Environ Sci Pollut Res
DOI 10.1007/s11356-016-6069-7

RESEARCH ARTICLE

Fluoride in weathered rock aquifers of southern India: managed aquifer recharge for mitigation

K. Brindha[1] · **G. Jagadeshan**[2] · **L. Kalpana**[2] · **L. Elango**[2]

Received: 28 August 2015 / Accepted: 6 January 2016

Abstract Climatic condition, geology, and geochemical processes in an area play a major role on groundwater quality. Impact of these on the fluoride content of groundwater was studied in three regions—part of Nalgonda district in Telangana, Pambar River basin, and Vaniyar River basin in Tamil Nadu, southern India, which experience semi-arid climate and are predominantly made of Precambrian rocks. High concentration of fluoride in groundwater above 4 mg/l was recorded in these areas. Human exposure dose for fluoride through groundwater was higher in Nalgonda than the other areas. With evaporation and rainfall being one of the major contributors for high fluoride apart from the weathering of fluorine-rich minerals from rocks, the effect of increase in groundwater level on fluoride concentration was studied. This study reveals that groundwater in shallow environment of all three regions shows dilution effect due to rainfall recharge. Suitable managed aquifer recharge (MAR) methods can be adopted to dilute the fluoride-rich groundwater in such regions which is explained with two case studies. However, in deep groundwater, increase in fluoride concentration with increase in groundwater level due to leaching of fluoride-rich salts from the unsaturated zone was observed. Occurrence of fluoride above 1.5 mg/l was more in areas in deeper groundwater environment. Hence, practicing MAR in these regions will increase the fluoride content in groundwater and so physical or chemical treatment has to be adopted. This study brought out the fact that MAR cannot be practiced in all regions for dilution of ions in groundwater and that it is essential to analyze the fluctuation in groundwater level and the fluoride content before suggesting it as a suitable solution. Also, this study emphasizes that long-term monitoring of these factors is an important criterion for choosing the recharge areas.

Keywords Hard rock terrain · Shallow water table · Granitic gneiss · MAR · Check dam · Recharge well · India

Introduction

Chemical composition of groundwater changes due to various processes including evaporation, weathering of rocks, and dissolution of minerals from the aquifer matrix. Weathering of rocks by hydrolysis increases the weakness of the mineral structure and the ionic bonding in them. This in turn increases the chance for leaching and replacement of ions between minerals and groundwater. These processes enhance the ionic concentration in groundwater. As the circulation of groundwater is less due to non-uniform rainfall pattern in the semi-arid regions, the contact time between the aquifer material and the groundwater will be more which in turn increases the release of ions from the rocks into the groundwater. As the availability of surface water resources is limited in arid and semi-arid regions of southern India, the population living in rural areas with no piped water supply relies on use of groundwater for drinking purposes. Long-term use of such water for drinking purpose leads to health problems. Fluoride is one such ion which is essential for good teeth and bones but at the same time if its concentration is below or above the desirable range of 0.6 to 1.5 mg/l (BIS 2012) in drinking water, it affects human health. Prolonged consumption of water with

---

Responsible editor: Philippe Garrigues

L. Elango
elango34@hotmail.com; elango@annauniv.edu

Q1 [1] International Water Management Institute, Vientiane, Lao People's Democratic Republic

[2] Department of Geology, Anna University, Chennai 600025, India

fluoride below 0.6 mg/l increases the chance for tooth decay but above 1.5 mg/l causes dental fluorosis, a disturbance of dental enamel and drinking water containing >3 mg/l leads to skeletal fluorosis. Fluoride is generally released to groundwater from aquifer material having minerals such as sellaite, fluorite, cryolite, fluorapatite, apatite, topaz, fluormica, biotite, epidote, amphibole, pegmatite, mica, clays, villuanite, phosphorite, etc. (Matthess 1982; Pickering 1985; Hem 1986; Handa 1988; Haidouti 1991; Gaumat et al. 1992; Gaciri and Davies 1993; Datta et al. 1996; Apambire et al. 1997; Kundu et al. 2001; Ayoob and Gupta 2006; Mohapatra et al. 2009; Kim et al. 2011).

Fluoride-rich groundwater is a major problem in many countries such as China, Japan, Sri Lanka, Iran, Pakistan, Turkey, Algeria, Mexico, Korea, Italy, Brazil, Malawi, Jordan, Ethiopia, Canada, Norway, Ghana, Kenya, and the USA (Brindha and Elango 2011; Ayoob and Gupta 2006; Fawell et al. 2006) apart from India. It can be commonly quoted that high evaporation and low rainfall regions in the arid to semi-arid parts of the world with aquifer formation containing fluorine are at a risk of elevated fluoride in groundwater. North western and southern parts of India are more prone to fluoride contamination due to various geochemical processes. Among the states in southern India, Telangana (formerly a part of Andhra Pradesh), Karnataka, and Tamil Nadu are holding higher fluoride bearing groundwater (Brunt et al. 2004). Because of fluoride prevalence in these southern states, several studies have been conducted by Mamatha and Rao (2010), Kantharaja et al. (2012), Tirumalesh et al. (2007) in Karnataka, Reddy et al. (2010), Brindha and Elango (2013), Mondal et al. (2009)) in Andhra Pradesh, and Karthikeyan et al. (2010), Viswanathan et al. (2009), Kalpana and Elango (2013), Jagadeshan and Elango (2012) in Tamil Nadu.

Mitigation of this problem is a major issue. Treatment of water to remove fluoride is available, but at a cost. In countries like India, people cannot afford to treat the water in spite of the availability of cost-effective treatment methods. Furthermore, the treatment methods have many limitations as it depends on the initial concentration of water to be treated, occurrence and removal of co-contaminants along with fluoride, disposal of sludge generated while treatment, etc. Hence, rather than treating the groundwater after pumping, the rainfall recharge can be increased and the quality of groundwater can be improved by dilution. Increase in recharge has been adopted through managed aquifer recharge (MAR) methods such as check dams (Bhagavan and Raghu 2005) and percolation ponds (Pettenati et al. 2014) in regions with high fluoride groundwater. Reactive transport modeling carried out by Pettenati et al. (2014) showed the beneficial effect of percolation tanks on fluoride in groundwater during the monsoon, whereas fluoride increased in groundwater during dry period because of evaporation. So, it is possible that the effect of these recharge methods may be variable and not always beneficial. Increase in fluoride concentration in groundwater at two locations has also been reported after the construction of check dams (Bhagavan and Raghu 2005). Thus, there are some contradicting findings on the applicability of MAR for in situ mitigation of high fluoride problem.

Earlier study by Brindha et al. (2011) indicated the classification for wells into two types based on the fluctuation in groundwater level and fluoride concentration. It is necessary to carry out long-term studies similar to this to identify areas where MAR can be adopted through check dams, recharge wells, infiltration ponds, and other recharge structures to ensure positive benefit. In this study, we have attempted to understand this long-term variation in groundwater level fluctuation and fluoride concentration so as to identify locations suitable for MAR for groundwater augmentation and improvement in groundwater quality by dilution. For this study, three regions falling in two administrative states of southern India, having different geological and climatic conditions as well as where groundwater is the primary source for drinking purposes were chosen. Objective of this study is to understand the temporal variation in groundwater level and fluoride concentration in three fluoride-rich groundwater regions of southern India along with assessing the effect of MAR as a mitigation measure.

Study area

Three regions in south India were considered in this study—a part of Nalgonda district in Telangana state and two regions in Tamil Nadu forming parts of the Pambar River basin and Vaniyar river basin (Fig. 1). In common, these places experience arid to semi-arid climate. Rivers in the study areas form dendritic to sub-dendritic drainage pattern and are seasonal with water flowing only during the monsoon. Therefore, groundwater forms major source for drinking and agricultural purposes in these areas. Groundwater occurs in the weathered and fractured parts under unconfined conditions. Agriculture in these areas is mainly depended on groundwater apart from the limited surface water source.

Nalgonda district

Study area in Nalgonda district is located about 80 km ESE of Hyderabad (Fig. 1), the capital of the state of Telangana and covers an area of about 724 km^2. This area is drained by Gudipalli Vagu River partly in the north, Pedda Vagu River in the south, and Nagarjuna Sagar reservoir in the southeast. Summer prevails mostly from March to May (30 to 46.5 °C) and winters from November to January (17 to 38 °C). Rainfall occurs during June to September contributed by the SW monsoon to about 600 mm/year. Topographically, the area is sloping toward SE with elevation ranging from 360 to 150 m

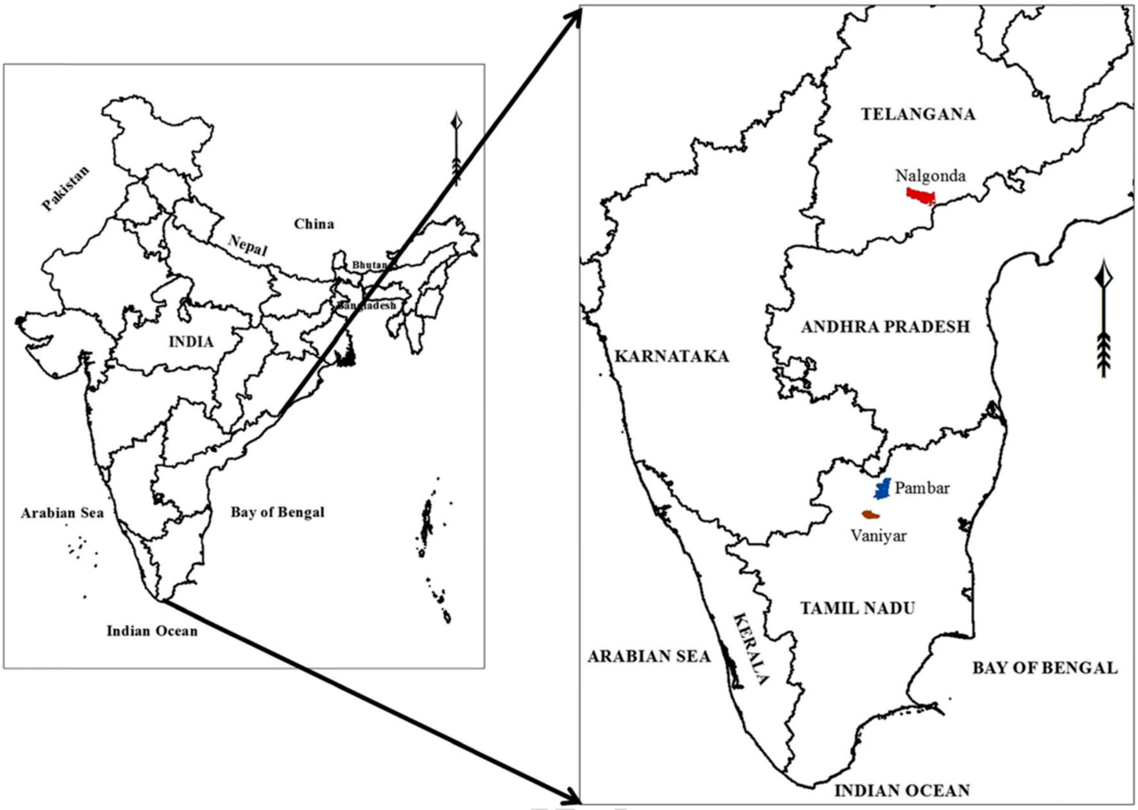


Fig. 1 Location of study areas

above mean sea level (amsl). This area is made of late Archean to early Proterozoic granites and granitic gneiss basement with intrusions of dolerite dykes and quartz veins. This is overlaid by Eparchean unconformity and is followed by Srisailam formation of Cuddapah supergroup which comprises of quartzite, shale, and limestone (Fig. 2).

Pambar river basin

This area (about 600 km^2) is situated in the northeastern part of Tamil Nadu (Fig. 1), located at 180 km SW of Chennai, the capital of the state of Tamil Nadu. The Pambar River basin drains a part of Vellore and Krishnagiri districts of Tamil Nadu. This river forms one of the northern tributaries of Ponnaiyar River and confluences with the main river through N-S trending Thurinjalar fault. This area experiences hot climate from March to June with temperature around 38 °C, and in winter between December and February the temperature is around 19 °C. Though SW (June to September) as well as NE (October to December) monsoon brings rain in this area, most of it is contributed by SW monsoon. Annual rainfall ranges from 750 to 900 mm. Elevation in this area varies from 1200 m amsl in the north to about 340 m amsl in the south. The basin is made of Archaen gneissic and charnockitic basement (Rao and Narayana 1988) with igneous intrusions of Proterozoic age. The intrusions are dolerite dykes, pyroxenites, syenites, and carbonatites (Fig. 2). Among these, Yelagiri syenite and Sevvatur and Samapaltti carbonatite are of geologic significance in Tamil Nadu.

Vaniyar river basin

Located in the south of Pambar river basin in the Dharmapuri district (Fig. 1), it forms one of the southern tributaries of Ponnaiyar River. It joins the main river along the Thurinjalar fault similar to the Pambar River basin. This study region covers 255 km^2 and experiences similar climatic conditions as that of the Pambar River basin with rainfall mostly during the SW monsoon ranging from 760 to 910 mm annually. Topographically, this area gently slopes toward the east. South and western parts of this area are mountainous. Archean gneisses and charnockites intruded with dolerite dykes (Fig. 2) of Proterozoic age are predominant in this area.

Methodology

Groundwater sampling was carried out once in 2 months from January 2009 to January 2010 in Nalgonda district, Telangana and from April 2011 to April 2012 in the two regions located in Tamil Nadu. Forty-five representative wells were chosen in Nalgonda, 37 in Pambar, and 44 in Vaniyar (Fig. 2). Polyethylene bottles (500 ml) were used to collect

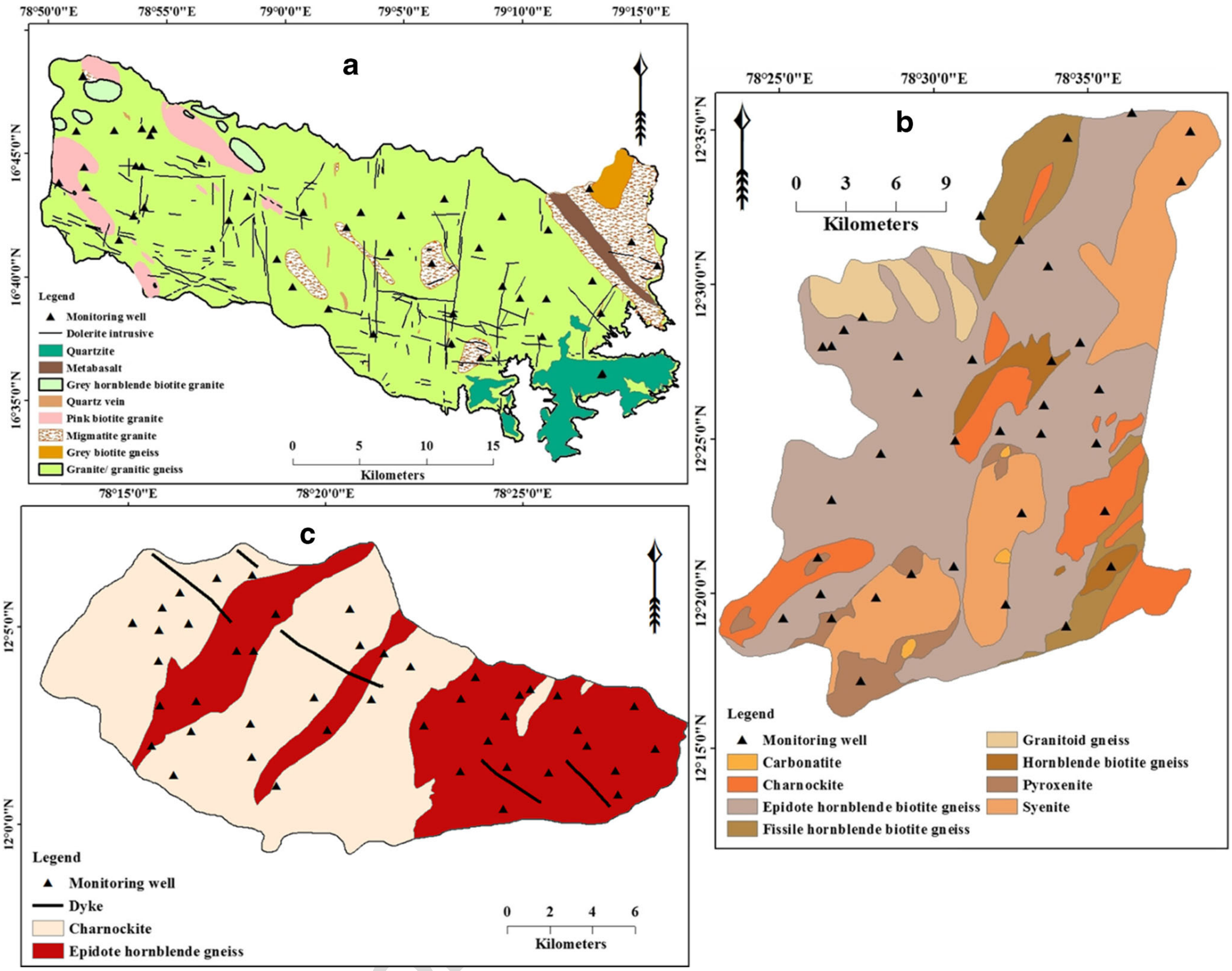


Fig. 2 Geology and location of monitoring wells in **a** Nalgonda, **b** Pambar, and **c** Vaniyar

groundwater samples. These bottles were washed in distilled water and rinsed with the sample before collecting the sample. Samples were collected from both open wells and bore wells. Water level indicator (Solinst 101) was used to measure the groundwater level in open wells and the samples from these wells were collected 30 cm below the water level using a depth sampler. For bore wells, water was pumped for about 10 min allowing sufficient time to collect the formation water. Electrical conductivity (EC in µS/cm) and pH were determined using portable meters. These meters were calibrated with 4.01, 7, and 10.01 buffer solution for pH and 84 and 1413 µS/cm conductivity solution for EC. Alkalinity of the groundwater samples was determined in the field by titration with diluted sulphuric acid (APHA 1998). Collected samples were filtered in the laboratory with a 0.2-µm filter paper, and the analysis for major and minor ions was done by Metrohm 861 advanced compact ion chromatograph. Recommended standards and blanks were run as per standard procedures to ensure accuracy in analysis. The ion balance error calculated was within ±5 %. However, this paper concentrates mainly on the fluoride dynamics in the groundwater samples. Total dissolved solids (TDS) in the groundwater samples were calculated from the EC, i.e., TDS = EC X 0.64 (Lloyd and Heathcote 1985).

Health risk of the individuals exposed to fluoride-rich groundwater which is mainly used for drinking purposes was ascertained by calculating the exposure dose. Fluoride exposure dose is calculated for infants, children, and adults based on the following generic equation,

$$\text{Exposure dose} = \frac{C \text{ x } \mathrm{WI}}{\mathrm{BW}}$$

Wherein *C* is the fluoride concentration (mg/l), WI is the water intake (l/d), and BW is the body weight (kg). It was assumed that the exposure is chronic and the concentration of fluoride assessed in groundwater is the total bioavailability of fluoride in water (Viswanathan et al. 2009; Ortiz et al. 1998). It was also assumed that the people rely only on groundwater as their drinking water source. But in reality, it is possible that packaged drinking water might be used in the semi-urban and urban areas. This is, however, mostly for drinking only and groundwater pumped from private bore wells located mostly in every household is used for cooking purpose. Water intake differs in individuals of different age—250 ml for infants, 1.5 l/day for children, and 3 l/day for adults. For infants, usually the water is boiled and used for mixing with milk formulas, and the risk of increase in the fluoride concentration due to evaporation was considered. Assuming as an extreme case that groundwater is used for this purpose, the concentration of fluoride was doubled (Grimaldo et al. 1995). Body weight for infants (0 to 6 months), children, and adults were considered as 6, 20, and 70 kg, respectively.

Results and discussion

A total of 484 groundwater samples from Nalgonda, 193 from Pambar, and 255 samples from Vaniyar were collected and analyzed.

EC and TDS

General quality of water can be determined from EC. Table 1 lists the minimum, maximum, and average of EC and TDS in groundwater of the three focal regions. Recorded average values of EC show that Pambar and Vaniyar are similar and are comparatively higher than Nalgonda. Classification of groundwater samples based on EC and TDS values (Table 2) imply that most of the groundwater samples in Nalgonda were fresh with respect to TDS (<1000 mg/l). More than 50 % of the samples were brackish in Pambar and Vaniyar regions. This shows that the occurrence of groundwater with high ionic concentration is very common in Pambar followed by Vaniyar river basin and then Nalgonda. Based on the suitability of groundwater for drinking purpose (Table 2), Nalgonda region was highly desirable. High concentration of ions in groundwater of Pambar and Vaniyar regions makes its suitable for irrigation rather than for drinking use.

pH and alkalinity

Analysis of groundwater shows that most of the samples are alkaline with pH above 7. Alkalinity of groundwater is controlled by its bicarbonate content (Arya et al. 2011), and titration-based analysis resulted in varying range of bicarbonate in groundwater. Among them, groundwater of Pambar basin is more alkaline with pH up to 9.5 and mean bicarbonate of 323.8 mg/l (Table 1). However, groundwater of Nalgonda and Vaniyar basin has comparatively less pH which ranges from 6.1 to 9.3 and 6.1 to 8.5, respectively. Bicarbonate levels in Nalgonda and Vaniyar were also lower than in Pambar with an average concentration of 288.3 and 280.3 mg/l, respectively.

Fluoride

Health impact of fluoride is both due to its low and high concentration through intake. Hence, the permissible limit for fluoride in drinking water proposed by WHO (1993) and BIS (2012) is between 0.6 and 1.5 mg/l. Table 1 gives the fluoride content measured in groundwater of this area during the sampling period. High concentration of fluoride greater than 4 mg/l was recorded in all the three regions. Figure 3 shows the number of samples with varying in fluoride content in the three areas for the total sampling period. Fluoride deficiency may cause dental carries (<0.6 mg/l); fluoride between 0.5 and 1.5 mg/l is optimum for dental health and hence beneficial, dental fluorosis may be caused while fluoride intake ranges between 1.5 and 4 mg/l which is designated in the low risk zone, 4 to 10 mg/l causes dental and skeletal fluorosis, and fluoride intake above 10 mg/l results in crippling skeletal fluorosis (Dissanayake 1991). These risk classification for fluoride is given by different authors, and the groundwater in these areas were classified based on Maithani et al. (1998) (Fig. 3). Fluorosis may not only be caused due to intake of

Table 1 Statistical details of various parameters in groundwater

Parameter	Nalgonda			Pambar			Vaniyar		
	Min	Max	Average	Min	Max	Average	Min	Max	Average
Groundwater level (m bgl)	0	14.6	4.04	1.8	19.2	9.05	5	27	13.9
EC (µS/cm)	144	5030	1008	150	6000	1928.5	366	4129	1763.2
TDS (mg/l)	92.2	3219.2	645.1	96	3840	1234.2	234.2	2642.6	1128.4
pH	6.1	9.3	–	6	9.5	–	6.1	8.5	–
Carbonate (mg/l)	0	0	0	0	60	8.4	0	78	8.1
Bicarbonate (mg/l)	68	592.8	288.3	42.7	671	323.8	72.5	576.9	280.3
Fluoride (mg/l)	0.1	8.8	1.3	0.1	4.3	1.3	0.2	6.9	2.2

Table 2 Classification of groundwater based on TDS

TDS (mg/l)	Water type/usability	Percentage of samples			Reference
		Nalgonda	Pambar	Vaniyar	
<1000	Fresh	94.7	39.9	47.8	Freeze and Cherry (1979)
1000–10,000	Brackish	5.3	60.1	52.2	
10,000–100,000	Saline	0.0	0.0	0.0	
>1,00,000	Brine	0.0	0.0	0.0	
<500	Desirable for drinking	32.6	5.7	10.8	Davis and DeWiest (1966)
500–1000	Permissible for drinking	62.2	34.2	36.9	
1000–3000	Useful for irrigation	4.4	59.1	52.2	
>3000	Unfit for drinking and irrigation	0.8	1.0	0.0	

fluoride-rich drinking water but also due to other diet habits. Fluoride was deficient, i.e., <0.6 mg/l in 20 % of groundwater in Nalgonda and 18.6 and 7.4 % in Pambar and Vaniyar River basins, respectively. Nearly 35 % of the groundwater samples had fluoride above 1.5 mg/l in Nalgonda and Pambar regions, whereas in Vaniyar, high fluoride content was recorded in 65 % of the region. Figure 4 gives the exposure dose for fluoride through groundwater used as drinking. Nalgonda has the highest exposure dose followed by Vaniyar and Pambar regions. As a representation, spatial distribution of the fluoride content in groundwater of the three sites is shown for one sampling period in Fig. 5. In general, the spatial variation in fluoride concentration of groundwater did not follow any systematic pattern (Fig. 5).

Sources of fluoride

Fluoride in groundwater of all three areas is of geological origin attributed to rock-water interaction and weathering of minerals. Though the rocks differ in these geographically distinct locations, these rocks possess minerals rich in fluorine that attribute to the fluoride content in groundwater. Groundwater occurring in some granitic regions is commonly affected by high fluoride in groundwater (Brindha et al. 2011; Brindha and Elango 2013; Reddy et al. 2010; Deshmukh et al. 1995; Kim and Jeong 2005). Nalgonda district comprises mainly of weathered and fractured granite and granitic gneisses which are widely known for their high fluoride contents than any part of the world (Rao et al. 1993). These rocks contain fluorine-rich minerals such as fluorite, biotite, and hornblende (Brindha et al. 2011; Brindha 2012; Brindha and Elango 2013) and the weathering of these rocks leads to release of fluoride into groundwater. Carbonatite complex of Pambar basin is also rich in fluoride. Carbonatite intrusions consisting of fluorite and fluorapatite, epidote hornblende biotite gneiss consisting of biotite and hornblende and charnockites have high fluoride. Vaniyar basin with Archaean gneisses, charnockites with dolerite dyke intrusions, and epidote hornblende gneiss also contain fluoride-bearing minerals. Weathering and release of fluoride from these rocks leads to fluoride-rich groundwater in these areas (Jagadeshan et al. 2015a, b).

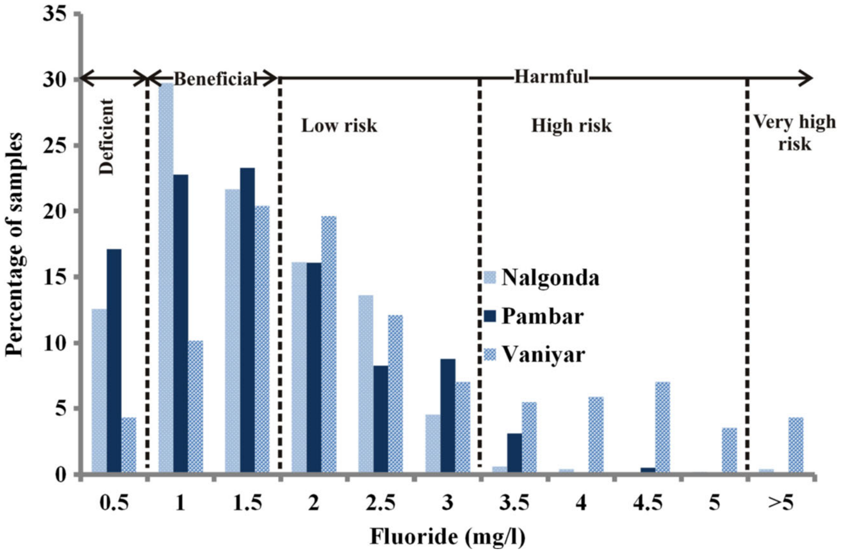
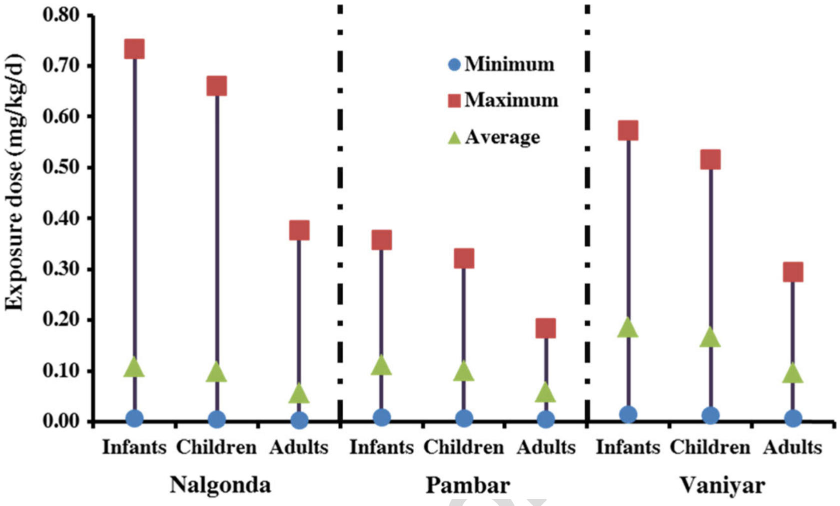


Fig. 3 Groundwater samples in different frequency of fluoride concentration and its risk (after Maithani et al. 1998)

Fig. 4 Fluoride exposure dose to humans in various regions



Geochemical processes

Generally, high fluoride concentration is present in Na-HCO$_3$ groundwater which is deficient in calcium (Apambire et al. 1997; Chae et al. 2007; Raju et al. 2012). Though this is widely accepted, mixed groundwater types have also been reported (Coetsiers et al. 2008; Davraz et al. 2008; Rafique et al. 2009) similar to the varied hydrochemical facies found in

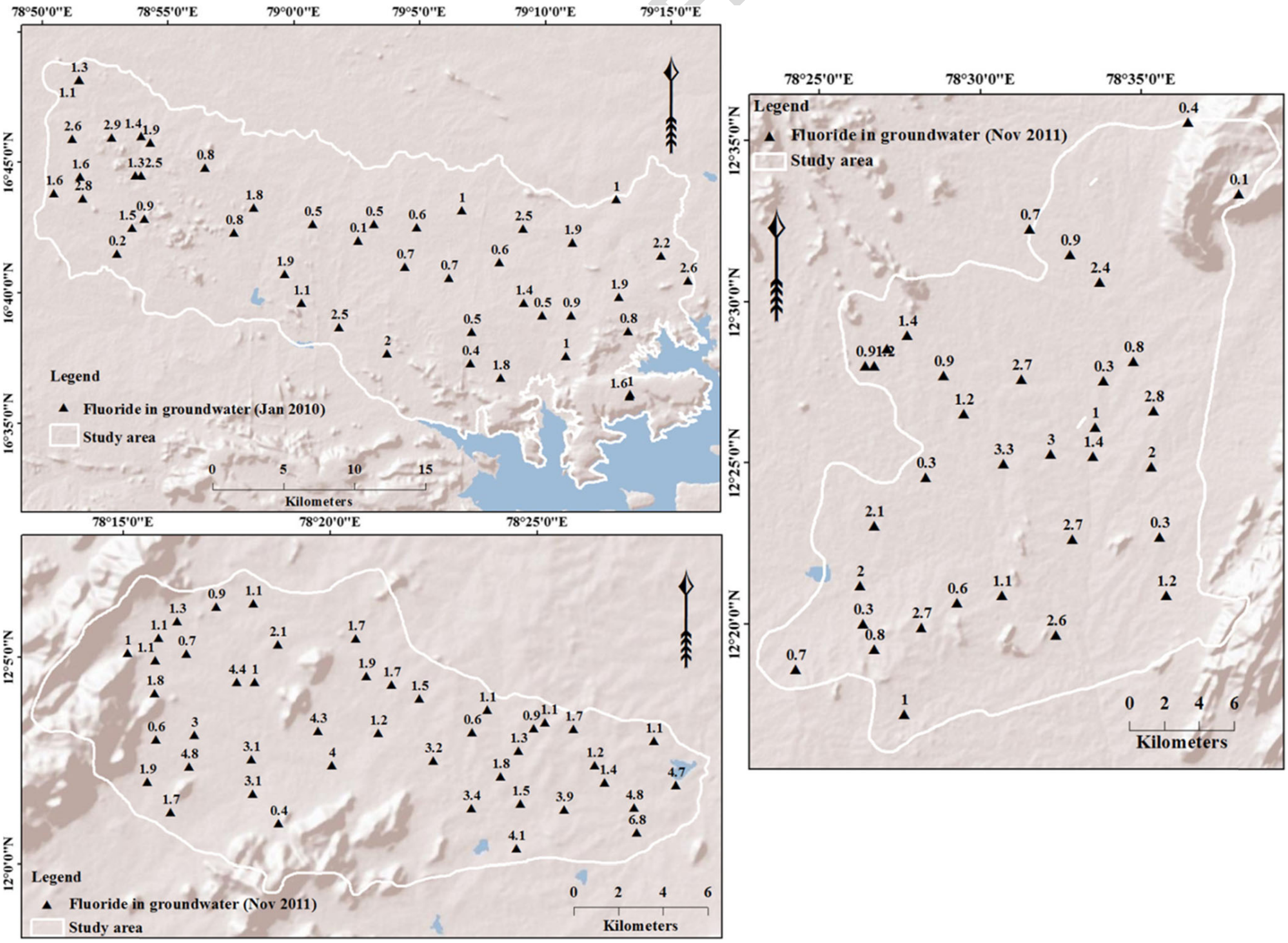


Fig. 5 Spatial distribution of fluoride concentration in the three study areas

these three regions. Ca-HCO_3, mixed Ca-Mg-Cl, and mixed Ca-Na-HCO_3 were the major groundwater type in Nalgonda region. Weathering and dissolution of silicate minerals were responsible for the concentration of cations, i.e., calcium, magnesium, sodium, and potassium (Rajesh et al. 2012) in addition to the ion exchange processes that involve the absorption of calcium and magnesium by clay minerals and subsequent release of sodium into groundwater. In Pambar region, groundwater type was in the order of mixed Ca-Na-HCO_3, Ca-HCO_3, Na-Cl, and mixed Ca-Mg-Cl. Ion exchange and evaporation were the main geochemical processes leading to these ions in groundwater (Kalpana 2014). Major groundwater type in Vaniyar basin was Na-Cl and mixed Ca-Mg-Cl where high sodium and low calcium contents in Vaniyar basin may be due to ion exchange (Jagadeshan et al. 2015b). Though most regions of Nalgonda and Pambar had high bicarbonate waters, contribution from chloride was also witnessed in some locations.

High TDS in groundwater can also enhance the ionic strength and lead to increase in fluoride solubility in groundwater (Rafique et al. 2009; Sreedevi et al. 2006; Rao 2003). A plot of fluoride and TDS of the samples in the three study areas in Fig. 6a–c shows that in Vaniyar basin increase in the fluoride concentration with increase in TDS is significant. In Nalgonda and Pambar regions, the relationship is not very prominent. High TDS can be attributed to higher intensity of weathering in Vaniyar basin compared to the other areas. These regions being located in arid to semi-arid zones experience high temperature leading to larger evaporation of water which too leads to high TDS. Contribution of evaporation process and weathering of rocks for high TDS is also evident from the Gibbs diagram for mechanisms controlling groundwater chemistry (Gibbs 1970) (Fig. 7).

Fluoride also depends on the alkalinity as alkaline groundwater is more vulnerable for fluoride leaching from the rocks in the aquifer matrix. Hence, mostly high fluoride occurs in groundwater rich in bicarbonate (Madhnure et al. 2007; Raju et al. 2012; He et al. 2013). Plot of fluoride against bicarbonate shows an increasing trend (Fig. 6d–f). Thus, fluoride varies directly with alkalinity, but inversely with hardness (Rao et al. 1993), i.e., fluoride will increase with increase in the ratio of $(HCO_3 + CO_3)/(Ca + Mg)$. Groundwater samples were divided into two groups based on the fluoride concentration being less than or greater than 2 mg/l in groundwater and the percentage of the water samples falling in the two groups were plotted against different range of ratio obtained from a sum of the concentration of carbonates and bicarbonates divided by the sum of the concentration of calcium and magnesium (Fig. 8). It is seen that as the range of this ratio increases, the number of samples having higher fluoride concentration also increases. This has also been

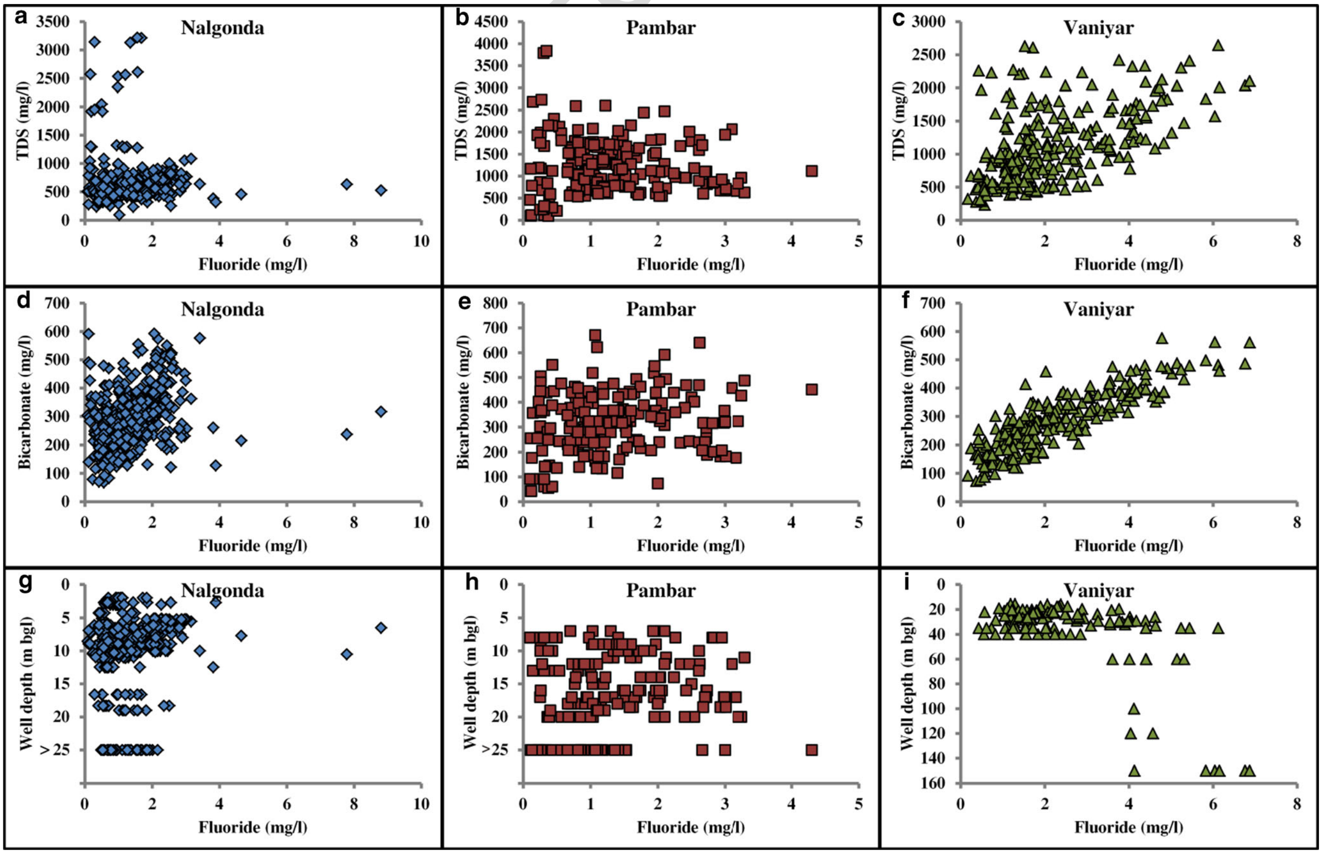
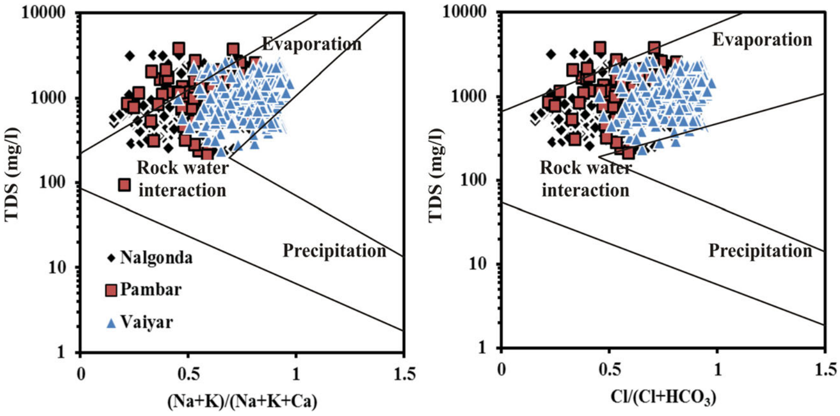


Fig. 6 Concentration of fluoride in groundwater versus **a**–**c** TDS, **d**–**f** bicarbonate. and **g**–**i** well depth

Fig. 7 Geochemical processes in the study areas



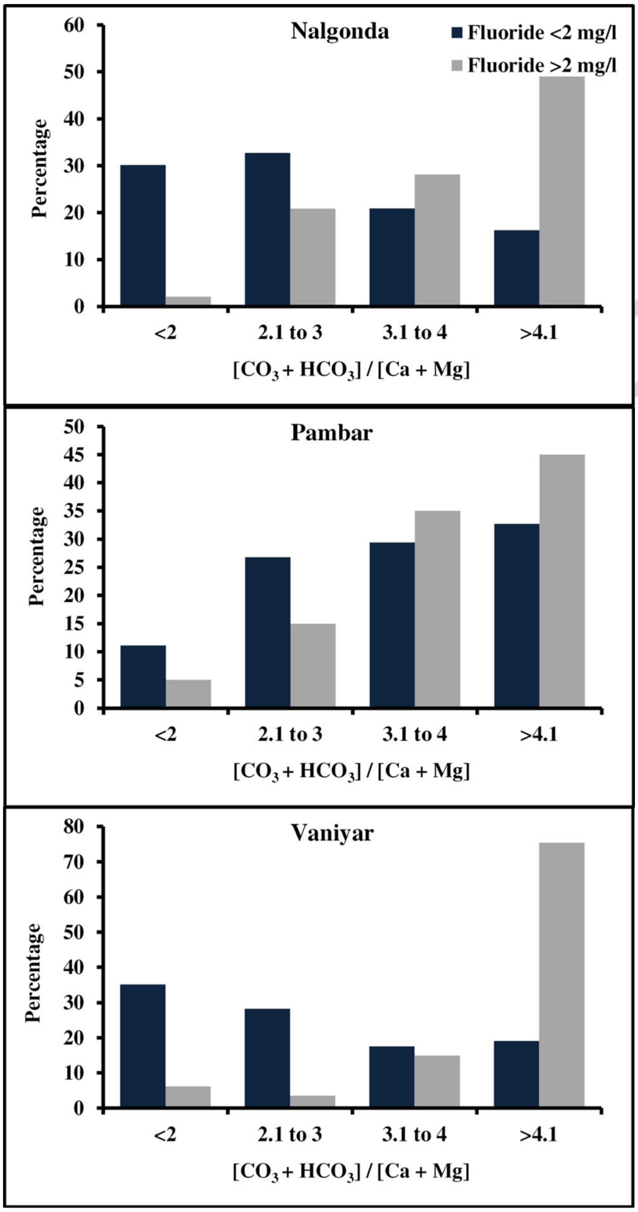


Fig. 8 Ratio of carbonates and hardness versus percentage of groundwater samples with fluoride above and below 2 mg/l

reported by Rao et al. (1993) while the similar trend was also observed by Brindha et al. (2011) for fluoride in groundwater ranging above and below 1 mg/l. Thus, it is evident in all three regions that the fluoride in groundwater increases with increase in carbonate and bicarbonate and decreases with increase in calcium and magnesium.

Temporal variation in groundwater level and fluoride

Intensity of weathering varies in the different areas and so also the depth of open dug wells. Maximum depth of open wells in Nalgonda and Pambar sub basin is about 20 m, whereas in the Vaniyar sub basin, it is more than 27 m. Depth of the wells play an important role in increasing the fluoride concentration in the extracted groundwater as reported by many researchers (Rafique et al. 2009; He et al. 2013; Jagadeshan et al. 2015a). Wells with greater depth have groundwater with relatively high concentrations of fluoride (Fig. 6g–i) due to longer residence time and interaction with the fractured and weathered fluorine bearing rocks. In Nalgonda, wells deeper than 11 m bgl had comparatively higher fluoride than the shallow wells (Fig. 6g) (Brindha and Elango 2013). Likewise, in Vaniyar region, wells with depth greater than 30 m bgl have more fluoride (Fig. 6h) (Jagadeshan et al. 2015a). Though a similar evident relation is not clearly observed in Pambar, dug wells at a minimum depth of 7 m bgl and bore wells deeper the 25 m has records of fluoride greater than 2 mg/l (Fig. 6i).

Groundwater level varied spatially and temporally during the study which is given in Table 1. Even though these locations are characterized by different rock types, the annual rainfall is similar and the maximum depth to groundwater level was high in Vaniyar region and less in Nalgonda. Fluctuation in groundwater level and the fluoride concentration was studied by plotting graphs for all the dug wells that were sampled and monitored. Since the depth to groundwater in bore wells of all three regions were not measured, they were exempted from this exercise. The rise or fall in fluoride concentration with that of groundwater level was analyzed. Also, the positive or negative trend of groundwater fluctuation with fluoride was compared with the different range of fluoride concentration. This study on temporal variation in fluoride concentration and groundwater level resulted in classification of wells into two types in all the three regions. In wells classified as type I, the groundwater level rise is associated with fall in fluoride concentration and vice versa. But in the case of wells classified as type II, the increase in groundwater level increases the fluoride concentration and vice versa. It was observed that the groundwater fluctuate in the upper part of the formation in type I, whereas in the wells grouped as type II, groundwater fluctuates at a comparatively greater depth. Analysis based on fluoride in groundwater samples of wells showing type I and II relation with groundwater level is shown for few sampling locations in Figs. 9 and 10. However, this classification based on the groundwater fluctuation in shallow and deep conditions varied at different depths for the three regions. Fluctuation in water levels up to 5 m bgl in Nalgonda (Brindha et al. 2011), up to 10 m bgl in Pambar, and up to 15 m bgl in Vaniyar represented the type I relationship. This variation is due to the local meteorological and hydrogeological conditions apart from the withdrawal of water by the people for various uses. Average groundwater levels recorded in these regions vary from 4, 9, and 14 m bgl for Nalgonda, Pambar, and Vaniyar, respectively (Table 1). As groundwater in these locations occur at shallow depth during rainfall recharge, dilution of groundwater results in decrease in the concentration of fluoride (Brindha et.al 2011) with increase in groundwater levels. Rise in fluoride concentration with decrease in groundwater level is attributed by direct evaporation from the open wells which are usually of large diameter (Brindha et al. 2011). Further during the lowering of groundwater level, abstraction and lateral flow lead to release of more fluorine from the comparatively fresher rocks at the bottom. In wells classified as type II, the groundwater level fluctuation is mostly below 5, 10, and 15 m bgl in Nalgonda, Pambar, and Vaniyar basins, respectively. As groundwater occurs comparatively at greater depth, percolation of rainwater leaches the salt deposited due to evaporation in the soil layer to the groundwater (Brindha et.al 2011). This flushing of salts with the infiltrating rainwater and also the rock-water interaction occurring at greater depths raise the fluoride concentration in groundwater along with the rise in water table. A schematic diagram of the type I and II relations between groundwater level and fluoride concentration is shown in Fig. 11.

Number of dug wells showing type I and II variations are given in Fig. 12a. In Nalgonda, more wells show type II condition where the leaching of salts from the unsaturated zone increase the fluoride content with raise in groundwater level. But in Pambar and Vaniyar regions, the effect of evaporation in increasing the fluoride concentration in the shallow groundwater and subsequent reduction by dilution effect (type I) was observed in more wells (Fig. 12b). Overall, the number of samples containing fluoride concentration above 1.5 mg/l was more in type II wells compared to the wells with type I relationship. It was observed that mostly the fluoride concentration is within the maximum permissible limit of 1.5 mg/l (BIS 2012) in wells where groundwater level fluctuates at shallow depths (type I). However, in the case of Vaniyar area, the fluoride concentration higher than 1.5 mg/l falls under both types (Fig. 12b). High intensity of weathering and

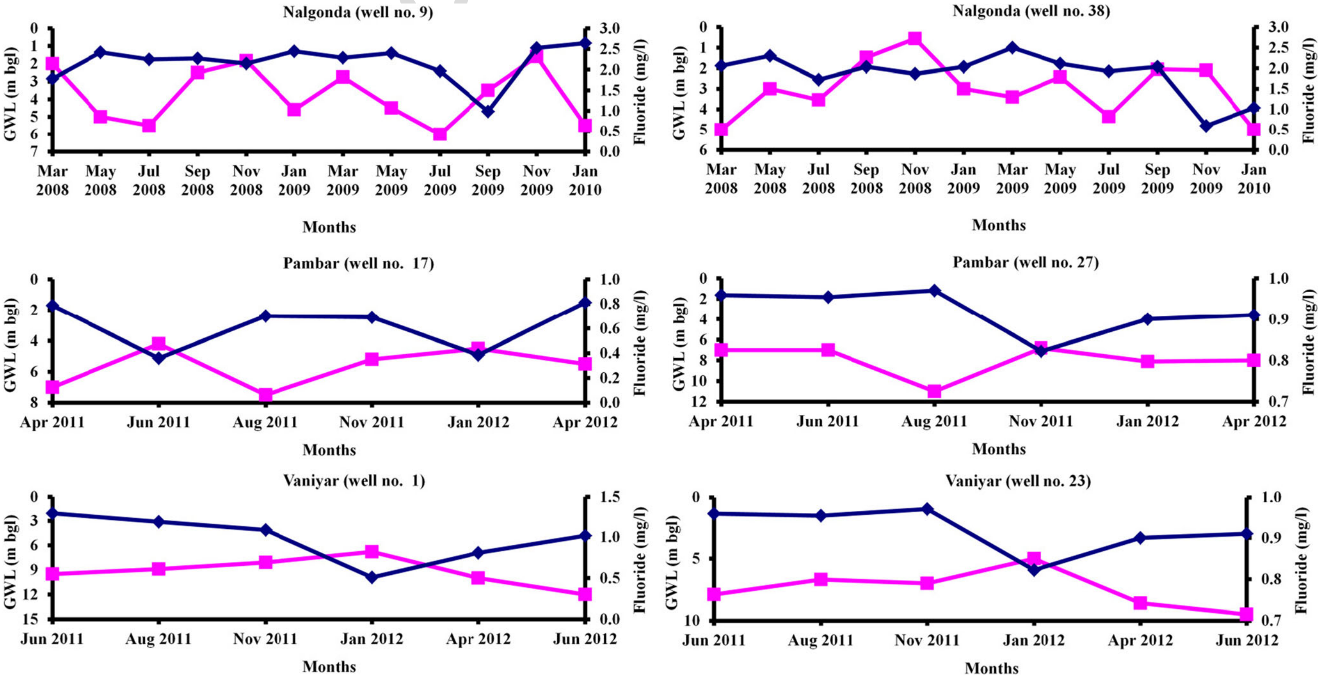


Fig. 9 Temporal variation in groundwater level and fluoride concentration (type I) in well with shallow water level fluctuation

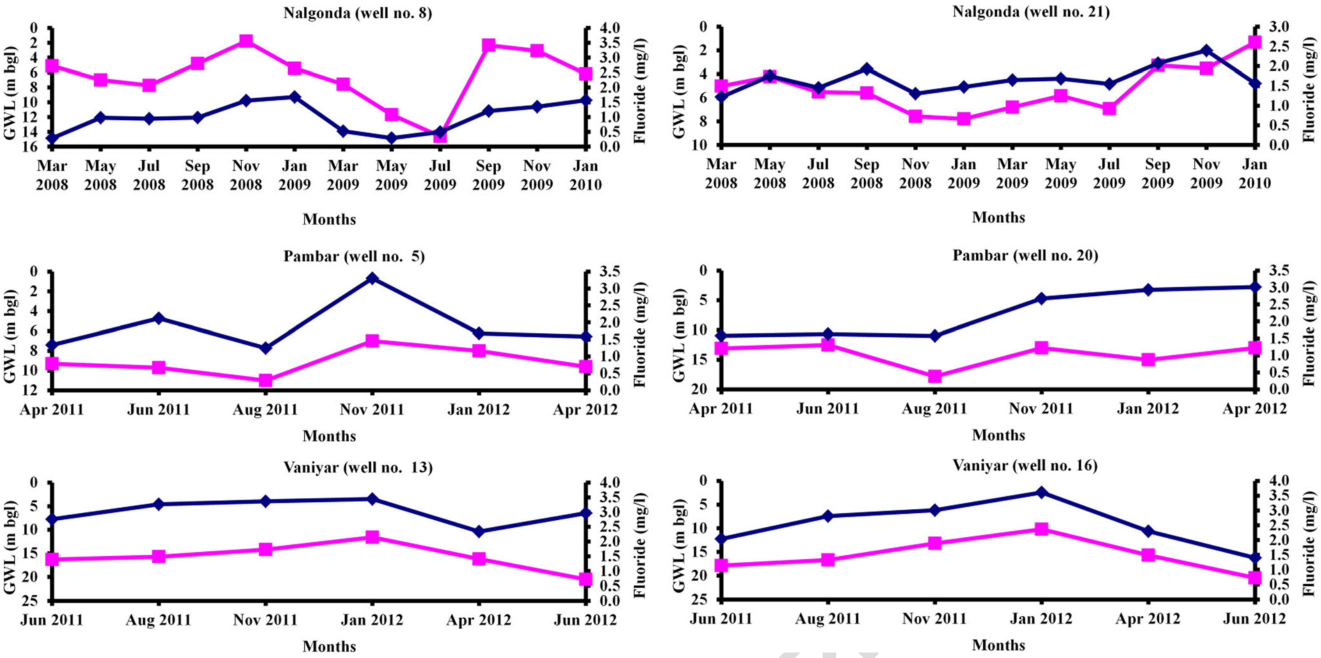


Fig. 10 Temporal variation in groundwater level and fluoride concentration (type II) in well with deep water level fluctuation

fracturing of rocks in Vaniyar region compared to the other regions has resulted into release of higher amount of fluoride into groundwater which was also evident from the TDS and bicarbonate contents (Fig. 6a–f).

MAR as a mitigation measure

Fluoride removal methods may be expensive and time consuming and might concentrate on the removal of one or few ions only. MAR is widely proposed as a suitable option to dilute the concentration of ions in groundwater and minimize the health effects due to consumption. Rao et al. (1992) and Rao and Tucker (1996) reported that the wells located downstream of surface water bodies such as tanks in parts of Nalgonda district had lower fluoride content in groundwater due to dilution by increased recharge. Similar results were observed by Andrade (2012) where a check dam and a percolation tank installed in a micro-watershed in Nalgonda district reduced fluoride from ~2 to 0.9 mg/l. In Anantapur district, Andhra Pradesh, impact of check dams on diluting fluoride-rich groundwater showed success rate at 58.6 % while two samples showed higher fluoride concentration after the construction of check dam indicating a negative impact. But these studies did not look into the temporal relation between groundwater level and fluoride concentration such as the present study. Having studied the relationship between fluoride and groundwater level fluctuation in three different areas, the increase in groundwater level by MAR is expected to reduce the fluoride concentration by dilution and make the groundwater potable especially in case of wells where water level fluctuates in shallow depth, i.e., type I wells. In the case of type II wells, if MAR is adopted, this might increase the concentration of fluoride up to a certain extent after which dilution may occur only in the event of long spells of rains during monsoon.

MAR as a measure of mitigation by a check dam and a dug well recharge system was assessed as a part of this study. Effect of dilution by MAR was verified by field observations in and

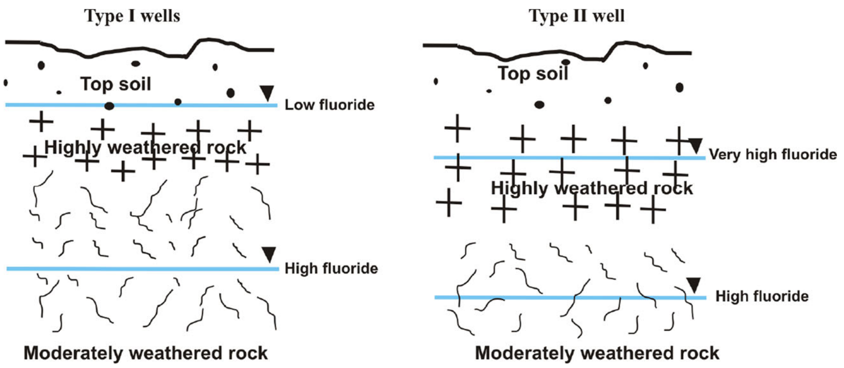


Fig. 11 Schematic representation of the relationship between groundwater fluctuation and fluoride concentration

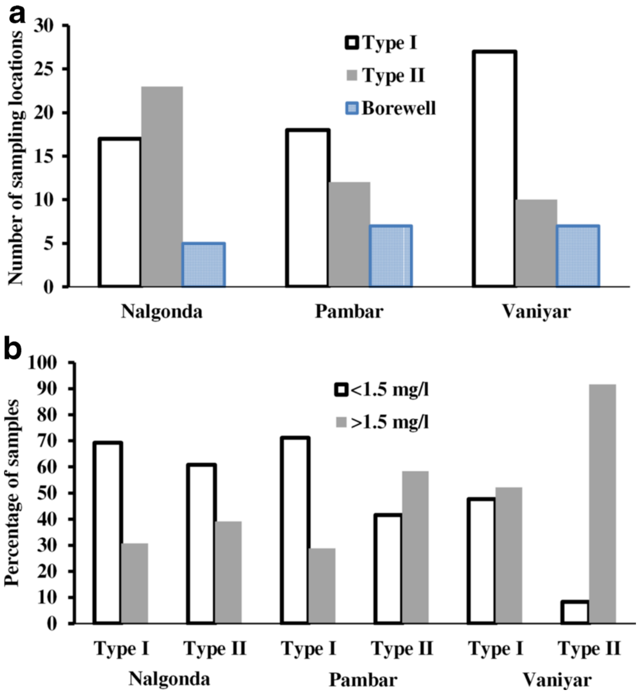


Fig. 12 **a** Wells classified into two types based on fluoride and groundwater fluctuation; **b** fluoride concentrations in different ranges in type I and II wells

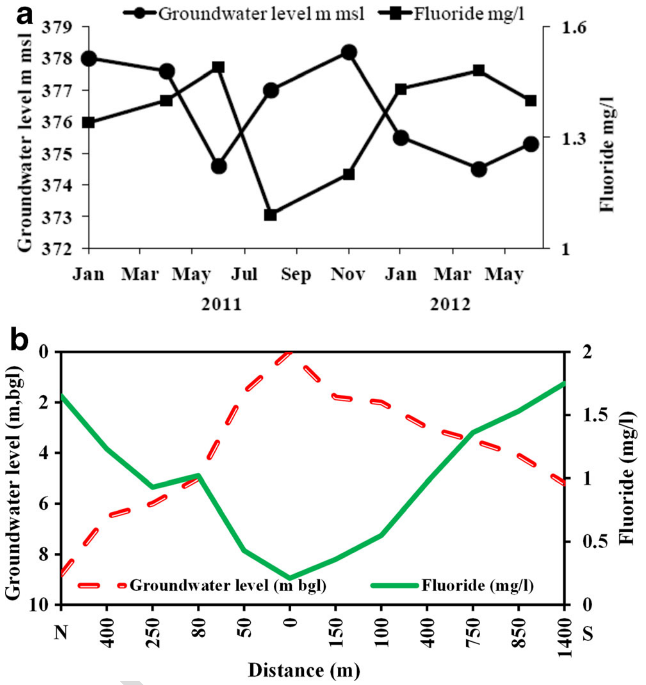


Fig. 13 **a** Temporal variation in groundwater level and fluoride concentration in the monitoring well located near the check dam; **b** groundwater level and fluoride concentration in wells on both banks of the river at different distances from the check dam

around a type I well of Pambar area where a check dam was constructed. A monitoring well located near the check dam in the western course of the Pambar River showed type I relation, i.e., dilution of fluoride concentration due to rise in groundwater level. As the well was near the check dam, the groundwater level was always shallow. Average groundwater level was at 4 m bgl and the fluoride concentration was in the range of 1.09 to 1.5 mg/l. Observed fluctuation of fluoride with groundwater level in the well is shown in Fig. 13a. Even though the rocks of this region are known for high fluoride content which is the source of fluoride in groundwater, the fluoride in this well is less due to dilution compared to those located farther for the check dam. Water in the well was potable with respect to fluoride content as the concentration did not exceed the maximum permissible limit of 1.5 mg/l. Variation in the concentration of fluoride and groundwater level in wells located on both banks of river and near the check dam is shown in Fig. 13b which establishes the reduction fluoride concentration in groundwater due to the MAR structure.

As a pilot experiment, a recharge well was constructed in the Vaniyar river basin of Dharmapuri district. A monitoring well close to the newly constructed recharge well was observed regularly for groundwater level and fluoride concentration which improved after installing the recharge structure (Fig. 14a). Water table raised from 14.5 to 9.1 m bgl, EC decreased from 1342 to 945 µS/cm, and fluoride reduced from 3.1 to 1.4 mg/l, i.e., within the permissible drinking water limits. This induced recharge benefited an area of about 1 km^2 (Fig. 14b) and sets as an example for using low-cost recharge structures to decrease fluoride in groundwater of affected areas.

Though these studies indicate the positive impact of MAR on mitigating fluoride in groundwater by dilution, this depends entirely on the quantity of rainfall that might be able to capture through MAR structures. With high evaporation in these arid to semi-arid regions, the increase in fluoride during the dry season is possible. It is thus highlighted that recharge can help to dilute the water and minimize fluoride pollution only in certain cases. Also, a systematic, long-term monitoring of water table and fluoride as carried out in the present study is essential to understand the processes and identify the relation between them to determine the possibilities for treatment. This exercise will help in the decision-making to adopt MAR and also help to identify suitable recharge areas for the MAR structures. In contrast to the general recommendation of artificial recharge structures in regions with greater depth to groundwater table, this study recommends such structures in areas of shallow water table which will result in improvement in groundwater quality with respect to fluoride.

Conclusion

This study aims to understand the variation in groundwater chemistry based on fluoride, the important health affecting ion with respect to the groundwater level fluctuation. Fluoride

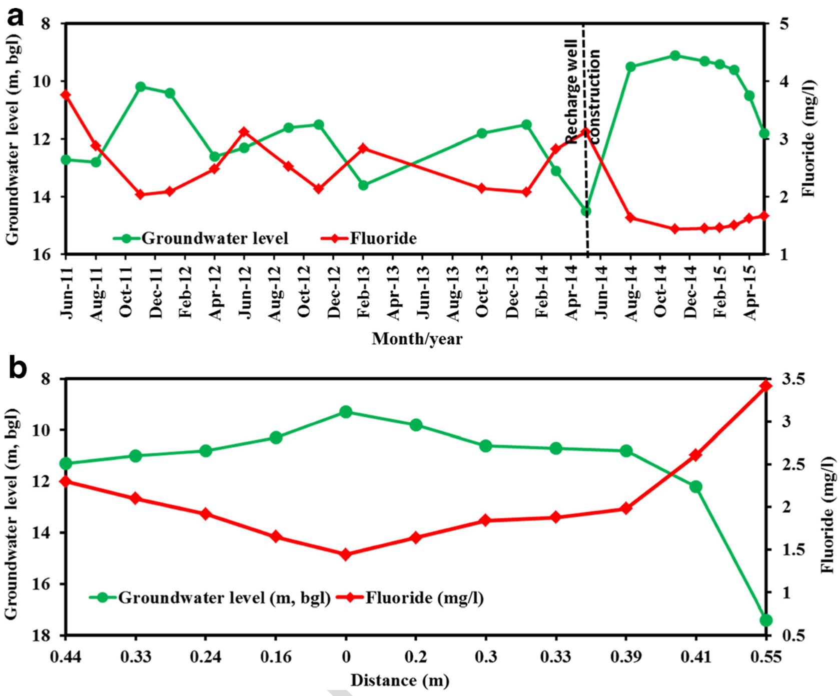


Fig. 14 **a** Temporal variation in groundwater level and fluoride concentration in a monitoring well before and after the construction of the recharge well; **b** groundwater level and fluoride concentration in wells on both sides of the recharge structure at different distances

contamination in groundwater of three areas in south India located in arid to semi-arid regions with high temperature and rainfall with similar drainage and distinct geological features was studied. Geological units of these areas contain fluoride-bearing minerals such as fluorite, fluorapatite, biotite, and hornblende. Maximum concentration of fluoride above 4 mg/l was recorded in all three regions. Fluoride concentration was above the maximum permissible limit of 1.5 mg/l in 36, 37, and 65 % of the groundwater samples in Nalgonda, Pambar, and Vaniyar regions, respectively. Fluoride exposure dose to humans was highest in Nalgonda followed by Vaniyar and Pambar regions. TDS levels recorded shows that the groundwater in these areas vary from fresh to brackish and are mostly alkaline with high pH and bicarbonate content. Correlation between fluoride and TDS as well as bicarbonate content in groundwater of these regions suggest that geochemical processes such as rock-water interaction and weathering attribute to high fluoride in groundwater. High pH, carbonates, and low hardness in groundwater lead to fluoride leaching from the inherent rocks and increase the concentration of fluoride. Study of groundwater level and fluoride fluctuation shows that most of the wells with shallow groundwater have comparatively less fluoride than wells with deep groundwater environment. However, the depth of groundwater level fluctuation of shallow wells differed in the three areas which was up to 5 m bgl in Nalgonda, 10 m bgl in Pambar, and 15 m bgl in Vaniyar. In wells where groundwater fluctuation is in shallow zone, it is associated with fall in fluoride concentration, whereas in deeper cases where the fluctuation is more in the weathered zone, the increase in groundwater level increases the fluoride concentration and the other way round. As dilution occurs in the former case, the artificial recharge is suggested in shallow water table regions to decrease the fluoride concentration. It is crucial not to adopt MAR in areas where groundwater fluctuation is in the deeper levels as it might increase the fluoride concentration. Hence, a study of this nature is essential before deciding on the type of treatment or mitigation method to be adopted. The analysis of mixing of surface water and groundwater studied in a location in the Pambar River basin around a check dam shows the reduction in fluoride concentration by MAR. Similar results were observed around a recharge well constructed specifically to decrease fluoride concentration in Vaniyar River basin. These studies evidences that the recharge of groundwater by MAR will improve the quality of groundwater.

Acknowledgments Work funded by the Board of Research in Nuclear Sciences, Department of Atomic Energy, Government of India (Grant no. 2007/36/35) in Nalgonda district, University Grants Commission (F.No.39-133/2010 (SR)) in Vaniyar River basin and the Centre with Potential for Excellence in Environmental Science scheme of University Grants Commission (Grant no. F.No.1-9/2004 (NS/PE)) in Pambar River basin are gratefully acknowledged. Authors would also like to thank the Department of Science and Technology's Funds for Improvement in Science and Technology scheme (Grant no. SR/FST/ESI-106/2010); University Grants Commission's Special Assistance Programme (Grant no. UGC DRS II F.550/10/DRS/2007 SAP-1) for their support in creating laboratory facilities, which helped in carrying out part of this work.

References

Andrade R (2012) Integrated use of geophysical, hydrological and geographic information system (GIS) methods in enhancing the groundwater quality in a fluoride-endemic terrain (Andhra Pradesh, India). Hydrogeol J 20(8):1589–1597

Apambire WM, Boyle DR, Michel FA (1997) Geochemistry, genesis, and health implications of fluoriferous groundwater in the upper regions of Ghana. Environ Geol 35(1):13–24

APHA (American Public Health Association) (1998) Standard Methods for the Examination of Water and Wastewater, 20th edn. American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA

Arya S, Kumar V, Minakshi A, Dhaka A (2011) Assessment of underground water quality: a case study of Jhansi city, Uttar Pradesh, India. Int Multidiscip Res J 1:11–14

Ayoob S, Gupta AK (2006) Fluoride in drinking water: a review on the status and stress effects. Crit Rev Environ Sci Technol 36:433–487

Bhagavan SVBK, Raghu V (2005) Utility of check dams in dilution of fluoride concentration in ground water and the resultant analysis of blood serum and urine of villagers, Anantapur District, Andhra Pradesh, India. Environ Geochem Health 27:97–108

BIS (2012) Indian standard drinking water specification, Second Revision ISO: 10500:2012, Bureau of Indian Standards, Drinking Water Sectional Committee, FAD 25, New Delhi, India

Brindha K (2012) Assessment of fluoride and uranium in groundwater and hydrogeochemical modelling in a proposed uranium tailings pond area, southern India. Ph.D. Thesis, Anna University, India (Unpublished thesis)

Brindha K, Elango L (2011) Fluoride in Groundwater: causes, implications and mitigation measures. In: Monroy S D (ed) Fluoride properties, applications and environmental management. Nova Publishers, p 111–136

Brindha K, Elango L (2013) Geochemistry of fluoride rich groundwater in a weathered granitic rock region, southern India. Water Qual Exposure Health 5:127–138

Brindha K, Rajesh R, Murugan R, Elango L (2011) Fluoride contamination in groundwater in parts of Nalgonda district, Andhra Pradesh. Environ Monit Assess 172:481–492

Brunt R, Vasak L, Griffioen J (2004) Fluoride in groundwater: probability of occurrence of excessive concentration on global scale. International groundwater resources assessment centre, Utrecht, Report nr. SP 2004–2, Available from: http://www.un-igrac.org/dynamics/modules/SFIL0100/view.php?fil_Id=125. Acessed on 9th May 2014

Chae GT, Yun ST, Mayer B, Kim KH, Kim SY, Kwon JS, Kim K, Koh YK (2007) Fluorine geochemistry in bedrock groundwater of South Korea, Sci. Total Environ 385(1–3):272–283

Coetsiers M, Kilonzo F, Walraevens K (2008) Hydrochemistry and source of high fluoride in groundwater of the Nairobi area, Kenya. Hydrol Sci J 53(6):1230–1240

Datta PS, Deb DL, Tyagi SK (1996) Stable isotope (180) investigations on the processes controlling fluoride contamination of groundwater. J Contam Hydrol 24:85–96

Davraz A, Sener E, Sener S (2008) Temporal variations of fluoride concentration in Isparta public water system and health impact assessment (SW-Turkey). Environ Geol 56(1):159–170

Deshmukh AN, Valadaskar PM, Malpe DB (1995) Fluoride in environment: a review. Gondwana Geol Mag 9:1–20

Dissanayake CB (1991) The fluoride problem in the ground water of Sri Lanka -environmental management and health. Int J Environ Stud 38(2):137–155

Fawell J, Bailey K, Chilton J, Dahi E, Fewtrell L, Magara Y (2006) Fluoride in drinking water. WHO, IWA publishing, p 1–144

Gaciri SJ, Davies TC (1993) The occurrence and geochemistry of fluoride in some natural waters of Kenya. J Hydrol 143:395–412

Gaumat MM, Rastogi R, Misra MM (1992) Fluoride level in shallow groundwater in central part of Uttar Pradesh. Bhu-Jal News 7(2&3):17–19

Gibbs RJ (1970) Mechanisms controlling worlds water chemistry. Science 170:1088–1090

Grimaldo M, Borja V, Ramirez AL, Ponce M, Rosas M, Diaz-Barriga F (1995) Endemic fluorosis in San Luis Potosi, Mexico. I. Identification of risk factors associated with human exposure to fluoride. Environ Res 68:25–30

Haidouti C (1991) Fluoride distribution in soils in the vicinity of a point emission source in Greece. Geoderma 49:129–138

Handa BK (1988) Fluoride occurrence in natural waters in India and its significance. Bhu-Jal News 3(2):31–37

He X, Ma T, Wang Y, Shan H, Deng Y (2013) Hydrogeochemistry of high fluoride groundwater in shallow aquifers, Hangjinhouqi, Hetao Plain. J Geochem Explor 135:63–70

Hem JD (1986) Study and interpretation of the chemical characteristics of natural water (3rd edn) USGS Water Supply Paper 2254

Jagadeshan G, Elango L (2012) Groundwater quality assessment in part of Vaniyar River Basin, Dharmapuri district, Tamil Nadu. Indian J Environ Prot 32(9):772–777

Jagadeshan G, Kalpana L, Elango L (2015a) Major ion signatures for identification of geochemical reactions responsible for release of fluoride from geogenic sources to groundwater and associated risk in Vaniyar River basin, Dharmapuri district, Tamil Nadu. India Environ Earth Sci. doi:10.1007/s12665-015-4250-9

Jagadeshan G, Kalpana L, Elango L (2015b) Hydrogeochemical characterization of fluoride rich groundwater of Vaniyar river basin, Dharmapuri District, Tamil Nadu, India. Geochem Int 53(6):554–564

Kalpana L (2014) Groundwater quality with special reference to fluoride and groundwater modelling for simulating the effect of managed aquifer recharge in Pambar basin, India. Ph.D. Thesis, Anna University, India (Unpublished thesis)

Kalpana L, Elango L (2013) Assessment of groundwater quality for drinking and irrigation purposes in Pambar River Sub-Basin, Tamil Nadu. Indian J Environ Prot 33(1):1–8

Kantharaja DC, Lakkundi TK, Basavanna M, Manjappa S (2012) Spatial analysis of fluoride concentration in groundwaters of Shivani watershed area, Karnataka state, South India, through geospatial information system. Environ Earth Sci 65(1):67–76

Karthikeyan K, Nanthakumar K, Velmurugan P, Tamilarasi S, Lakshmanaperumalsamy P (2010) Prevalence of certain inorganic constituents in groundwater samples of Erode district, Tamilnadu, India, with special emphasis on fluoride, fluorosis and its remedial measures. Environ Monit Assess 160:141–155

Kim K, Jeong GY (2005) Factors influencing natural occurrence of fluoride rich ground waters: a case study in the southeastern part of the Korean Peninsula. Chemosphere 58(10):1399–1408

Kim Y, Kim J-Y, Kim K (2011) Geochemical characteristics of fluoride in groundwater of Gimcheon, Korea: lithogenic and agricultural origins. Environ Earth Sci 63(5):1139–1148

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

Lloyd JW, Heathcote JA (1985) Natural inorganic hydrochemistry in relation to groundwater. Clarendon, Oxford

Madhnure P, Sirsikar DY, Tiwari AN, Ranjan B, Malpe DB (2007) Occurrence of fluoride in the groundwaters of Pandharkawada area, Yavatmal district, Maharashtra, India. Curr Sci 92(5):675–679

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 effect of human health. Curr Sci 74(9):773–777

Mamatha P, Rao SM (2010) Geochemistry of fluoride rich groundwater in Kolar and Tumkur Districts of Karnataka. Environ Earth Sci 61(1):131–142

Matthess G (1982) The properties of groundwater. Wiley & Sons, New York, p 498

Mohapatra M, Anand S, Mishra BK, Giles DE, Singh P (2009) Review of fluoride removal from drinking water. J Environ Manag 91:67–77

Mondal NC, Prasad RK, Saxena VK, Singh Y, Singh VS (2009) Appraisal of highly fluoride zones in groundwater of Kurmapalli watershed, Nalgonda district, Andhra Pradesh (India). Environ Earth Sci 59:63–73

Ortiz D, Castro L, Turrubiartes F, Milan J, Diaz-Barriga F (1998) Assessment of the exposure to fluoride from drinking water in Durango, Mexico using a geographic information system. Fluoride 31(4):183–187

Pettenati M, Picot-Colbeaux G, Thiéry D, Boisson A, Alazard M, Perrin J, Dewandel B, Maréchal J-C, Ahmed S, Kloppmann W (2014) Water quality evolution during managed aquifer recharge (MAR) in Indian crystalline basement aquifers: reactive transport modeling in the critical zone. Geochemistry of the Earth's Surface meeting, GES-10, Procedia Earth and Planetary Science 10,) 82–87

Pickering WF (1985) The mobility of soluble fluoride in soils. Environ Pollut Ser B 9:281–308

Rafique T, Naseem S, Usmani TH, Bashir E, Khan FA, Bhanger MI (2009) Geochemical factors controlling the occurrence of high fluoride groundwater in the Nagar Parkar area, Sindh, Pakistan. J Hazard Mater 171:424–430

Rajesh R, Brindha K, Murugan R, Elango L (2012) Influence of hydrogeochemical processes on temporal changes in groundwater quality in a part of Nalgonda district, Andhra Pradesh, India. Environ Earth Sci 65:1203–1213

Raju NJ, Dey S, Gossel W, Wycisk P (2012) Fluoride hazard and assessment of groundwater quality in the semi-arid Upper Panda River basin, Sonbhadra district, Uttar Pradesh, India. Hydrol Sci J 57(7): 1433–1452

Rao NS (2003) Groundwater quality: focus on fluoride concentration in rural parts of Guntur districts, Andhra Pradesh, India. Hydrol Sci J 48(5):877–892

Rao DR, Narayana BL (1988) Origin and evolution of Gneiss-Charnockite rocks of Dharmapuri district, Tamil Nadu, India. Lunar and Planetary Inst., Workshop on the Deep Continental Crust of South India, p 147–148

Rao RS, Tucker SP (1996) Integrated remote sensing based approach to identify low fluoride drinking water sources – A case study of Nalgonda & Anantapur Districts of Andhra Pradesh, India. In: Proceedings of the National Workshop on Application of Remote Sensing & GIS Techniques to Integrated Rural Development, SIII.15–SIII.38

Rao RS, Krupanidhi KVJR, Venkata Swamy M, Rama Krishna GVA, Mastan Rao C, Subba Rao AV (1992) Integrated remote sensing based approach to identify low fluoride drinking water sources – a case study in part of Nalgonda District, AP. In: Sahai B, Kachhwaha TS, Ravindran KV, Roy AK, Sharma ND, Sharma PK (eds) Proceedings of the National Symposium on Remote Sensing for Sustainable Development, pp 219–223

Rao NVR, Suryaprakasa Rao K, Schuiling RD (1993) Fluorine distribution in waters of Nalgonda District, Andhra Pradesh, India. Environ Geol 21:84–89

Reddy DV, Nagabhushanam P, Sukhija BS, Reddy AGS, Smedley PL (2010) Fluoride dynamics in the granitic aquifer of the Wailapally watershed, Nalgonda District, India. Chem Geol 269(3–4):278–289

Sreedevi PD, Ahmed S, Made B et al (2006) Association of hydrological factors in temporal variations of fluoride concentration in a crystalline aquifer in India. Environ Geol 50:1–11

Tirumalesh K, Shivanna K, Jalihal AA (2007) Isotope hydrochemical approach to understand fluoride release into groundwaters of Ilkal area, Bagalkot District, Karnataka, India. Hydrogeol J 15(3):589–598

Viswanathan G, Jaswanth A, Gopalakrishnan S, Sivailango S (2009) Mapping of fluoride endemic areas and assessment of fluoride exposure. Sci Total Environ 407:1579–1587

WHO (World Health Organisation) (1993) Guidelines for drinking water quality, vol. 1, 2nd edn, Recommendations, WHO, Geneva, pp 130

AUTHOR QUERIES

AUTHOR PLEASE ANSWER ALL QUERIES.

Q1. Please check if the affiliations are presented correctly.
Q2. “TDS” was expanded to “Total dissolved solids.” Please check if correct.
Q3. Please check if the equation is presented correctly.
Q4. Please check Table 2 if data are presented correctly.