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Influence of stone quarries on groundwater quality and health in Fatehpur Sikri, India

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Abstract

Fatehpur Sikri block is a well known tourist place, also famous for sandstone and limestone quarries. Dental and skeleton fluorosis is a common disease among children (>10 years) and adults of all age groups. To understand the factors causing the dental and skeletal fluorosis diseases and their source in groundwater a study based on water quality analysis of aquifers in and around stone quarries, was carried out. All the dug wells are dry and majority of the hand pumps are equipped with the jet pumps in the block. Water samples were collected from hand pumps and tube wells in June 2012 and February 2013. Fluoride zonation and groundwater salinity maps were generated for shallow and deep aquifers. These analyses show drastic changes in the salinity levels of shallow and deep aquifers. The deep aquifers are more saline as compared to the shallow aquifers. On the contrary, the concentration of chemical constituents such as Na^+, K^+, Cl^- and F^- was more in the shallow aquifers compared to the deep aquifers. Concentration of fluoride was found more in villages near or within the stone quarries (shallow aquifers between 1.7 to 3.8 mg/l and 1.5 to 3.6 mg/l in June 2012 and February, 2013 respectively and in deep aquifers between 1.2 to 2.7 mg/l and 1.1 to 2.7 mg/l in June 2012 and February, 2013 respectively) as compared to the villages approximately 1–1.5 km far from these quarries. Study reveals escalation in both groundwater salinity and fluoride in aquifers and direct and indirect contribution of sandstone and limestone quarries in increasing hazardous materials in groundwater.

Keywords: Stone quarries; Quaternary aquifers; Fluoride; Groundwater salinity; Shallow and deep aquifers

1. Introduction

Groundwater salinity and high concentration of fluoride are major quality problems worldwide, which are directly or indirectly associated with the local or regional geological features and climatic conditions. Moreover it is also influenced by human actions such as irrigation, and anthropogenic activities. Fluoride is one of the most abundant chemicals after Cl among the halogens (Rankama and Sahama, 1950) that has been extensively studied (WHO, 1970, 1984a) and fluoride related health and environmental concerns have reached an alarming proportion in several regions of the world. More than 23 countries in the world including India have problems with F^- in the drinking water (Susheela et al., 1993). In India problem of fluorosis has been known since a longtime. The dental fluorosis earlier called "mottled enamel" was first reported by Viswanathan (1935) to be prevalent in human beings. Similar type of

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Table 1
Fluoride concentration in drinking water and its effect on human health (source: International drinking water standards (1971) WHO, Geneva).

S.NO.	Fluoride concentration	Effects
1	Nil	Limited growth and fertility
2	<0.5	Dental caries
3	0.5–1.5	Promote dental health and prevent tooth decay
4	1.5–4.0	Dental fluorosis (mottling and pitting of teeth
5	4.0–10.00	Skeletal fluorosis
6	>10.00	Crippling fluorosis

diseases in cattle in certain parts of old Hyderabad state was reported by Mahajan (1934). However, Short (1937) was the first person to identify the disease as "fluorosis" in human beings in the Nellore district of Andhra Pradesh. Fluoride plays a very important role on the formation of dental enamel and normal mineralization in bones but can cause dental fluorosis and adversely affect the central nervous system, bones and joints at high concentrations (Agrawal et al., 1997). At low concentration (<2 mg/l) soluble fluoride in the drinking water may cause mottled enamel during the formation of teeth, but at higher levels other toxic effects may be observed (Weast and Lide, 1990). Excessive intake of fluoride results in skeletal and dental fluorosis (Czarnowski et al., 1999). Several symptoms lead to death, when fluoride doses reach 250–450 mg/ml (Luther et al., 1995). Moreover, it has been found that IQ of the children living in the high fluoride areas (>3.15 mg/ml) was significantly lower (Lu et al., 2000). Table 1 shows the effects of fluoride on human health. Daily consumption of fluoride varies widely and depends on various sources of exposure. It is believed that fluoride is incorporated into the teeth and bones and its incorporation into the teeth and skeletal tissues is reversible. Fluoride is excreted via urine, faces and sweat (IPCS, 1984; US EPA, 1985; Janssen et al., 1988). Fluoride as inhaled particles is also absorbed, the extent of absorption depends on the size of the particles and the solubility of fluoride compounds present (IPCS, 2002).

Fluorine is the thirteenth most abundant (0.06 to 0.09%) element in the earth's crust (Environment Canada, 1976; Smith, 1983). Fluorine is the most electronegative and reactive of all the known elements (Pauling, 1960). Its abundance in continental crust is about 626 μg/g (Henderson, 1982; Periakali et al., 2001). The maximum tolerance limit of fluoride in drinking water specified by the World Health Organization (WHO, 1984b) is 1.5 mg/l. The major source of fluoride in groundwater aquifer is fluoride bearing bed rocks in the subsurface. The important fluoride minerals are fluorite, fluor-apatite and apatite, which are accessory minerals in many types of rocks. Fluorite contains nearly half of fluorine by weight, therefore its contribution in rocks and groundwater is high, even though the mineral is present in small quantity (Correns, 1956). Fluorine also occurs in limestone, sandstone and in clay minerals. More than 90% of natural fluorine in soil is bound to clay particles (Lahermo and Backman, 2000). In groundwater fluoride occurs as fluoride ion and is released into the groundwater, via, weathering of rocks and minerals (HEM, 1989).

Fig. 1. Open sandstone quarry exposed to surface and precipitated water in Fatehpur Sikri block deteriorating groundwater quality.

Fig. 2. Exposed weathered sandstone rocks in Fatehpur Sikri block deteriorating groundwater quality.

Fig. 3. Hand pump equipped with jet pump in Mandimirja Kha village, Fatehpur Sikri block.

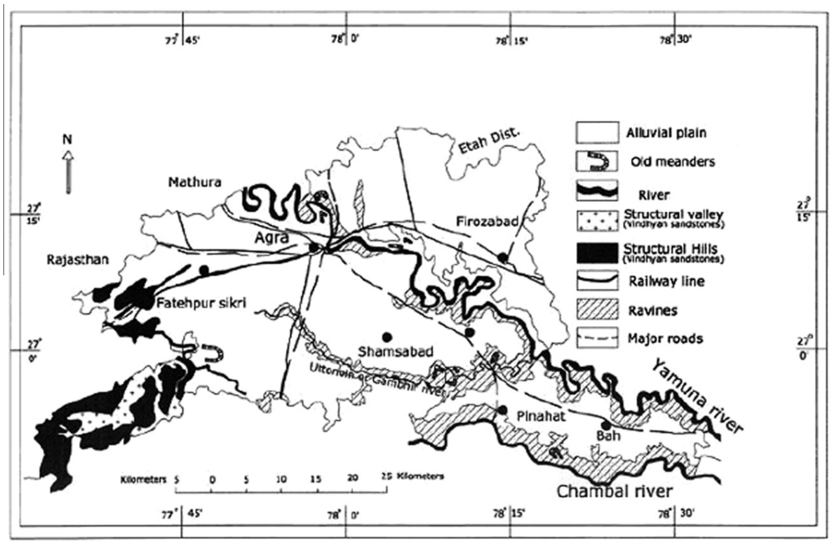

Fig. 4. Hydrogeographical map of Agra district (Source: Misra and Mishra, 2007a).

Table 2
Fluoride concentration in groundwater in different parts of India and its sources based on the literature (after Brindha and Elango, 2011).

State, district/place (in alphabetical order)	Source	General range of fluoride concentration in groundwater	Reference
Andhra Pradesh, Kurmapalli watershed	Fluoride rich rocks	Up to 21.0 mg/l	Mondal et al. (2009)
Andhra Pradesh, Nalgonda	Fluoride rich grantic rocks	0.4–20 mg/l	Ramamohana Rao et al. (1993)
Andhra Pradesh, part of Nalgonda district	Fluoride rich granitic rocks	0.1–8.8 mg/l	Brindha et al. (2011)
Andhra Pradesh, Vamsadhara river basin	Pyroxene amphibolites and pegmatites	Up to 3.4 mg/l	Srinivasa Rao (1997)
Andhra Pradesh, Visakhapatnam	Granitic rocks	0.6–2.1 mg/l	Subba Rao (2009)
Andhra Pradesh, Wailapally watershed	Hornblende, biotite, apatite, fluorite and fluoride rich calcretes	0.5–7.6 mg/l	Reddy et al. (2010a)
Andhra Pradesh, Wailapally watershed	Fluorite bearing rocks	0.97–5.83 mg/l	Reddy et al. (2010b)
Andhra Pradesh and Jharkhand	Coal ash	0.1 to >4 mg/l	Prasad and Mondal (2006)
Assam, Guwahati	Granite	0.18–6.88 mg/l	Das et al. (2003)
Delhi	Irrigation water and brick industries	0.1–16.5 mg/l	Datta et al. (1996)
Gujarat, Mehsana	Granite, gneiss and pegmatite	0.94–2.81 mg/l	Salve et al. (2008)
Gujarat, Mehsana	Calcite and dissolution of dolomite	1.5–5.6 mg/l	Dhiman and Keshari (2006)
Haryana, Bhiwani	Rook	0.14–86 mg/l	Garg et al. (2009)
Karnataka, Bellary	Apatite, hornblende and biotite	0.33–7.8 mg/l	Wodeyar and Sreenivasan (1996)
Keral , Palghat	Hornblende and biotite gneiss	0.2–5.75 mg/l	Shaji et al. (2007)
Maharashtra, Yavatmal	Amphibole, biotite and fluoroapatite	0.30–13.41 mg/l	Madhnure et al. (2007)
Rajasthan, Hanumangarh	Fluoride bearing host rocks	1.01–4.42 mg/l	Suthar et al. (2008)
Tamil Nadu, Erode	Host rocks and weathering of fluorite	0.5 and 8.2 mg/l	Karthikeyan et al. (2010)
Uttar Pradesh, Kanpur	–	0.14 to 5.3 mg/l	Sankararamakrishnan et al. (2008)
Uttar Pradesh, Mathura	Clay and Silt bed	0.1–2.5 mg/l	Misra and Mishra (2007a,b)
West Bengal, Hooghly	Super phosphate fertilizer	0.01–1.18 mg/l	Kundu and Mandal (2009)

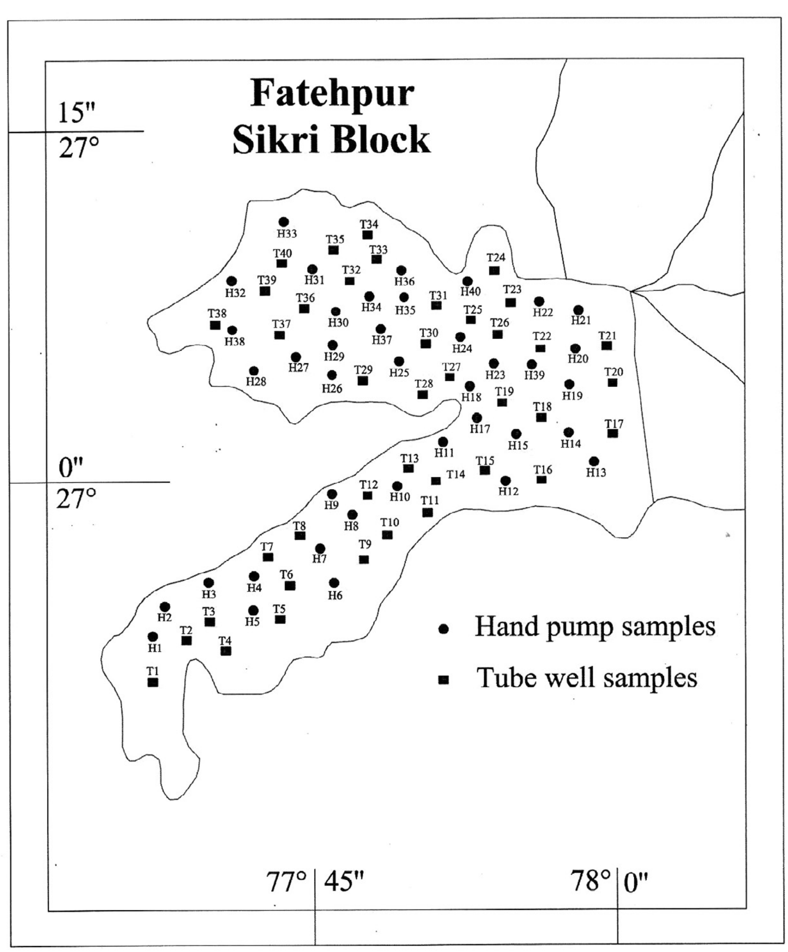

Fig. 5. Fatehpur Sikri map showing sampling locations of hand pump and tube well samples based on GPS measurements.

Table 3
Groundwater quality classification using specific conductance (source: Tamta 1999).

S.No	Class	Specific conductance (μmho/cm) at 25 °C
1	Non-saline	Less than 2000
2	Slightly saline	2000–4000
3	Saline	4000–6000
4	Very Saline	>6000

In Agra district, the quality of groundwater is quite variable. A major part of the district is located in the marginal alluvial plain, with some portion falling in the central alluvial plain of the Ganga Plain. The western portion of Agra district is Fatehpur Sikri block, which is facing severe problem of groundwater salinity and fluoride along with severe water scarcity problems. Fatehpur Sikri block was recognized as a critical (dark) block in 1998 by the state groundwater department. The problem of dental and skeletal fluorosis is very common in majority of the villages in this area. It seems that the problem of continuously deteriorating groundwater quality is directly or indirectly related with open limestone and sandstone quarries. The limestone and sandstone quarries are contaminating the fresh groundwater aquifers of the region by increasing fluoride concentration and salinity in groundwater in this region. The surface and precipitated waters are directly exposed to these quarries. Sandstone and limestone rocks easily get weathered and broken down especially when it comes in contact with water. Figs. 1 and 2 show some of the sandstone and limestone quarries exposed to the surface water in the study area. Almost all the wells in the region are dry and the hand pumps equipped with jet pumps are only able to provide some water. Fig. 3 shows hand pump equipped with jet motors in Fatehpur Sikri block. In view of the persistent problem of groundwater fluoride and salinity in the region, the study of stone quarries and their impact on groundwater quality in shallow and deep aquifers was carried out in June 2012 and February, 2013. The study of stone quarries and assessment of their impact on water quality is difficult because it might take many years to separate their causes and effects. The present study is an attempt to examine the factors causing escalation, variation and deterioration in water quality and scarcity problems of the shallow and deep aquifers in the Fatehpur Sikri block.

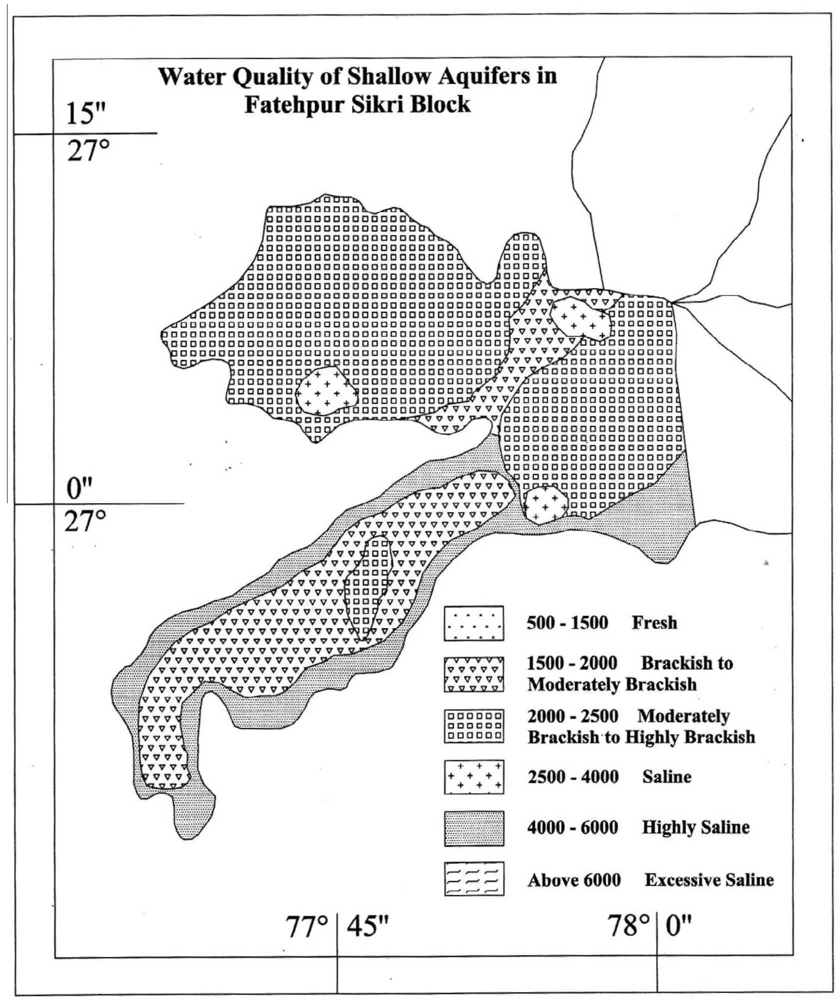

Fig. 6. Map showing the water quality in shallow aquifers in Fatehpur Sikri block, Agra district, Uttar Pradesh.

2. Study area

Agra district is located at the southwestern part of Uttar Pradesh (India) state and is bounded by the state of Rajasthan in the west and the state of Madhya Pradesh in the south. Fatehpur Sikri block is the western most part of the Agra district and belongs to the marginal plain (Ganga Plain). Fatehpur Sikri is located 40 km from Agra city. Fatehpur Sikri was once the capital of the mughal empire in the 16th century. It was established by Emperor Akbar from the twin villages of Fatehpur and Sikri as tribute to the famous Sufi saint, Sheikh Salim Chishti. At that time it was abandoned by its residents due to water quality and scarcity problems. The entire area is marked by the hilly ranges of the sandstone and limestone of Vindhyan group, which are also overlain in some areas by a thick pile of unconsolidated sediments of the Ganga Plain. The study area is situated between 26° 45″ and 27° 15″N latitudes and between 77° 30″ and 78° 0″ E longitudes at approximately 180 m above sea level. The study area has a semi-arid to arid climate with an average monthly temperature varying between 38 and 46 °C in the summer and between 25 and 32 °C in the winter. The average weather conditions allow recognizing six well marked traditional seasons, i.e. spring (March–April), summer (May–June), monsoon (July–August), early autumn (September–October), late autumn (November–December) and winter (January–February). The average annual rainfall variation is between 450 and 550 mm.

3. Hydrogeology of the area

The Agra district is a part of the Ganga Plain. Majority of the study area is covered by Gangetic alluvial deposits of the quaternary period comprising gravel, sand, silt, clay and kankar in various proportions (Misra and Mishra, 2006). The thickness of the alluvial covered around the study area ranges from 200 to 250 m. In the lower part just above the basement, thick horizons of arkosic gravel–coarse sand are present. They are followed by a clay–kankar (calcrete nodules) succession with thin, fine sand intercalations. The topmost 10 m are invariably made up of clay with kankar and distinct calcrete horizons (Singh, 1996). The ground water behaviour in the entire study area is

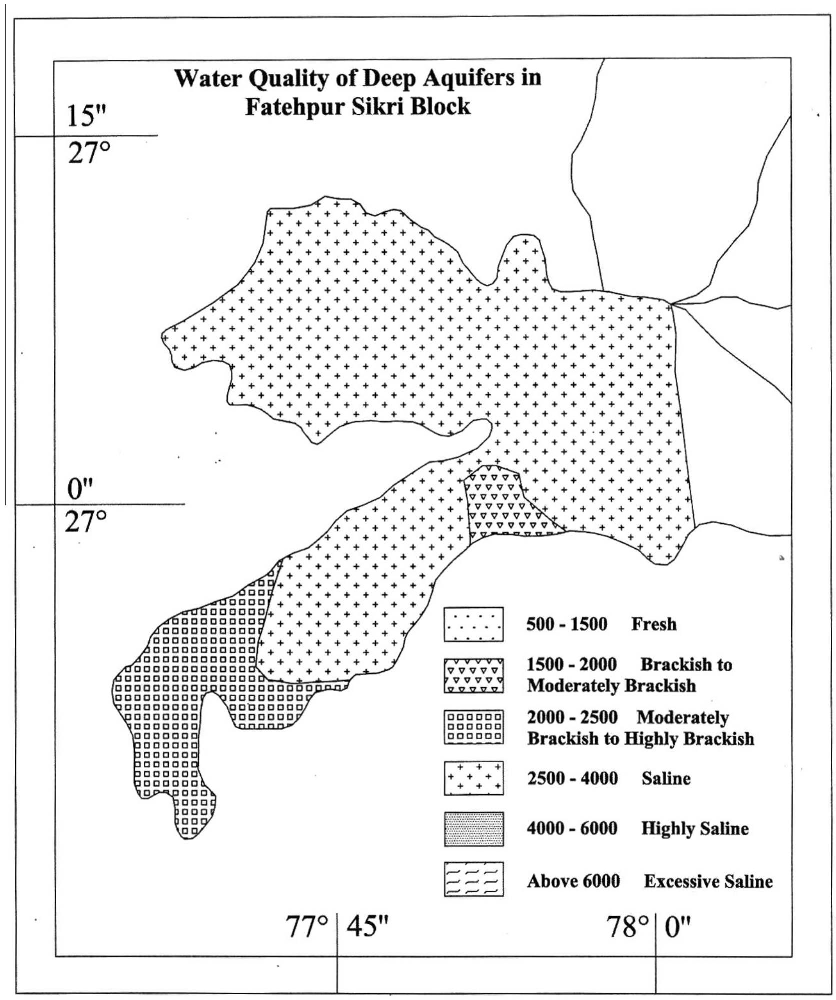

Fig. 7. Map showing the water quality in the deep aquifers in Fatehpur Sikri block, Agra district, Uttar Pradesh.

highly complicated due to the occurrence of diversified geological formations with considerable lithological and climatological dissimilarities and various hydrochemical conditions. River Yamuna acts as a lifeline and is the main river flowing through the district. In the entire region the major part of the ground water withdrawal takes place from the upper unconfined aquifers, which are also the active recharge zones and hold the replenishable ground water resource. Most areas of Agra district are facing problems related with water quality. Even in Agra city, the groundwater environment is plagued by the dual ills of saline water occurrence below 30/40 meters as well as the sporadic presence of fluorides and nitrates much above the permissible limits (Misra and Mishra, 2007a).

Hydrogeomorphologically, Agra district can be divided (Fig. 4) into five major units: alluvial plain, structural valley, valley fills, structural hills and ravines. The alluvial plains are mostly composed of gravel, pebbles, sand and silt. The groundwater prospects appear to be good in this unit. Structural valleys in the region are composed of fine to medium sand, which is highly porous and permeable. In this area, the water table position ranges from 30 to 60 m. The valley fills mostly lie very close to hilly ranges in the structural valleys, consisting of boulders, cobbles, pebbles, gravels, sand, silt and clay. The shallowest water table position is recorded in these areas. The structural hills are composed of Vindhyan sandstones and lime stones.

4. Distribution of fluoride in the study area and India

Groundwater is the only source of water available for domestic, irrigational and industrial purposes in entire study area. The supply of treated Yamuna river water is limited to urban areas of Agra district. The groundwater recharge of the study area totally depends on the rainfall that percolates below the ground surface and passes through the joints, fractures and voids of the rocks. The water potential of the study area is the main source of surface and groundwater, which experiences very low annual precipitation. The water table in the entire Fatehpur Sikri varies between 30 and 65 m. Since no comprehensive and scientific investigations have been carried out in the region so far as part of a complete hydrological appraisal of the watershed, information on baseline hydrological

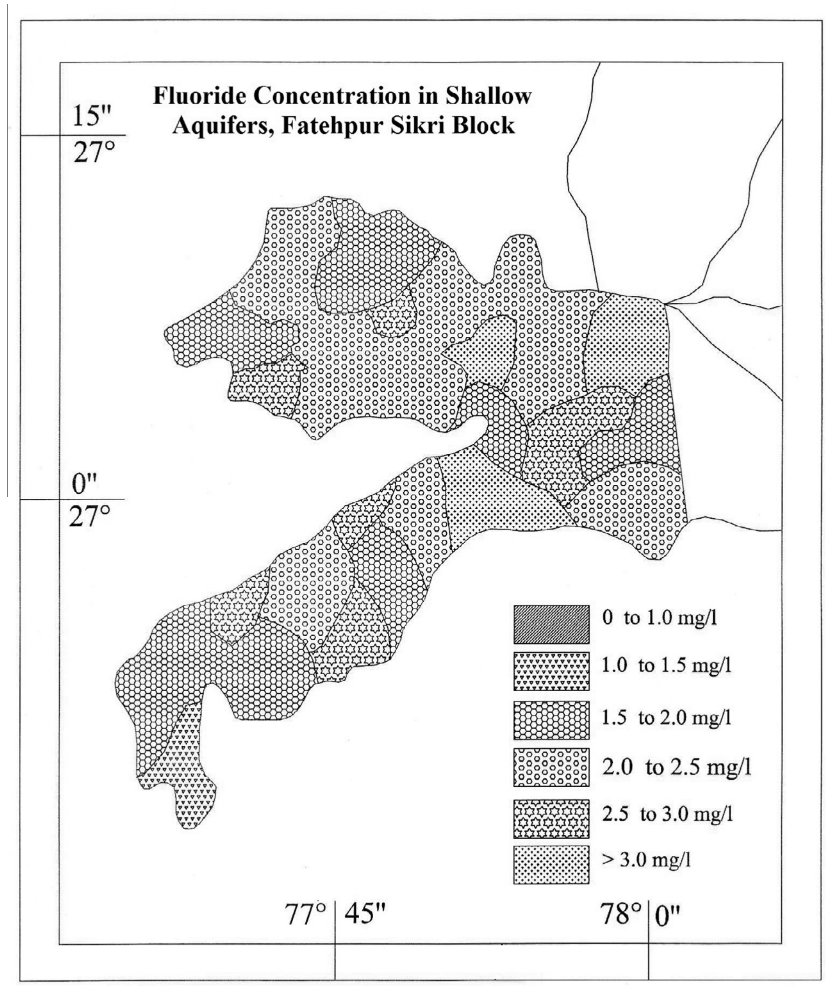

Fig. 8. Map showing fluoride concentration in shallow aquifers in Fatehpur Sikri block, Agra district, Uttar Pradesh.

characteristics and also on spatio-temporal aspects of water resources is not available.

In the entire Agra district ground water quality in 77 villages was studied (Gupta et al., 1994). According to this study the fluoride concentration in the study area ranged from 0.28 to 22.0 mg/l of the analysed 138 samples (45%) were in the range of 0–1.0 mg/l, 129 samples (42%) in the range of 1.0–1.5 mg/l, 37 samples (12%) in the range of 1.5–3.0 mg/l and only 3 samples (1%) were above 3.0 mg/l. The highest concentration (22.0 mg/l) was recorded at Bainkhera village.

Studies show that out of 85 million tons of fluoride deposits in the earth's crust, 12 million are found in India (Teotia and Teotia, 1994). In India approximately 27 million people in 16 states are consuming fluoride over 1.5 mg/l through drinking water and are under severe threat of fluorosis (Adyalkar and Radhakrishna, 1974; Bhakuni et al., 1969; Singh et al., 1982; Pathak, 1999; Susheela, 1993; Choubisa and Sompura, 1996). The endemic fluorosis is prevalent in India since 1937 (Shortt, 1937). Most of the areas of north west and southern India are heavily affected with fluorosis (Agrawal et al., 1997; Yadav et al., 1999). However the incidence of fluorosis in people living in other parts of India has also been reported. The fluoride concentration and their sources in different parts of India are mentioned in Table 2.

5. Objective of the study

The major objective of the present work is to study the impact of sandstone and limestone quarries on the quaternary aquifers and analyse their direct and indirect impact on continuously increasing salinity and fluoride levels in shallow and deep aquifers of Fatehpur Sikri block. This study had three main objectives: (1) to evaluate the salinity and fluoride levels in shallow and deep aquifers and classify the areas with their salinity levels (2) to evaluate the impact of sandstone and limestone quarries on some of the major constituents of groundwater such as Na^+, K^+, Cl^-, TDS and F^- in shallow and deep aquifers and (3) find out the exact reason of dental and skeletal fluorosis in the region.

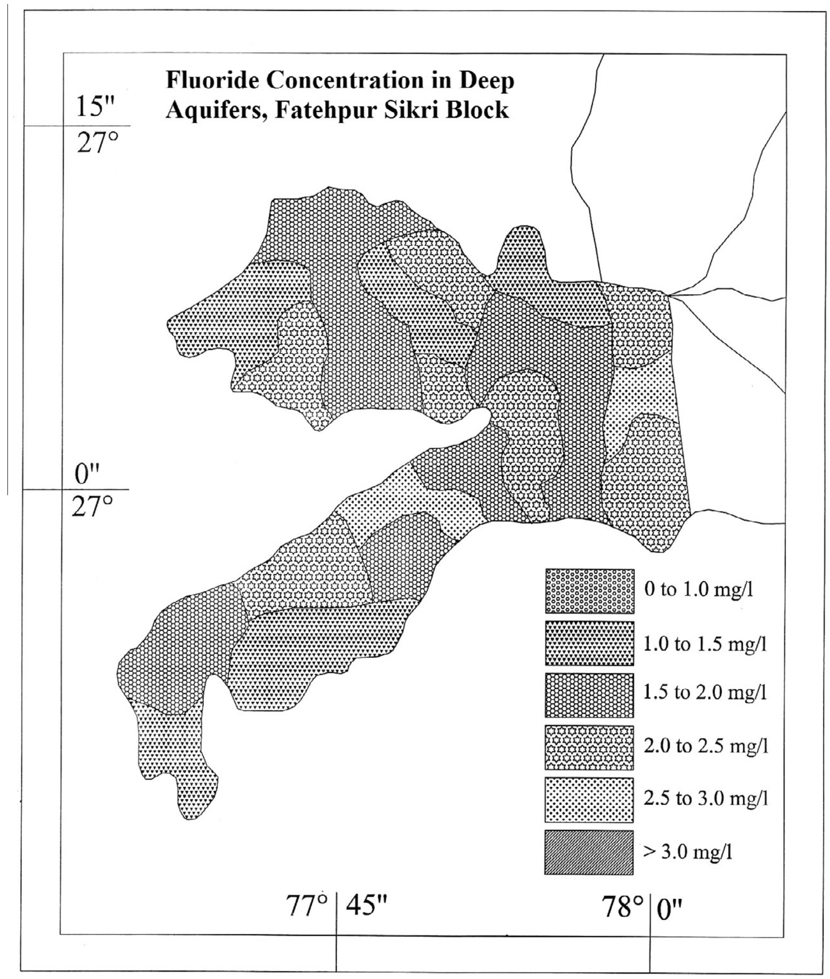

Fig. 9. Map showing fluoride concentration in deep aquifers in Fatehpur Sikri block, Agra district, Uttar Pradesh.

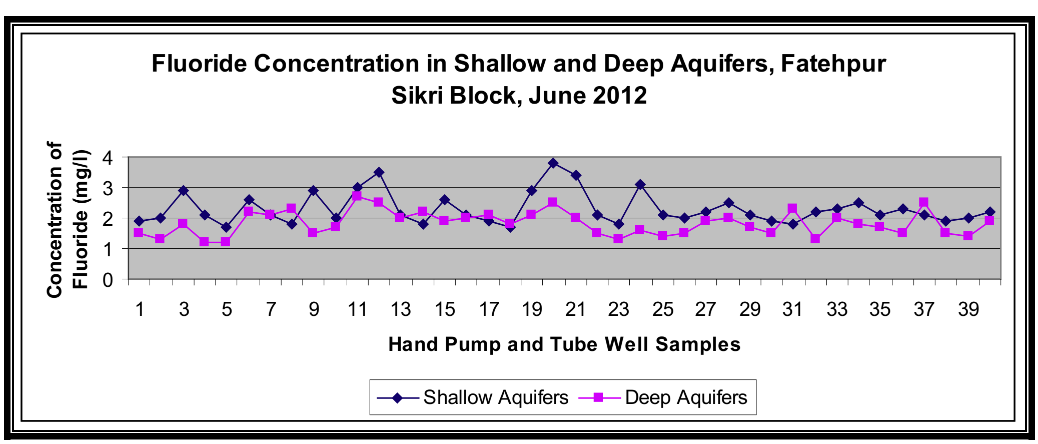

Fig. 10. Map showing fluoride concentration in shallow and deep aquifers in Fatehpur Sikri block, Agra district, Uttar Pradesh, June 2012.

This work would help in the understanding of the groundwater quality in this region.

6. Methodology

Total 150 samples were collected and 40 samples each from hand pumps and tube wells were collected in very close proximity of the sandstone and limestone quarries in June 2012 and February, 2013 (Fig. 5) for the comparative study of salinity and fluoride levels in the shallow and deep aquifers. In most of the cases, the samples collected from hand pumps and tube wells were used for several hours prior to sampling. The groundwater samples were collected in glass bottles after rinsing with the sample

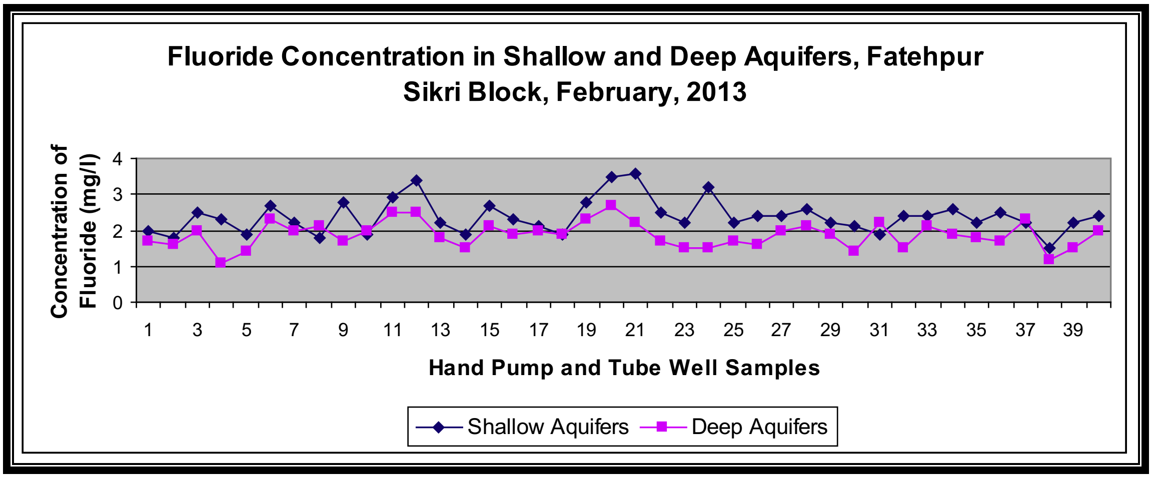

Fig. 11. Map showing fluoride concentration in shallow and deep aquifers in Fatehpur Sikri block, Agra district, Uttar Pradesh, February 2013.

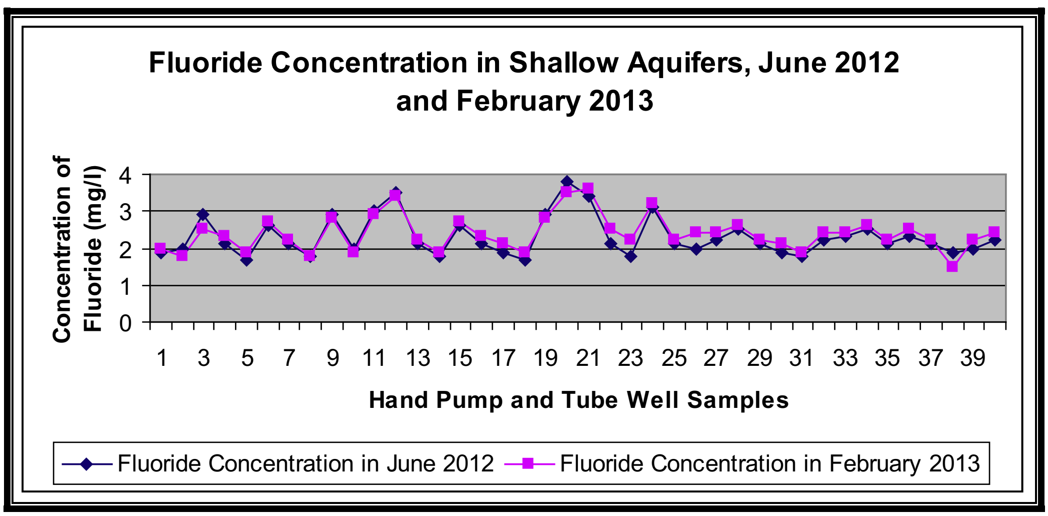

Fig. 12. Map showing fluoride concentration in shallow aquifers in Fatehpur Sikri block, Agra district, Uttar Pradesh, June 2012 and February 2013.

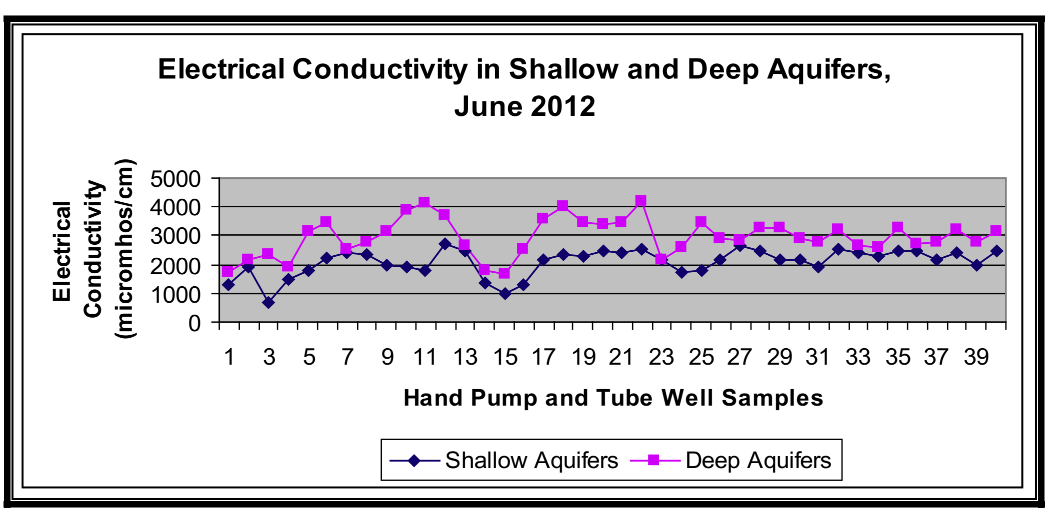

Fig. 13. Map showing electrical conductivity in shallow and deep aquifers, Fatehpur Sikri block, Agra district, Uttar Pradesh, June 2012.

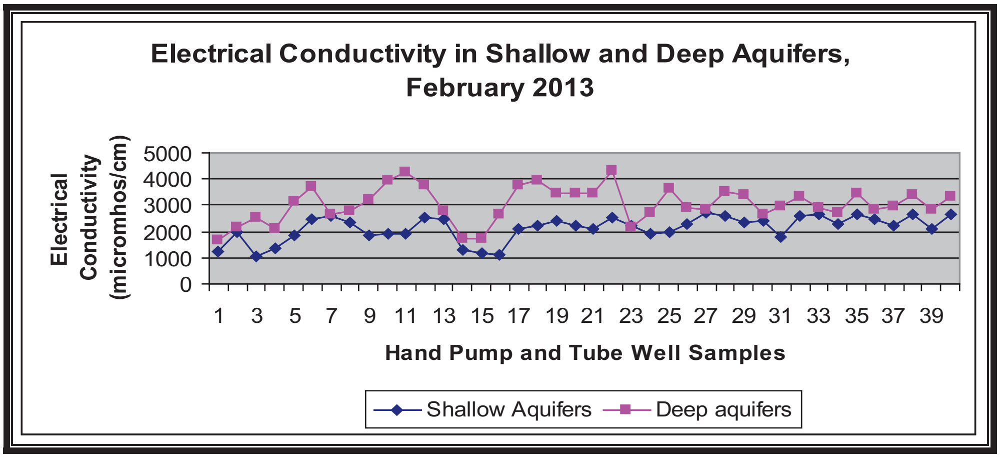

Fig. 14. Map showing electrical conductivity in shallow and deep aquifers, Fatehpur Sikri block, Agra district, Uttar Pradesh, February 2013.

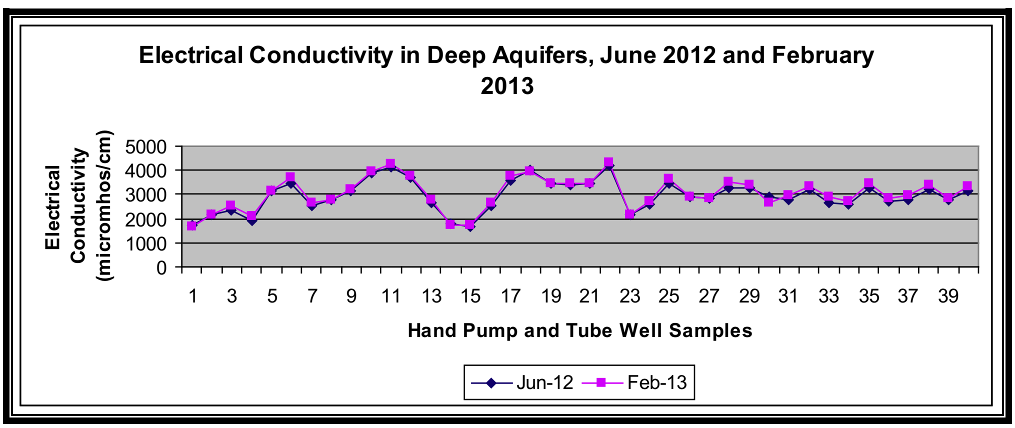

Fig. 15. Map showing electrical conductivity in deep aquifers, Fatehpur Sikri block, Agra district, Uttar Pradesh, June 2012 and February 2013.

water. The sample bottles were immediately sealed using rubber stoppers and aluminium protective caps crimped with a handheld crimping device. The hand pumps and tube wells range in depth from 30 to 40 m and 80 to 140 m, respectively. The electrical conductivity (EC) and pH of the 150 samples were analysed on the spot, while 40 samples each of hand pumps and tube wells were also analysed for other chemical constituents in the laboratories.

The salinity levels in the aquifers as mentioned in Table 3 are classified (Tamta, 1999; MOWR, 1997) on the basis of their electrical conductivity. The same standard is used to classify the groundwater quality in aquifers. Water samples for fluoride were analysed by using the SPADNS colorimetric method. A calibration standard ranging from 0 to 6.0 mg F^{-}/l was prepared by diluting an appropriate volume of standard F^{-} solution. To 60 ml of standard solution, 10.0 ml of the SPADNS reagent was added and mixed well. The double beam UV VIS spectrophotometer (UV5704 M) was set at a wavelength of 580 nm, and a calibration graph was prepared from different standard F^{-} concentrations. When the graph gave a straight line, the instrument was considered ready for measurement of F in the samples. The total dissolved solid was calculated using the formula given by Todd (Todd, 1959). The chemical constituents, such as Na^{+}, K^{+} and Cl^{-}, were analysed on the basis of the standard water quality procedures (APHA-AWWA, 1980) in the environmental engineering lab, Department of civil and environmental engineering, ITM University, Gurgaon.

7. Results and discussion

Several studies have shown that high fluoride in groundwater is generally expected in the areas where F^{-} bearing minerals are abundant in the rocks, because F^{-} leaches out and dissolves in groundwater during weathering and circulation of water in rocks and soils (Carrillo-Rivera et al., 2002; Naseem et al., 2010; He et al., 2012). In the study area (Fatehpur Sikri) also sandstone and limestone are present in abundance both on surface and subsurface. The results of the study are indicated in Figs. 6 and 7 that show the salinity levels and in Figs. 8 and 9, which show

Table 4
Chemical composition of the Hand pump water in Fatehpur Sikri block in June 2012.

Hand Pump samples	pH	EC	TDS	K^+	Na^+	Cl^-	F^-
H1	7.1	1278	780	5	70	187	1.9
H2	7.4	1890	1345	4	123	214	2.0
H3	8.0	700	1707	12	65	367	2.9
H4	7.9	1477	1233	16	90	176	2.1
H5	7.6	1789	650	21	211	256	1.3
H6	7.1	2232	980	7	156	289	2.6
H7	7.2	2398	560	6	167	269	2.1
H8	7.5	2343	680	3	176	432	1.8
H9	7.9	1967	789	2	156	356	2.9
H10	8.1	1934	537	8	172	378	2.0
H11	8.3	1800	1211	24	113	217	3.0
H12	7.8	2689	1456	16	89	257	3.5
H13	7.5	2456	1482	19	84	160	2.1
H14	7.3	1345	621	11	90	278	1.4
H15	7.5	967	890	9	59	410	2.6
H16	7.3	1267	1278	3	52	267	2.1
H17	7.4	2176	1600	6	65	378	1.9
H18	7.3	2345	2100	8	129	315	1.7
H19	7.8	2267	1400	5	163	275	2.9
H20	8.4	2475	1344	16	165	159	3.8
H21	8.5	2412	1178	11	231	144	3.4
H22	7.8	2512	845	17	205	223	2.1
H23	7.3	2162	728	21	189	372	1.8
H24	7.0	1754	1532	27	245	378	3.1
H25	7.5	1798	1653	2	156	276	2.1
H26	7.2	2185	1287	5	161	265	2.0
H27	7.6	2651	734	6	113	167	2.2
H28	7.5	2453	645	20	87	149	2.5
H29	8.0	2187	667	7	93	248	2.1
H30	8.1	2176	947	5	165	274	1.9
H31	7.5	1895	948	4	136	352	1.8
H32	7.6	2512	936	12	187	316	2.2
H33	7.9	2415	934	15	216	341	2.3
H34	7.7	2289	1273	19	251	267	1.2
H35	8.3	2451	1184	21	145	284	2.1
H36	8.4	2439	834	5	173	193	2.3
H37	8.1	2165	934	7	158	164	2.1
H38	7.9	2418	942	9	201	273	1.9
H39	7.3	1964	693	7	142	210	2.0
H40	7.8	2462	834	11	161	274	2.2

H = Hand pump (all values are in mg/l, except pH and EC. Units of EC are mmho/cm).

Table 5
Chemical composition of the Tube well water in Fatehpur Sikri block in June 2012.

Tube well samples	pH	EC	TDS	K^+	Na^+	Cl^-	F^-
T1	7.8	1700	934	11	290	202	1.5
T2	7.5	2150	756	21	210	267	1.3
T3	8.2	2367	960	7	189	344	1.8
T4	8.0	1890	1109	5	90	387	1.2
T5	7.2	3154	1004	12	74	187	1.2
T6	7.0	3456	785	8	79	164	2.2
T7	6.9	2513	745	6	59	267	2.1
T8	7.6	2789	945	5	127	234	2.3
T9	7.2	3178	1356	9	156	167	1.5
T10	7.5	3890	1654	8	184	365	1.7
T11	7.4	4130	983	9	149	418	2.7
T12	8.0	3701	874	21	265	426	2.5
T13	7.9	2670	830	30	243	376	2.0
T14	7.4	1820	928	9	219	518	2.2
T15	7.6	1687	1094	8	281	421	1.9
T16	7.4	2540	1056	6	56	233	2.0
T17	7.6	3562	938	4	82	341	2.1
T18	7.9	3987	940	6	98	367	1.8
T19	7.5	3452	1260	8	108	156	2.1
T20	7.4	3421	1045	7	115	162	2.5
T21	7.0	3471	1084	6	142	149	2.0
T22	7.1	4190	1109	10	198	175	1.5
T23	7.9	2180	1398	15	59	265	1.3
T24	7.4	2567	845	6	117	325	1.6
T25	7.6	3465	560	11	158	176	1.4
T26	7.7	2894	534	14	173	378	1.5
T27	7.4	2843	947	17	297	256	1.9
T28	7.8	3245	830	8	321	261	2.0
T29	7.4	3267	934	5	183	177	1.7
T30	7.9	2896	1165	9	276	153	1.5
T31	7.1	2790	1102	5	249	267	2.3
T32	7.4	3212	1247	13	228	364	1.3
T33	7.0	2678	783	11	174	255	2.0
T34	8.1	2563	630	17	216	262	1.8
T35	8.0	3289	1159	4	173	347	1.7
T36	7.8	2690	1205	8	128	356	1.5
T37	7.4	2789	1045	4	63	311	2.5
T38	7.5	3187	1349	12	72	247	1.5
T39	7.8	2765	934	16	121	365	1.4
T40	7.2	3143	830	21	155	244	1.9

T = Tube well water (all values are in mg/l, except pH and EC. Units of EC are mmho/cm).

the fluoride concentration in shallow and deep aquifers based on electrical conductivity of the hand pump and tube well water sample analysis in June 2012 and February 2013. The finding shows fluoride concentration in shallow aquifers is more as compared to the deep aquifers, while deep aquifers are more saline compared to shallow aquifers. Variation and escalation in fluoride and salinity levels are also recorded. Such variations in the water quality of deep and shallow aquifers are most probably due to the poor hydraulic conductivity between the shallow and deep aquifer systems in the region.

Moreover the hydrochemical properties of groundwater, as well as the lithological features of the area are also contributing for high fluoride and salinity in groundwater in the region. The continuous escalation of fluoride and salinity in the groundwater is due to the long-term water–rock interaction within the stone quarries, fluoride and salt from these stone quarry rocks are released out and then accumulated in the groundwater aquifers in the region. Fig. 10–15 show the actual variation and escalation in fluoride and salinity levels. The hydrochemical property of groundwater, as well as the lithological features of the area seems to be contributing factors for high Fluoride and Salinity in groundwater. The continuous escalation of fluoride and salinity in the groundwater is due to the long-term water–rock interaction within the stone quarries, fluoride and salt from these stone quarry rocks are released out and then accumulated in the groundwater aquifers in the region. The variation in the water quality of deep and shallow aquifers is attributed to the poor hydraulic

Table 6
Comparison of the hand pump samples data (F) June, 2012 & February, 2013.

Hand pump samples	F^{-}	F^{-}
H1	1.9	2.0
H2	2.0	1.8
H3	2.9	2.5
H4	2.1	2.3
H5	1.7	1.9
H6	2.6	2.7
H7	2.1	2.2
H8	1.8	1.8
H9	2.9	2.8
H10	2.0	1.9
H11	3.0	2.9
H12	3.5	3.4
H13	2.1	2.2
H14	1.8	1.9
H15	2.6	2.7
H16	2.1	2.3
H17	1.9	2.1
H18	1.7	1.9
H19	2.9	2.8
H20	3.8	3.5
H21	3.4	3.6
H22	2.1	2.5
H23	1.8	2.2
H24	3.1	3.2
H25	2.1	2.2
H26	2.0	2.4
H27	2.2	2.4
H28	2.5	2.6
H29	2.1	2.2
H30	1.9	2.1
H31	1.8	1.9
H32	2.2	2.4
H33	2.3	2.4
H34	2.5	2.6
H35	2.1	2.2
H36	2.3	2.5
H37	2.1	2.2
H38	1.9	1.5
H39	2.0	2.2
H40	2.2	2.4

Table 7
Comparison of the hand pump samples data (EC) June, 2012 & February, 2013.

Hand pump samples	EC	EC
H1	1278	1250
H2	1890	1976
H3	700	1060
H4	1477	1388
H5	1789	1855
H6	2232	2455
H7	2398	2589
H8	2343	2344
H9	1967	1855
H10	1934	1910
H11	1800	1944
H12	2689	2550
H13	2456	2455
H14	1345	1320
H15	967	1180
H16	1267	1100
H17	2176	2100
H18	2345	2244
H19	2267	2411
H20	2475	2233
H21	2412	2125
H22	2512	2555
H23	2162	2234
H24	1754	1900
H25	1798	1987
H26	2185	2256
H27	2651	2700
H28	2453	2567
H29	2187	2345
H30	2176	2388
H31	1895	1789
H32	2512	2577
H33	2415	2657
H34	2289	2262
H35	2451	2678
H36	2439	2450
H37	2165	2234
H38	2418	2642
H39	1964	2087
H40	2462	2633

conductivity between the shallow and deep aquifer systems in the region.

The water quality of the shallow aquifers in approximately 80% of area ranges between brackish to highly brackish. While the salinity level in deep aquifers was found to be moderately brackish to saline in more than 90% of the area. Most of the deep aquifers in the study area were found to be of unconfined to semi-confined in nature. The semi-confined aquifers possess some hydrostatic pressure and whenever these aquifers were drilled with bore wells, the pressure caused the upward movement of water, leading to deterioration of shallow aquifers (Misra and Mishra, 2006). Further, majority of the rivers of the Ganga Plain originate from the Himalayan mountain ranges, where precipitation is generally high and the concentration of total dissolved solids (TDS) in the rivers is low. But when these rivers flow through arid to semi-arid regions of the Ganga Plain, the concentration of salts in their lower reaches rises through evaporation. When this water is diverted to canals for irrigation, the salt concentration is escalated by evapotranspiration and it increases the soil and groundwater salinity (Misra et al., 2006). This could also be one of the reasons for the continuous escalation of salinity in the shallow and deep aquifers in the study area.

Tables 4–9 show the chemical composition of groundwater collected from the, hand pumps and tube wells in the study area in June 2012 and February 2013. It is noted that in most of the areas the groundwater of the shallow aquifers is characterized by a high concentration of Na^{+},

Table 8
Comparison of the Tube well samples data (F) June, 2012 & February, 2013.

Tube well samples	F^- (June, 2012)	F^-(February, 2013)
T1	1.5	1.7
T2	1.3	1.6
T3	1.8	2.0
T4	1.2	1.1
T5	1.2	1.4
T6	2.2	2.3
T7	2.1	2.0
T8	2.3	2.1
T9	1.5	1.7
T10	1.7	2.0
T11	2.7	2.5
T12	2.5	2.5
T13	2.0	1.8
T14	2.2	1.5
T15	1.9	2.1
T16	2.0	1.9
T17	2.1	2.0
T18	1.8	1.9
T19	2.1	2.3
T20	2.5	2.7
T21	2.0	2.2
T22	1.5	1.7
T23	1.3	1.5
T24	1.6	1.5
T25	1.4	1.7
T26	1.5	1.6
T27	1.9	2.0
T28	2.0	2.1
T29	1.7	1.9
T30	1.5	1.4
T31	2.3	2.2
T32	1.3	1.5
T33	2.0	2.1
T34	1.8	1.9
T35	1.7	1.8
T36	1.5	1.7
T37	2.5	2.3
T38	1.5	1.2
T39	1.4	1.5
T40	1.9	2.0

Table 9
Comparison of the tube well samples data (EC) June, 2012 & February, 2013.

Tube well samples	EC	EC
T1	1700	1670
T2	2150	2160
T3	2367	2507
T4	1890	2090
T5	3154	3160
T6	3456	3697
T7	2513	2675
T8	2789	2807
T9	3178	3190
T10	3890	3945
T11	4130	4267
T12	3701	3776
T13	2670	2765
T14	1820	1745
T15	1687	1732
T16	2540	2643
T17	3562	3765
T18	3987	3960
T19	3452	3442
T20	3421	3474
T21	3471	3476
T22	4190	4320
T23	2180	2150
T24	2567	2743
T25	3465	3650
T26	2894	2900
T27	2843	2832
T28	3245	3534
T29	3267	3377
T30	2896	2650
T31	2790	2988
T32	3212	3344
T33	2678	2876
T34	2563	2744
T35	3289	3455
T36	2690	2855
T37	2789	2975
T38	3187	3375
T39	2765	2865
T40	3143	3345

K^+, Cl^-, F^- and TDS than the deep aquifers. The variation in these parameters between the waters of the two types of aquifers is believed to result from the interplay of the following factors.

(a) Poor hydraulic conductivity between shallow and deep aquifer systems.
(b) Salt rich geological formations.
(c) Exposure of salt rich rocks to weathering and erosion through stone quarries.

Furthermore, the extremely low hydraulic conductivity between the shallow and deep zones also suggests that the recharge sources for both deep and shallow zones are different; otherwise all the aquifers would have similar water quality (Misra et al., 2006).

The concentration of fluoride in all the 40 samples of shallow aquifers (hand pump samples) was found above the maximum permissible limit i.e. 1.5 mg/l. The maximum concentration of fluoride in shallow aquifers was found to be 3.8 mg/l. In deep aquifers the fluoride concentration is low as compared to shallow aquifers. The maximum concentration in deep aquifers was recorded as 2.7 mg/l. Due to the high concentration of fluoride intake through drinking water, dental fluorosis has become a household disease. Dental fluorosis symptoms, such as chalkiness of teeth, brown strain on teeth and mottling of teeth are common among people of all age groups. No case of acute to chronic skeletal fluorosis was found in entire Fatehpur Sikri block, because exposure of high fluoride (>4.0 mg/l) over a prolonged period of time causes acute or chronic skeletal fluorosis. This perception is based on the report of National Research

Council, 1993, which has stated that crippling skeletal fluorosis might occur in people, who have ingested 10–20 mg/l of fluoride per day for over 10–20 years. In the majority of the villages symptoms of early stage of skeletal fluorosis such as pain in bones and joints, muscle weakness, sporadic pain and stiffness of joints etc. were found among children (12–18 year), adults and elderly people. In some adults (25–35 year) and elderly people the effect of skeletal fluorosis is more prominent as their bones and joints become completely weak and they are not able to walk and work without help.

The open stone quarries which are one of the main contributing factors for continuous escalation in salinity and fluoride levels in the groundwater in this region can be filled with soil and covered with vegetation, it will not only prevent further erosion and weathering of salt and fluorine rich minerals but also prevent escalation of the fluoride and salinity levels in aquifers.

8. Conclusion and recommendation

It is evident from the outcome of the study that Fatehpur Sikri block is facing severe water quality and scarcity problems. The widespread incidence of dental and skeletal fluorosis in the region bearing both health and social problems are of great concern. The study demonstrates the following points:

1. The main source of fluoride and salt in groundwater is the availability of salt rich geological formation in Fatehpur Sikri block. Hundreds of open stone quarries directly exposed to the surface and precipitated water are escalating weathering and erosion of salt rich minerals.
2. By the long-term water–rock interaction within the stone quarries, fluoride and salt from these stone quarry rocks are released out and then accumulated in the groundwater aquifers in the region.
3. The intake of fluoride above the permissible limit in drinking water is the major reason for both dental and skeletal fluorosis diseases in the study areas.
4. Symptoms of early stage skeletal fluorosis are very much prominent among the people of all age groups (>12 years) and in the absence of any prevention measure, entire region may come under the impact of acute to chronic skeletal fluorosis in future.
5. The variation in the water quality of deep and shallow aquifers can be attributed to the poor hydraulic conductivity between the shallow and deep aquifer systems in the region.
6. The open stone quarries can be filled with soil and covered with vegetation ; it will prevent further erosion and weathering of salt and fluorine rich minerals and also escalation of the fluoride and salinity levels in aquifers.

Further high concentration of fluoride can be managed through artificial recharge and rainwater harvesting techniques. A study carried out by Bhagavan and Raghu, 2005 shows that the construction of check dams in Anantapur district, India has helped widely to reduce fluoride concentration in groundwater. Groundwater recharge via, recharge pits, ponds, rainwater harvesting techniques and by constructing vertical and horizontal shafts may help in improving the groundwater quality and preventing the further depletion of water table. The study area imperatively needs implementation of water management and recharge schemes. As an immediate solution, to alleviate the human suffering in the region, defluoridation of groundwater and supply of safe drinking water are also recommended along with the use of Nalgonda technique of defluoridation.

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