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# Vulnerability of intensively-exploited hard-rock aquifers to fluoride contamination in India: impact of global change

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**ABSTRACT:** A geochemical study was conducted to obtain a comprehensive understanding of fluoride concentration increase in groundwater from a crystalline (hard-rock) aquifer in a small Indian agricultural watershed, where groundwater is intensively abstracted for paddy irrigation. A reactive 1-D geochemical model using PHREEQC was used to reproduce fluoride concentrations under rice paddies taking into account evaporation and return flow related to paddies and water-rock interactions processes, namely dissolution of biotite, allanite and fluoro-apatite as well as absorption onto Al and Fe-hydroxides. This model can be applied to evaluate vulnerability to high fluoride concentration for several land use and climate change scenarios.

## 1 INTRODUCTION

Groundwater with a high F concentration is encountered in many places around the world and various geological settings (Edmunds & Smedley, 2005), whereas an excessive intake of F is dangerous for human health and provokes a potentially highly disabling disease called fluorosis. In India, endemic fluorosis has been identified in 17 states, affecting more than 60 million people because of consumption of water with high fluoride concentration (Rao et al., 1974). The Maheshwaram watershed is a typical Southern India rural watershed; in response to the development of agricultural activities, its hard rock aquifer is overexploited leading to a progressive depletion of water resources as indicated by declining water tables (Maréchal et al., 2006). This watershed has also to face groundwater quality problems and an increase of fluoride concentration has been reported for several years, leading to cases of dental fluorosis (Pauwels et al., 2010). The present work, based on the detailed study of chemical and isotopes composition of groundwater under paddy fields in the Maheshwaram watershed and supported by chemical modeling, aims at determining: 1) the key parameters of fluoride accumulation in groundwater in response to paddy fields development; 2) evaluate the potential impact of land use and climate change on fluoride concentration.

## 2 METHOD

### 2.1 General feature of the watershed

The Maheshwaram watershed is located 35 km south of Hyderabad, Andhra Pradesh, Southern India (Fig. 1). With an annual potential evapotranspiration close to 2,000 mm and an annual rainfall of 750 mm over a 4- to 5-months monsoon period, the climate of the region is classified as semi-arid. The geology is relatively homogeneous and composed of Archean granites, which is representative of the whole region. It is also a typical rural watershed with a population of 15,000 inhabitants, whose principal economic activity is agriculture: rice, vegetables and flowers being the main crops. Irrigated agriculture has developed since the beginning of 1980', im-

plying a significant water table depletion, leading to an endoreism of the basin (i.e., basin closure). The irrigation return flow (IRF) is largely variable in the area and is a function of the land use (higher in rice paddies than in flower- or vegetable plots).

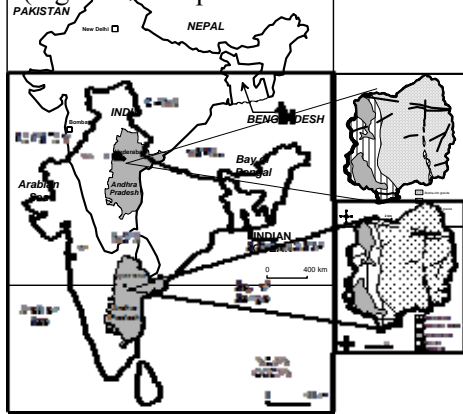


Figure 1: Site Location

## 2.2 Sampling and analytical techniques

Samples were collected from i) some of the 900 borewells drilled for irrigation which are equipped with submersible pumps and ii) boreholes drilled for scientific purpose at selected depth by using a down hole hammer. Water samples were collected for major and trace elements determination using ionic chromatography and ICP-MS. Water samples were also collected for stable isotopes measurements using a Finnigan MAT 252 mass spectrometer with a precision of 0.1‰ vs. SMOW (e.g. Standard Mean Ocean Water) for  $\delta^{18}\text{O}$  and 0.8‰ for  $\delta^2\text{H}$ .

## 2.3 Modeling

The software PHREEQC (Parkust and Appelo, 1999) is used to simulate and confirm some of the hydrogeochemical processes that occur during infiltration of water from paddy fields to groundwater.

# 3 RESULTS AND DISCUSSION

## 3.1 Impact of paddy fields and return flow on F accumulation

Groundwater F concentrations depend on the land use activities and are mostly above the drinking-water limit (1.5 mg/l) where the paddy fields prevail, whereas they remain at more acceptable levels elsewhere (Fig.2). Stable isotopes of the water molecule present also a particular signature in groundwater beneath paddy fields compared to other areas. From the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  of groundwater and monsoon rainfall samples, it has been possible to calculate the “D-excess”, namely the deviation from the Local Meteoric Water Line, represented by the formulae (Negrel et al., 2011):

$$\delta^2\text{H} = 7.64 \pm 0.26 \delta^{18}\text{O} + 7.80 \pm 1.18 \quad (R^2 = 0.989, n = 12)$$

Actually, the ‘D-excess’ in groundwater is always below 10 and generally within the -0.6 to 7.6 range, with a value as low as -4. The “D-excess” values of around 7 and 8 are considered as being inherited from precipitation with a minor evaporation (Negrel et al., 2011), whereas the lower value, particularly those less than 5 suggest significant evaporation of water. It is worth

pointing out that all values below 3.5 are related to groundwater where paddy fields prevail, indicating a higher evaporation in these areas (Fig. 2).

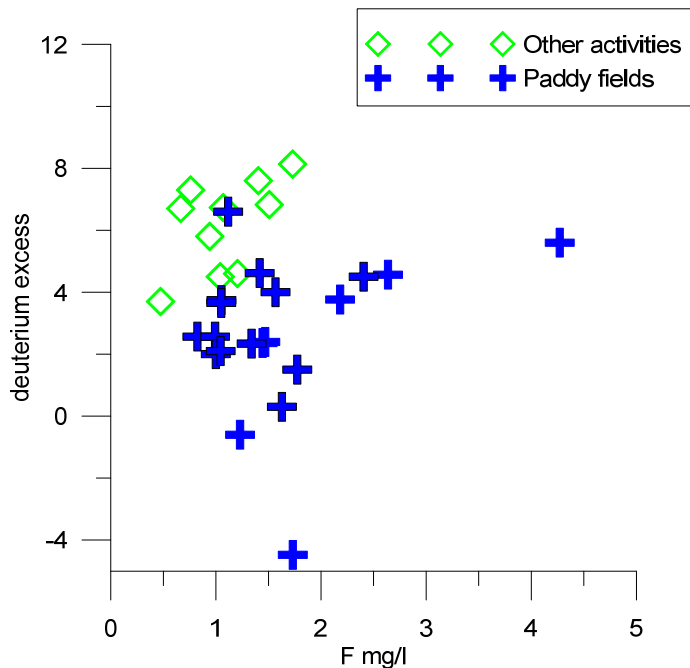


Figure 2: ‘D-excess’ vs. fluoride plot for groundwater from the Maheshwaram watershed

From a balance between yield and recharge at the scale of the watershed, the extent of Irrigation Return Flow (IRF) mainly related to paddy fields has been already highlighted by Maréchal et al. (2006). From the present study, it is clear that IRF leads to a significant evaporation of water, which is known for its negative impact on groundwater quality because it increases the overall salinity of water. This result is also in agreement with a solute recycling model, which includes the reservoir geometry and hydraulic properties, the pumping rate and the irrigation surface area of the watershed (Perrin et al., 2011) and which simulates an increase in concentration of any mobile element by 2.8 over the last 13 years.

### 3.2 Simulating F accumulation beneath a paddy field

Fluoride concentrations as well as evaporation linked to IRF are higher beneath paddy fields suggesting the impact of evaporation on F accumulation. However, the lack of clear relationship between “D-excess” and fluoride suggest the occurrence of other processes involved within fluoride accumulation, among them contribution from variability of water-rock interactions processes and inputs from fertilizers.

A 1D PHREEQC column has been conceptualized in order to understand the relative contributions of the above mentioned processes on the control of fluoride accumulation in groundwater (Fig. 3). In this model, return flow is simulated by successive infiltration of pumped groundwater (last cell in column PHREEQC) after flowing through the column. At each daily step of recharge, an average evaporation flux is applied to the inflowing solution. The calculations are made for an average thickness of 20m above the groundwater level and an average infiltration velocity corresponding to the geometric mean of hydraulic conductivity in the laminated layer of  $5.1 \times 10^{-5} \text{ m.s}^{-1}$  (about 4.4 m/day) (Dewandel et al., 2006).

Water-rock interactions processes taken into account are based on observations. Biotite, apatite, allanite and sphene are the main F-bearing minerals of the granite from the watershed. As

sphene is an unalterable phase, it cannot be considered as a main contributor to F accumulation. Therefore, only biotite (F: 1.08%), fluorapatite (F: 3.42%) and allanite (F: 0.97%) must account for the fluoride accumulation. On one hand, the presence of some undesirable elements such as uranium at concentrations that can exceed the drinking water limit supports the contribution of allanite (U= 0.3%). On the other hand, a lack of vanadium in some of the high-F-groundwater samples, despite the significant content in biotite (V=0.03% ) and allanite (V= 0.03%), suggests a significant contribution from fluorapatite (V<0.003%) in some samples. Thus, the three F-bearing minerals almost certainly contribute through water-rock interaction processes and have been taken into account in the PHREEQC 1D conceptual model of water infiltration beneath a paddy field.

In the calculations, thermo-kinetic dissolution of primary aluminosilicate phases (allanite and biotite, among others) and iron oxides (goethite) are based on the general form:

$$R_i = k_i S_i \left( \frac{a_i}{K_i} \right)^n \left( 1 - \frac{Q_i}{K_i} \right)$$

Where  $k_i^{m,eff}$  is the rate constant,  $Q_i$  is the ion activity product and  $K_i^m$  is the thermodynamic equilibrium constant for the reaction (Lasaga, 1998). Dissolution rate of fluorapatite ( $Ca_{10}(PO_4)_6F_2$ ) depends on pH and is expressed according to Chairat et al. (2007). Precipitation of secondary mineral at thermodynamic equilibrium is allowed for chalcedony, calcite, fluorite, gibbsite, kaolinite, dolomite, ferrihydrite. Adsorption processes, including fluoride adsorption, are described by Dzombak and Morel (1990) theory for both ferrihydrites and gibbsite minerals. The model also includes ion exchange capacity of clays.

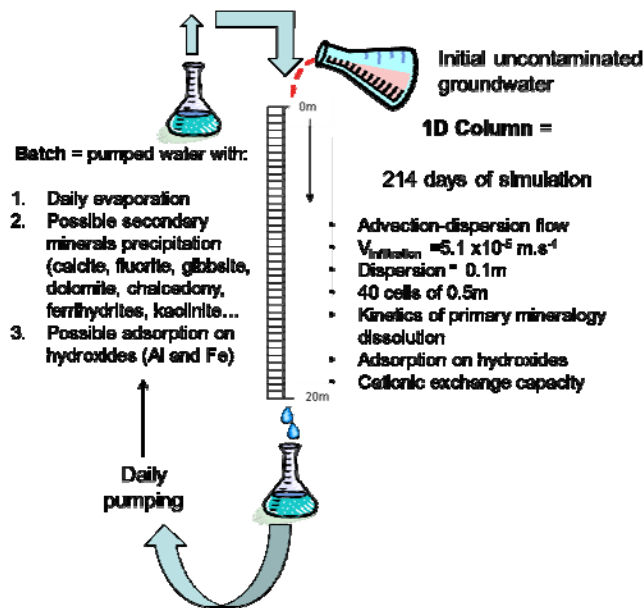
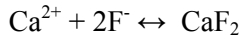


Figure 3. PHREEQC 1D Column conceptual model of return flow simulation beneath a paddy field.

The evolution of the chemical composition is simulated as a function of time and depth (Fig.4). During infiltration, through-flow column and return flow, pH value stays near neutrality because of the buffering effect due to calcite precipitation. Cl<sup>-</sup> concentration increases yearly by 9.4%. Fluoride concentration varies with depth in response to infiltration of evaporated water and water-rock interaction processes. It also increases with time despite possible fluoride adsorption onto precipitating mineral phases and the potential fluorite (CaF<sub>2</sub>) precipitation according to the reaction:



Fluoride concentration increase exceeds that of chloride but depends on the dissolution rate of the primary mineralogy (biotite, allanite and fluorapatite). The strong mobilization of F is due to the inhibition of fluorite precipitation by calcite stability in the system, which precipitation consumes calcium, making it unavailable for fluorite.

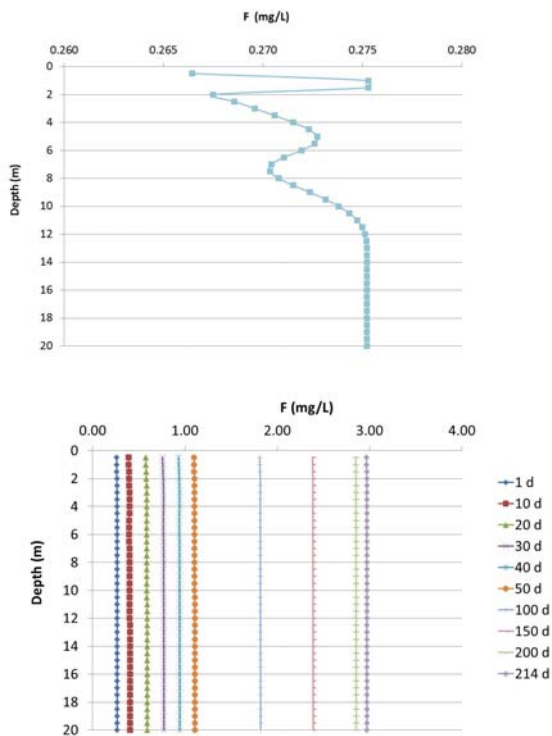


Fig.4: F concentration pattern with depth on a daily basis and at different periods of time.

### 3.3 Impact of climate change

The 1D PHREEQC column can be applied to evaluate groundwater vulnerability to high fluoride concentration for several land use and climate change scenarios. In particular, climate change, by changing rainfall rates and temperature may have an additional negative impact on groundwater quality, notably by enhancing F accumulation. Increase of temperature contributes to evaporation increase. With the change of rainfall rates, they promote salinization of the groundwater system. For the considered study area, by applying a lumped reservoir model, Perrin et al. (2011) simulated the concentration evolution of any conservative elements for different scenarios during the next 35 years (2010-2044). Decrease of rainfall rates by 10 % would lead to an increase of any conservative element concentration by a factor of about 2 and evaporation

increase by 10 % would increase concentration by about 1.8 compared to today's values. For fluoride, higher factors have even to be expected because of additional dissolution of F-bearing primary minerals. Apart from evaporation, temperature increase may also modify water-rock interactions and in turn impacts F concentration. Thus, we have shown that calcite stability within soils is a key parameter of fluoride increase in groundwater, and increase of temperature favors calcite stability, although the sensitivity of this parameter need to be assessed. According to these results, F concentration in groundwater beneath paddy fields would systematically exceed the drinking water limit rapidly (1.5 mg/l).

## CONCLUSIONS

Fluoride accumulation in groundwater constitutes a threat to drinking water for local communities in hard-rock regions of India. Although fluoride originates from dissolution of rock aquifer during groundwater flow, some land use practices can contribute to its accumulation. Our work shows that evaporation in paddy fields and subsequent water-rock interaction during return flow increases F concentration by several mg/l, by a factor higher than that of overall salinity and leading rapidly to groundwater exceeding the drinking water limit. The 1D geochemical model can be applied to evaluate groundwater vulnerability to high fluoride concentration for several land use and climate change scenarios. Climate change is expected to enhance F accumulations in groundwater, in particular through the decrease of rainfall and increase of evaporation. Within a near future, all groundwater around paddy fields would reach F concentration exceeding drinking water limit.

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