

Full Length Research Paper

# Geochemical evaluation of high-fluoride and nitrate groundwater: A Case Study from Qinkenpao area, Daqing, China

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Groundwater quality problems have emerged in many geographical areas due to natural environmental processes and human intervention in the geosystems. Hydrogeochemical appraisal of fluoride contaminated groundwater in Qinkenpao area, Daqing State, China is carried out by means of groundwater quality investigations. Results obtained from aqueous speciation modeling using AQUACHEM 5.1 reveal that the groundwater is undersaturated with fluorite and with calcite. The samples also contained high concentrations of nitrate, which is a serious water quality issue due to the impact of human activity. Factor analysis modeling demonstrated that  $\text{NO}_3^-$  in the system are produced by anthropogenic sources. Strong correlation observed between  $\text{NO}_3^-$  and  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{F}^-$ , suggesting that they have the same origin. The factor analysis indicates that sodium plus nitrate bicarbonate groundwater have a high loading factor for fluoride, whereas that for calcium chloride and magnesium chloride groundwater is low. The plausible geochemical reactions in the area of study are dissolution of calcite and dolomite, carbon dioxide and sulphate minerals with ion exchange.

**Key words:** Aqueous speciation modeling, fluoride, nitrate, groundwater, hydrogeochemical, factor analysis.

## INTRODUCTION

Water is an essential natural resource for sustaining life and environment that we have always thought to be available in abundance and a free gift of nature. However, chemical composition of surface or subsurface is one of the prime factors in which the suitability of water for domestic, industrial or agricultural purpose depends. Freshwater occurs as surface water and groundwater.

Though groundwater contributes only 0.6% of the total water resources on earth, it is the major and preferred source of drinking water in rural as well as urban areas, particularly in developing countries like China because treatment of the drinking water, including disinfection is often not required. But in the area of economical growth, groundwater is getting polluted due to urbanization and

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industrialization.

Presence of various hazardous contaminants like fluoride, nitrate, arsenic, pesticides, other heavy metals etc. in groundwater has been reported from different parts of China. The occurrence of high fluoride and nitrate concentration in groundwater has now become one of the most important health-related geoenvironmental issues in many countries of the world. Fluoride and arsenic are the two main contaminants in groundwater present naturally and artificially in China, India, Egypt, Morocco, Saudi Arabia, Argentina, Canada etc., causing a set of health symptoms known commonly as fluorosis and arsenicosis (Mameri, 1998).

In groundwater, the natural concentration of fluoride depends on the geological, chemical and physical characteristics of the aquifer, the porosity and acidity of the soil and rocks; the temperature, the action of other chemical elements like calcium and bicarbonates, and the depth of the aquifer (Chandra et al., 1981; Largent, 1961).

Fluoride has a significant mitigating effect against dental caries if the concentration is approximately 1 mg/L. However, continuing consumption of higher concentrations can cause dental fluorosis and in extreme cases even skeletal fluorosis. The maximum tolerance limit of fluoride in drinking water specified by the World Health Organization (WHO, 1984) is 1.5 mg/L. High fluoride concentrations are especially critical in developing countries, largely because of lack of suitable infrastructure for treatment.

If fluoride concentration in drinking water is more than 1.0 mg/L, it would result in fluorosis (dental fluorosis and skeletal fluorosis) for human beings, especially for children and pregnant woman. This is a result of the destruction of metabolic calcium and phosphorus, as well as inhibition of active enzymatic processes in the human body. Thus, the function of the endocrine system gets interrupted, leading to fluorosis (Khandare et al., 2005).

Once nitrates get into the groundwater, the greatest danger is for babies less than 1 year old. Small babies have bacteria in their digestive tract that converts nitrate into nitrite, which is toxic. Nitrite reacts with a substance in the blood called hemoglobin. When nitrites are present, hemoglobin will preferentially combine with nitrite instead of oxygen. The new substance formed is called methemoglobin and does not carry oxygen. As the amount of methemoglobin increases, the amount of oxygen in the blood decreases, eventually causing internal suffocation (Walton, 1951; WHO, 1996; USEPA, 1997).

The most common symptom of nitrate poisoning in babies is a bluish color to the skin, particularly around the baby's eyes and mouth. The blood will also turn a chocolate-brown color, which reflects the lack of oxygen. These symptoms of nitrate toxicity are commonly referred to as the "blue-baby" syndrome.

Except the municipality of Shanghai, every province in China has areas that are afflicted with endemic fluorosis

(Zan-dao and Yan, 2002). Unfortunately, the problem is often serious and is usually difficult to prevent or correct. The major sources of fluoride ingestion are from drinking water, coal burning, and tea bricks. For the prevention of dental caries, a drinking water standard for fluoride of 1.0 to 1.5 mg/L had been widely adopted. In China, the standard in the 1950s was 1.5 mg/L. In 1970s, it was lowered to 0.5 to 1.0 mg/L, where it has remained till date (Zan-dao and Yan, 2002).

Recently, factor analysis has been used with remarkable success by many investigators as a tool in the study of groundwater chemistry (Lawrence and Upchurch, 1983). In this study, hydrogeochemical evaluation of high-fluoride and nitrate groundwater in Daqing City, Qinkenpao area, China, is carried out (i) to characterize fluoride and nitrate contamination in the groundwater; and (ii) to identify plausible geochemical reactions under the prevailing hydrogeological conditions, as well as their role in mobilizing fluoride and nitrate concentration.

## METHODOLOGY

### Area of study

Located in the North Temperate Zone, Daqing belongs to the continental monsoon climate and is affected by the cold air mass from inland Mongolia and the monsoon comes from the warm air mass of the ocean. The area of study located between latitudes 46°32'28" N - 46°42'18" N and longitudes 125°04'19" E - 125°25'14" E covers an area of 549 km<sup>2</sup> (Figure 1). It is semi-arid area characterized by hot dry summers 24°C (April to June) and cold dry winters -26°C (November to February). The annual rainfall is 418 mm, mainly during June to September. Most of the area is flat and plain, where the surface elevation ranges between 174 to 149 m a.s.l.

### Geology and hydrogeology

Quaternary sediments are widely distributed in this area, and the thickness ranges from 20 to 40 m. The shallow groundwater belongs to unconfined and confined groundwater, which is located in the quaternary sediment. Unconfined aquifer lies below loess-like loam, and the permeability coefficient is 0.5 m/d. This aquifer lithology is sand and gravel, with the thickness changes from 1 to 10 m and groundwater depth below ground varies from 2 to 8 m. Confined aquifer mainly occurs in sand and gravel, which has a close hydraulic connection with unconfined aquifer. It is important to note that there is a lack of tertiary sediment in this area, and the mudstone aquiclude (about 30 m), which belongs to cretaceous sediment, exists in the underlying cretaceous gravel aquifer and the upper quaternary aquifer. The hydraulic gradient in this area is not large, and the runoff cycle is poor. Moreover, the main recharge of groundwater in this area is from atmospheric precipitation and groundwater runoff, and discharge is via evaporation and lateral runoff (Figure 2).

### Sampling and analytical procedure

Groundwater quality monitoring was carried out for 19 well locations in the area of study during post-monsoon 2010. The details of

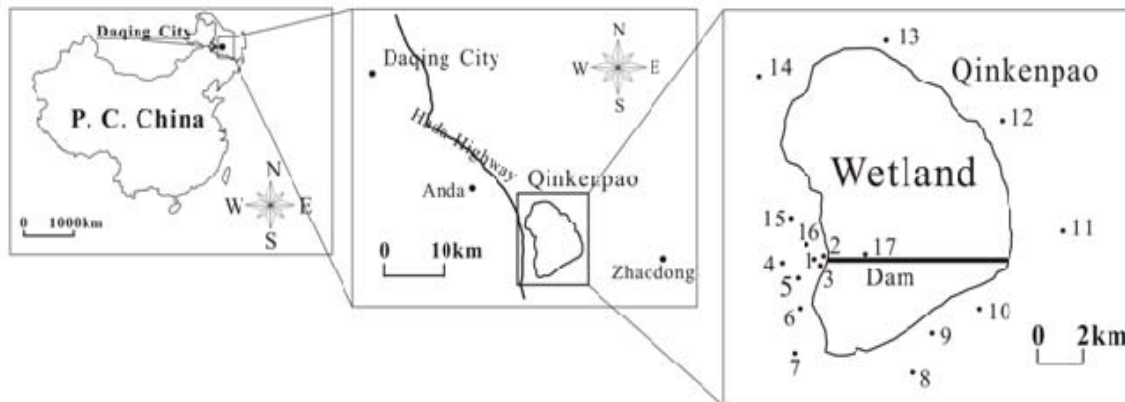


Figure 1. Map of Sartu District, Daqing City, China.

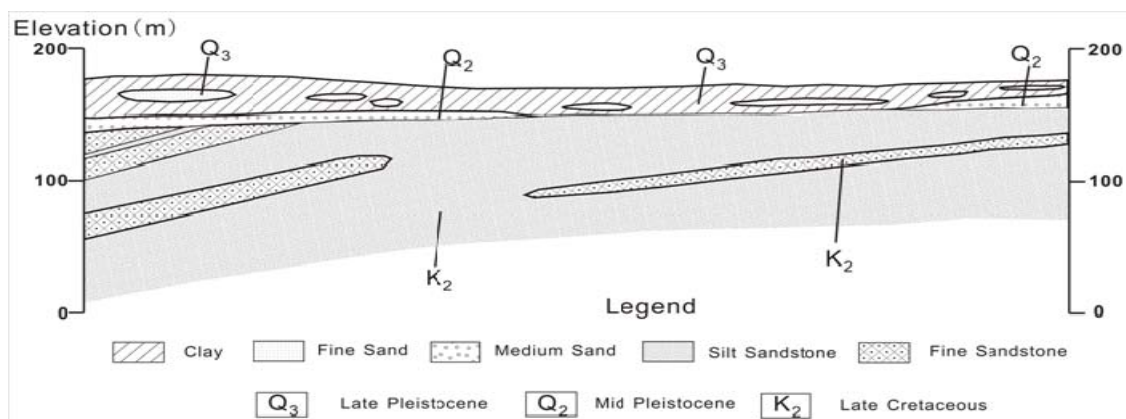


Figure 2. Geological sketch of aquifers in the study area.

location, type and depth of wells are given in Table 1. The polyethylene bottles were used to collect the samples of surface water and groundwater. Water samples were collected from September, 2010. Physicochemical parameters, including temperature, pH, electrical conductivity (EC) and total dissolved solid (TDS), were conducted in the field. Other samples were transported to the laboratory for testing. Major components ( $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  and  $\text{F}^-$ ) were measured in laboratory within 10 days of sampling. Samples were stored in the dark in a cold room at  $4^\circ\text{C}$ . All of these negative and positive ions are tested using DX-120 ion chromatography, and the detection limits are shown in Table 2 (EPA, 2009).

The cation-anion balance error of 17 samples collected in post-monsoon 2010 is within the permissible limit of 5% and the remaining 2 samples with higher ion balance error were not considered in the study.

## RESULTS AND DISCUSSION

### Fluoride and Nitrate hydrogeochemistry and aqueous speciation modeling

Concentrations of various groundwater quality parameters obtained for samples collected in post-

monsoon 2010 are shown in Table 2. The water type for each sample is also indicated. It is evident that groundwater consists mainly of types  $\text{Na-HCO}_3$ ,  $\text{Ca-HCO}_3$  and  $\text{Ca-NO}_3$ . The calcium concentration ranges between 6.25 and 193.5 mg/L, fluoride between 0.58 and 3.4 mg/L and nitrate between 0 and 624.1 mg/L. The correlation coefficients among various groundwater quality parameters were obtained to investigate their interdependence. The correlation matrix for the hydrochemical data of September 2010 is shown in Table 3. This shows that fluoride and nitrate have a positive relationship with all species, but sulfate and pH for nitrate, and further pH for fluoride have a negative relationship.

The  $\text{NO}_3^-$  concentrations at some locations (60% of the wells) exceeded the 50 mg/L limit specified by the WHO drinking water standard.

Groundwater also contained high concentrations of  $\text{NO}_3^-$ , which indicates a serious water quality issue. This  $\text{NO}_3^-$  originates from the soil surface and enters the groundwater via infiltration. However, due to the influence of land use, there was still a high level of horizontal

**Table 1.** Well location, and depth of well.

Location	Latitude, N	Longitude, E	Altitude (m a.m.s.l.)	Depth of well (m b.g.l.)
1	46°19'07.1"	125°29'07.0"	163.2	100.0
2	46°19'08.4"	125°29'11.1"	156.9	40.0
3	46°19'05.4"	125°29'08.7"	158.3	34.0
4	46°19'04.0"	125°28'09.0"	170.6	20.0
5	46°18'47.3"	125°28'34.0"	167.5	65.0
6	46°18'02.4"	125°28'42.1"	164.7	10.0
7	46°17'01.0"	125°28'30.0"	163.5	32.0
8	46°16'35.0"	125°32'44.0"	174.2	10.0
9	46°17'30.0"	125°33'21.0"	166.4	20.0
10	46°18'02.8"	125°35'04.0"	164.5	20.4
11	46°19'47.5"	125°38'03.9"	153.8	20.0
12	46°22'16.5"	125°35'50.2"	150.3	7.8
13	46°24'07.6"	125°31'42.5"	156.7	20.0
14	46°23'16.8"	125°27'15.6"	165.3	50.0
15	46°20'04.6"	125°28'23.1"	162.4	37.0
16	46°23'16.8"	125°27'15.6"	167.8	50.0
17	46°19'06.6"	125°29'52.4"	152.8	-

**Table 2.** Hydrochemical parameters for post-monsoon 2010 (concentrations are in mg/L).

Location	TDS	pH	K	Na	Ca	Mg	Cl	F	SO <sub>4</sub>	HCO <sub>3</sub>	NO <sub>3</sub>	Water Type
1	365.44	8.77	0.56	58.50	51.22	21.76	53.23	1.82	13.60	159.26	5.49	Ca-HCO <sub>3</sub>
2	671.96	7.88	0.03	112.06	68.52	28.54	36.45	1.44	190.80	214.33	19.78	Na-SO <sub>4</sub>
3	419.29	8.83	0.72	61.82	55.05	25.12	11.51	1.75	13.05	215.52	34.74	Ca-HCO <sub>3</sub>
4	1003.87	7.26	0.61	69.03	147.50	39.42	166.21	0.86	22.64	223.56	334.05	Ca-NO <sub>3</sub>
5	429.70	7.82	0.64	100.23	44.17	13.57	34.62	0.58	30.18	176.23	29.48	Na-HCO <sub>3</sub>
6	576.19	8.23	0.57	44.71	103.14	26.87	75.19	1.18	25.17	164.62	134.75	Ca-HCO <sub>3</sub>
7	345.95	8.24	0.95	61.69	42.44	12.68	16.45	0.65	19.98	191.11	0.00	Na-HCO <sub>3</sub>
8	1228.24	7.36	0.43	39.72	193.50	39.62	198.30	1.30	36.00	157.77	561.60	Ca-NO <sub>3</sub>
9	501.95	7.46	0.33	39.15	89.94	26.31	17.25	1.01	20.28	247.07	60.62	Ca-HCO <sub>3</sub>
10	1451.51	7.78	3.20	99.04	166.96	49.53	315.25	2.25	88.90	310.48	415.90	Ca-Cl
11	1910.79	7.65	2.24	340.78	90.72	39.06	314.30	3.40	91.05	405.14	624.10	Na-NO <sub>3</sub>
12	1731.95	9.75	1.26	451.12	31.23	38.27	186.24	1.36	124.13	717.41	180.93	Na-HCO <sub>3</sub>
13	1123.04	7.66	1.47	121.08	130.06	42.29	201.50	0.96	75.85	276.84	272.98	Ca-Cl
14	532.49	7.70	0.95	71.59	75.36	29.10	26.84	1.52	8.81	262.85	55.47	Ca-HCO <sub>3</sub>
15	654.17	7.98	1.02	121.18	72.93	30.59	66.52	2.94	31.37	294.70	32.91	Na-HCO <sub>3</sub>
16	1120.36	7.89	0.74	59.67	161.13	42.04	190.99	1.46	24.81	178.61	460.91	Ca-NO <sub>3</sub>
17	1181.18	9.40	1.30	340.01	6.25	9.58	207.98	0.97	0.00	363.17	251.92	Na-HCO <sub>3</sub>
Detection limit			0.10	0.10	0.10	0.10	0.10	0.10	0.25	3	0.20	

variation in groundwater quality in the upper aquifer. NO<sub>3</sub> and cation concentrations (Ca<sup>2+</sup> and Mg<sup>2+</sup>) showed strong correlations indicating that they originated from the same sources (Figure 3).

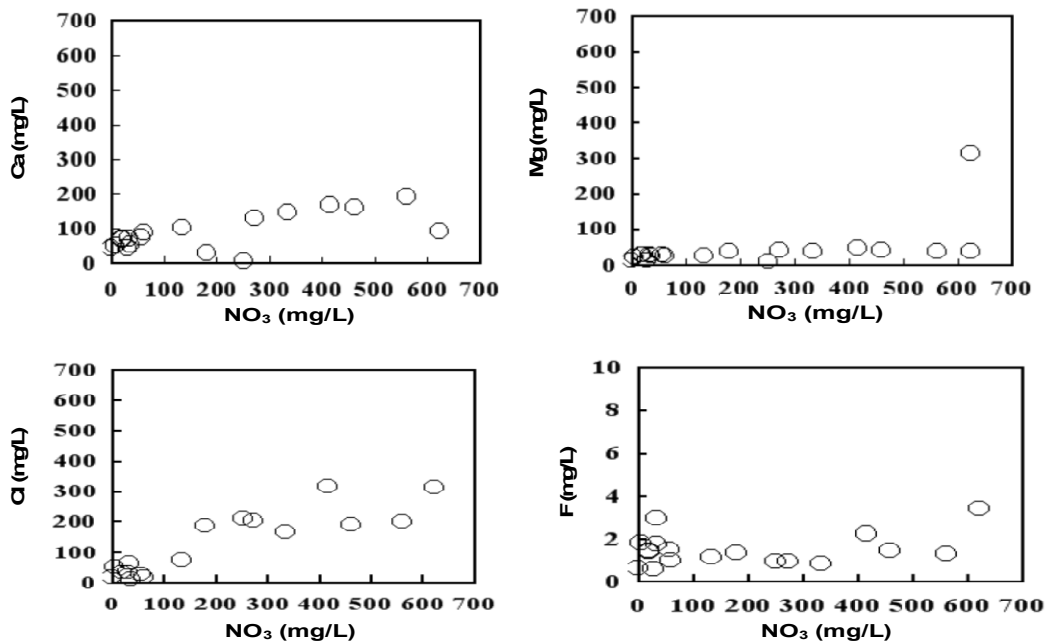
The upper limits of the point distribution for observed fluoride and calcium concentrations form a hyperbolic curve that suggests solubility of calcium- and fluoride-containing minerals controlling the fluoride concentration

(Figure 4). High fluoride with very low calcium and magnesium in water may be due to prior precipitation of CaCO<sub>3</sub> from water and only limited incorporation of fluoride in the calcite structure, so that there is always a net balance of fluoride in the solution.

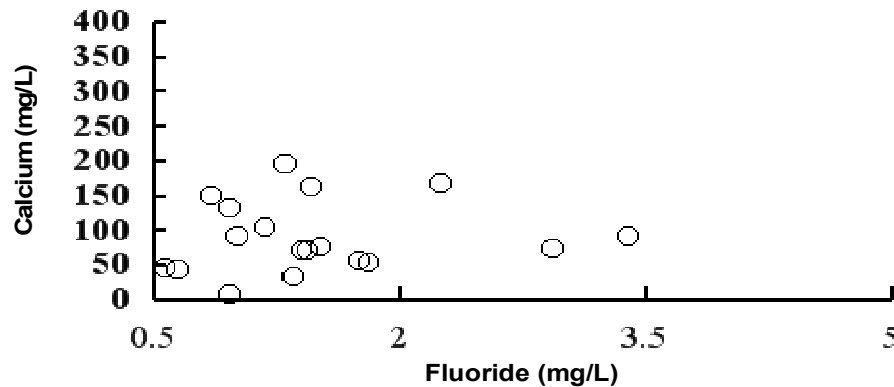
Aqueous speciation modeling was carried out using PHREEQC (Parkhurst and Appelo, 1999) geochemical code via AquaChem 5.1 (Waterloo Hydrogeologic Inc.,

**Table 3.** Correlation coefficients matrix for post-monsoon 2010 hydrochemical data.

Element	Ca	Mg	Na	K	Cl	F	SO <sub>4</sub>	HCO <sub>3</sub>	NO <sub>3</sub>	TDS	pH
Ca	1	0.784	-0.441	0.188	0.478	0.1	-0.13	-0.314	0.656	0.319	-0.691
Mg		1	0.025	0.424	0.637	0.4	0.226	0.236	0.627	0.637	-0.388
Na			1	0.397	0.489	0.259	0.441	0.896	0.227	0.702	0.597
K				1	0.754	0.486	-0.013	0.442	0.528	0.632	0.053
Cl					1	0.373	0.143	0.429	0.888	0.92	-0.046
F						1	0.126	0.25	0.271	0.395	-0.05
SO <sub>4</sub>							1	0.339	-0.06	0.334	0.107
HCO <sub>3</sub>								1	0.145	0.676	0.547
NO <sub>3</sub>									1	0.806	-0.287
TDS										1	0.079
pH											1



**Figure 3.** Cation (Ca<sup>2+</sup> and Mg<sup>2+</sup>) and anion (F<sup>-</sup> and Cl<sup>-</sup>) versus NO<sub>3</sub><sup>-</sup> concentrations in groundwater.



**Figure 4.** Relationship between calcium and fluoride concentration.

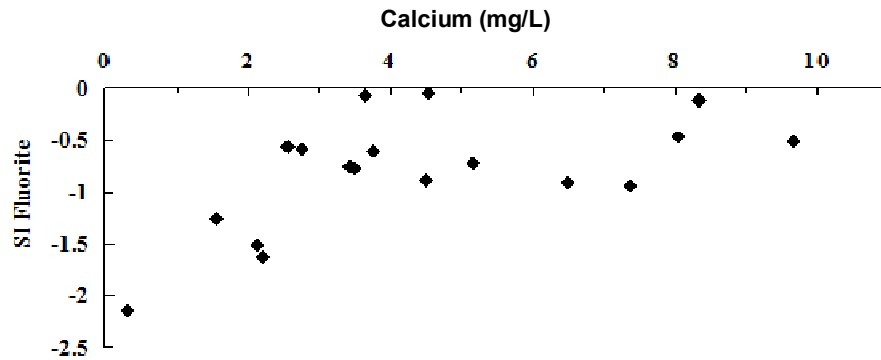


Figure 5. Plot of saturation indices of fluorite versus calcium concentration.

Table 4. Saturation index.

Well No.	SI anhydrite	SI aragonite	SI calcite	SI dolomite	SI fluorite	SI gypsum	SI halite
1	-2.0696	-0.3273	-0.1799	-0.4365	-0.0453	-1.8335	-5.6201
2	-2.3956	-0.4054	-0.258	-0.6096	-0.0716	-2.1586	-6.6778
3	-1.7993	-0.1499	-0.0024	-0.2443	-0.1128	-1.5628	-6.1418
4	-2.8094	-0.7648	-0.6174	-1.3233	-0.5607	-2.5723	-7.0696
5	-2.8246	-0.6192	-0.4717	-1.0003	-0.5872	-2.5875	-7.7168
6	-2.9105	-0.4228	-0.2753	-0.679	-0.6089	-2.6735	-7.2957
7	-2.3311	-0.3763	-0.2288	-0.7522	-0.4667	-2.0946	-6.5728
8	-1.6651	-0.6075	-0.4601	-1.0192	-0.7503	-1.4281	-6.975
9	-1.6293	-0.5938	-0.4463	-0.9955	-0.7734	-1.3923	-6.9723
10	-2.3233	-0.5106	-0.3632	-0.3509	-1.2585	-2.0868	-5.7029
11	-2.1222	-0.3693	-0.2219	-0.8428	-0.5083	-1.8858	-6.7409
12	-2.3643	-0.5152	-0.3677	-1.0342	-0.7208	-2.1273	-7.0639
13	-2.4764	-0.3743	-0.2269	-0.7026	-0.8849	-2.2394	-7.7493
14		-1.4277	-1.2803	-2.0872	-2.1392		-5.7602
15	-1.9107	-0.2697	-0.1223	-0.445	-0.9089	-1.6741	-6.2329
16	-2.3758	-0.297	-0.1496	-0.5838	-0.9375	-2.1391	-6.5602
17	-2.6851	-0.7539	-0.6064	-1.4538	-1.5082	-2.4479	-7.5497

2009). The saturation indices of fluorite were computed for all three sets of temporal data, sampled as well as earlier hydrochemical data. Figure 5 shows the plot of these saturation indices versus calcium concentrations. Results show that the groundwater is undersaturated with calcite, having a saturation index of -0.0024 to -0.6174 with an equilibrium state. The groundwater is undersaturated with fluorite, having a saturation index of -0.0453 to -2.1392 (Table 4).

### Multivariate analysis

The factor analysis was carried out using the hydrochemical data of the area of study. These data were considered for multivariate analysis without combining sampled data to make the homogeneous data set with

reference to dynamic changes in hydraulic stresses, land-use characteristics and pollutant sources. The chemical constituents considered for factor analysis for the unconfined aquifer were calcium, magnesium, sodium, potassium, bicarbonate, sulphate, chloride, fluoride, nitrate, pH and TDS. The principal component analysis was carried out using Statistical Package for Social Services (SPSS) software. The two-factor model results revealed that the first two eigenvalues extracted from the matrix account for more than 72% of total variance, which shows that the hydrochemical data is well posed. A varimax rotated component matrix with Kaiser (1958) normalization was used for principal component analysis. The interpretation of factors was made in terms of the square of the coefficients of that factor. The rotated component matrix for the geochemical data is given in Table 5. There is almost identical loading for sodium,

**Table 5.** Rotated component matrix.

Parameter	Factor 1	Factor 2
NO <sub>3</sub>	0.910	0.121
Mg	0.870	-0.228
Cl	0.858	0.411
Ca	0.833	-0.510
TDS	0.746	0.630
K	0.600	0.455
F	0.420	0.329
Na	0.324	0.973
HCO <sub>3</sub>	0.365	0.919
pH	-0.277	0.823
SO <sub>4</sub>	0.185	0.352

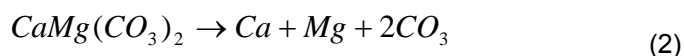
magnesium, nitrate and bicarbonate. Therefore, the variance in the chemical composition of the hydrochemical system is controlled by sources of sodium and bicarbonate. For Factor 1, the sum of the squares of calcium and magnesium (1.45) is approximately that of nitrate and chloride bicarbonate, sulphate and chloride (1.56). Thus, the combined relationship suggests that there is more than one component or more than one solid phase that adds or removes calcium, magnesium, nitrate and chloride into the groundwater. For Factor 1, there is no replacement mechanism as there is a lack of mutually exclusive components. Nitrate is naturally present in groundwater at very low concentrations, and its source is human activity such as domestic or industrial waste or agricultural. Factor 1 shows calcium chloride and magnesium chloride waters. Factor 2 shows that the sum of the squares of sodium and potassium (1.15) is approximately that of bicarbonate, sulphate and chloride (1.37). The combined relationship suggests that there is more than one component or more than one solid phase that adds or removes sodium, potassium, bicarbonate, sulphate and chloride. The presence of negative correlations indicates that some components are controlled by equilibrium with the minerals in the aquifers. Thus, there is a reaction path by which one set of chemical products replaces another set. Moreover, it is observed that there is positive correlation between calcium and fluoride for both the factors.

For Factor 1, there is probably dissolution of fluorite, calcite and dolomite, whereas for Factor 2, the decrease in fluoride may be due to adsorption on clay surfaces. Thus, these results obtained from factor analysis help in understanding the possible grouping of chemical constituents in the groundwater.

### Geochemical reactions

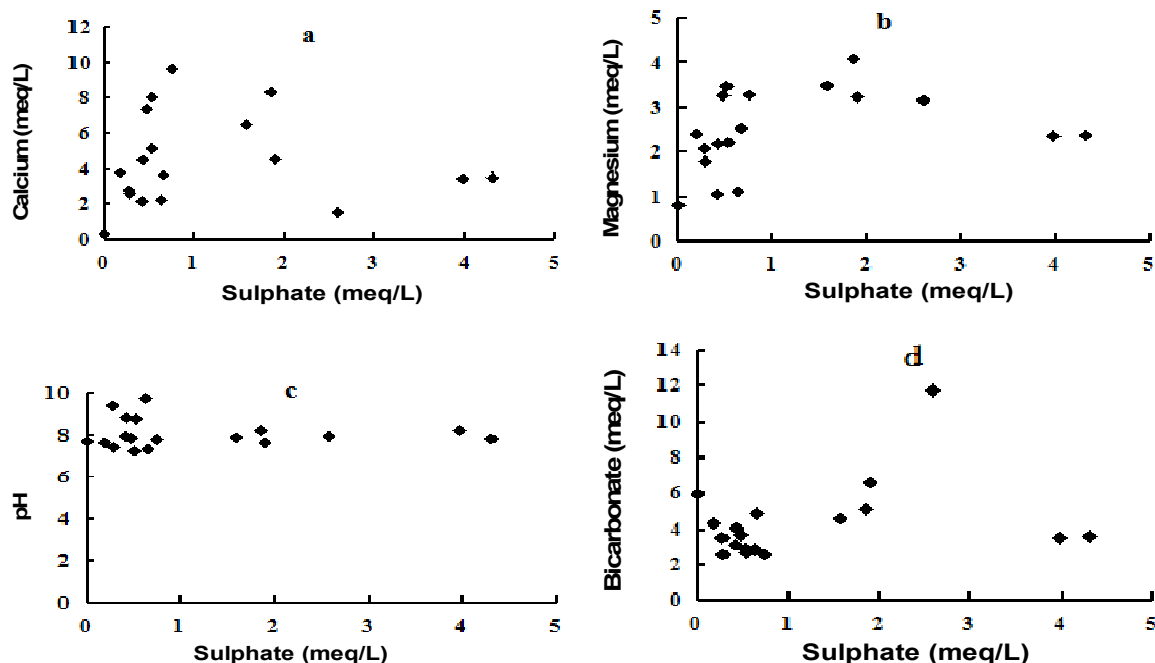
The actual changes in concentrations of chemical species as a function of sulphate concentration help in

obtaining the information on possible geochemical reactions that may be occurring in the area of study. To investigate this, analysis was carried out using hydrochemical data. The increase in calcium and magnesium and pH as sulphate increases are shown in Figure 6a-c. The groundwater in the area of study is undersaturated with calcite and dolomite (Table 4), and dissolution of calcite and dolomite adds calcium and magnesium to the groundwater. Calcite dissolution causes a pH increase due to consumption of H<sup>+</sup> by carbonate during the dissolution process. The decrease in the CO<sub>2</sub> in the solution leads to the dissolution of calcite and dolomite and CO<sub>2</sub> dissolution, thereby increasing the magnesium and calcium concentration in the solution. The geochemical equations for possible reactions in the aquifer are as follows:



Where (g) in Equation 4 refers to the gaseous phase and (aq) to the aqueous phase.

Although the trends in calcium, magnesium and pH with sulphate are evident in the groundwater in the area of study, there is variation in the temperature and other reactions in addition to dedolomitization or dissolution of carbonates. Dedolomitization is a specific geochemical process and has been reported by Plummer et al. (1990)



**Figure 6.** Plot of calcium, magnesium, pH and bicarbonate alkalinity as a function of sulphate.

and Kloss and Goebelbecker (1992). The plot of bicarbonate alkalinity as a function of dissolved sulphate concentration (Figure 6d) shows that bicarbonate alkalinity is decreasing as sulphate increases, and is possibly indicative of dedolomitization or carbonate dissolution. Cation exchange with calcium and magnesium cations could contribute to additional bicarbonate on the flow path with uptake of calcium and magnesium and release of sodium from exchange sites on clay minerals causing dissolution of carbonate minerals. The molar concentrations of sodium plus potassium are slightly more than the concentration of chloride. This is indicative of presence of evaporites. These waters have high bicarbonate concentration. Thus, there is a tendency to form sodium-bicarbonate waters. For the groundwater in the area of study of Qinkenpao area, the sodium bicarbonate water is derived from the dissolution of carbonate minerals.

## Conclusion

Fluoride (0.58 to 3.4 mg/L) and nitrate (0 to 624.1 mg/L) concentrations in groundwater are observed in large parts of the Qinkenpao area, Daqing, China, and are a matter of concern for drinking water supply since it exceeds the maximum permissible fluoride concentration of 1.5 mg/L and nitrate concentration of 50 mg/L for public water supply systems. Factor analysis showed that sodium bicarbonate waters have high fluoride, whereas calcium chloride and magnesium chloride waters have

low factor loading for fluoride. Results obtained from aqueous speciation modeling reveal that the groundwater is undersaturated with calcite, indicating dissolution of calcite and dolomite, and undersaturated with fluorite, possibly indicative of its dissolution. The geochemical reactions in the area of study indicate dissolution of calcite and dolomite, carbon dioxide and sulphate-bearing minerals with ion exchange.

## Conflict of Interest

The author(s) have not declared any conflict of interest.

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