text{O}_8$), essentially contains amphibole mineral $[(\text{Ca}, \text{Na}, \text{K})_2\text{-}3(\text{Mg}, \text{Fe}_2^+, \text{Fe}_3^+, \text{Ti}, \text{Al})_5(\text{Si}, \text{Al})_8\text{O}_{22}(\text{OH}, \text{F})_2]$ which may contribute F^- to the groundwater. Madhnure et al. (2011) have also reported that minerals such as amphibole, mica and zeolite are the contributory minerals for excess of F^- in groundwater from shallow basalt aquifers. Similarly, calcretes from the basalts in shallow aquifer also provide a source of F^- to groundwater. Near-surface exposures of basalt in the study area show that calcrete occurs as an intrusion in the form of vein or patches. Reddy et al. (2010) have reported that calcrete deposits have acted as a sink for co-precipitation and/or adsorption of fluoride in Wailapalli watershed, Nalgonda district of Telangana State.

Groundwater facies

For identification of characteristics of groundwater and chemistry, a Piper diagram is widely used as it gives the best graphical representation (Hill 1940; Piper 1944). Groundwater from shallow basalt aquifer (phase 1 and phase 2 samples, 24 in quantity) is mainly of Ca- HCO_3 -Cl type (12 in quantity) followed by Ca-Na- HCO_3 -Cl type (5), Ca-Cl type (4) and Ca-Na-Cl type (3) (Fig. 6a), whereas groundwater from deeper granite aquifer (phase 2 samples, 5 in quantity) is mainly of Ca-Na-Cl type (3) and Na-Cl type (2) (Fig. 6b).

Relationships between fluoride and major ions

The relationship between F^- and four major ions (pH, Ca^{2+} , Na^+ and HCO_3^-) is studied for both aquifers (Fig. 7a–h). The plot of F^- vs. pH shows a moderate degree of positive correlation in shallow basalt aquifers ($R^2 = 0.63$) and a weak positive degree in deeper granite aquifers ($R^2 = 0.28$), indicating that higher alkalinity in groundwater promotes leaching of F^- (Agrawal et al. 1997; Saxena and Ahmed 2001; Madhnure et al. 2007; Madhnure et al. 2016). The correlation plot between F^- vs. Ca^{2+} shows a weak negative correlation ($R^2 = 0.21$ and 0.23) in both aquifers, and a similar observation was also made by Jacks et al. (2005). The plot of Na^+ vs. F^- shows a weak positive degree of correlation in both aquifers

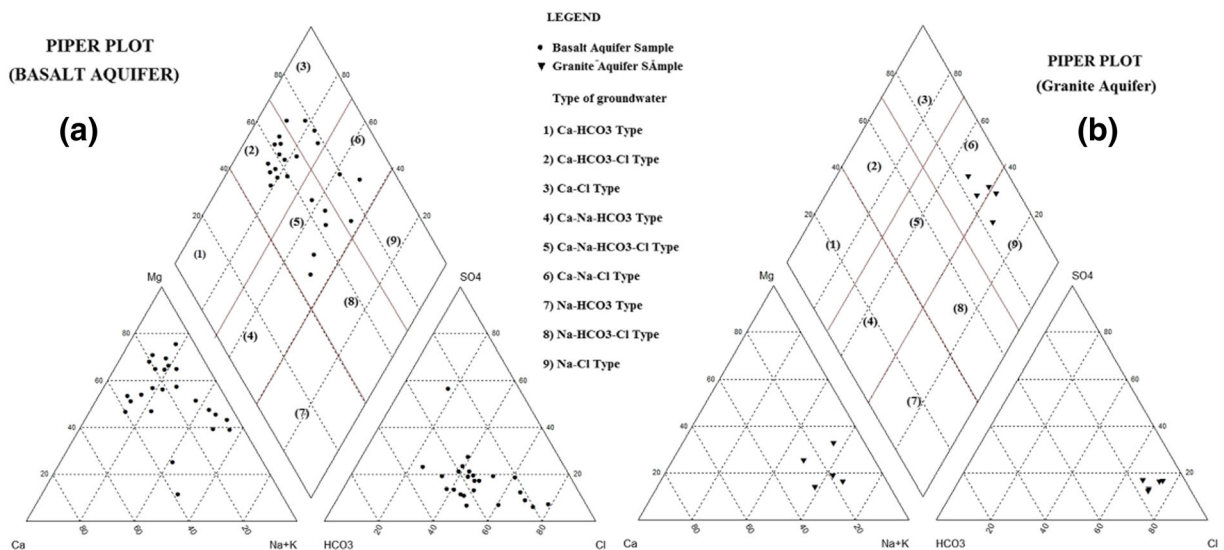


Fig. 6 a, b Groundwater facies (Piper plot)

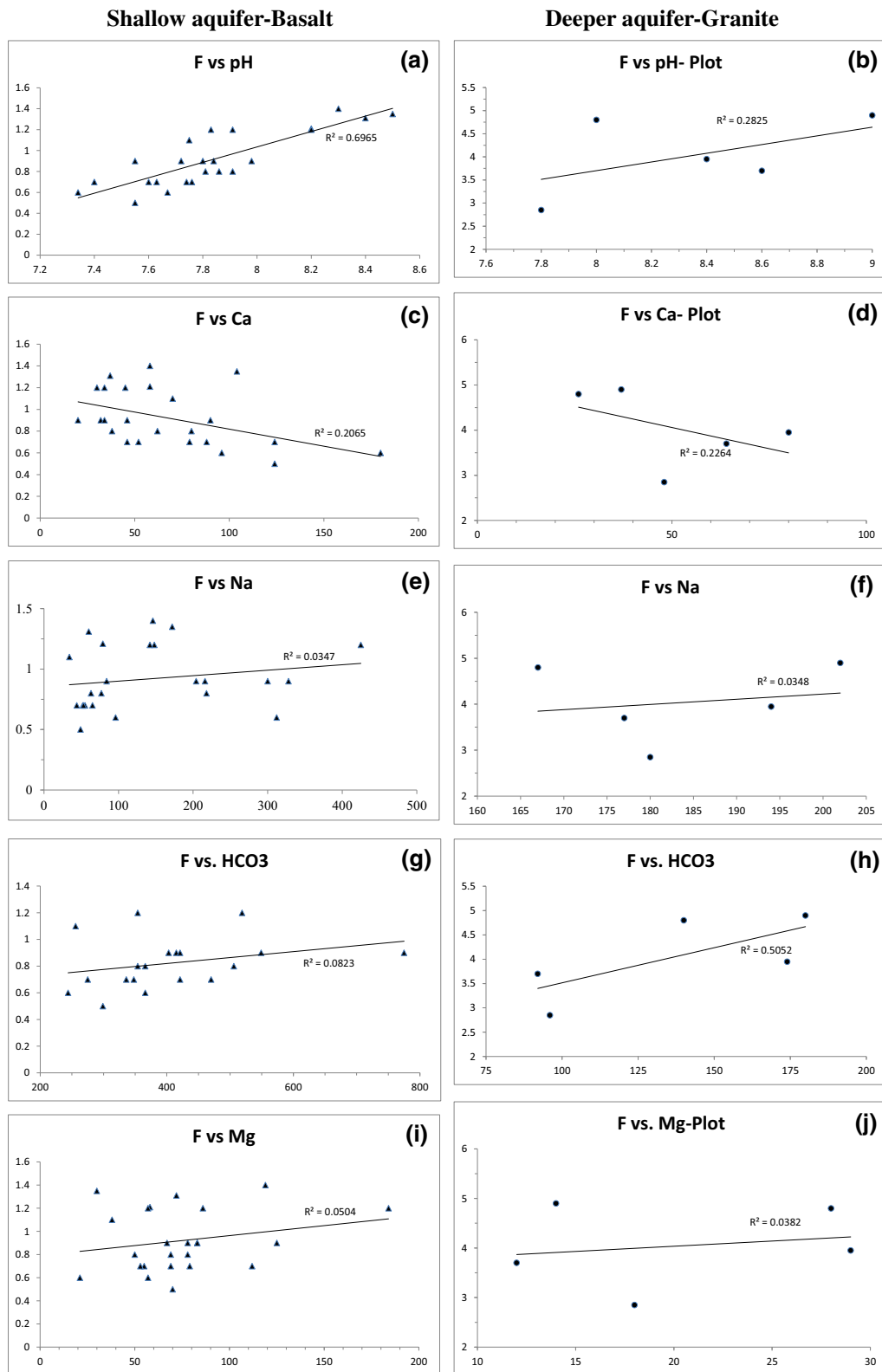


Fig. 7 a–j Relationships between F and other major ions (basalt and granite aquifers)

($R^2 = 0.034$ and 0.034). Apambire et al. (1997) and Madhnure et al. (2016) have also observed that Na^+ concentration increases with F^- , thereby increasing the solubility of fluorite in water. The fluoride and HCO_3^- pair has shown a weak positive correlation in both aquifers ($R^2 = 0.08$ and 0.05), and a similar relationship is also observed by Madhnure et al. (2016).

Groundwater management and augmentation options

In order to assess the management and augmentation options in the city, an assessment based on rainwater availability from rooftop and runoff water availability from open spaces and roads is made. (Madhnure 2004) estimated 1.987 MCM of rainwater available from rooftop, out of which 1.35 MCM can be recharged to groundwater or can be stored in emergency conditions, which is sufficient to cater for the needs of ~40,800 people (135 l/day/person for 245 days); Madhnure also estimated ~0.54 MCM of runoff from open spaces.

Conclusions and recommendations

Deeper granite aquifer is contaminated with high fluoride (geogenic), and shallow basalt aquifer is free from fluoride contamination, but contaminated with nitrate (anthropogenic). High concentrations of F^- in deeper granite aquifer are due to source rocks containing fluoride-bearing accessory minerals, higher residence time, low recharge due to prevailing drought conditions and higher alkalinity. Due to increasing urbanization coupled with prevailing drought conditions, demand of drinking water is not satisfied by the normal recharge process resulting in desaturation of shallow aquifer particularly in the northwestern part of the city, and people are tapping deeper aquifers. As a recommendation, it is suggested to utilize 1.35 MCM of net rainwater available from rooftop along with 0.54 MCM from surface runoff with suitable rainwater-harvesting structures like recharge shafts. Fluoride-rich groundwater from deeper aquifers may be used for drinking purposes by blending with treated surface water and/or for other purposes. Most effective defluoridation techniques like electrolytic defluoridation (EDF), ion exchange and reverse

osmosis may be adopted along with integrated fluorosis mitigation measures (Godfrey 2007).

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