

Distribution and assessment of hydrogeochemical processes of F-rich groundwater using PCA model: a case study in the Yuncheng Basin, China

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Abstract Hydrogeochemistry and factor analysis were conducted together to assess the distribution and the major geochemical processes in fluoride-contaminated shallow groundwater in the Yuncheng Basin. Spatially, fluoride concentration was low (< 1.5 mg/L) in the southern piedmont plain, medium (< 4 mg/L) in the central basin, and high (up to 14.1 mg/L) in Kaolao lowland areas in shallow aquifers. A three-factor principal component analysis model explained over 75.1% of the total variance. Sediment weathering leaching and evapotranspiration were recognized as the first primary hydrochemical processes response for the groundwater chemistry and explained the largest portion (42.1%) of the total variance. Factor two reflects the negative influence of human activities, with a positive loading of NO_3^- and HCO_3^- , and negative loading of well depth. Fluoride-bearing mineral dissolution and

alkaline condition was ranked as the third factors responding for groundwater chemistry and explained 11.2% of the total variance.

Keywords Fluoride · Groundwater chemistry · PCA model · Hydrogeochemical processes · Yuncheng Basin

1 Introduction

Groundwater plays a significant role in the water supply and economic development in China, especially in the arid and semi-arid areas in northern China. About one-third of the total population in China relies on groundwater for drinking water supply. However, potentially toxic elements, e.g. fluorine and arsenic, may reach hazardous concentrations in groundwater as a result of specific hydrogeological and geochemical processes. F-rich groundwaters are found in many areas around the world, including India (Choubisa 2013; Jacks et al. 2005; Rao 2001; Reddy et al. 2010; Srikanth et al. 2013; Vikas et al. 2013), Brazil (Souza et al. 2013), Mexico (Aguilar-Diaz et al. 2011; Daessle et al. 2008; Irigoyen et al. 1995; Reyes-Gómez et al. 2015), and China (Amini et al. 2008; Ando et al. 2001; Cao et al. 1997; Gao et al. 2007; Smedley et al. 2003), yet notably in Asia and Africa (Appelo and Postma 2005; Hu et al. 2013; Mondal et al. 2014; Sajil-Kumar et al. 2015).

The Yuncheng Basin in North China is one of the representative fluoride-polluted areas. The basin is surrounded by mountains to the south, east, and north, forming a NE–SW semi-closed rifted basin. Zhongtiao Mountain lies down the south and east boundary, with elevation at the main peaks of 1200–1900 m. To the northeast, north, and northwest boundary of the Yuncheng Basin are Zijin

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Mountain, Jiwang Mountain, and Gufeng Mountain, respectively. To the west is the Yellow River (Fig. 1). As a semi-closed inter-mountainous basin, Yuncheng Basin is subject to numerous environmental issues such as shortage of water resources and deterioration of groundwater quality, especially the widely distributed F-rich groundwater.

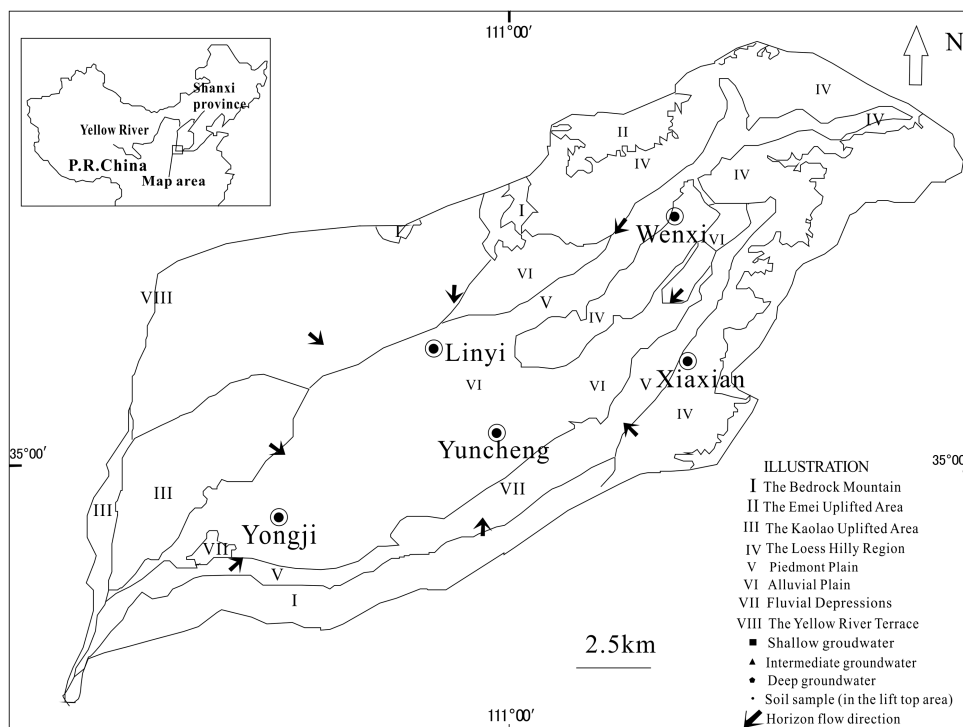
Endemic fluorosis was first confirmed at Yuncheng Basin in the 1980s. In 2005, Gao et al. focused on the occurrence of fluoride in rocks as the original source of fluoride in the groundwater. Then, Gao et al. (2007) studied the effect of salt lake water intrusion on shallow groundwater, which result in fluoride elevations. A study by Zhang (2010) revealed the leacheability of fluoride in soils from the Yuncheng Basin. Currell et al. (2010, 2011) demonstrated natural mineral sources of fluoride in groundwater in the central basin with some limited field-work. As a further work, the hydrochemistry of F-rich groundwater was reported by Khair et al. (2014), Li et al. (2015, 2016, 2018), Luo et al. (2018) and Li and Gao (2018).

Based on the previous researches, several hydrogeochemical processes, including water–rock interaction, evaporation, saline water intrusion, and polluted water leakage were considered to be the major sources for fluoride in groundwater in the basin. Additionally, alkaline pH values are favorable for fluoride desorption from the sediments (Jacks et al. 2005; Smedley et al. 2005; Bhattacharya et al. 2006). The mechanisms may include: 1) high pH could affect the ion charge of F^- and properties of

solid surface, and further to promote the adsorption of anions; 2) considerable OH^- in groundwater could precipitate Ca^{2+} , Fe^{3+} , and Al^{3+} , preventing F^- from complexing with cations, which results in copious release of F^- in groundwater; and 3) under alkaline condition, OH^- could be exchanged by F^- adsorbed in clay minerals, humus, and soil colloid. However, further understanding the extent of the hydrogeochemical processes involved requires an understanding of the contributions of these major geochemical factors, which are not well stated in the studies mentioned above. Multivariate statistical method (Principal Component Analysis) is a useful tool in providing additional information on groundwater chemistry interpretation. Principal Component Analysis reduces a large data matrix to a new matrix with fewer dimensions where the new references axes are the main variation directions. The geological interpretation of components yields insight into the main hydrogeochemical processes which may govern the distribution of hydrochemical variables (Belkhir et al. 2010; Cloutier et al. 2008; Dassi 2011; Galazoulas and Petalas 2014; Gao et al. 2011; Masoud 2014; Singh et al. 2013; Suk and Lee 1999; Wang et al. 2001).

The aims of this study were: (1) to investigate the hydrochemistry of groundwater in the Yuncheng Basin; (2) to evaluate the distribution of F^- in groundwater in the Yuncheng Basin; and (3) to identify and assess the potential contribution of major hydrochemical processes on hydrochemistry of fluoride contaminated groundwater.

Fig. 1 A simple geomorphology map of the Yuncheng basin, China (→ groundwater flow direction; Line AB, position of cross-section in Fig. 2)



2 Geology and hydrogeology

Basin geology and hydrogeology is discussed by Currell et al. (2010) and Li et al. (2015), hence only a brief summary is given here. The Yuncheng Basin comprises a 300–500 m thick Quaternary sediments (Q1–Q4), which are composed of aeolian loess, lacustrine clays, fluvial sands, and gravels. Basement rock outcrops in the south of the area are Archean metamorphic rock. This rock formation (Arsm) is composed of granite, biotite plagioclase gneiss, quartzite, and migmatite; the major minerals in the rocks include feldspar, biotite, quartz, chlorite, and so on. Elsewhere, sedimentary rocks, mainly Neogene mudstone and Cambro-Ordovician limestone, underlie the Quaternary sediments.

Due to the thick loose sediments accumulated in the Yuncheng Basin, groundwater is stored in the Quaternary alluvium that forms several aquifers (Fig. 2). On account of the differences in runoff conditions, shallow groundwater flows from the mountain fronts towards the center of the basin. The hydraulic gradient is 6–12‰ in the mountain front, 7‰ in the Emei tableland, and 3‰ in the flatlands (Chen et al. 1993). Phreatic and artesian aquifers are the main water resources for exploitation in the study area. Based on the distribution characteristics of aquifers and the hydraulic features, pore waters in the Yuncheng Basin

could be classified into three types: (1) phreatic aquifers (5–70 m) which are supplied by precipitation, canal seepage, infiltrating of irrigation return flow, reservoir seepage, and lateral recharge, whose discharge is dominated by artificial exploitation and by evaporation; (2) intermediate semi-confined artesian aquifers (70–120 m), which are recharged mainly by lateral runoff from mountain fronts, and discharged dominantly by artificial exploitation; (3) semi-confined phreatic-artesian aquifers (130–500 m), which are remotely recharged and their hydrogeological conditions are controlled by leakage through aquitards.

3 Sampling and methods

A total of 79 samples, including one rainwater, six surface water, 22 groundwater from shallow aquifers, 9 groundwater from intermediate aquifers and 41 groundwater from deep aquifers were collected across the Yuncheng Basin in August 2013. When sampling, water samples were collected only after the in situ physicochemical parameters, including temperature, pH, and electrical conductivity (EC) were stable and all these parameters were measured within several minutes by portable meters.

Each sample was collected in three polyethylene bottles, one for anion analysis, one for cation analysis and the rest

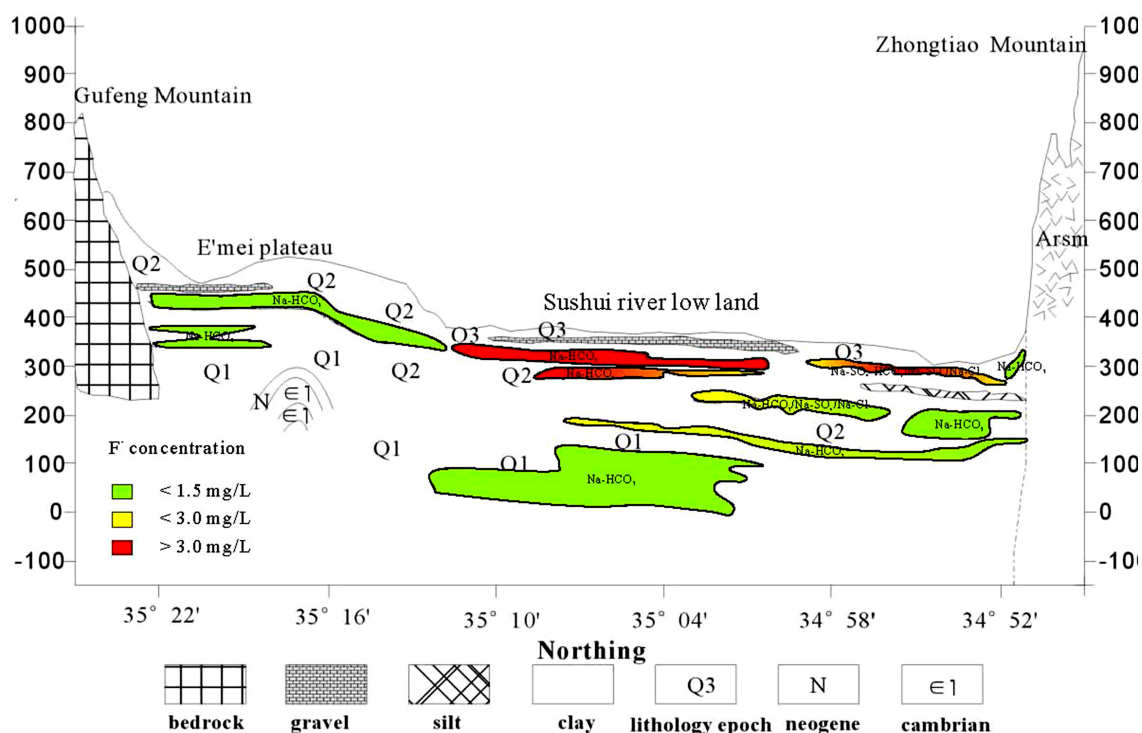


Fig. 2 A schematic diagram for the distribution of major aquifers, hydrochemistry facies and F^- concentration in groundwater; Q1, Lower Pleistocene; Q2, Middle Pleistocene; Q3, Upper Pleistocene

kept in a refrigerator for future experimental use. The total alkalinity was measured on the sampling day using the Gran titration method with the triple repetition analyze error $< \pm 2\%$. The concentrations of HCO_3^- and CO_3^{2-} were computed by the software PHREEQC 2.8. Hydrochemical analyses were performed at the Key Laboratory of Biological and Environmental Geology, China University of Geosciences (Wuhan, China). The concentrations of Cl^- , SO_4^{2-} , and NO_3^- were determined using ion chromatography (IC, Dionex 120, Dionex, Sunnyvale, CA, USA). For cation analysis, reagent-quality HNO_3 was added to one of these polyethylene bottles until the pH of samples was less than 2. Major cations, K^+ , Na^+ , Ca^{2+} , and Mg^{2+} , were measured using inductively coupled plasma-atomic emission spectrometry (ICP-AES, IRIS Intrepid XSP, Thermo Elemental, Madison, WI, USA). The analytical precision for the measurements of cations and anions is indicated by the ionic balance error, which is observed to be within the standard limit of $\pm 5\%$.

Box plot and principal component analyses of the water hydrochemical data were performed using the SPSS software version 9.0 (SPSS Inc. 2008). Factor extraction was carried out by principal component analysis. Varimax rotation was applied to obtain unrelated components (Kaiser 1958) and a three-factor model is determined. In this present study, the dataset was made up, including 79 samples and 11 chemical parameters (pH, well depth, F^- , NO_3^- , Cl^- , HCO_3^- , SO_4^{2-} , Ca^{2+} , K^+ , Mg^{2+} , and Na^+).

4 Results and discussions

4.1 Groundwater chemistry

The major properties and hydrochemistry of all water samples are summarized in Table 1. The chemistry of the groundwater in the area shows a wide variation in concentration ranges (Fig. 3). SO_4^{2-} is found to be an extremely variable component, ranging between 17.5 and 8295 mg/L, followed by Cl^- (6.73 – 3044 mg/L) and HCO_3^- (66.45 – 1094 mg/L). Concentrations of Na^+ , the major dominant cation, span over a wide range of 8.28–4967 mg/L. Other cations, including Ca^{2+} , Mg^{2+} , and K^+ , are relatively stable. Ca^{2+} and Mg^{2+} are two secondary dominant cations in groundwater, with average concentrations of 51.53 and 75.17 mg/L, respectively. K^+ , having had little impact on groundwater quality, is detected at a low concentration with an average value of 3.96 mg/L.

Based on the burial depth and regional hydrogeological conditions, groundwater samples were divided into three categories: shallow groundwater, intermediate groundwater, and deep groundwater. Shallow groundwater from the Kaolao lowland and the southern piedmont plain belong to Na- HCO_3 type with low F contents (Fig. 2). While shallow groundwater from the central basin area gives the highest TDS values, up to 17,452 mg/L. These groundwaters belong to Na- SO_4 - HCO_3/Cl or Na- Cl - SO_4 type (Fig. 4), with Na^+ as the dominant cation and SO_4^{2-} and/or Cl^- as

Table 1 Summary of major physical–chemical parameters of groundwater in Yucheng Basin (in mg/L, except for well depth, temperature and pH)

Water type	Well depth (m)	Temperature (°C)	pH	HCO_3^-	F	Cl	SO_4	NO_3	Ca	Mg	K	Na	TDS
<i>Shallow groundwater</i>													
Max	70	23.4	9.2	1094	14.1	3044	8295	67.9	280.5	489.6	14.1	4967	17,452
Min	9	16.5	7.1	148.3	0.53	10.86	18.51	3.10	4.00	4.80	0.30	8.28	362.4
Mean	37	18.2	7.9	581.2	4.80	393.4	918.4	17.4	51.9	98.4	2.37	673.1	2445
Medium	32	17.9	7.9	571.5	3.80	117.7	295.4	13.9	33.6	54.3	1.61	283.5	1.026
SD	20.1	1.57	0.5	256.9	4.13	700.9	1815	14.1	62.2	124.9	2.99	1073	3.765
<i>Intermediate groundwater</i>													
Max	120	21.3	8.4	717.6	3.15	156.6	230.5	16.3	73.1	45.9	4.12	363.6	1128
Min	85	16.50	7.6	66.5	0.40	11.39	42.5	1.17	8.21	16.2	0.97	16.7	231.1
Mean	106	18.9	8.1	393.4	1.53	62.99	131.1	6.73	31.8	29.1	2.53	161.4	622.3
Medium	110	19.0	8.1	271.3	1.51	38.49	134.2	4.83	17.4	30.1	2.25	142.3	653.2
SD	13.5	2.02	0.3	232.3	0.82	48.98	55.0	5.01	25.6	12.3	1.03	122.6	304.5
<i>Deep groundwater</i>													
Max	500	20.7	8.6	830.9	2.90	1402	2106	23.9	268.5	470.4	10.1	1074	5253
Min	130	17.2	7.3	175.6	0.10	6.73	17.5	1.31	12.0	10.9	0.96	16.3	228.8
Mean	234	20.2	8.0	385.4	1.22	192.9	359.2	7.17	51.4	65.3	3.49	260.3	1132
Medium	220	19.9	8.0	372.1	1.22	74.0	144.4	5.82	31.9	39.9	2.70	205.3	731.4
SD	72.1	1.97	0.3	143.4	0.75	307.7	477.6	4.59	52.4	81.0	2.43	230.6	1110

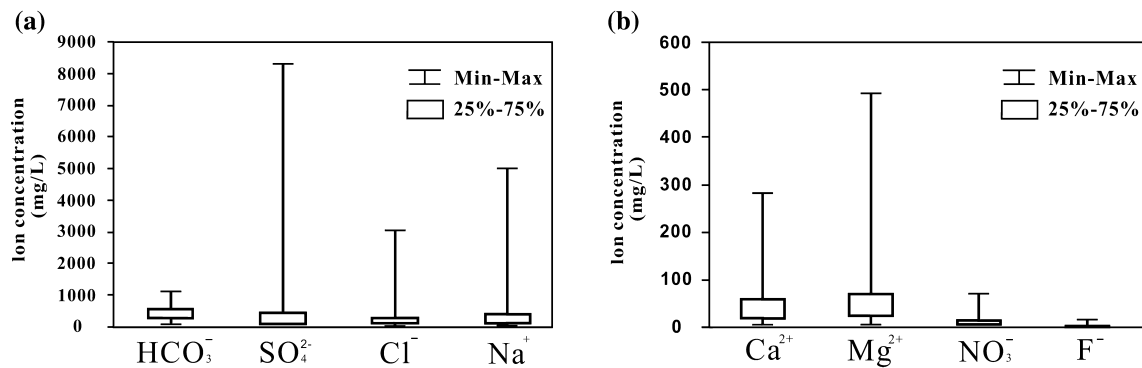
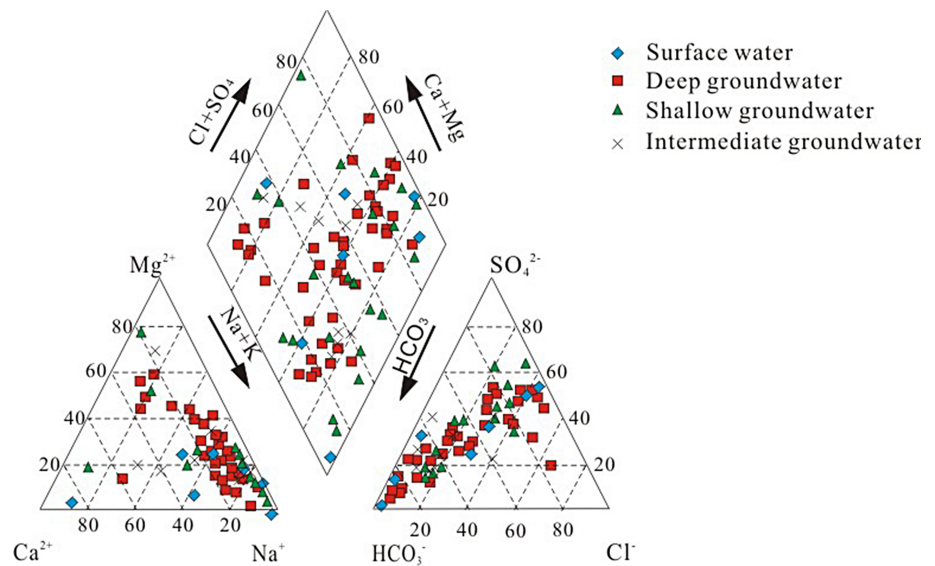


Fig. 3 Box plots of major ions in the water samples of Yuncheng basin

Fig. 4 Piper diagram of water samples from the Yuncheng basin (filled diamond surface water, filled square deep groundwater; filled triangle shallow groundwater; cross mark intermediate groundwater)



the dominant anions. The concentrations of Na^+ , Cl^- and SO_4^{2-} are up to 4967, 3044 and 8295 mg/L, respectively, in these higher TDS groundwaters. Evaporation tends to concentrate all the species in the shallow groundwater (Li et al. 2015), therefore, strong evaporation is believed to be one of the major factors inducing the enrichment of sulfate and chloride concentration in shallow groundwater at Yuncheng Basin. Gypsum dissolution and anthropogenic activities, like agricultural fertilizers, may also contribute to the groundwater chemistry. Soluble gypsum is widely distributed in the middle Pleistocene and, hence, can be regarded as one of the primary sources of sulfate in shallow groundwater in the Yuncheng Basin (Gao et al. 2007; Shanxi Province Geological Survey 1982). More than 70% of the shallow groundwater contains NO_3^- in excess of the WHO standard for drinking water (10 mg/L). On account of the lack of natural nitrate in most geologic formations, NO_3^- concentrations > 5 mg/L are generally indicative of water contamination by animal wastes, fertilizers, and/or effluents (Heaton 1986). The highest NO_3^- content

(67.9 mg/L) is observed in shallow groundwater, implying an anthropogenic source in this area.

Intermediate and deep groundwaters are all alkaline, with a pH range of 7.3–8.6. Most of them are freshwaters with TDS lower than 1000 mg/L and belong to Na- HCO_3 type water. About 30% of intermediate and deep groundwater collected from the Kaolao lowland and central basin areas belong to Na- SO_4 - HCO_3 /Cl or Na-Cl- SO_4 type with TDS > 1000 mg/L. The sources of salt in these waters may either come from evaporite (e.g. gypsum, halite, and mirabilite) dissolution (Li et al. 2015) or leakage of saline shallow groundwater. High NO_3^- concentrations are also observed in intermediate and deep groundwaters. Due to the low background nitrate concentrations in intermediate and deep groundwater samples, the elevated NO_3^- concentrations in these groundwaters indicate the downwards vertical leakage of irrigated water and/or polluted shallow groundwater.

4.2 Fluoride pollution in groundwater

Rainwater, surface water and groundwater are collected for fluoride were analyzed in this case study. Rainwater contains a low fluoride concentration of 0.32 mg/L. Generally, fluoride content in precipitation is lower than the detection limit, but seawater spray and atmospheric pollutants are the major sources of fluoride in precipitation. As an inland catchment, the fluoride in rainwater at the Yuncheng Basin mainly derives from atmospheric pollution from local industries and coal consumption (Luo et al. 2018).

Concentrations of fluoride in surface waters vary between 0.32 and 11.2 mg/L with an average value of 4.1 mg/L. Fluoride concentration is low in the surface water samples collected from mountain areas and the piedmont plain areas and higher in lakes and reservoir where human activities are frequent and intensive. This suggests that human activities are partly responsible for the enrichment of fluoride in these waters.

Groundwater has severely suffered from fluoride pollution in Yuncheng Basin (Cao 2005; Gao et al. 2007; Li et al. 2015). Over 68% of the shallow wells contain fluoride concentrations above the WHO provisional drinking water guide value of 1.5 mg/L (WHO 2004). The concentration of fluoride in groundwater is not uniform in the study area. In the case of shallow aquifer, fluoride concentrations range between 0.32 and 14.1 mg/L with an arithmetical mean value of 4.27 mg/L. The fluoride concentration is low in the shallow groundwater from the south piedmont plain areas (Fig. 2), whereas the highest fluoride concentration (14.1 mg/L) is found in shallow groundwater from the Kaolao lowland area in the Shushui river basin. Increase of fluoride content is supposed to be controlled by hydrological and geochemical processes in this area (e.g., irrigation leaching, dissolution of fluorine minerals, cation exchange, and evaporation). Shallow groundwater that has medium to high fluoride contents with elevated Ca and

TDS contents are observed from the north part of the salt lake.

Intermediate and deep groundwater samples are characterized by low to medium F^- concentration values, ranging from 0.19 to 3.2 mg/L and 0.1 to 2.9 mg/L, respectively. Forty percent of the intermediate wells and thirty percent of the deep wells fall above the 1.5 mg/L threshold. The wide distribution of F-rich groundwater in intermediate and deep groundwater suggests that the fluoride pollution is a non-point source pollution.

The spatial variation of the fluoride concentration is presented in a spatial distribution map (Fig. 2). It can be seen that high fluoride groundwater is concentrated mostly in the central areas rather than in the margins (Figs. 1, 2).

4.3 Assessment of major geochemical processes using PCA

In general, PCA (principle component analysis) extracts correlations and reduces the amount of data into components that explain a portion of the total variances between chemical parameters. These variances are mainly related to the chemical parameters showing the highest loading factors obtained by using the varimax rotation. Those high loaded components are further regarded as references for identifying the geochemical processes involved. In this case study, three factors are defined and 75.11% of the total cumulative variances are obtained (Tables 2, 3; Fig. S1).

Factor one, associated with high positive loadings for Cl^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , and Na^+ , explains the largest portion of the total variance (42.1%). This factor can be explained by chemical weathering and evapotranspiration processes. In general, groundwater in the Yuncheng basin is recharged by precipitation and discharged by abstraction and evapotranspiration. During the movement of groundwater from the margins to the central areas, the chemical constituents in groundwater are naturally sourced from the dissolution of sediment/rock minerals. The major minerals

Table 2 Eigenvalues, percent of variance, cumulative eigenvalue, cumulative percent of variance for the factor analysis of physical–chemical parameters

Factors	Eigenvalue	Percent of variance	Cumulative Eigenvalue	Cumulative percent of variance
1	4.825	43.864	4.825	43.864
2	2.200	19.997	7.025	63.861
3	1.237	11.247	8.262	75.108
4	0.949	8.629	9.211	83.737
5	0.681	6.191	9.892	89.929
6	0.500	4.543	10.392	94.471
7	0.301	2.734	10.693	97.205
8	0.166	1.507	10.859	98.712
9	0.111	1.009	10.970	99.721
10	0.031	0.279	11.000	100
11	4.63e ⁻⁸	4.21e ⁻⁷	11.000	100

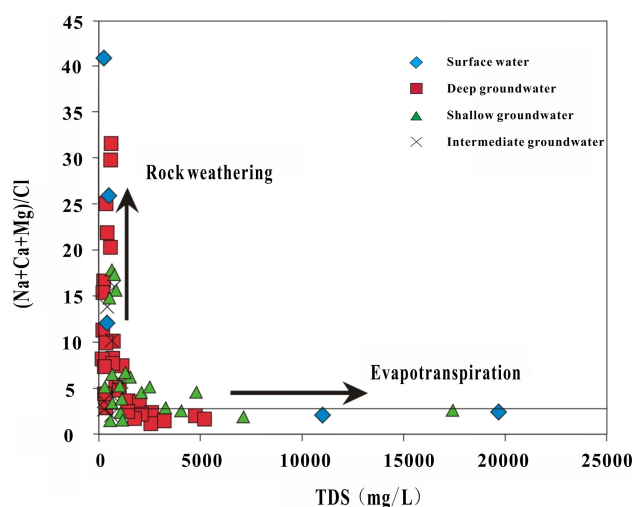
Table 3 Loading for varimax rotated factor matrix of three-factor model explaining 75.1% of the total variance

Parameters	Factor 1	Factor 2	Factor 3
Well depth	− 0.107	− 0.702	− 0.032
pH	− 0.356	− 0.142	0.785
F [−]	0.319	0.337	0.804
Cl [−]	0.984	0.025	0.079
SO ₄ ^{2−}	0.937	0.173	0.096
HCO ₃ [−]	0.074	0.668	0.412
NO ₃ [−]	0.311	0.685	0.108
K ⁺	0.235	− 0.550	0.188
Na ⁺	0.904	0.214	0.242
Ca ²⁺	0.883	− 0.195	− 0.243
Mg ²⁺	0.886	0.164	− 0.194

Bold text means correlation is significant at the 0.05 level (two-tailed)

Table 4 Summary of major minerals in sediments from Yuncheng Basin, China (according to Li et al. 2015)

Minerals (weigh percent)	Max	Min	Average	SD
Quartz	68.25	19.71	40.02	9.40
Chlorite	14.14	0.26	4.12	2.95
Mica	31.52	0.86	11.71	6.69
Calcite	44.38	0.24	8.79	5.83
Albite	41.09	1.58	23.10	8.26
K-feldspar	43.26	0.17	8.96	7.61
Amphibole	5.50	0.45	2.15	0.95
Dolomite	9.60	0.09	1.50	2.10

**Fig. 5** Scatter map of (Na + Ca + Mg)/Cl ratios versus TDS values in water samples from Yuncheng Basin, China

in sediments are quartz, albite, k-feldspar, mica, calcite, chlorite, and some amphibole and dolomite in the Yuncheng Basin (Table 4, Li et al. 2015). Minor contents of

gypsum, mirabilite, and halite are also reported for sediments from the basin (Gao et al. 2007; Shanxi Province Geological Survey 1982). As a consequence, the weathering leaching of these minerals yields high contents of HCO₃[−], SO₄^{2−}, Na⁺, Cl[−], Ca²⁺, and Mg²⁺ in Quaternary groundwater.

However, the involvement of additional hydrochemical processes in this stage is suggested by the low loading of HCO₃[−] in factor one. Evapotranspiration is regarded as another crucial factor affecting groundwater chemistry. If groundwater undergoes the evapotranspiration process, there would be a consistency of (Na + Ca + Mg)/Cl ratios of samples with increasing TDS value. As shown in Fig. 5, the distribution of the water samples shows two trends: (1) parallel to the X-axis reflecting the influence of evapotranspiration and (2) close to the Y-axis indicating a sustained increase of Na/Ca/Mg-bearing mineral dissolution. Block groundwater samples, collected from intermediate and deep aquifers, located close to the Y-axis showed a low TDS value and increased (Na + Ca + Mg)/Cl ratio. Some surface water and shallow groundwater samples, collected from the piedmont plain areas, also dropped into this group. The increasing (Na + Ca + Mg)/Cl ratio and low TDS in this group suggest that water chemistry components here were obtained by natural mineral weathering leaching process, which was controlled by the kinetic dissolution rate of minerals.

Two surface water samples and several shallow groundwater samples, collected from the central basin, displayed a significant increase of TDS value with little change in (Na + Ca + Mg)/Cl ratio. Several deep groundwater samples were classified into this group too. Evapotranspiration generally increases the concentration of major ions and TDS in groundwater without making a significant change of the ion ratios. The constant (Na + Ca + Mg)/Cl ratio and the elevated TDS value in these waters suggest a significant influence of evapotranspiration on groundwater chemistry. Considering the fact that deep groundwater is not affected by evapotranspiration, deep samples that appeared in this group may be due to the leakage of shallow groundwater or surface water subjected to evapotranspiration.

Factor two, which explains 19.997% of the total variance, is dominated by well depth (− 0.702), NO₃[−] (0.685), and HCO₃[−] (0.668). The negative loading of well depth and positive loading of HCO₃[−] and NO₃[−] suggest a reverse correlation between burying depth and groundwater chemistry components. Basically, deep burying depth stands for a weak surface leakage and/or interference of human activities. Hence, high concentrations found in wells with lower depth indicates heavier human activity influence.

Due to the lack of natural source in the geologic formations in the area, high loading value of NO_3^- indicates a significant human activity input, e.g. animal wastes, agricultural fertilizers and/or effluents. The highest NO_3^- content (67.9 mg/L, Table 1) observed in shallow groundwater implies an anthropogenic source in this area. Given the low background nitrate concentrations in deep groundwater, the high NO_3^- concentrations in some deep samples with depth over 200 m may be due to mixing with irrigation return water and/or shallow polluted groundwater.

The common source of HCO_3^- is derived from carbonate weathering dissolution due to the lack of organic sources in the sediment aquifers (Currell et al. 2011). But the negative loading of Ca^{2+} and low loading of Mg^{2+} suggest that carbonate minerals dissolution may be masked by a high degree of cation exchange. Briefly, the association of well depth, NO_3^- , and HCO_3^- reflects the influence of anthropogenic processes on pollution of groundwater and can thus be termed as the ‘anthropogenic factor’.

Fluoride bearing mineral dissolution and alkaline condition was ranked as the third factors responding for groundwater chemistry. Factor three, containing only two high loading factors F^- (0.804) and pH (0.785), reflects the influence of fluorine as a pollutant in the area, and could be defined as the ‘F pollution factor’. Natural water–rock interactions and hydrogeological processes are the key factors controlling groundwater fluoride mobilization. In general, F^- is preferentially adsorbed to sediment mineral surfaces under neutral conditions (Smedley et al. 2005; Bhattacharya et al. 2006). pH is one of the major factors that govern the liberation and mobility of fluoride into groundwater. Thus, pH is considered to be the most important factor causing F mobilization (Osei et al. 2016; Tang and Zhang 2016; Zhang et al. 2015). Nonetheless, as a mutable parameter in groundwater, pH is not an independent parameter and it is closely associated with the relevant hydrogeochemical processes mentioned above.

5 Conclusion

Groundwater in the Yuncheng Basin showed wide variations in major ions and fluoride concentration. $[\text{F}]$ is low in the shallow groundwater from the south piedmont plain areas, whereas the highest fluoride concentration (14.1 mg/L) is found in shallow aquifers from the Kaolao lowland area in the Shushui river basin. Intermediate and deep groundwater are characterized by low to medium F^- concentrations (0.19 ~ 3.2 mg/L).

Integrated hydrogeochemistry and principal component analysis provide important clues for understanding the major processes controlling the hydrochemistry of fluoride

contaminated groundwater at Yuncheng Basin. Natural water–rock interactions including dissolution of sediment/rock minerals (e.g., fluoride bearing minerals, evaporites) and evapotranspiration were recognized as the prime process impacting the high fluoride groundwater. Anthropogenic activities have affected the hydrochemistry of fluoride contaminated shallow groundwater, as indicated by high NO_3^- contents, the negative loading of well depth and positive loading of HCO_3^- and NO_3^- in Factor 2. Alkaline condition is considered to be the most important factor leading to F mobilization.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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