

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

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11 **Abstract**

12 High concentrations of fluoride (up to 7.6 mg/L) are a recognized feature of the Wailapally
13 granitic aquifer of Nalgonda District, Andhra Pradesh, India. The basement rocks provide
14 abundant sources of F in the form of amphibole, biotite, fluorite and apatite and whole-rock
15 concentrations of F in the aquifer are in the range 240–990 mg/kg. Calcretes from the shallow
16 weathered horizons also contain comparably high concentrations of F, in the range 635–
17 950 mg/kg. The concentrations of water-soluble F in the granitic rocks and the calcretes are
18 usually low (1% of the total or less) but broadly correlate with the concentrations observed in
19 groundwaters in the local vicinity. The water-soluble fraction of calcretes is relatively high in
20 weathered calcretes compared to fresh samples.

21 Groundwater major-ion composition shows a well-defined trend with flow downgradient in
22 the Wailapally aquifer, from Na-Ca-HCO₃-dominated waters in the recharge area at the upper
23 part of the catchment, through to Na-Mg-HCO₃ and ultimately to Na-HCO₃ and Na-HCO₃-Cl
24 types in the discharge area in the lowest part. The evolution occurs over a reach spanning
25 some 17 km. Groundwater chemistry evolves by silicate weathering reactions, although
26 groundwaters rapidly reach equilibrium with carbonate minerals, favouring precipitation of
27 calcite, and ultimately dolomite in the lower parts of the watershed. This precipitation is also
28 aided by evapotranspiration. Decreasing Ca activity downgradient leads to a dominance of
29 fluorite-undersaturated conditions and consequently to mobilisation of F. Despite the clear
30 downgradient evolution of major-ion chemistry, concentrations of F remain relatively uniform
31 in the fluorite-undersaturated groundwaters, most being in the range 3.0–7.6 mg/L. The rather
32 narrow range is attributed to a mechanism of co-precipitation with and/or adsorption to
33 calcrite in the lower sections of the aquifer. The model may find application in other high-F
34 groundwaters from granitic aquifers of semi- arid regions.

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

36 **1. Introduction**

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

57 This paper outlines the origin of F in groundwater in a granitic watershed located in Nalgonda
58 District, about 70 km south of Hyderabad, India. Nalgonda District is one of the poorest

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

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

82 This study uses a multifaceted approach to understand the mechanism responsible for the

83 spatial distribution and dynamics of F across a small watershed composed of a single bedrock
84 geological unit (granitic gneiss), based on the chemical analysis of 433 groundwater samples
85 and a number of soil profiles, rock and calcrete samples.

86 **2. Regional setting**

87 **2.1. Study area**

88 The study area (130 km²) lies in a semi-arid region, between 17.03° to 17.13° N latitude and
89 78.8° to 79.0° E longitude, located about 70 km southeast of Hyderabad, Andhra Pradesh,
90 India (Fig. 1). The granite exposures are seen as rugged dissected hills (600–650 m a msl)
91 with a N-S trend in the western part, as domed hillocks or sheet-like exposures in the middle
92 part and as undulating terrain with black alkaline soils in the eastern part of the study area.
93 These alkaline soils in the east likely formed due to high evaporation rates and a historic
94 shallow water table.

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

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

106 area and in particular the higher concentrations are from porphyroblastic and pink granites.

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

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

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

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

129 SW monsoon. However, rainfall is erratic from year to year, with a variation from 400–
130 1000 mm. Temperature varies from 9°C during winter (minimum) to 42°C during summer
131 (maximum), although average daytime temperatures remain around 30°C for most of the year.
132 As a result of the high temperature, average potential evaporation is about 1400 mm, which is
133 more than twice the average annual rainfall (measured at the Wailapally village, centre of the
134 watershed).

135 **2.2. Hydrogeology**

136 Groundwater is present in both the weathered zone and bedrock fractures. Significant
137 deformation has produced a network of intersecting fractures in the weathered zone which
138 provides hydraulic continuity between the two systems. Groundwater occurs mainly under
139 unconfined conditions, although semi-confined and confined conditions exist locally due to
140 sheet joints in the basement rock. Erratic rainfall and over-exploitation of groundwater in
141 recent years has led to severe water shortages for irrigation and drinking. About 2500 wells
142 exist in the catchment, including both dug wells and boreholes, as inventoried in the 88 km²
143 non-hill terrain of the watershed. Of these, almost all dug wells of ≤ 15 m depth are dry, as are
144 some 40% of the boreholes drilled down to depths ranging to 120 m. Discharge from the
145 remaining boreholes is poor, typically in the range 1.5 to 3 L/s.

146 The watershed is almost a closed basin with only one outlet to the east. The ground elevation
147 difference between the stream area in the central part and the watershed boundary is about
148 20–25 m. No external sources of water supply exist in the watershed either for irrigation or for
149 drinking purposes. The main input source to the groundwater is rainfall recharge. A recharge
150 study (Reddy et al., 2009), conducted in this area using environmental chloride, indicates that
151 the bulk of the vertical recharge in the western elevated land occurs through preferred
152 pathways and that a small fraction occurs through the soil matrix. The dominating

153 preferential flow is high (\sim 16% of the annual average rainfall) in the valley fills, but
154 decreases to 5–5.5% in the plains, whereas the matrix (piston flow) recharge is only 1–1.5%
155 of rainfall. Furthermore, considerable lateral movement of groundwater down the slope allows
156 sequential hydrochemical changes to occur (Reddy et al., 2009).

157 The groundwater sampling campaign for this study was carried out under pre-monsoon
158 drought conditions during June 2004. At the time, the depth to water table varied from 40 m
159 in the west to 7 m in the east (380 to 270 m a msl, Fig. 2), with an average hydraulic gradient
160 7.5 m/km. The gradient was steeper in the west.

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

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

170 **2.3. Groundwater samples**

171 As almost all open wells were dry, groundwater samples were taken only from boreholes. Out
172 of 433 boreholes sampled from the watershed during the well inventory period (pre-monsoon
173 period of 2004–2005), about 10% were drilled for domestic use, the others being used for
174 agriculture. Being in hard-rock terrain, boreholes are not screened except in the top few
175 metres of the highly weathered zone to avoid borehole collapse. The collected samples

176 generally represent mixed waters abstracted from a range of depths within a borehole.
177 However, a few boreholes were abstracting water exclusively from sheet joints at greater
178 depths. Most of the domestic boreholes are fitted with hand pumps and almost all agricultural
179 boreholes have 5 HP submersible pumps.

180 Electrical conductance and pH of the water samples were measured using the Consort C533
181 portable multi-parameter analyzer. Carbonate alkalinity was measured by titration. Other
182 anions and cations were measured using a Dionex ion chromatograph. An AS-14A Ion Pac
183 was used with 8.0 mM sodium carbonate and 1.0 mM bicarbonate as eluent and H₂SO₄ as
184 regenerant with a mixed standard of F, Cl, NO₂, Br, NO₃, PO₄ and SO₄ made in the required
185 proportions from the standards purchased from Merck, Germany. A CS-17 column was used
186 for cation separation with 6 mM methanesulfonic acid as eluent, and a mixed standard of Li,
187 Na, K, Mg and Ca prepared in accordance with the approximate sample values. As a result of
188 the high TDS values (>600 mg/L), the samples were diluted to measure both anions and
189 cations. Several routine checks on standards were made to ensure data quality. Measurements
190 have a precision of ±5% of the total value. The majority of analysed samples had ionic charge
191 imbalances of <5%.

192 **2.4. Rock and soil samples**

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

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

199 Geophysical Research Institute (NGRI) using a Philips MagiX PRO PW 2440, wavelength-
200 dispersive XRF spectrometer coupled with a PW 2540 autosampler. The MagiX PRO is a
201 sequential instrument with a single goniometer-based measuring channel encompassing the
202 entire spectral range from F to U in the concentration range of a few mg/kg to % levels.
203 International reference materials from USGS, Canadian and NIST standards (SO-1, SO-2, JB-
204 2, JP-1, G-2, JG-1A) were used in the preparation of calibration graphs.

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

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

216 **3. Results**

217 Although more than 480 groundwater samples were collected and analysed in the study, 50
218 samples were excluded from consideration due to anthropogenic contamination determined
219 from associated high nitrate (≥ 50 mg/L) and chloride (> 100 mg/L) concentrations. These
220 samples were in all cases located within and close to villages where groundwater suffers
221 locally from contamination by latrines and animal wastes. Thus the data for 433 non-

222 contaminated groundwater samples have been used for analysis and interpretation (Fig. 2).

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

228 **3.1. Hydrochemical variation**

229 **3.1.1. Major ions**

230 A statistical summary of the groundwater chemical data for the watershed is given in Table 1.
231 The complete dataset is provided in the Supplemental Data. For the watershed as a whole, the
232 average pH value is 7.7 with a range of 6.6 to 8.9 and average electrical conductivity is 925
233 $\mu\text{S}/\text{cm}$ (TDS 492 mg/L) with a range of 230 to 2130 $\mu\text{S}/\text{cm}$ (TDS 120–1130 mg/L).
234 Groundwater temperature is around 30°C. Concentrations of major constituents Na, K, Ca,
235 Mg, Cl, SO_4 , HCO_3 and CO_3 also show wide variation from a few mg/L to a few hundreds of
236 mg/L.

237 There is significant variation in the average values of different chemical constituents in the
238 different zones (Table 1). Some chemical constituents show a linearly increasing trend from
239 zone I to zone IV, while others show a decreasing trend. From zone I to zone IV, the spatial
240 variation in the average values of various chemical constituents are: pH 7.4–8.5; EC 525–
241 1400 $\mu\text{S}/\text{cm}$; Na 57–310 mg/L; HCO_3 270–660 mg/L; CO_3 <0.1–30 mg/L; Cl 18–110 mg/L
242 and SO_4 12–90 mg/L. However, average Mg increases from zone I to III (16–47 mg/L) and
243 decreases in zone IV (26 mg/L) and Ca decreases downgradient from 27–8 mg/L.

244 3.1.2. Spatial variability in fluoride concentration

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

252 Relatively little variation in groundwater F concentration occurs down the groundwater flow
253 gradient. The median fluoride concentrations in zones I to IV are respectively 3.6, 3.6, 2.7 and
254 4.3 mg/L. The relatively low zone-III median is due to dilution of groundwater by surface
255 water from the surface tank/pond in that area (Fig. 2) and to a contribution of fresh young
256 recharge water being added from the southern hillocks. Fluoride concentrations in this water
257 are in the range 0.5–1.5 mg/L in zone III. This is the only area within the watershed where
258 groundwater has F concentrations within the permissible limits for drinking.

259 High-F groundwaters in other parts of the world are often of Na-HCO₃ type with low Ca
260 concentrations and neutral to alkaline pH values. Several studies have demonstrated positive
261 correlations between F and both HCO₃ and Na in high-F groundwaters as well as an inverse
262 relationship between F and Ca concentrations in fluorite-saturated groundwaters (e.g. Handa,
263 1975; Kundu et al., 2001; Wang and Cheng, 2001; Smedley et al., 2002; Ozsvath, 2005;
264 Edmunds and Smedley, 2005; Valenzuela et al., 2006; Qinghai Guo et al., 2006). For the
265 groundwaters from the Wailapally watershed, there is no clear correlation between these
266 parameters when considering the sample set as a whole (Table 2). Correlations are also
267 generally poor within zones. However, Table 2 indicates that for groundwaters with low F

268 concentrations (0.5–1.5 mg/L), relatively good positive correlations exist between F and Mg
269 (r^2 0.74) and between F and HCO_3 (r^2 0.59). This group comprises only 14 samples, the
270 majority being from a small area around the pond in zone III and indicating the effect of
271 dilution by surface water and by fresh recharge from the southern side of the watershed.

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

276 **3.1.3. Variation in fluoride concentration with depth**

277 Some studies (e.g. Edmunds and Smedley, 2005; Kim and Jeong, 2005; Hudak and Sanmanee,
278 2003), have found a positive correlation between borehole/well depth and concentration of F
279 in groundwater, although relationships are not always apparent (e.g. Apambire et al., 1997). In
280 the Wailapally catchment, borehole depths are mostly in the range 30–120 m and groundwater
281 occurs in fractures at variable depths within the bedrock. No relationship has been found
282 between F concentration and borehole depth (Fig. 4).

283 **3.1.4. Groundwater saturation indices**

284 Ranges and means of saturation indices for calcite, dolomite and fluorite (PHREEQC;
285 Parkhurst and Appelo, 1999) are given for the different zones in Table 1. An SI range of
286 0 ± 0.25 has here been taken as an indication of near-saturated condition. Most groundwaters
287 from the catchment are saturated or near-saturated with respect to calcite. Around 28% of the
288 samples are oversaturated (SI >0.25). Most of the calcite-undersaturated groundwaters are
289 from the peripheral areas of zones I and II. The degree of calcite saturation increased
290 downgradient. All calcite-oversaturated samples are from the low-lying areas, particularly in

291 zone IV (Fig. 5).

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

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

302 **3.2. Chemical variation in rocks and soils**

303 **3.2.1. Fluoride in granite samples**

304 The important fluoride minerals in the granitic rocks of the area are fluorite (CaF_2) and apatite
305 [$\text{Ca}_5(\text{Cl},\text{F},\text{OH})(\text{PO}_4)_3$]. Amphiboles (hornblende) and biotite also contain abundant fluoride
306 which substitutes for hydroxyl in the crystal lattices (Natarajan and Murthy, 1974; Rammohan
307 Rao et al., 1993; Edmunds and Smedley, 2005). The basement and weathered rocks of the
308 area contain substantial quantities of these F-bearing minerals, especially in the porphyritic
309 pink granites.

310 The average F concentration in surface rock samples collected from the watershed varies from
311 242 to 990 mg/kg (Table 3). The lowest value is found in a grey granite sample from the
312 eastern part; the highest represents an average of seven measurements (ranging from 19 to
313 3125 mg/kg) on different aliquots of a single sample of pink granite from the western part.

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

317 The highest observed F concentration is very similar to that found for rocks from the same
318 area by Rammohan Rao et al. (1993). They reported F concentration ranges in granitic rocks
319 from Nalgonda district from 325 to 3200 mg/kg with a mean of 1440 mg/kg. In neighbouring
320 Hyderabad, Rammohan Rao et al. (1993) reported mean F concentrations in granitic rocks of
321 910 mg/kg, although groundwater F concentrations in this area were generally found to be
322 lower because of relatively high solute Ca concentrations. A mean F concentration of
323 360 mg/kg was found for granites in non-endemic areas of India (Rammohan Rao et al., 1993).

324 In the adjacent Hyderabad district, where F concentrations in groundwaters are almost at
325 permissible limits (except certain pockets), the granites have an average F concentration of
326 910 mg/kg, which is about 1.5 times less than the Nalgonda Granite (Ramamohana Rao et al.,
327 1993).

328 **3.2.2. Chemistry of calcretes**

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

333 The analysed calcrete samples display a positive correlation (r^2 0.6) between MgO and F. This
334 suggests that a relationship exists between the concentration of F and the dolomite content of
335 the calcretes. Jacks et al. (2005) also found very high concentrations of F in calcrete samples
336 collected from arid areas of the Indian granitic terrain. They quoted a range of 510–9000

337 mg/kg in 25 analysed calcrete samples. They also noted that highest F concentrations
338 occurred in dolomitic calcretes (>5 mol% Mg) in downslope positions in the valley sites
339 studied. This accords with the observed F distributions in calcretes in this study.

340 **3.2.3. Total and soluble fluoride in depth profiles and rocks**

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

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

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

355 Two profiles from zone II, Lachammagudem (to 1.2 m depth, Fig. 6) and Wailapally (to
356 3.6 m) each have average water-soluble F concentrations of 10 mg/kg. The Lachammagudem
357 water-soluble profile increases with depth, with concentrations up to 17 mg/kg at 110 cm
358 depth. The average total F in the soil profile at the site is 1015 mg/kg and has relatively little
359 variation (Fig. 6). The water-soluble component of F at Lachammagudem is therefore just

360 under 1% of the total F. Local groundwater at the Lachammagudem site has 7.0 mg/L F.
361 Local groundwater F concentrations at the Wailapally site are also relatively high, at 5.5 mg/L.
362 Three shallow profiles (to depths of 0.5 to 1 m) from zone III contain average water-soluble F
363 concentrations in the range 1.4–4.9 mg/kg, compared to average total F values of 343–
364 568 mg/kg. Groundwater F at these sites is around 5 mg/L. The lowest value of soluble F is
365 from a shallow profile in the alkaline soils (Gattuppall-Yelamakanna Road) where the water-
366 soluble and groundwater F concentrations are 1.4 mg/kg and 5 mg/L respectively. In all zone
367 III profiles, water-soluble F concentrations represent less than 1% of the total solid F.
368 One profile from zone IV (Yelamakanna, Fig. 6) has an average water-soluble F concentration
369 of 5 mg/kg and an average total F concentration of 670 mg/kg (water-soluble fraction 0.7% of
370 the total solid F concentration). Groundwater F concentration at this site is 4 mg/L.
371 Figure 7 shows the relationship between average water-soluble F in the soil profiles and F in
372 the local groundwaters. A relatively good correlation is apparent, except for two profiles:
373 Dubbagadda Tanda and Gattuppall-Yelamakanna Road (in the alkaline soils). The overall
374 correlation suggests that groundwater F concentration is related to the presence of readily
375 leachable F in the solid phase. At Dubbagadda Tanda, in the recharge area (zone I), the
376 average water-soluble F is comparatively low, 0.5 mg/kg. This may be attributed to the
377 combined effect of low clay content of the profiles (relatively high permeability), and
378 comparatively high recharge (93% of total recharge through preferential flow) in this area
379 (Reddy et al., 2009). The reason for the lack of correlation between water-soluble F and
380 groundwater F concentration in the alkaline soil profile (discharge area; zone IV) is less clear.

381 **3.2.4. Soluble fluoride in calcretes**

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

383 7.5 mg/kg (Table 3). The great variation in the water-soluble F concentrations appears largely
384 to be controlled by the degree of weathering. For example, despite the high concentration of
385 total F in fresh nodules collected from the ground surface at Wailapally (average 950 mg/kg),
386 the water-soluble concentration is below detection limit (Table 3). Likewise, water-soluble
387 concentrations in fresh calcrete (without etching pits) from Gattuppall-Yelamakanna Road
388 average 0.7 mg/kg, despite the average total F concentration being 685 mg/kg. Of the
389 weathered calcrete samples (with etching pits), average water-soluble concentrations are as
390 high as 7.6 mg/kg compared to a total F concentration of 700 mg/kg.

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

394 **4. Discussion**

395 **4.1. Controls on the down gradient evolution of groundwater chemistry**

396 The chemical variation of groundwaters from the Wailapally watershed indicates that they are
397 strongly impacted by geochemical reactions with the granitic host rocks. Recharge occurs
398 predominantly in zone I and groundwater flow occurs under mainly oxic conditions. Lowest
399 pH values in zone I (down to 6.6) are found in groundwaters with lowest TDS values. These
400 represent recently recharged groundwater. Most groundwaters in zone I are of Na-Ca-HCO₃
401 type, reflecting the importance of reaction of silicate minerals, notably sodic feldspar in the
402 presence of acid generated from soil-derived CO₂:



404 This generates dissolved Na, consumes protons, and also leads to increasing alkalinity. A

405 minority of groundwaters in zone I are of Ca-Na-HCO₃ type.

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

418 Downgradient of zone I, the groundwaters evolve from Na-Ca-HCO₃ type through a Na-Mg-
419 HCO₃ type in zone II, to Na-Mg-Cl-HCO₃ type in zone III, and ultimately to Na-HCO₃ or Na-
420 HCO₃-Cl type in discharge zone IV. Groundwater pH also increases downgradient, from a
421 median of 7.3 in zone I to 8.5 in zone IV, the increase in response to silicate-mineral
422 dissolution, and potentially also degassing of CO₂ in the discharge zone. Downgradient
423 increases in Cl concentration from values close to 10 mg/L in zone I to concentrations of
424 typically 150 mg/L and extremes up to 350 mg/L in zone IV are supporting evidence for the
425 influence of evapotranspiration. The observed evolution in geochemical composition of the
426 groundwaters occurs along a flow path of some 17 km.

427 **4.2. Controls on fluoride mobility**

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

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

450 **4.3. Calcretes as a potential sink of fluoride**

451 Calcretes are abundant in the weathered material overlying the granitic rocks. The

452 petrology of these has not been studied in detail, but calcretes elsewhere are dominantly
453 composed of microcrystalline calcite, with variable but usually low concentrations of Mg
454 (typically less than 3 mol % MgCO₃). Concentrations of MgO in the analysed calcretes are
455 usually <3 weight % but reach up to 15.6 weight % (Table 5). Watts (1980) suggested that the
456 concentration of Mg was related to the rate of evaporation, higher rates favouring higher
457 concentrations. Jacks and Sharma (1995) found a progressively increasing proportion of Mg
458 in calcretes with distance downgradient in a catchment in southern India. Additional minerals
459 in calcretes can include forms of silica (quartz, chalcedony) and clay minerals. Of these,
460 palygorskite, sepiolite and smectite have frequently been recorded (Hay and Wiggins, 1980;
461 Watts, 1980; Rodas et al., 1994; Kadir and Eren, 2008). Sepiolite and palygorskite are
462 typically authigenic in origin although both authigenic and detrital smectite have been
463 described (Wright and Tucker, 1991).

464 The concept of removal of F from solution by co-precipitation with calcite and dolomite is
465 well established (Carpenter, 1969, Jacks et al., 2005). It is also supported by the observed
466 high concentrations of F in the calcrete samples analysed in this study. Fan et al. (2003)
467 demonstrated that sorption of F on calcite surfaces can also occur. Turner et al. (2005) showed
468 with extensive laboratory experiments, that F adsorption occurs rapidly over the entire calcite
469 surface with fluorite precipitating at step edges and kinks, where dissolved Ca²⁺ concentration
470 is highest. Sepiolite, palygorskite and smectite, if present in the calcrete deposits, also
471 represent potential sites for F sorption. Further investigation is needed to establish the relative
472 role of such accessory mineral phases.

473 A conceptual model depicting the various processes controlling the F concentration is shown
474 in the Fig. 8. The main source of F is from weathering of parent granitic rock with F-rich
475 minerals, with mobilization occurring during the percolation of rainwater in vertical/lateral

476 flow. Groundwater flows laterally downgradient and F concentration increases from relatively
477 low values (typically 1.6 mg/L) in the west of zone I to around 5 mg/L near the eastern limit
478 of zone I, a stretch of some 3.5 km. The relatively low concentrations are attributed to
479 comparatively high recharge rate, facilitated by large vertical permeability in the form of a
480 greater density of fractures. In zones II to IV, calcite saturation is achieved and calcite
481 precipitation can occur. From evidence of groundwater Mg concentrations, dolomite
482 precipitation appears to be restricted to the low-lying areas of zone IV, in response to
483 increased evapotranspiration. Groundwaters in zones II to IV contain a rather uniform F
484 concentration, usually of 4–7 mg/L. A small exception in zone III exists because groundwater
485 is locally diluted by low-F pond recharge. As calcretes contain large concentrations of F, the
486 rather uniform F concentrations in the groundwaters from the lower reaches of the watershed
487 could be limited by co-precipitation with calcite, or adsorption of F to carbonate mineral
488 surfaces.

489 **5. Conclusions**

490 The Wailapally granitic watershed, characterized by high-F groundwater (up to 7.6 mg/L), is
491 composed of distinct geomorphological segments which experience notable variations in
492 groundwater chemical composition. The western part contains a thick weathered zone (valley
493 fill deposits) which acts as the main recharge area for the watershed and groundwater flows
494 laterally towards the eastern part which forms a discharge zone. Hydrochemical facies evolve
495 from Na-Ca-HCO₃ and Ca-Na-HCO₃ in the west to Na-HCO₃ and Na-HCO₃-Cl in the eastern
496 (discharge) area. Irrespective of chemical facies of groundwater in different geomorphological
497 segments the F concentration in the dominantly fluorite-undersaturated groundwaters remains
498 relatively constant, at around 3–7 mg/L. Abundant F sources, in the form of hornblende,
499 biotite, apatite, fluorite and F-rich calcretes, a closed hydrological basin and dry climate

500 provide favorable conditions for the release of F to groundwater. It is hypothesized that the
501 rather uniform concentrations of F in zones II to IV are due to removal of F from the
502 groundwater by co-precipitation with, and/or adsorption to, calcrete deposits in the weathered
503 horizons of the aquifer. This is supported by the high concentrations of F found in the calcrete
504 samples analysed in the study.

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

509 ACKNOWLEDGEMENTS

510 The authors are thankful to the Director NGRI for the permission to publish the paper and
511 Regional Director, CGWB Southern Region for his kind cooperation during the well
512 inventory work. B.S. Sukhija thanks CSIR for the award of Emeritus Scientist scheme. We
513 also thank Dr. Krishna, NGRI, for analyzing the rock and soil samples for total fluoride and
514 Dr. J.S. Bhargava, Hydrochemical wing of CGWB, for valuable discussions. This work has
515 been carried out under the CSIR Network Project on Groundwater (COR-0005).

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629 Fig.1 Location of Wailapally watershed (Nalgonda district, Andhra Pradesh, India) showing
630 the different geomorphological units (zones), along with soil profiles investigated.

631 Fig. 2 Location of sampled boreholes and distribution of fluoride in groundwater in the
632 Wailapally watershed. The water-table contours (m amsl) show groundwater flow from
633 west to east. The inset shows a histogram of F distributions.

634 Fig. 3. Variation of groundwater fluoride concentration in the flow direction in a 3.5 km
635 stretch of the valley fill/recharge area (zone I). Fig. 3a to d: relationship between F and other
636 major ions in the groundwaters from the same transect.

637 Fig. 4. Fluoride concentration in the groundwater as a function of borehole depth.

638 Fig. 5. Variation in saturation indices and concentrations of calcium, magnesium and fluoride
639 in groundwaters with distance down the flow gradient.

640 Fig. 6. Depth distribution of total and water-soluble fluoride in the soil depth profiles: a)
641 Dubbagadda Tanda (DT, recharge area, zone I), b) Lachammagudem (LG, zone II) and
642 c) Yelamakanna (YK, discharge area, zone IV).

643 Fig. 7. Average soluble fluoride in various depth profiles as a function of fluoride
644 concentration in the respective groundwater. Pink triangle: Dubbagadda Tanda, red circle:
645 Gattuppal-Yelamakanna Road.

646 Fig. 8. A conceptual model of the mechanism and processes that control the fluoride
647 concentration in the granitic aquifer.

648

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 (n=433)	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
	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 (n=118)	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
	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 (n=218)	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
	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 (n=60)	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
	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 (n=37)	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
	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 samples 1 – 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 ₂ O ₃ %	Fe ₂ O ₃ (T) %	MnO %	MgO %	CaO %	Na ₂ O %	K ₂ O %	TiO ₂ %	P ₂ O 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