
Modeling of High Fluoride Groundwaters in India using PHREEQC

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Abstract—The development of conceptual geochemical models is enhanced by saturation index calculations that can identify the equilibrium state of minerals. Speciation modeling provides saturation indices that indicate reactions thermodynamically possible, minerals dissolving and precipitating in an aquifer system. In the present study, aqueous speciation modeling is carried out for the high fluoride groundwaters of some monitoring wells in Uttar Pradesh, Haryana, Rajasthan, Gujarat and Orissa using PHREEQC geochemical code. Speciation modeling results indicate that the groundwaters are oversaturated with calcite and undersaturated with fluorite and oversaturated with fluorite for some monitoring wells in Rajasthan, Orissa and Haryana districts.

Keywords: Ground water speciation modeling, fluorite, Geochemical model.

I. Introduction

Occurrence of fluorine in groundwater has drawn attention due to its adverse impact on human physiology. The maximum tolerance limit of fluoride in drinking water specified by the World Health Organization is 1.5 mg l⁻¹ [20]. The high concentration of fluoride in the groundwater has been reported in many parts of Indian subcontinent and is becoming a serious concern for the drinking water supply [4, 9, 12]. Normally fluorine exists in form of fluoride in natural waters because of its high reactivity [14]. Fluorine occurs mainly as free fluoride ion in natural waters, though fluoride complexes of Al, Be, B, and Si are also encountered under specific conditions. One hundred fifty fluorine bearing minerals (63 silicates, 34 halides, and 22 phosphates, 30 others) are reported [18], but many minerals may contain minor amounts of F⁻ replacing OH⁻ or O²⁻. The main natural sources of fluoride in soil are fragments of minerals such as apatite, cryolite, fluorite or fluorspar and topaz (Al silicates containing F). These can be supplemented by inputs of man-made material. Industries, which use raw materials containing even small amounts of fluorine, can release enough gaseous (HF, SiF₄) and / or particulate fluorides (AlF₃, Na₃AlF₆, CaF₂) to enhance elemental levels in the surrounding areas. Pollutant sources include manufacturers of bricks, iron fertilizers and glass, coal-fired power stations and aluminium smelters. Minerals like fluorite, fluoroapatite, fluormica (phlogopite), cryolite, epidote, topaz, phosphorite, tremolite villuanite and certain varieties of mica contribute fluo-

ride [5, 6, 7, 8, 15]. The occurrence of fluoride both in igneous and sedimentary rocks is reported to be similar [2]. Fluoride in the range 30 to 21000 ppm is present in amphiboles present in metamorphic rocks [5, 19]. The fluoride contamination can be from fertilizers [6, 7, 11].

II. Present Study

A. Theory

Groundwater may undergo a variety of inorganic chemical reactions as it moves and interacts with the solid framework materials and associated gases. The main reactions are precipitation / dissolution, oxidation / reduction, aqueous complexation, hydrolysis, sorption and desorption, exsolution and dissolution of gases. In the recent past, a number of geochemical codes have been developed to model the water rock interactions. These geochemical codes can be used for mass balance modeling, equilibrium speciation / saturation modeling and equilibrium mass transfer modeling. The geochemical codes for modeling water rock interactions include PHREEQC, MINTEQA2, WATEQ, BALANCE, NETPATH, EQ3NR, MINEQL and HYDROGEOCHEM. The development of conceptual geochemical models is enhanced by saturation index calculations that can identify the equilibrium state of minerals. Speciation modeling provides saturation indices that indicate which reactions are thermodynamically possible, which minerals may be dissolving and which may be precipitating in an aquifer system. Speciation models calculate the thermodynamic properties of aqueous solutions, including the molalities and activities of aqueous species and saturation indices of minerals. Ion-association and specific-interaction are the two current approaches to calculate the above mentioned properties. In dilute aqueous solutions, the activity of solute species is defined as:

$$a_i = \frac{m_i}{\gamma_i} \quad (1)$$

in which m_i is the concentration of species i in molal units, γ_i is the activity coefficients. An alternative means of calculating ion activity coefficients in dilute solutions is provided by Debye-Huckel theory, which attempts to calculate the effect of electrostatic interactions among ions

on their free energies of formation. To evaluate the cumulative effect of attractive and repulsive forces, a charge-weighted function of species concentration known as ionic strength (I) is defined as:

$$I = 0.5 \sum m_i z_i^2$$

in which z_i is the charge on an ion of species i . The Debye Huckel equation takes into account not only the ionic strength of the electrolyte solution, but also effective size of the hydrated ion of interest. The activity coefficient for ion i , is given as:

$$\log_{10} \gamma_i = -Az_i^2(I)^{0.5} / (1 + Ba(I)^{0.5}) \quad (3)$$

where a is size parameter for ionic species and A and B are empirical parameters. A and B are functions of only pressure and temperature.

The primary purpose of speciation modeling is to calculate mineral saturation indices, which are indicators of saturation state of a mineral with respect to a given water composition. Thermodynamically, the potential for dissolution or precipitation of solid can be expressed as the computed saturation index (SI):

$$SI = \log_{10}(IAP / K_{sp}) \quad (4)$$

where, IAP is the empirical ion-activity product for a given mineral in the water of interest, and, K_{sp} is the equilibrium solubility product constant (Table 1) for the same mineral at the temperature and pressure of the water.

Net dissolution of solid phase should occur if the groundwater is undersaturated with respect to the solid in the adjacent aquifer as indicated by a negative value of SI. Net precipitation of solid can occur only if the SI has a positive value. An SI value of zero means that there is no thermodynamic tendency for net dissolution or net precipitation of the mineral. Thus, saturation index indicates what should happen thermodynamically however, it does not indicate the rate at which the process will proceed.

A. PHREEQC

The USGS geochemical code PHREEQC version 2 is a computer program written in the C programming language. Parkhurst and Appelo (1999) developed this geochemical code. It is designed to perform a wide variety of low-temperature aqueous geochemical calculations. PHREEQC is based on an ion-association aqueous model and has the following capabilities;

(1) Speciation and saturation-index calculations;

(2) Batch-reaction and one-dimensional (1D) transport calculations involving reversible reactions, which include aqueous, mineral, gas, solid-solution, surface-complexation, and ion-exchange equilibria, and irreversible reactions, which include specified mole transfers of reactants, kinetically controlled reactions, mixing of solutions, and temperature changes; and

(3) Inverse modeling, which finds sets of mineral and gas mole transfers that account for differences in composition between waters, within specified compositional uncertainty limits.

B. Hydrochemical data

High fluoride in the groundwater samples has been reported by Chadha and Tamta [1] for some villages in Unnao district in Uttar Pradesh, Sirsa and Karnal district in Haryana and Jalor, Jaisalmer, Jodhpur, Bikaner and Barmer district in Rajasthan. Kundu et al [13] have reported high fluoride in the groundwater of Nayagarh district in Orissa. Jethra [10] has reported high fluoride in the groundwater of Dungarpur district, while Phadtare [17] has reported high fluoride in the groundwater of Mehsana district. The hydrochemical data reported by these investigators are used in this study for aqueous speciation modeling by using a geochemical code PHREEQC. The chemical composition high fluoride groundwater of some villages reported by Chadha and Tamta [1], Kundu et al [13], Jethra [10] and Phadtare [17] is given in Table 2.

III. RESULTS AND DISCUSSIONS

The groundwater samples of Unnao district, Uttar Pradesh and Sirsa and Karnal district, Haryana are from unconsolidated formation consisting of quaternary sediments of recent and older alluvium. The high fluoride in groundwater in groundwater of Unnao district in UP, Sirsa and Karnal district in Haryana is accompanied with low calcium concentration [1]. High fluoride groundwaters also occur in the villages of Nayagarh district of Orissa (Kundu et al. [13], petrographic studies of the country rock granite gneiss with bands of quartzo-feldspathic minerals and ferromagnesian minerals revealed the presence of biotite, hornblende and orthopyroxene. Groundwater in unconfined aquifer of Mehsana district in Gujarat has high fluoride concentration in the northeastern part of the district which has weathered granite formations.

Table 1 Equilibrium solubility product constant of some mineral phases.

Phases	Equilibrium constant Log K_{sp}	Phases	Equilibrium constant Log K_{sp}
Anhydrite	-4.360	Fluorite	-10.600
Aragonite	-8.336	Goethite	-1.000
Calcite	-8.480	Gypsum	-4.580
CO ₂ (g)	-1.468	Halite	1.582
Dolomite	-17.090	Jarosite-K	-9.210
Fe(OH) ₃	4.891	Melanterite	-2.209

Table 2 Chemical composition of the groundwater from monitoring wells in India

Uttar Pradesh

Unnao district	pH	EC	Total Alk.	Cl	F	Ca	Mg	Na	K
Bandla Khera	8.5	1615	569	73	5.4	7	35	340	7.1
Garhi	8.4	672	352	11	5.8	12	19	142	1.0

Haryana

Location and district	pH	EC	HCO ₃	Cl	F	SO ₄	Ca	Mg
Dabwali, Sirsa	8.2	2155	1069	123	12.8	86	4.4	3.9
Diwana, Sirsa	7.65	1368	799	26	10.4	59	21	13
Pucca Khera, Karnal	7.65	3594	1097	267	6.85	435	36	69

Orissa

Location and District	pH	HCO ₃	F	Cl	Ca	Mg	Na	K	Al
Sagargaon, Nayagarh	7.7	366	2.71	45.3	38.5	7.2	130.6	2.1	0.4
Singhpur, Nayagarh	7.6	325	2.8	1148	93.	67.4	647.6	74.2	0.1
Balasingi, Nayagarh	7.6	362	8.49	420	64.7	30.7	388.4	9.5	0.7

Gujarat

Location and district	pH	EC	HCO ₃	Cl	SO ₄	F	Ca	Mg	Na	K
Vadnagar	8.05	10025	2306	1503	984	5.6	20	36	1886	624
Malekpur	8.75	990	378	71	34	1.7	60	73	53	-
Dabhoda	8.3	625	183	64	724	1.9	20	12	97	-
Sipur	7.8	1845	610	277	43	3.8	32	24	363	-
Bheesal Vasana	8.2	1860	573	284	58	1.6	44	36	322	8

Rajasthan

Location and District	pH	EC	CO ₃	HCO ₃	Cl	SO ₄	F	Ca	Mg	Na	K
Sankholi, Jalore	8.6	1960	72	476	234	139	6.5	28	27	382	3
Ranau, Jaisalmer	7.8	2020	0	439	312	190	4.65	16	17	425	7
Salwas, Jodhpur	8.6	5480	96	939	625	537	8.5	24	58	1173	18
Arjansar, Bikaner	9	2960	120	488	496	110	12.9	16	15	621	4.7
Dhadlawas, Barmer	8.6	3190	36	171	788	302	4.5	42	43	621	25
Bhilura, Dungarpur	7.95	880	-	329	121	80	1.6	80	44	74	10
Nayagaon, Dungarpur	8.20	370	-	244	540	116	3.1	120	56	253	19
Hatai, Dungarpur	8	750	-	403	57	58	6	48	44	83	4
Aspur, Dungarpur	7.7	1080	-	244	206	49	3	60	49	92	8

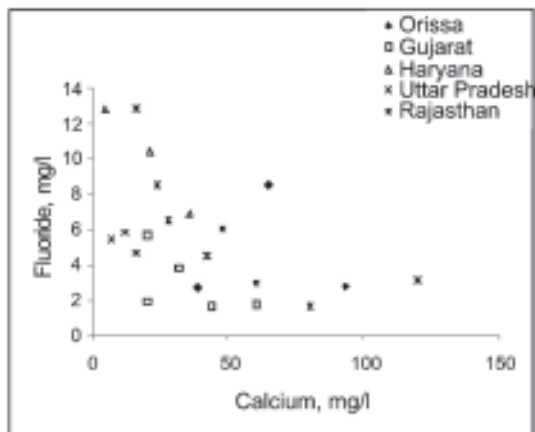


Figure 1. Plot of relationship between calcium and fluoride

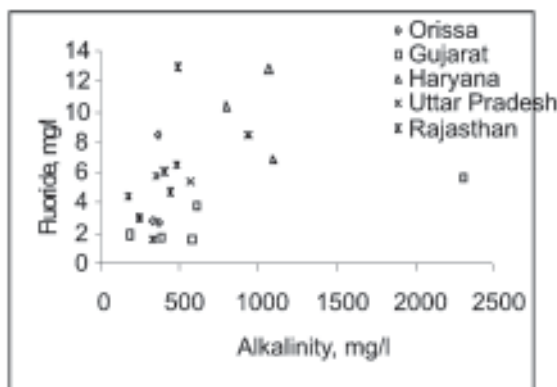


Figure 2. Plot of relationship between alkalinity and fluoride

Table 3 Saturation indices of calcite and fluorite

Location	Ionic strength	SI Calcite	SI Fluorite
Bandala Khera (UP)	1.71×10^{-2}	0.55	-0.72
Garhi (UP)	8.8×10^{-3}	0.59	-0.29
Dabwali (Haryana)	1.51×10^{-2}	0.31	-0.16
Diwana (Haryana)	1.15×10^{-2}	0.16	0.42
Pucca Khera (Haryana)	2.79×10^{-2}	0.61	0.05
Sargagaon (Orissa)	9.53×10^{-3}	0.44	-0.42
Singhpur (Orissa)	4.43×10^{-2}	0.5	-0.29
Balasinghi (Orissa)	2.36×10^{-2}	0.46	0.64
Vadnagar (Gujarat)	1.08×10^{-1}	0.82	-0.65
Malekpur (Gujarat)	1.442×10^{-2}	1.68	-0.78
Dabhoda (Gujarat)	2.1×10^{-2}	0.96	-1.38
Sipor (Gujarat)	2.1×10^{-2}	0.57	-0.35
Bheesal Vasana (Gujarat)	2.15×10^{-2}	1.05	-1
Sankholi (Rajasthan)	2.11×10^{-2}	1.53	-0.07

Ranau (Rajasthan)	2.36×10^{-2}	0.1	-0.5
Salwas (Rajasthan)	5.6×10^{-2}	1.34	-0.09
Arjansar (Rajasthan)	2.95×10^{-2}	1.43	0.19
Dhadlawas (Rajasthan)	3.6×10^{-2}	1.29	-0.23
Bhilura (Rajasthan)	1.59×10^{-2}	0.88	-0.69
Nayagaon (Rajasthan)	2.77×10^{-2}	1.1	-0.02
Hatai (Rajasthan)	1.34×10^{-2}	0.87	0.26
Aspur (Rajasthan)	1.69×10^{-2}	0.39	-0.26

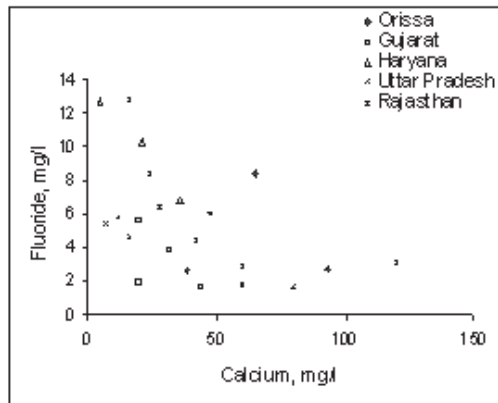


Figure 2. Plot of relationship between alkalinity and fluoride

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Dabwali (Harvana)	1.51×10^{-2}	0.31	-0.16
Diwana (Harvana)	1.15×10^{-2}	0.16	0.42
Pucca Khera (Haryana)	2.79×10^{-2}	0.61	0.05
Sagargaon (Orissa)	9.53×10^{-3}	0.44	-0.42
Singhpur (Orissa)	4.43×10^{-2}	0.5	-0.29
Balasinghi (Orissa)	2.36×10^{-2}	0.46	0.64
Vadnagar (Gujarat)	1.08×10^{-1}	0.82	-0.65
Malekpur (Gujarat)	1.442×10^{-2}	1.68	-0.78
Dabhoda (Gujarat)	2.1×10^{-2}	0.96	-1.38
Sipor (Gujarat)	2.1×10^{-2}	0.57	-0.35
Bheesal Vasana (Gujarat)	2.15×10^{-2}	1.05	-1
Sankholi (Rajasthan)	2.11×10^{-2}	1.53	-0.07
Ranau (Rajasthan)	2.36×10^{-2}	0.1	-0.5
Salwas (Rajasthan)	5.6×10^{-2}	1.34	-0.09
Arjansar (Rajasthan)	2.95×10^{-2}	1.43	0.19
Dhadlawas (Rajasthan)	3.6×10^{-2}	1.29	-0.23
Bhilura (Rajasthan)	1.59×10^{-2}	0.88	-0.69
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Table 3 Saturation indices of calcite and fluorite

These high fluoride waters also have low calcium concentration [17]. The high fluoride groundwater of Sankholi, Ranau, Salwas, Arjansar and Dhadlawas in Rajasthan are sampled from the semi-consolidated formations and are accompanied by high concentration of sodium, chloride and sulphate and indicative of dissolution of fluoride bearing minerals [1]. The groundwater from shallow wells in Dungarpur district for Bhilura village sampled from gneiss formation, Nayagaon and Aspur phyllite/schist and phyllite formation Hatai village have high fluoride [10]. The plots of fluoride versus calcium and alkalinity are shown in Figs. 1-2. A negative relation is observed between fluoride and calcium and a positive relation with alkalinity. The SI of calcite and fluorite for

respective villages are given in Table 3. The plot of SI_{fluorite} versus SI_{calcite} is shown in Fig. 3. PHREEQC is based on the ion association theory and can be used for speciation modeling for dilute aqueous solution with ionic strength less than 0.5. The groundwater samples considered have ionic strength in the range 9.53×10^{-3} to 1.088×10^{-1} .

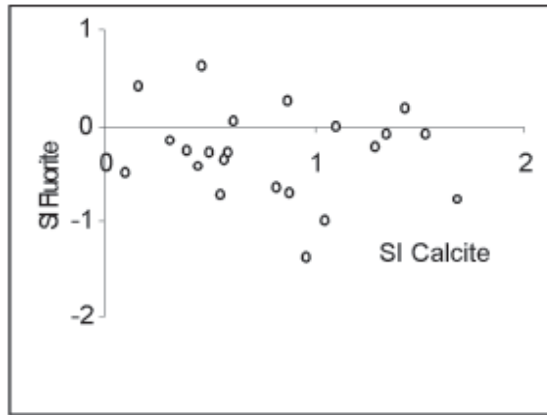


Figure 3. Plot of relationship between saturation index of calcite and fluorite

The groundwater is undersaturated and oversaturated at certain places with fluorite and the saturation index values of fluorite are in the range of -1.38 to 0.64. At Hatia (Rajasthan), Balasinghi (Orissa), Diwana and Pucca khera (Haryana) the groundwater is oversaturated with fluorite. Results of aqueous speciation modeling of high fluoride groundwaters reveal that the groundwater is oversaturated with calcite, the saturation index values of calcite are in the range of 0.1- 1.68.

I. Conclusions

Geochemical codes has been used for mass balance, equilibrium speciation / saturation index and equilibrium mass transfer modeling. The thermodynamic properties of aqueous solutions, including the molalities and activities of aqueous species and saturation indices of minerals has been calculated using speciation models. PHREEQC geochemical code is used for speciation modeling for the high fluoride groundwaters of Uttar Pradesh, Haryana, Orissa, Gujarat and Rajasthan. Saturation index calculation results show that the groundwaters are oversaturated with calcite and undersaturated with fluorite at most of the places, however it is oversaturated with fluorite at certain places.

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