Fluoride dynamics in the granitic aquifer of the Wailapally watershed, Nalgonda District, India

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Abstract

High concentrations of fluoride (up to 7.6 mg/L) are a recognized feature of the Wailapally granitic aquifer of Nalgonda District, Andhra Pradesh, India. The basement rocks provide abundant sources of F in the form of amphibole, biotite, fluorite and apatite and whole-rock concentrations of F in the aquifer are in the range 240–990 mg/kg. Calcretes from the shallow weathered horizons also contain comparably high concentrations of F, in the range 635–950 mg/kg. The concentrations of water-soluble F in the granitic rocks and the calcretes are usually low (1% of the total or less) but broadly correlate with the concentrations observed in groundwaters in the local vicinity. The water-soluble fraction of calcretes is relatively high in weathered calcretes compared to fresh samples.

Groundwater major-ion composition shows a well-defined trend with flow downgradient in the Wailapally aquifer, from Na-Ca-HCO_3-dominated waters in the recharge area at the upper part of the catchment, through to Na-Mg-HCO_3 and ultimately to Na-HCO_3 and Na-HCO_3-Cl types in the discharge area in the lowest part. The evolution occurs over a reach spanning some 17 km. Groundwater chemistry evolves by silicate weathering reactions, although groundwaters rapidly reach equilibrium with carbonate minerals, favouring precipitation of calcite, and ultimately dolomite in the lower parts of the watershed. This precipitation is also aided by evapotranspiration. Decreasing Ca activity downgradient leads to a dominance of fluorite-undersaturated conditions and consequently to mobilisation of F. Despite the clear downgradient evolution of major-ion chemistry, concentrations of F remain relatively uniform in the fluorite-undersaturated groundwaters, most being in the range 3.0–7.6 mg/L. The rather narrow range is attributed to a mechanism of co-precipitation with and/or adsorption to calcrete in the lower sections of the aquifer. The model may find application in other high-F groundwaters from granitic aquifers of semi- arid regions.

Keywords: Fluoride; groundwater; health, granite; soil profiles; calcrete

1. Introduction

The detrimental effects of long-term ingestion of high concentrations of fluoride in drinking water are well known and include physiological disorders, dental and skeletal fluorosis, thyroxine changes and kidney damage (Grandjean et al., 1992). High-fluoride groundwaters have been reported from many parts of the world, particularly in arid and semi-arid areas of India, China, Sri Lanka, Spain, Mexico and many countries in Africa, western USA and south America (Edmunds and Smedley, 2005; Ayoob and Gupta, 2006). The serious health risks associated with high F concentrations in drinking water (exceeding the WHO guideline value of 1.5 mg/L; WHO, 2004) warrant investigations of fluoride chemistry encompassing a wide spectrum of hydrochemical and geochemical analyses and appropriate methods of remediation. Granitic rocks contain a relative abundance of fluoride-rich minerals such as micas, apatite and amphiboles. Fluorite (CaF_2) is the principal fluoride mineral, mostly present as an accessory mineral in granites. Dissolution of such minerals can constitute a major source of F in groundwater (Ramesham and Rajagopalan, 1985; Abu Rukah and Alsokhny, 2004; Edmunds and Smedley, 2005, Shaji et al., 2007). High concentrations in groundwater also result from evapotranspiration which may trigger calcite precipitation and result in a reduction in the activity of Ca (e.g. Jacks et al., 2005). Several studies have noted an increase in dissolved F concentrations with increasing groundwater residence time (Nordstrom and Jenne, 1977; Apambire et al., 1997; Genxu and Guodong, 2001; Edmunds and Smedley, 2005). Relatively high F concentrations have been found in some deeply circulating groundwaters along fault lines (Kim and Jeong, 2005, Kundu et al., 2001).

This paper outlines the origin of F in groundwater in a granitic watershed located in Nalgonda District, about 70 km south of Hyderabad, India. Nalgonda District is one of the poorest and most drought-prone districts of Andhra Pradesh in southern India. The area has long been associated with high groundwater fluoride concentrations which have been reported to reach up to 20 mg/L (Rammohan Rao et al., 1993). The district has given its name to an established water defluoridation technique, the Nalgonda technique, developed in the 1970s by NEERI (National Environmental Engineering Research Institute, Nagpur, India) under a UNDP Program (Nawlakhe et al., 1975). Thousands of inhabitants with paralysing bone diseases, deformities of vertebrae, hands and legs, deformed teeth, blindness and other conditions are a common manifestations of this natural hazard in the district. The first fluorosis problem in Nalgonda district was reported by Siddiqui (1968). A comprehensive study of fluoride in the granitic rocks was carried out by the Geological Survey of India (1974). This study reported fluoride concentrations up to 7 mg/L in both groundwater and streamwater around Wailapally, attributed to fluorite-rich zones in the bedrock (Natarajan and Mohan Rao, 1974). Clusters of fluorite were found disseminated as grains or in vein fills in the porphyritic granite gneiss (Natarajan and Murthy, 1974).

Rammohan Rao et al. (1993) concluded that the two main factors governing fluoride in groundwater from the Nalgonda District are the presence of acid-soluble F minerals and low concentrations of Ca and Mg in rocks and soils, with high concentrations of HCO_3 in circulating groundwater. Reddy (2002) reported that the F distribution in groundwaters of the Wailapally watershed is variable and does not follow any pattern in relation to topography, gradient or weathered-zone thickness. However, neither of these studies aimed to delineate systematically the spatial distributions in fluoride across the area and to understand the origins of the fluoride. A better understanding of fluoride geochemistry in the study area is important for evaluating the contamination process more precisely.

This study uses a multifaceted approach to understand the mechanism responsible for the spatial distribution and dynamics of F across a small watershed composed of a single bedrock geological unit (granitic gneiss), based on the chemical analysis of 433 groundwater samples and a number of soil profiles, rock and calcrete samples.

2. Regional setting

2.1. Study area

The study area (130 km^2) lies in a semi-arid region, between 17.03^o to 17.13^o N latitude and 78.8^o to 79.0^o E longitude, located about 70 km southeast of Hyderabad, Andhra Pradesh, India (Fig. 1). The granite exposures are seen as rugged dissected hills (600–650 m a msl) with a N-S trend in the western part, as domed hillocks or sheet-like exposures in the middle part and as undulating terrain with black alkaline soils in the eastern part of the study area. These alkaline soils in the east likely formed due to high evaporation rates and a historic shallow water table.

The aquifer is composed of Archaean basement rocks of the Peninsular Gneissic Complex. These comprise biotite-rich grey or pink granite, porphyritic granite and migmatitic granite gneiss (Natarajan and Murthy, 1974). Younger intrusions of pink granite are also common in this area, especially in the western region.

The rocks are medium- to coarse-grained and composed of greyish or white feldspars, bluish grey or white translucent to opaque quartz, biotite, and hornblende. Fluorite occurs as anhedral grains disseminated in the grey and pink porphyritic gneiss. Quartz and apatite veins, and dolerite dykes are aligned along the major N-S or E-W oriented fractures (Reddy, 2002). Petrographic investigations show the presence of F-containing minerals: fluorite (0-3.3%), biotite (0.1-1.7%) and hornblende (0.1-1.1%) (Rammohan Rao et al., 1993). Natarajan and Mohan Rao (1974) reported F concentrations 0.31 to 1.1% in the whole rock from the same area and in particular the higher concentrations are from porphyroblastic and pink granites.

The weathered zone overlying the bedrock varies in thickness from 30–40 m in the west to less than 10 m in the east. The thick weathered zone in the west has developed as a result of abundant joints and fractures in the granite and accumulation of colluvial deposits due to the hilly terrain. In the east, the weathered zone is thinner because of less jointing and flatter topography.

Calcrete is well-developed in the weathered zone over much of the watershed, notably the central and low-lying eastern parts. It is however, absent from the western section (zone I) and the watershed periphery. Calcrete deposits are observed at the ground surface in the alkaline soils in the east but are also observed in several areas at depths of 10–15 m from dug-well sections. Surface and near-surface exposures occur as hard layers, sometimes extensive but typically as discrete patches. Nodular forms of calcrete also occur in some places. Calcretes found in the dug-well sections are highly weathered.

Topographic elevation varies from 420 m in the west to 280 m in the east with an average topographic gradient of 8 m/km. The gradient is steeper in the western half than in the east. There is no well-developed drainage system in the area, although streams originating in the western hills flow eastwards (Fig. 1). The main stream, Wailapally Vagu, flows from the central part of the catchment and terminates at the man-made irrigation tank at Yelmakanna (Fig. 1). Similarly, south of Wailapally Vagu, many small streams end abruptly after flowing a short distance eastwards, reflecting the high permeability of the soils. There are a few artificially made irrigation tanks across the streams where the surface water storage is for a limited period (a few days to 1–2 months depending on rainfall).

Annual average rainfall is around 650 mm, most falling during July to September from the

SW monsoon. However, rainfall is erratic from year to year, with a variation from 400–1000 mm. Temperature varies from 9^{o}C during winter (minimum) to 42^{o}C during summer (maximum), although average daytime temperatures remain around 30^{o}C for most of the year. As a result of the high temperature, average potential evaporation is about 1400 mm, which is more than twice the average annual rainfall (measured at the Wailapally village, centre of the watershed).

2.2. Hydrogeology

Groundwater is present in both the weathered zone and bedrock fractures. Significant deformation has produced a network of intersecting fractures in the weathered zone which provides hydraulic continuity between the two systems. Groundwater occurs mainly under unconfined conditions, although semi-confined and confined conditions exist locally due to sheet joints in the basement rock. Erratic rainfall and over-exploitation of groundwater in recent years has led to severe water shortages for irrigation and drinking. About 2500 wells exist in the catchment, including both dug wells and boreholes, as inventoried in the 88 km^2 non-hill terrain of the watershed. Of these, almost all dug wells of ≤15 m depth are dry, as are some 40% of the boreholes drilled down to depths ranging to 120 m. Discharge from the remaining boreholes is poor, typically in the range 1.5 to 3 L/s.

The watershed is almost a closed basin with only one outlet to the east. The ground elevation difference between the stream area in the central part and the watershed boundary is about 20–25 m. No external sources of water supply exist in the watershed either for irrigation or for drinking purposes. The main input source to the groundwater is rainfall recharge. A recharge study (Reddy et al., 2009), conducted in this area using environmental chloride, indicates that the bulk of the vertical recharge in the western elevated land occurs through preferred pathways and that a small fraction occurs through the soil matrix. The dominating preferential flow is high (~16% of the annual average rainfall) in the valley fills, but decreases to 5–5.5% in the plains, whereas the matrix (piston flow) recharge is only 1–1.5% of rainfall. Furthermore, considerable lateral movement of groundwater down the slope allows sequential hydrochemical changes to occur (Reddy et al., 2009).

The groundwater sampling campaign for this study was carried out under pre-monsoon drought conditions during June 2004. At the time, the depth to water table varied from 40 m in the west to 7 m in the east (380 to 270 m a msl, Fig. 2), with an average hydraulic gradient 7.5 m/km. The gradient was steeper in the west.

In addition to the quantity problems, the area is facing a severe water-quality problem. High concentrations of naturally-occurring F in the groundwater make it unsuitable for drinking, and alternative sources of drinking water are currently not available.

Based on the relatively high water-level increase (27–35 m) during above-normal rainfall conditions in 2005, low Cl concentrations in the groundwater (average 17 mg/L), and its pulse movement to groundwater recharge (preferential recharge), the western part of the study area (zone I) is demarcated as a recharge zone (Fig. 1). The eastern part (zone IV) is demarcated as a discharge zone based on low water-level fluctuation (ca. 4 m), lower recharge rate (ca. 1%) and higher groundwater Cl concentration (average 120 mg/L) (Reddy et al., 2009).

2.3. Groundwater samples

As almost all open wells were dry, groundwater samples were taken only from boreholes. Out of 433 boreholes sampled from the watershed during the well inventory period (pre-monsoon period of 2004–2005), about 10% were drilled for domestic use, the others being used for agriculture. Being in hard-rock terrain, boreholes are not screened except in the top few metres of the highly weathered zone to avoid borehole collapse. The collected samples generally represent mixed waters abstracted from a range of depths within a borehole. However, a few boreholes were abstracting water exclusively from sheet joints at greater depths. Most of the domestic boreholes are fitted with hand pumps and almost all agricultural boreholes have 5 HP submersible pumps.

Electrical conductance and pH of the water samples were measured using the Consort C533 portable multi-parameter analyzer. Carbonate alkalinity was measured by titration. Other anions and cations were measured using a Dionex ion chromatograph. An AS-14A Ion Pac was used with 8.0 mM sodium carbonate and 1.0 mM bicarbonate as eluent and H_2SO_4 as regenerent with a mixed standard of F, Cl, NO_2, Br, NO_3, PO_4 and SO_4 made in the required proportions from the standards purchased from Merck, Germany. A CS-17 column was used for cation separation with 6 mM methanesulfonic acid as eluent, and a mixed standard of Li, Na, K, Mg and Ca prepared in accordance with the approximate sample values. As a result of the high TDS values (>600 mg/L), the samples were diluted to measure both anions and cations. Several routine checks on standards were made to ensure data quality. Measurements have a precision of ±5% of the total value. The majority of analysed samples had ionic charge imbalances of <5%.

2.4. Rock and soil samples

Soil samples were collected from vertical profiles at nine sites across the study area (Fig. 1). These were extracted by machine-operated auger and were sampled with a sampling interval of 10 cm. The depth of the profiles varied from 1 m to 3.6 m.

Fifteen samples of calcrete and granite were also collected from the study area. Calcrete samples are from the surface as well as at different depths in the weathered zone. Samples were analysed for major elements and total F by XRF spectrometry at the National

Geophysical Research Institute (NGRI) using a Philips MagiX PRO PW 2440, wavelength-dispersive XRF spectrometer coupled with a PW 2540 autosampler. The MagiX PRO is a sequential instrument with a single goniometer-based measuring channel encompassing the entire spectral range from F to U in the concentration range of a few mg/kg to % levels. International reference materials from USGS, Canadian and NIST standards (SO-1, SO-2, JB-2, JP-1, G-2, JG-1A) were used in the preparation of calibration graphs.

The soils and calcrete samples were also used in batch leaching experiments. Samples were first air-dried; 50 g of solid sample were then weighed and 50 mL of milli-Q water added (1:1 ratio). Samples were stirred several times and after 2 hours, the supernatant was decanted (Whatman No.1 filter paper) (Sharma and Hughes, 1985; Johnston, 1987; Sukhija et al., 1988). Sukhija et al. (1988) adopted a similar procedure for investigation of soluble Cl in depth profiles. Soluble F concentration was then measured in the supernatant solution using ion chromatography.

In a further experiment, samples of calcrete were leached (1:1 ratio) for a week and the supernatant liquid analysed for F in order to investigate dissolution over a longer timescale. Another experiment with 50 g of calcrete and 100 mL milli-Q water (1:2 ratio) was also undertaken to investigate the effect of solid/solution ratio.

3. Results

Although more than 480 groundwater samples were collected and analysed in the study, 50 samples were excluded from consideration due to anthropogenic contamination determined from associated high nitrate (≥50 mg/L) and chloride (>100 mg/L) concentrations. These samples were in all cases located within and close to villages where groundwater suffers locally from contamination by latrines and animal wastes. Thus the data for 433 noncontaminated groundwater samples have been used for analysis and interpretation (Fig. 2).

To describe the hydrochemical evolution and processes in the aquifer, the watershed has been divided into four zones based on the geomorphology and hydrogeological conditions. Zone I covers the valley fills (mostly thick weathered zone with some colluvium) in the western part of the watershed, zone II is pediment, zone III moderately weathered pediplain and zone IV is shallow weathered pediplain in the eastern part of the watershed (Fig. 1).

3.1. Hydrochemical variation

3.1.1. Major ions

A statistical summary of the groundwater chemical data for the watershed is given in Table 1. The complete dataset is provided in the Supplemental Data. For the watershed as a whole, the average pH value is 7.7 with a range of 6.6 to 8.9 and average electrical conductivity is 925 µS/cm (TDS 492 mg/L) with a range of 230 to 2130 µS/cm (TDS 120–1130 mg/L). Groundwater temperature is around 30ºC. Concentrations of major constituents Na, K, Ca, Mg, Cl, SO_4, HCO_3 and CO_3 also show wide variation from a few mg/L to a few hundreds of mg/L.

There is significant variation in the average values of different chemical constituents in the different zones (Table 1). Some chemical constituents show a linearly increasing trend from zone I to zone IV, while others show a decreasing trend. From zone I to zone IV, the spatial variation in the average values of various chemical constituents are: pH 7.4–8.5; EC 525–1400 µS/cm; Na 57–310 mg/L; HCO_3 270–660 mg/L; CO_3 <0.1–30 mg/L; Cl 18–110 mg/L and SO_4 12–90 mg/L. However, average Mg increases from zone I to III (16–47 mg/L) and decreases in zone IV (26 mg/L) and Ca decreases downgradient from 27–8 mg/L.

3.1.2. Spatial variability in fluoride concentration

Both the mean and median fluoride concentrations in the groundwater are 3.6 mg/L with a range of 0.5 to 7.6 mg/L. The frequency distribution of concentrations in the 433 groundwater samples shows that no samples have <0.5 mg/L, only 3% have fluoride concentrations ≤1.5 mg/L (the WHO guideline value), 30% lie in the range 1.6–3 mg/L, 34% have 3–4 mg/L, 23% contain 4–5 mg/L and the remaining 10% have concentrations in the range 5–7.6 mg/L (Fig. 2 inset). Groundwaters with F concentrations >4 mg/L F cover almost three quarters of the study area (Fig. 2).

Relatively little variation in groundwater F concentration occurs down the groundwater flow gradient. The median fluoride concentrations in zones I to IV are respectively 3.6, 3.6, 2.7 and 4.3 mg/L. The relatively low zone-III median is due to dilution of groundwater by surface water from the surface tank/pond in that area (Fig. 2) and to a contribution of fresh young recharge water being added from the southern hillocks. Fluoride concentrations in this water are in the range 0.5–1.5 mg/L in zone III. This is the only area within the watershed where groundwater has F concentrations within the permissible limits for drinking.

High-F groundwaters in other parts of the world are often of Na-HCO_3 type with low Ca concentrations and neutral to alkaline pH values. Several studies have demonstrated positive correlations between F and both HCO_3 and Na in high-F groundwaters as well as an inverse relationship between F and Ca concentrations in fluorite-saturated groundwaters (e.g. Handa, 1975; Kundu et al., 2001; Wang and Cheng, 2001; Smedley et al., 2002; Ozsvath, 2005; Edmunds and Smedley, 2005; Valenzuela et al., 2006; Qinghai Guo et al., 2006). For the groundwaters from the Wailapally watershed, there is no clear correlation between these parameters when considering the sample set as a whole (Table 2). Correlations are also generally poor within zones. However, Table 2 indicates that for groundwaters with low F concentrations (0.5–1.5 mg/L), relatively good positive correlations exist between F and Mg (r^2 0.74) and between F and HCO_3 (r^2 0.59). This group comprises only 14 samples, the majority being from a small area around the pond in zone III and indicating the effect of dilution by surface water and by fresh recharge from the southern side of the watershed.

Despite the overall lack of spatial trend in F concentrations, some systematic lateral variations are observed in small areas. A 3.5 km stretch in the valley fill/recharge area of zone I shows a progressive downgradient increase in F from 1.6 mg/L to 4.5 mg/L (Fig. 3). However, there is no significant correlation between F and other major ions in these groundwaters (Fig. 3a-d).

3.1.3. Variation in fluoride concentration with depth

Some studies (e.g. Edmunds and Smedley, 2005; Kim and Jeong, 2005; Hudak and Sanmanee, 2003), have found a positive correlation between borehole/well depth and concentration of F in groundwater, although relationships are not always apparent (e.g. Apambire et al., 1997). In the Wailapally catchment, borehole depths are mostly in the range 30–120 m and groundwater occurs in fractures at variable depths within the bedrock. No relationship has been found between F concentration and borehole depth (Fig. 4).

3.1.4. Groundwater saturation indices

Ranges and means of saturation indices for calcite, dolomite and fluorite (PHREEQC; Parkhurst and Appelo, 1999) are given for the different zones in Table 1. An SI range of 0±0.25 has here been taken as an indication of near-saturated condition. Most groundwaters from the catchment are saturated or near-saturated with respect to calcite. Around 28% of the samples are oversaturated (SI >0.25). Most of the calcite-undersaturated groundwaters are from the peripheral areas of zones I and II. The degree of calcite saturation increased downgradient. All calcite-oversaturated samples are from the low-lying areas, particularly in zone IV (Fig. 5).

Similarly, most groundwaters are saturated or over-saturated with respect to dolomite. Almost all undersaturated groundwaters derive from zone I and saturation index progressively increases downgradient (Fig. 5), although there is an apparent slight decrease in degree of saturation in samples from zone IV. The saturated state of most of the groundwaters with respect to these minerals is consistent with the presence of calcrete deposits, as well as occurrence of alkaline soils, in the lower parts of the catchment.

Despite the large range and often high concentrations of F in the groundwaters, most samples are undersaturated with respect to fluorite (around 95% have $SI_{fluorite}$ <0; Fig. 5). Only two samples from the dataset are oversaturated with respect to fluorite (SI >0.25). Almost all saturated samples are from zone I.

3.2. Chemical variation in rocks and soils

3.2.1. Fluoride in granite samples

The important fluoride minerals in the granitic rocks of the area are fluorite (CaF_2) and apatite [$Ca_5(Cl,F,OH)(PO_4)_3$]. Amphiboles (hornblende) and biotite also contain abundant fluoride which substitutes for hydroxyl in the crystal lattices (Natarajan and Murthy, 1974; Rammohan Rao et al., 1993; Edmunds and Smedley, 2005). The basement and weathered rocks of the area contain substantial quantities of these F-bearing minerals, especially in the porphyritic pink granites.

The average F concentration in surface rock samples collected from the watershed varies from 242 to 990 mg/kg (Table 3). The lowest value is found in a grey granite sample from the eastern part; the highest represents an average of seven measurements (ranging from 19 to 3125 mg/kg) on different aliquots of a single sample of pink granite from the western part.

The wide variation in F concentration from different aliquots of one sample can be attributed to the presence or absence of fluorite grains. The data indicate that the pink granite contains abundant F-bearing accessory minerals.

The highest observed F concentration is very similar to that found for rocks from the same area by Rammohan Rao et al. (1993). They reported F concentration ranges in granitic rocks from Nalgonda district from 325 to 3200 mg/kg with a mean of 1440 mg/kg. In neighbouring Hyderabad, Rammohan Rao et al. (1993) reported mean F concentrations in granitic rocks of 910 mg/kg, although groundwater F concentrations in this area were generally found to be lower because of relatively high solute Ca concentrations. A mean F concentration of 360 mg/kg was found for granites in non-endemic areas of India (Rammohan Rao et al., 1993).

In the adjacent Hyderabad district, where F concentrations in groundwaters are almost at permissible limits (except certain pockets), the granites have an average F concentration of 910 mg/kg, which is about 1.5 times less than the Nalgonda Granite (Ramamohana Rao et al., 1993).

3.2.2. Chemistry of calcretes

Chemical analyses of 11 calcrete samples from three zones determined by XRF are given in Table 4. The concentrations of CaO vary between 30–50% and of MgO between 1.5–16%. Fluoride concentration varies between 440 and 1160 mg/kg. The fluoride concentration is very similar to that found in the granitic rocks of the area.

The analysed calcrete samples display a positive correlation (r^2 0.6) between MgO and F. This suggests that a relationship exists between the concentration of F and the dolomite content of the calcretes. Jacks et al. (2005) also found very high concentrations of F in calcrete samples collected from arid areas of the Indian granitic terrain. They quoted a range of 510–9000 mg/kg in 25 analysed calcrete samples. They also noted that highest F concentrations occurred in dolomitic calcretes (>5 mol% Mg) in downslope positions in the valley sites studied. This accords with the observed F distributions in calcretes in this study.

3.2.3. Total and soluble fluoride in depth profiles and rocks

The relationship between total and water-soluble F concentrations has been investigated in the nine soil profiles from all four zones in order to assess the lability of F in the solid phase. Data for average total and water-soluble concentrations from profiles, together with concentrations in granitic bedrocks and in groundwater from nearby boreholes are given in Table 3.

Of the soil profiles, that from Wailapally is the thickest (to a depth of 3.6 m) and that from Puttapaka is the thinnest (to 0.5 m depth; Table 3). Average water-soluble F concentration in different profiles varies from 0.5 to 10 mg/kg and within the profile the variation is 2–4 times the average concentration. Average water-soluble F in the depth profile at Dubbagadda Tanda (to depth 1.7 m; zone I) is only 0.5 mg/kg, although it increases slightly with depth (0.2–0.8 mg/kg; Fig. 6). Total F concentration in the profile averages 626 mg/kg with relatively little variation. Water-soluble F therefore represents less than 0.1% of the total. Fluoride concentration in the groundwater around this site is 3.7 mg/L.

A profile in zone I at Gangamolla Tanda (to 2.5 m depth) shows an average water-soluble F concentration of 3.0 mg/kg, while the local groundwater has a concentration of 2.5 mg/L.

Two profiles from zone II, Lachammagudem (to 1.2 m depth, Fig. 6) and Wailapally (to 3.6 m) each have average water-soluble F concentrations of 10 mg/kg. The Lachammagudem water-soluble profile increases with depth, with concentrations up to 17 mg/kg at 110 cm depth. The average total F in the soil profile at the site is 1015 mg/kg and has relatively little variation (Fig. 6). The water-soluble component of F at Lachammagudem is therefore just under 1% of the total F. Local groundwater at the Lachammagudem site has 7.0 mg/L F. Local groundwater F concentrations at the Wailapally site are also relatively high, at 5.5 mg/L.

Three shallow profiles (to depths of 0.5 to 1 m) from zone III contain average water-soluble F concentrations in the range 1.4–4.9 mg/kg, compared to average total F values of 343–568 mg/kg. Groundwater F at these sites is around 5 mg/L. The lowest value of soluble F is from a shallow profile in the alkaline soils (Gattuppal-Yelamakanna Road) where the water-soluble and groundwater F concentrations are 1.4 mg/kg and 5 mg/L respectively. In all zone III profiles, water-soluble F concentrations represent less than 1% of the total solid F.

One profile from zone IV (Yelamakanna, Fig. 6) has an average water-soluble F concentration of 5 mg/kg and an average total F concentration of 670 mg/kg (water-soluble fraction 0.7% of the total solid F concentration). Groundwater F concentration at this site is 4 mg/L.

Figure 7 shows the relationship between average water-soluble F in the soil profiles and F in the local groundwaters. A relatively good correlation is apparent, except for two profiles: Dubbagadda Tanda and Gattuppal-Yelamakanna Road (in the alkaline soils). The overall correlation suggests that groundwater F concentration is related to the presence of readily leachable F in the solid phase. At Dubbagadda Tanda, in the recharge area (zone I), the average water-soluble F is comparatively low, 0.5 mg/kg. This may be attributed to the combined effect of low clay content of the profiles (relatively high permeability), and comparatively high recharge (93% of total recharge through preferential flow) in this area (Reddy et al., 2009). The reason for the lack of correlation between water-soluble F and groundwater F concentration in the alkaline soil profile (discharge area; zone IV) is less clear.

3.2.4. Soluble fluoride in calcretes

Water-soluble concentrations of fluoride in the analysed calcretes vary from not detectable to

7.5 mg/kg (Table 3). The great variation in the water-soluble F concentrations appears largely to be controlled by the degree of weathering. For example, despite the high concentration of total F in fresh nodules collected from the ground surface at Wailapally (average 950 mg/kg), the water-soluble concentration is below detection limit (Table 3). Likewise, water-soluble concentrations in fresh calcrete (without etching pits) from Gattuppal-Yelamakanna Road average 0.7 mg/kg, despite the average total F concentration being 685 mg/kg. Of the weathered calcrete samples (with etching pits), average water-soluble concentrations are as high as 7.6 mg/kg compared to a total F concentration of 700 mg/kg.

Leaching experiments on the weathered calcretes indicated that the concentrations of water-soluble F almost doubled in three samples out of six when leached for 1 week instead of 2 hours. No significant change with time was observed in the unweathered calcretes.

4. Discussion

4.1. Controls on the down gradient evolution of groundwater chemistry

The chemical variation of groundwaters from the Wailapally watershed indicates that they are strongly impacted by geochemical reactions with the granitic host rocks. Recharge occurs predominantly in zone I and groundwater flow occurs under mainly oxic conditions. Lowest pH values in zone I (down to 6.6) are found in groundwaters with lowest TDS values. These represent recently recharged groundwater. Most groundwaters in zone I are of Na-Ca-HCO_3 type, reflecting the importance of reaction of silicate minerals, notably sodic feldspar in the presence of acid generated from soil-derived CO_2:

$$2NaAlSi_3O_8 + 2H^+ + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 4H_4SiO_4.$$

This generates dissolved Na, consumes protons, and also leads to increasing alkalinity. A minority of groundwaters in zone I are of Ca-Na-HCO_3 type.

Downgradient, the groundwaters rapidly become saturated with respect to calcite, with resultant precipitation of this mineral, as manifested by the occurrence of calcretes, in zones II to IV. Rapid saturation with respect to dolomite also occurs but the degree of oversaturation and the increasing concentrations of Mg downgradient in zones II and III suggest that dolomite does not precipitate readily. However, a notable reduction in Mg concentrations in zone IV, suggests that precipitation of dolomite occurs in the low-lying part of the catchment, likely promoted by increased evapotranspiration in the zone of discharge. A study by Jacks and Sharma (1995), also in granitic terrain in southern India, found a downgradient change in the mineralogy of calcrete deposits, with upslope concretions being dominantly of calcite and with increasing dolomite content in lower-lying valley sites. No systematic changes in Mg/Ca ratio of calcretes with distance downgradient are observed in the Wailapally catchment however (Table 4).

Downgradient of zone I, the groundwaters evolve from Na-Ca-HCO_3 type through a Na-Mg-HCO_3 type in zone II, to Na-Mg-Cl-HCO_3 type in zone III, and ultimately to Na-HCO_3 or Na-HCO_3-Cl type in discharge zone IV. Groundwater pH also increases downgradient, from a median of 7.3 in zone I to 8.5 in zone IV, the increase in response to silicate-mineral dissolution, and potentially also degassing of CO_2 in the discharge zone. Downgradient increases in Cl concentration from values close to 10 mg/L in zone I to concentrations of typically 150 mg/L and extremes up to 350 mg/L in zone IV are supporting evidence for the influence of evapotranspiration. The observed evolution in geochemical composition of the groundwaters occurs along a flow path of some 17 km.

4.2. Controls on fluoride mobility

Initial inputs of F from rainfall are likely to be relatively low. Satsangi et al. (1998) observed concentrations of around 0.3 mg/L in rainfall from rural areas of Uttar Pradesh, although Jacks et al. (2005) suggested that the concentration could be as high as 1 mg/L in southern India as a result of an important component contributed by dry deposition. The granitic rocks of the watershed contain abundant primary mineral sources of F, including amphibole, biotite, fluorite and apatite. The high concentrations of F in calcrete observed in this study also indicate that this could be a potential source of dissolved F given suitable conditions for release to solution. The apparent correlation between concentration of water-soluble F and concentration of F in local groundwaters demonstrates a relatively rapid release rate from leachable mineral sites. In zone I where concentrations of dissolved Ca are relatively high, some groundwaters are saturated with respect to fluorite. However, groundwaters become undersaturated in zone I and throughout zones II to IV in response to decreasing Ca activities, signifying that fluorite is not controlling F concentrations throughout most of the watershed. Increasing pH and alkalinity downgradient are also more conducive to F mobilisation (Wang and Cheng, 2001).

Several workers (Jacks et al., 1993; Gaciri and Davies, 1993; Tirumalesh et al., 2007) have observed increasing F concentrations in groundwater in granitic terrains going downgradient from recharge to discharge areas. However, in the Wailapally catchment, little spatial pattern in F concentrations is observed despite the distinct downgradient evolution in major-ion composition. The groundwater F concentration varies mostly over the range 3.0–7.6 mg/L (Table 3). It is suggested that the limited range of concentrations of F in the fluorite-undersaturated waters is due to buffering by co-precipitation with, or adsorption to, calcrete.

4.3. Calcretes as a potential sink of fluoride

Calcretes are abundant in the weathered material overlying the granitic rocks. The petrology of these has not been studied in detail, but calcretes elsewhere are dominantly composed of microcrystalline calcite, with variable but usually low concentrations of Mg (typically less than 3 mol % $MgCO_3$). Concentrations of MgO in the analysed calcretes are usually <3 weight % but reach up to 15.6 weight % (Table 5). Watts (1980) suggested that the concentration of Mg was related to the rate of evaporation, higher rates favouring higher concentrations. Jacks and Sharma (1995) found a progressively increasing proportion of Mg in calcretes with distance downgradient in a catchment in southern India. Additional minerals in calcretes can include forms of silica (quartz, chalcedony) and clay minerals. Of these, palygorskite, sepiolite and smectite have frequently been recorded (Hay and Wiggins, 1980; Watts, 1980; Rodas et al., 1994; Kadir and Eren, 2008). Sepiolite and palygorskite are typically authigenic in origin although both authigenic and detrital smectite have been described (Wright and Tucker, 1991).

The concept of removal of F from solution by co-precipitation with calcite and dolomite is well established (Carpenter, 1969, Jacks et al., 2005). It is also supported by the observed high concentrations of F in the calcrete samples analysed in this study. Fan et al. (2003) demonstrated that sorption of F on calcite surfaces can also occur. Turner et al. (2005) showed with extensive laboratory experiments, that F adsorption occurs rapidly over the entire calcite surface with fluorite precipitating at step edges and kinks, where dissolved Ca^{2+} concentration is highest. Sepiolite, palygorskite and smectite, if present in the calcrete deposits, also represent potential sites for F sorption. Further investigation is needed to establish the relative role of such accessory mineral phases.

A conceptual model depicting the various processes controlling the F concentration is shown in the Fig. 8. The main source of F is from weathering of parent granitic rock with F-rich minerals, with mobilization occurring during the percolation of rainwater in vertical/lateral flow. Groundwater flows laterally downgradient and F concentration increases from relatively low values (typically 1.6 mg/L) in the west of zone I to around 5 mg/L near the eastern limit of zone I, a stretch of some 3.5 km. The relatively low concentrations are attributed to comparatively high recharge rate, facilitated by large vertical permeability in the form of a greater density of fractures. In zones II to IV, calcite saturation is achieved and calcrete precipitation can occur. From evidence of groundwater Mg concentrations, dolomite precipitation appears to be restricted to the low-lying areas of zone IV, in response to increased evapotranspiration. Groundwaters in zones II to IV contain a rather uniform F concentration, usually of 4–7 mg/L. A small exception in zone III exists because groundwater is locally diluted by low-F pond recharge. As calcretes contain large concentrations of F, the rather uniform F concentrations in the groundwaters from the lower reaches of the watershed could be limited by co-precipitation with calcrete, or adsorption of F to carbonate mineral surfaces.

5. Conclusions

The Wailapally granitic watershed, characterized by high-F groundwater (up to 7.6 mg/L), is composed of distinct geomorphological segments which experience notable variations in groundwater chemical composition. The western part contains a thick weathered zone (valley fill deposits) which acts as the main recharge area for the watershed and groundwater flows laterally towards the eastern part which forms a discharge zone. Hydrochemical facies evolve from Na-Ca-HCO_3 and Ca-Na-HCO_3 in the west to Na-HCO_3 and Na-HCO_3-Cl in the eastern (discharge) area. Irrespective of chemical facies of groundwater in different geomorphological segments the F concentration in the dominantly fluorite-undersaturated groundwaters remains relatively constant, at around 3–7 mg/L. Abundant F sources, in the form of hornblende, biotite, apatite, fluorite and F-rich calcretes, a closed hydrological basin and dry climate provide favorable conditions for the release of F to groundwater. It is hypothesized that the rather uniform concentrations of F in zones II to IV are due to removal of F from the groundwater by co-precipitation with, and/or adsorption to, calcrete deposits in the weathered horizons of the aquifer. This is supported by the high concentrations of F found in the calcrete samples analysed in the study.

The study has an important practical utility as it helps to locate groundwaters with F concentrations below the WHO guideline value and to explain their origin. Sources of drinking water with acceptably low F concentrations in the watershed are mainly located in areas of preferential flow recharge and surface water bodies.

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REFERENCES

Abu Rukah, Y., Alsokhny, K., 2004. Geochemical assessment of ground water contamination with special emphasis on fluoride concentration in North Jordan. Chemie der Erde, 64, 171-181.

Apambire, W.B, Boyle, D.R., Michel, F.A., 1997. Geochemistry, genesis, and health implications of fluoriferous ground waters in the upper regions of Ghana. Environmental

Geology 33 (1), 13-24.

Ayoob, S., Gupta, A. K., 2006. Fluoride in Drinking Water: A Review on the Status and Stress Effects, In: Critical Reviews in Environmental Science and Technology, 36:6, 433-487. DOI: 10.1080/10643380600678112

Carpenter, R. 1969. Factors controlling the marine geochemistry of fluorine. Geochimica et Cosmochimica Acta 33, 1153-1167.

Edmunds, W.M., Smedley, P.L., 2005. Fluoride in natural waters. In: Selinus O (Ed) Essentials of Medical Geology. Elsevier Academic Press, London, pp 301–329.

Fan, X., Parker, D.J., Smith, M.D., 2003. Adsorption kinetics of fluoride on low cost materials. Water Research 37, 4929-4937.

Gaciri, S.J., Davies, T.C., 1993. The occurrence and geochemistry of fluoride in some natural waters of Kenya. Journal of Hydrology 143, 395–412

Genxu, W., Guodong, C., 2001. Fluoride distribution in water and the governing factors of environment in arid north-west China. Journal of the Arid Environment 49, 601-614.

Geological Survey of India, 1974. Hydrogeochemical investigation for fluoride bearing minerals in Kangal and Halia river basin, Nalgonda district, AP. Unpublished GSI Report, Hyderabad, India.

Grandjean, P., Olsen, J.H., Jensen, O.M., Juel, K., J., 1992. Cancer incidents and mortality in workers exposed to fluoride. National Cancer Institute (Bathesda), 84, 1903-1909.

Handa, B.K. (1975) Geochemistry and genesis of fluoride-containing ground waters in India. Ground Water 13, 275–281.

Hay, R.L. and Wiggins, B. 1980. Pellets, ooids, sepiolite and silica in three calcretes of the southwestern United States. Sedimentology 27, 559-576.

Hudak, P.F. Sanmanee, S., 2003. Spatial patterns of nitrate, chloride, sulphate and fluoride concentrations in the Woodbine aquifer of north-central Texas. Environmental Monitoirng and Assessment 82(3), 311-320.

Jacks, G., Rajagopalan, K., Alveteg, T. Jonsson, M., 1993. Genesis of high-F groundwaters, southern. India. Applied Geochemistry, Supplimetary Issue no. 2, 241-244.

Jacks, G., Bhattacharya, P. Choudary, V. Singh, K.P., 2005. Controls on the genesis of some high fluoride ground waters in India. Applied Geochemistry 20, 221-228.

Jacks G, Sharma, V.P., 1995. Geochemistry of calcic horizons in relation to hillslope processes, southern India. Geoderma 67, 203-214.

Johnston, D.C., 1987. Distribution of Environmental chloride in relation to subsurface Hydrology. Journal of Hydrology, 94, 67-88.

Kadir, S. and Eren, M. 2008. The occurrence and genesis of clay minerals associated with Quaternary caliches in the Mersin area, southern Turkey. Clays and Clay Minerals 56, 244-258.

Kim, K. Jeong, G.Y., 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

Kundu, N., Panigrahi, M.K., Tripathy, S., Munshi, S., Powell, M.A., Hart, B.R., 2001. Geochemical appraisal of fluoride contamination of groundwater in the Nayagarh District of Orissa, India. Environmental Geology 41, 451-460.

Natarajan, V Mohan Rao V.R., 1974. Hydrogeochemical investigation for fluoride bearing minerals in Kangal and Halia river basin, Nalgonda district, AP. Vol. Of Symposium on Fluorosis, Indian Academy of Geosciences, Hyderabad.

Natarajan, V. Murthy, S.R.N., 1974. Fluorite bearing granites of sivanagudem area, Nalgonda Disrticrt, Andhra Pradesh. Proc. Of the Sym. On Fluorosis. Held at Hyderabad 1974.

Nawlakhe, W.G., Kulkarni, D.N., Pathak, B.N Bulusu, K.R., 1975. De-fluoridation of water by Nalgonda technique. Indian Journal of Environmental Health 17, 26-65.

Nordstrom, D.K., Jenne, E.A. 1977. Fluorite solubility equilibria in selected geothermal waters. Geochimica Cosmochimica Acta 41, 175-188.

Ozsvath, D.L. 2005. Marathon County, Wisconsin. Environmental Geology 50 (1), 132 – 138.

Parkhust, D.L., Appelo, C.A.J. 1999. User's Guide to PHREEQC (Version 2) – A computer program for speciation, batch reaction, one-dimensional transport, and inverse geochemical calculations. U.S.G.S. Water Resources Investigations Report 99-4259, U.S.G.S, Denver, USA.

Qinghai Guo, wang, Yanxin., Ma, Teng Ma Rui 2006. Geochemical processes controlling the elevated fluoride concentrations in groundwaters of the Taiyuan Basin, Northern China. Journal of Geochemical Exploration doi:10.1016/ j.gexplo.2006.07.001.

Rammohan Rao, N.V., Rao, N., Rao, KS.P., Schuiling, R.D., 1993. Fluorine distribution in waters of Nalgonda District, Andhra Pradesh, India. Environmental Geology 21(1-2), 84–89.

Ramesham, V. Rajagopalan, K., 1985. Fluoride ingestion into the natural waters of hard-rock areas, Peninsular India, Journal of the Geological Society of India 26, 125-132.

Reddy, A.G.S., 2002. Occurrence, genesis and control strategies of fluoride, Wailapally watershed, Nalgonda district, Andhra Pradesh. CGWB, Southern region report.

Reddy, D.V., Nagabhushanam, P., Sukhija, B.S., Reddy, A.G.S., 2009. Geochemical Signatures: Source area, Recharge Processes and dynamic behavior of groundwater in Wailapally Granitic Watershed, Nalgonda Dist., AP, India. Journal of Hydrology DOI: 10.1002/hyp.7236.

Rodas, M., Luque, F.J. Mas, R. and Garzon, M.G. 1994. Calcretes, palycretes and silcretes in the Palaeogene detrital sediments of the Duero and Tajo Basins, central Spain. Clays & Clay Minerals 29, 273-285.

Shaji, E., Bindu, Viju, J., Thambi, D.S., 2007, High fluoride in groundwater of Palghat district, Kerala. Current Science 92, 240-245.

Satsangi, G.S., Lakhani A., Khare P., Singh S.P., Kumari K.M. and Srivastava, S.S. 1998. Composition of rain water at a semi-arid rural site in India. Atmospheric Environment 32, 3783-3793.

Sharma, M.L. Hughes, M.W., 1985. Groundwater recharge estimation using Chloride, Deuterium, Oxygen-18 profile in the deep coastal sands of Western Australia. Journal of Hydrology 81, 93-109.

Siddiqui, A.H. 1968. Fluorosis in Nalgonda district Hyderabad, India. Fluoride, 1-2, 76-85.

Smedley, P.L., Nicolli H. B., Macdonald D. M. J., Barros A. J., and Tullio J. O. 2002. Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from

La Pampa, Argentina. Applied Geochemistry 17, 259-284.

Sukhija, B.S., Reddy, D.V., Nagabhushanam, P., Chand, R., 1988. Validity of the environment chloride method for the recharge evaluation of coastal aquifers, India. Journal of Hydrology 99, 349-366.

Tirumalesh, K., Shivanna, K., and H.V., Jalihal, A.A. 2007. Isotope, hydrochemical approach to understand fluoride release into ground waters of Ilkal area, Bagalkot dist., Karnataka, India. Hydrogeology Journal 15, 589-598.

Turner, B.D., Binning, P., Stipp, L.S.S. 2005. Fluoride removal by calcite: evidence for fluoride precipitation and surface adsorption. Environmental Science & Technology 39, 9561-9568.

Valenzuela, L.V., Ramirez, J.H., Reyes, J.L., Sol, A.U., Lazaro O.M. 2006. The origin of fluoride in groundwater supply to Hermosillo City, Sonora, Mexico. Environmental Geology 51, 17-27.

Wang, G., Cheng, G., 2001. Fluoride distribution in water and the governing factors of environment in arid north-west China. Journal of the Arid Environment 49, 601–614.

Watts, N.L. 1980. Quaternary pedogenic calcretes from the Kalahari (southern Africa): mineralogy, genesis and diagenesis. Sedimentology 27, 661-686.

WHO, 2004. Guidelines for Drinking-Water Quality, Third Edition. World Health Organization, Geneva, 212 pp.

Wright, V.P. and Tucker, M.E. (eds.) 1991. Calcretes. Reprint Series 2, International Association of Sedimentologists. Blackwell, Oxford.

LIST OF FIGURES

Table 1. Statistical summary of the hydrochemical data set of Wailapally groundwater samples.

Zone		pH	EC µS/cm	Na mg/L	K mg/L	Mg mg/L	Ca mg/L	Cl mg/L	SO_4 mg/L	HCO_3 mg/L	CO_3 mg/L	NO_3 mg/L	F mg/L	SI_C log	SI_D log	SI_F log
Whole watershed	ave	7.66	891	121.1	1.8	32.2	20.8	59.4	24.4	433	3	16.6	3.6	-0.044	0.363	-0.529
(n=433)	std	0.40	374	86.0	2.8	17.3	9.7	59.5	34.3	174	11	9.4	1.2	0.383	0.960	0.398
	min	6.57	230	21.6	<0.2	3.0	3.1	4.0	4.1	134	0	0.0	0.5	-1.374	-3.086	-2.037
	max	8.93	2130	513	28.1	91.7	82.1	349.9	501.2	869	105	49.7	7.6	0.923	2.675	0.381
Zone I	ave	7.38	525	57.1	0.7	15.5	27.1	17.7	11.6	272		14.7	3.6	-0.304	-0.582	-0.276
(n=118)	std	0.37	123	15.6	0.3	5.5	9.1	11.4	4.8	60		8.1	0.8	0.422	0.907	0.266
	min	6.57	230	21.6	0.3	3.0	12.5	4.0	4.1	134		0.0	1.6	-1.374	-3.086	-0.922
	max	8.30	828	91.6	2.2	33.9	56.6	52.4	25.9	447		49.4	5.4	0.588	1.302	0.381
Zone II	ave	7.65	918	108	1.7	38.2	20.4	59.5	17.6	446		16.9	3.6	-0.023	0.504	-0.515
(n=218)	std	0.26	254	43.0	1.5	14.8	8.8	47.6	10.1	147		9.7	1.1	0.298	0.622	0.339
	min	6.93	322	40.3	0.3	6.7	4.7	5.5	5.3	193		0.0	1.3	-0.825	-1.915	-1.645
	max	8.38	1710	253	13.1	85.6	82.1	302.8	69.5	775		49.7	7.6	0.923	2.422	0.241
Zone III	ave	7.76	1210	179	4.8	47.1	17.9	110.6	35.6	564		18.7	3.0	0.086	0.876	-0.856
(n=60)	std	0.23	386	80.2	5.3	17.0	6.1	84.2	28.1	163		8.3	1.5	0.230	0.579	0.432
	min	7.41	447	37.8	0.9	15.6	5.5	10.9	4.4	189		0.9	0.5	-0.428	-0.711	-2.024
	max	8.50	1960	346	28.1	91.7	33.0	349.9	176.5	869		39.5	6.0	0.733	2.228	-0.087
Zone IV	ave	8.45	1380	311	1.9	26.4	7.7	108	87.1	655	32	17.6	4.3	0.450	1.709	-0.882
(n=37)	std	0.20	361	94.5	4.0	12.8	2.7	65.3	84.2	110	25	12.0	1.3	0.245	0.392	0.396
	min	7.95	777	133	<0.2	7.6	3.1	16.7	8.1	397	0	0.0	1.1	-0.117	0.713	-2.037
	max	8.93	2130	513	25.1	61.0	14.4	238.0	501.2	848	105	45.2	7.0	0.922	2.675	-0.225

Table 2. Correlation coefficient (r^2) between fluoride and other chemical constituents in groundwater for different ranges of fluoride concentration.

F range (mg/L)	0.5 to 7.6	0.5 to 1.5	1.6 to 3.0	3.1 to 5.0	5.1 to 7.6
No. samples	433	14	129	246	44
pH	0.200	0.465	-0.007	0.128	0.016
Conductivity	0.191	0.354	0.036	0.143	0.254
Na	0.243	0.374	0.071	0.179	0.217
K	-0.133	-0.625	-0.260	0.077	0.021
Mg	0.077	0.741	-0.078	0.047	0.103
Ca	0.001	-0.370	0.137	0.014	-0.137
Cl	0.061	0.352	0.059	0.033	0.169
HCO_3	0.287	0.591	0.035	0.198	0.160
CO_3	0.235	-0.207	0.275	0.271	0.023
SO_4	0.092	0.197	0.015	0.154	0.362

Table 3. Total fluoride concentrations in the country rock and soil profile, and soluble fluoride in the soil profile and fluoride in the groundwater.

Profile location	Zone	Total F in rocks (mg/kg)	Profile depth (m)	Average total F in soil profile (mg/kg)	Average water-soluble F in profile (mg/kg)	F in nearby groundwater (mg/L)
Dubbagadda Tanda	I	989@[1]	1.7	626	0.5	3.7
Gangamolla Tanda	I		2.5		3.0	2.5
Lachammagudem	II	338@[2]	1.2	1015	10	7.0
Lacham'm calcrete	II	875	-	-	1.8	7.0
Wailapally	II	-	3.6	-	10	5.5
Wailapally calcrete	II	947*	-	-	nd	5.0
Darma Tanda	III	716@[3]	1.0	343	3.6	2.2
Gattuppal	III		3.2		6.2	5.0
Puttapaka	III		0.5	568	4.9	2.5
Puttapaka calcrete		635			nd	
Gattuppal-Yelamakanna Road	III	288[4]	0.8	384	1.4	5.0
G-VR calcrete		700[5]			7.6	
G-VR calcrete	III	685*	-	-	0.7	6.0
Yelamakanna	IV	242@	3.4	685	5.0	4.0

@ rock samples1 – average of 7 samples; 2 – average of 2 samples; 3 – average of 3 samples; 4 – average of 3 samples; 5 – average of 5 weathered calcrete samples; *fresh surface calcrete (two samples each); nd – F is not detected

Table 4. Chemical composition of calcretes from the Wailapally watershed.

Sample	Sample names	Zone	SiO_2 %	Al_2O_3 %	Fe_2O_3(T) %	MnO %	MgO %	CaO %	Na_2O %	K_2O %	TiO_2 %	P_2O_5 %	Sum %	F
1	Calcrete over alkaline soil	II	13.99	3.44	1.57	0.08	3.09	37.95	0.46	0.70	0.30	0.04	61.62	583
2	CLC-LG	II	16.04	4.28	1.88	0.2	2.13	35.16	1.04	0.74	0.30	0.03	61.8	875
3	CLC over alkaline soil -WP	II	18.08	4.64	1.66	0.11	13.5	29.22	1.11	0.97	0.30	0.01	69.64	948
4	CLC YKGT-RD	III	13.26	3.03	1.49	0.17	9.06	37.03	0.33	0.6	0.29	0.02	65.28	691
5	Nodules YKGT-RD	III	12.64	2.73	1.41	0.08	1.54	41.28	0.08	0.57	0.29	0.02	60.64	441
6	CLC YKGT-RD	III	14.34	3.63	1.71	0.14	15.6	32.63	0.97	0.65	0.3	0.01	69.98	1158
7	CLC YKGT-RD	III	13.71	3.22	1.59	0.13	6.56	37.23	0.25	0.60	0.29	0.01	63.59	684
8	CLC below red soil	III	14.84	4.14	1.70	0.13	1.78	36.89	0.44	0.87	0.30	0.02	61.11	634
9	Calcrete GT-YK road	III	14.16	3.47	0.86	0.02	11.98	51.13	1.19	0.36	0.10	0.02	83.29	660
10	CLC/weathered	IV	14.27	3.55	1.62	0.08	2.21	37.63	0.89	0.64	0.30	0.01	61.2	538
11	CLC kk	IV	14.81	3.61	1.55	0.23	1.84	37.08	0.51	0.89	0.29	0.02	60.83	457