Hydrochemical Characteristics and Water Quality of Groundwater in the Thick Loess Deposits

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1 Hydrochemical characteristics and water quality of groundwater

2 in the thick loess deposits

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Abstract: Water quality and quantity should be paid more attentions for regions with arid climate and thick vadose zones since the limited groundwater cannot be replenished rapidly once polluted. This study focused on the Loess Plateau of China to investigate the geochemical mechanism affecting groundwater chemistry and to calculate contribution rates of multiple sources to groundwater solutes. We employed multiple methods (diagrams, bivariate analyses, hierarchical cluster analysis (HCA), sodium adsorption ratio (SAR), water quality index (WQI), correlation analysis, forward simulation) for the above purposes. We collected 64 groundwater samples in the thick loess deposits in June 2018 (flood season) and April 2019 (dry season). The average concentrations of cation were in the order of $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ in the flood season, and $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ in the dry season. The order of anions contents in the flood season and the dry season was $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$. The major hydrochemical facies were Ca-HCO_3 and Ca-Mg-HCO_3 in the flood season, and $\text{Na-Ca-HCO}_3\text{-SO}_4$ and Na-HCO_3 in the dry season, respectively. Most of the groundwater (95% in the flood season and 96% in the dry season) was suitable for drinking, and overall water quality (except samples F28 and D13) was acceptable for irrigation. Mineral dissolution and cation exchange were important natural processes affecting groundwater chemistry. A forward model showed that the contribution of atmospheric input, anthropogenic input, evaporite dissolution, silicate weathering and carbonate weathering to solutes in groundwater was $2.3 \pm 1.5\%$, $5.0 \pm 7.1\%$, $19.3 \pm 21.4\%$, $42.8 \pm 27.3\%$ and $30.6 \pm 27.1\%$ in the flood season, and $9.1 \pm 6.4\%$, $3.4 \pm 5.2\%$, $20.3 \pm 15.9\%$, $56.6 \pm 23.2\%$, and $10.7 \pm 15.4\%$ in the dry season, respectively. Although the overall contribution of anthropogenic inputs was minor, it was the dominant source of solutes for some groundwater samples. This study provides fundamental information for water management in arid areas.

Keywords: Arid climate; Thick vadose zones; Hydrochemistry; Hierarchical cluster analysis; Solute sources; Chinese Loess Plateau

1 Introduction

Groundwater in arid regions is crucial to support sustainable socio-economic development since they are the only available and stable water sources with large reserves (Li et al. 2016, 2019a; Aghababazadeh et al. 2016; Wang et al. 2017). However, groundwater is currently severely threatened by excessive extraction and pollution (Brindha et al. 2011; Alarcon-Herrera et al. 2013; Subba Rao 2020). The growing demand for water resources leads to the excessive groundwater extraction (López-Alvis et al. 2019; Subba Rao et al. 2020). Simultaneously, the deterioration of water quality indirectly reduces the available groundwater amount (Wu and Sun 2016; Brindha et al. 2016; Li et al. 2017a). Particularly, water pollution treatment is hardly to be conducted for groundwater, which extends the risk of contaminated groundwater (Liu et al. 2018). In consequence, the scarcity of groundwater in arid regions caused by the arid climate and water pollution has been paid increasing attentions.

Groundwater, especially those stored in deep aquifers, should be of high priority for protection. These groundwater resources generally have large reserves sustaining regional development, but they have slow renewal rate and are difficult to be replenished. However, the global-scale analysis showed that the water storage of several major aquifers in arid mid-latitudes have declined severely from 2002 to 2013 (Famiglietti 2014), and contemporary pollutants may be able to reach deep aquifers (Jasechko et al. 2017). As such, it is fundamental to investigate the changes in quantity and quality of groundwater resources in regions with deep vadose zones and aquifers.

Investigating the hydrogeochemical characteristic is the prerequisite for the analysis of water quality and potential pollution sources (Ahada et al. 2013). However, the hydrochemical characteristics of groundwater are affected by both the long-term geological evolution and immediate anthropogenic activities (Yong-Hong et al. 2007).

With such complicated sources and processes, the hydrochemical characteristics and water quality may vary spatially and temporally. For example, López-Alvis et al. (2019) discovered that the groundwater quality of Siwa Oasis in Egypt had been deteriorating in alarming rate over the past 11 years due to unsafe groundwater extraction from deep sandstone aquifers. Zanotti et al. (2019) reflected the significant spatial difference in groundwater quality between the higher and lower plains of Oglio River basin. Xiao et al. (2015) found that the concentrations of ions in groundwater of the Tarim River Basin varied significantly with a higher concentration in the dry season than in the wet season. The spatiotemporal variations in groundwater hydrochemical characteristics highlights the importance of dynamic sampling on a large spatial scale to provide detailed information for water resources management.

The Loess Plateau in China is the largest area covered by loess deposit up to 350 m deep (Zhu et al. 2018). The thick loess stores huge groundwater reservoirs, which dominates the watershed-scale hydrological processes (Li et al. 2019b). The groundwater recharge mechanism and the groundwater depletion has been widely reported (Huang et al. 2018). However, the hydrochemical characteristics and water quality have not been fully investigated. For example, Li et al. (2014) assessed the shallow groundwater in the Zhongwei section of the Loess Plateau, and concluded that the excessive Cl^- and SO_4^{2-} made groundwater in most areas unsuitable for direct human consumption. Although groundwater quality evaluation based on a single sampling (Yu et al. 2020) has been conducted for some limited regions, it cannot represent the hydrochemical characteristics on a large scale considering seasonality. As such, groundwater quality investigation considering the spatial and temporal variability in this region can provide valuable information for other regions with thick vadose zones and aquifers.

The objective of this research is to investigate the hydrochemical characteristics and

assess the groundwater quality in the Loess Plateau. In specific, we will ask the following questions: (1) What are the hydrochemical characteristics and quality of groundwater in the thick loess? (2) Why do the hydrochemical characteristics and water quality vary spatiotemporally? (3) What processes are driving the hydrochemical characteristics? To answer the above questions, we launched two groundwater sampling campaigns across the whole loess-covered regions considering the seasonality. After determining the ion contents, we analyzed the general characteristics, hydrochemical facies and water quality for drinking and irrigation purpose. Our results will be helpful for groundwater management in other loess-covered regions or other region with thick vadose zones and aquifers.

2 Materials and Methods

2.1 Study area

The Loess Plateau in north China (Fig. 1) is the largest loess-covered area in the world (Xiao 2016). It extends from the Riyue and Helan Mountains in the west to the Taihang Mountains in the east, from the Yinshan Mountains in the north to the Qinling Mountains in the south, covering an area of approximately $64 \times 10^5 \text{ km}^2$. The area spans a semiarid to subhumid climate from west to east, with a mean annual temperature of 14.3°C in the east and 4.3°C in the west. The mean annual precipitation varies from 150 mm in the west to 800 mm in the east, and most of the rainfall is concentrated from June to September (Li et al. 2010). Generally, the Quaternary loess is layered deposits consisted of Wucheng loess (Q_1), Lishi loess (Q_2) and Malan loess (Q_3) from bottom to top. The Wucheng loess has low permeability, the Lishi loess is considered to be a good aquifer due to the relatively large porosity, and the Malan loess is the top soil (Huang et al. 2017). However, due to the severe soil erosion, the thickness of loess and the topography vary greatly in space, which has a great impact on the water level and reserves of groundwater (Gates et al. 2011).

124 As the most common minerals in carbonates and Quaternary sediments, calcite,
125 dolomite, feldspar, gypsum, and halide provide abundant soluble components for
126 groundwater (Xiao 2016). Moreover, human activities may also have a certain impact
127 on quality of groundwater. As a traditional agricultural area and an important national
128 energy base, the incidents of groundwater pollution in the Loess Plateau by industrial
129 sewage and agricultural activities have been widely reported (Li 2018; Huang et al.
130 2018).

Fig. 1 (a) Geographical location of the Loess Plateau and groundwater sampling sites. (b) Land use of the Loess Plateau.

2.2 Sample collection and analysis

In this study, we focused on the unconfined groundwater that discharges into rivers instead of getting recharge from rivers. The above-mentioned groundwater is generally stored in high-altitudes areas where surface water is scarce and groundwater become

the only water source. The groundwater level in these areas is generally 10 m below the ground surface. These groundwater samples exclude the impacts of surface water, thus highlighting the impacts of anthropogenic activities.

We collected 64 groundwater samples in the thick loess deposits, among which 37 samples were collected during the flood season (August 2018) and 27 samples from the dry season (April 2019). In order to eliminate the negative effects of stagnant water, the wells were pumped for at least 10 minutes before sampling. All groundwater samples were stored in plastic bottles and kept in a portable fridge. The samples were delivered back to the laboratory by fast delivery at the end of each day to ensure that the hydrochemical components can be determined in the next day. The temperature, pH, total dissolved solids (TDS), electrical conductivity (EC) were measured by a portable meter (HANNA, HI98130) in situ. Major cations (K^+ , Na^+ , Ca^{2+} , and Mg^{2+}) were determined by a coupled plasma-atomic emission spectrometry. Cl^- , SO_4^{2-} , and NO_3^- were determined by ion chromatography (DIONEX ICS-1100, Thermal Fisher Scientific, USA). The HCO_3^- content was measured by titration with hydrochloric acid (Table 1).

Table 1 Chemical composition of groundwater samples and water quality assessment results for irrigation and drinking purposes in the study area.

Sample No.	Group	Well		pH	EC (μS/cm)	TDS (mg·L ⁻¹)	Ion concentration (mg·L ⁻¹)								Quality assessment		
		depth (m)	Landuse				Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	SAR	%Na	WQI
Flood Season																	
F28	F-Group 1	11	Cropland	6.84	2848	1410	168.57	69.76	226.42	3.83	476.41	177.99	63.58	461.09	1.97	24.79	122.11
F30	F-Group 1	18	Built-up land	6.66	1795	978	238.71	79.06	137.95	4.15	851.69	168.22	165.93	159.21	3.69	41.11	131.87
F11	F-Group 2	-	Cropland	7.32	1663	834	66.72	33.54	49.02	2.08	322.15	68.70	22.28	44.14	0.14	4.19	56.52
F12	F-Group 2	23	Cropland	7.48	1100	550	31.37	24.54	70.85	1.40	263.72	86.45	9.38	16.13	0.30	6.87	36.17
F15	F-Group 2	50	Grassland	7.02	736	371	149.39	10.65	6.53	3.17	410.51	88.22	1.95	4.35	0.33	9.68	18.13
F16	F-Group 2	12	Built-up land	7.54	867	433	116.28	19.88	56.35	2.08	484.22	43.18	42.02	16.27	0.37	8.11	31.56
F17	F-Group 2	15	Cropland	7.57	890	477	105.87	35.05	24.25	3.02	456.90	12.76	73.75	14.21	0.37	15.88	41.80
F19	F-Group 2	19	Grassland	7.50	1967	953	105.53	19.83	144.00	1.97	490.57	141.45	3.27	78.05	0.38	10.58	28.71

F2	F-Group 2	-	Cropland	7.30	771	385	159.26	26.05	15.30	3.21	212.85	166.68	26.84	123.77	0.38	9.29	33.84
F25	F-Group 2	80	Built-up land	7.54	608	303	73.59	29.08	18.70	1.63	395.30	6.82	10.99	5.62	0.45	14.33	43.66
F27	F-Group 2	180	Cropland	7.01	566	284	78.52	24.30	15.08	1.89	371.09	10.79	13.58	4.56	0.45	13.62	50.93
F29	F-Group 2	20	Grassland	6.83	1123	566	79.21	38.25	89.75	12.62	558.77	50.31	8.53	36.49	0.47	12.29	53.31
F3	F-Group 2	-	Built-up land	7.86	1250	647	22.88	15.89	136.16	2.42	347.09	102.32	12.35	34.90	0.52	12.11	22.63
F31	F-Group 2	210	Cropland	7.46	595	298	72.40	21.47	20.66	2.27	344.51	13.58	12.97	8.01	0.55	15.02	23.47
F32	F-Group 2	80	Built-up land	8.20	539	270	74.56	21.09	12.52	1.70	341.25	6.96	10.15	6.04	0.65	16.32	45.95
F33	F-Group 2	70	Built-up land	8.30	593	294	139.69	31.07	18.55	1.49	591.66	13.27	15.58	6.79	0.87	16.91	23.56
F34	F-Group 2	120	Built-up land	8.33	613	306	131.23	24.89	18.34	3.38	560.59	5.85	5.28	4.35	1.22	26.27	21.00
F35	F-Group 2	60	Built-up land	8.41	657	328	47.95	18.09	75.16	5.46	418.30	2.73	16.61	4.62	1.27	25.10	32.30
F36	F-Group 2	6	Cropland	8.12	525	262	76.77	5.08	12.45	10.25	284.72	13.53	1.53	3.24	2.06	37.16	28.91
F37	F-Group 2	-	Built-up land	8.49	702	351	78.17	16.54	17.01	3.67	342.53	5.17	11.18	7.71	2.29	46.30	27.15
F38	F-Group 2	-	Built-up land	8.63	781	391	40.36	27.01	82.68	3.45	423.00	19.46	20.92	9.76	2.34	46.60	25.04
F39	F-Group 2	40	Built-up land	8.58	751	375	48.34	49.86	122.58	1.95	555.22	72.18	32.60	29.10	2.46	46.31	24.58
F40	F-Group 2	180	Built-up land	8.52	721	360	143.26	29.88	44.08	1.85	672.33	5.12	20.79	5.42	2.94	45.01	29.23
F5	F-Group 2	40	Built-up land	7.84	495	247	62.44	15.82	15.28	3.05	320.25	3.10	5.34	0.98	3.36	47.67	40.87
F9	F-Group 2	5	Grassland	7.69	847	423	111.97	15.96	27.70	5.72	468.34	9.37	7.94	9.88	5.33	70.79	36.46
F1	F-Group 3	-	Grassland	7.60	510	255	48.28	10.43	10.78	1.76	190.46	23.29	4.19	4.34	0.21	7.99	15.71
F10	F-Group 3	-	Grassland	7.35	825	413	26.09	10.30	45.63	3.33	205.66	28.74	3.38	7.36	0.22	12.80	13.35
F13	F-Group 3	-	Grassland	7.40	640	320	39.09	16.08	26.88	1.21	135.87	60.37	6.12	32.32	0.37	13.53	11.85
F14	F-Group 3	14	Cropland	7.49	790	392	79.58	12.73	7.79	3.86	178.12	17.86	132.97	5.93	0.39	16.12	23.09
F21	F-Group 3	11	Cropland	7.74	1130	565	23.48	11.70	129.74	3.27	140.34	50.42	100.24	103.17	0.84	26.45	19.17
F22	F-Group 3	45	Grassland	7.50	903	482	26.33	21.05	23.96	2.44	176.47	33.56	14.95	12.13	0.91	26.69	21.04
F23	F-Group 3	-	Grassland	7.23	663	333	42.00	13.43	11.37	4.85	181.48	11.16	21.24	10.20	0.97	35.09	61.84
F24	F-Group 3	130	Cropland	7.27	616	308	27.38	10.61	36.09	1.54	208.42	8.94	8.87	4.11	1.48	41.66	62.37
F26	F-Group 3	150	Cropland	7.05	529	265	47.65	15.45	51.49	1.81	335.84	3.37	15.40	4.64	1.65	38.37	23.15
F4	F-Group 3	-	Cropland	7.66	831	415	18.46	9.23	20.42	1.04	140.25	6.82	4.37	3.36	1.91	48.89	23.95
F7	F-Group 3	-	Grassland	7.60	417	453	19.08	5.58	4.17	1.04	88.62	3.33	2.46	2.30	2.23	50.14	15.86
F8	F-Group 3	-	Grassland	7.95	705	350	21.15	17.82	57.79	1.75	219.98	24.58	19.17	23.88	5.44	72.70	20.90

Dry Season

D13	D-Group 1	75	Cropland	7.51	2030	1015	33.13	61.67	1213.50	2.03	2960.39	316.35	78.50	114.35	28.62	88.60	148.78
D1	D-Group 2	5	Grassland	7.22	840	420	116.01	31.80	37.87	2.35	342.70	176.31	11.72	24.03	0.16	5.10	43.00
D12	D-Group 2	32	Cropland	7.32	560	280	36.92	35.21	20.18	1.89	284.00	13.95	25.71	12.26	0.49	12.99	29.11
D17	D-Group 2	52	Grassland	7.74	1220	610	62.52	43.30	155.32	3.26	465.77	176.32	11.55	73.68	0.57	16.23	26.33
D18	D-Group 2	-	Cropland	7.66	500	250	61.28	20.38	33.45	2.46	290.79	22.36	32.44	18.58	0.80	16.80	36.12
D20	D-Group 2	40	Cropland	7.20	660	330	108.37	16.60	6.85	2.65	194.35	15.51	118.11	62.25	0.93	22.34	48.56
D22	D-Group 2	61	Cropland	7.94	960	480	29.76	42.95	140.24	2.26	365.28	117.79	40.72	75.37	0.94	24.16	23.69

D23	D-Group 2	19	Grassland	8.13	1930	965	7.06	9.44	109.17	0.88	38.34	131.14	6.12	86.96	1.27	32.38	29.59
D26	D-Group 2	19	Grassland	7.55	940	470	45.65	39.66	177.37	3.60	655.11	83.60	5.49	29.17	1.82	36.65	23.99
D27	D-Group 2	-	Grassland	7.42	520	260	82.19	24.60	19.68	2.49	389.60	18.42	6.11	7.46	3.22	49.78	51.27
D3	D-Group 2	3	Grassland	7.76	720	360	58.15	28.29	67.78	3.84	410.31	23.32	11.02	32.68	3.54	57.62	29.35
D30	D-Group 2	23	Cropland	8.13	1000	500	24.49	35.48	183.01	1.87	577.40	78.83	14.67	29.87	3.68	50.38	62.35
D4	D-Group 2	-	Grassland	8.08	690	345	36.03	20.09	107.21	2.50	396.50	59.17	6.76	12.74	3.83	54.85	48.89
D5	D-Group 2	-	Cropland	7.83	940	470	45.19	37.39	121.40	1.97	458.21	94.33	11.07	37.24	4.36	53.48	38.43
D6	D-Group 2	6	Cropland	7.61	1270	635	68.89	46.54	191.94	2.80	690.16	139.07	3.56	52.21	4.61	58.28	38.39
D7	D-Group 2	300	Grassland	7.60	640	320	46.12	17.40	39.92	2.44	214.16	53.81	7.54	28.42	5.50	65.69	22.79
D9	D-Group 2	20	Grassland	7.42	820	410	56.04	32.99	35.57	1.96	312.51	40.63	18.45	31.25	6.29	80.71	37.22
D10	D-Group 3	120	Cropland	7.34	440	220	24.26	9.91	9.73	1.27	133.81	3.48	5.42	5.00	0.42	18.25	14.92
D11	D-Group 3	80	Built-up land	7.33	530	265	26.81	12.16	78.57	2.41	325.42	4.24	15.42	5.69	0.63	27.81	14.74
D14	D-Group 3	180	Built-up land	7.85	540	270	11.72	10.32	16.41	1.05	104.21	6.94	9.23	6.56	0.70	22.77	10.96
D15	D-Group 3	80	Built-up land	7.70	540	270	22.71	18.04	88.74	1.33	351.23	15.21	13.15	8.66	0.84	33.85	20.39
D16	D-Group 3	-	Grassland	7.53	490	245	39.88	24.17	42.85	1.57	317.88	12.80	12.85	8.05	1.32	32.19	11.89
D2	D-Group 3	200	Built-up land	7.61	460	230	38.78	13.46	19.99	1.29	213.85	8.34	8.05	5.47	1.44	45.36	20.30
D21	D-Group 3	35	Unused	8.05	510	255	10.80	10.88	36.43	1.41	140.90	10.15	20.45	7.64	1.86	52.84	19.73
D28	D-Group 3	-	Built-up land	7.31	790	395	14.78	10.18	29.58	1.23	114.61	25.99	3.62	15.11	2.07	48.45	16.75
D29	D-Group 3	75	Built-up land	7.54	590	295	13.85	10.09	12.77	1.39	101.42	5.72	8.29	7.40	3.15	59.63	15.04
D8	D-Group 3	-	Cropland	7.74	490	245	21.60	17.12	53.38	1.35	263.90	8.30	4.67	10.21	3.36	59.60	12.28

EC = electrical conductivity; TDS = total dissolved solids; SAR = sodium adsorption ratio; %Na = the Sodium percentage; WQI = water quality index.

To investigate the accuracy of chemical analysis, the ionic charge balance error (ICBE) of anions and cations was calculated by the following formula (Eq.1):

$$ICBE = \frac{\sum Cations - \sum Anions}{\sum Cations + \sum Anions} \times 100 \quad (1)$$

where the concentrations unit of cations and anions are meq/L. The calculation results of ICBE in the study area were within $\pm 5\%$, which indicated that the quality of groundwater chemical data is reliable (Ismail et al. 2019).

2.3 Multivariate data analysis

The Q-mode hierarchical cluster analysis (HCA) was employed to divide samples into various groups using the Ward's method (J.C. 1974). For those water quality indices not normally distributed, a log transformation was conducted (Ismail et al. 2019). HCA can present information about the evolution of groundwater bodies, and determine the hydrochemical facies.

We investigated whether there were seasonal differences in groundwater by comparing solute concentrations of groundwater between flood season and dry season with a Wilcoxon paired rank sum test. A non-parametric test was used because the concentrations of ions were not normally distributed (Bernal et al. 2015). It was observed that only HCO_3^- of flood season and pH and K^+ of dry season were normally distributed. Therefore, it is necessary to substitute the original data of other non-normal distribution parameters into the formula of $x' = \log_{10}(x)$ for log-transformation. The calculation results showed that the remaining parameters were corrected to be normalized except Cl^- of flood season and thus it was excluded.

2.4 Water Quality Analysis

The groundwater quality for drinking purposes was assessed based on an improved form of water quality index (WQI, Eq.2-3) (Aghababazadeh et al. 2016):

$$W_i = \frac{w_i}{\sum w_i} \quad (2)$$

$$WQI = \sum [W_i \times (\frac{C_i}{S_i}) \times 100] \quad (3)$$

where W_i and w_i are the weight and relative weight of the i_{th} parameter, respectively (Table 3); C_i is the concentrations of the i_{th} parameter; S_i is the permissible limit for the

i_{th} parameter. Based on WQI values, groundwater quality can be divided into five groups: excellent (< 50), good (50-100), poor (100-200), very poor (200-300), and unsuitable (≥ 300).

For irrigation purpose, Na^+ in groundwater can change the salinity of the soil and offset the osmotic pressure of the crops, which further affects the plant root water uptake and photosynthesis (FK et al., 2015). The sodium hazard can be estimated by the sodium adsorption ratio (SAR, Eq.4) (Banoeng-Yakubo et al.) and soluble sodium percentage (%Na, Eq.5) (Santacruz et al. 2017):

$$SAR = \frac{[Na^+]}{\sqrt{\frac{[Ca^{2+}] + [Mg^{2+}]}{2}}} \quad (4)$$

$$\%Na = \frac{Na^+}{Na^+ + K^+ + Ca^{2+} + Mg^{2+}} \times 100\% \quad (5)$$

where all ions are expressed in meq/L. According to SIAR values, sodium hazard can be classified into four categories, i.e., low (< 10), medium (10 -18), high (18 - 26), and very high (≥ 26). Also, the classification of irrigation water quality based on %Na is as follows: suitable (< 30), marginally suitable (30-60), and unsuitable (≥ 60). The salinity hazard is divided into four ranks by EC ($\mu S/cm$): low (< 250), medium (250 -750), high (750-2250), and very high (≥ 2250).

To show the spatial variation of hydrochemical parameters (i.e., TDS, Ca^{2+} , Na^+ , NO_3^-) and WQI values, the ordinary kriging was used in this study since it overall outperformed other methods.

2.5 Quantifying contribution of different solute sources

The forward model was applied to quantify the relative contributions of atmospheric

inputs and rock weathering to dissolved solutes (Wu et al., 2005). In this study, anthropogenic input was also considered as one of the solutes sources by using nitrate as an indicator (Li et al. 2019c; Xiao et al. 2015). The overall flow chart and specific equations used for quantification of source contribution to dissolved solutes were presented in Fig. 2.

Fig. 2 Overall framework of forward model for quantification of source contribution to dissolved solutes in groundwater.

216 According to Xiao et al. (2016), the mean value of $\text{Ca}^{2+}/\text{Na}^{+}$ in bedrock from the upper
 217 to lower reaches of the Yellow River is 0.24–0.31, and the average value of $\text{Mg}^{2+}/\text{Na}^{+}$
 218 is 0.35–0.51 (Xiao 2016). In this study, we took the mean values of $\text{Ca}^{2+}/\text{Na}^{+}$ (0.26) and
 219 $\text{Mg}^{2+}/\text{Na}^{+}$ (0.47) in bedrock to calculate the contribution of silicate weathering.

220 3 Results

221 3.1 Hydrochemical characteristics

222 Table 2 listed the hydrochemical statistics of groundwater samples in different seasons
 223 on the Loess Plateau. In the flood season, pH ranged between 6.66 and 8.63 with an
 224 average of 7.65, and the TDS concentration ranged from 247 to 1410 mg/L with an
 225 average of 445 mg/L. Ca^{2+} (average 76.80 mg/L) and Na^{+} (average 50.90 mg/L) were
 226 the dominant cations, while HCO_3^{-} (average 355.82 mg/L) was the dominant anion. The
 227 contents of ions were in the order of $\text{Ca}^{2+} > \text{Na}^{+} > \text{Mg}^{2+} > \text{K}^{+}$ and $\text{HCO}_3^{-} > \text{SO}_4^{2-} > \text{Cl}^{-} >$
 228 NO_3^{-} .

229 **Table 1** Descriptive statistics of hydrochemical parameters of groundwater in different seasons on
 230 the Loess Plateau

Statistics		pH	EC	TDS	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	SO_4^{2-}	NO_3^{-}	Cl^{-}
<i>Flood Season (37 samples)</i>												
F-group 1	Mean	6.75	2322	1194	203.64	74.41	182.19	3.99	664.05	173.10	114.76	310.15
	SD	0.13	745	305	49.60	6.58	62.56	0.23	265.37	6.91	72.38	213.46
F-group 2	Mean	7.81	842	422	87.64	24.08	47.52	3.47	418.95	41.22	16.78	20.63
	SD	0.55	367	182	39.00	9.73	42.42	2.78	115.74	47.80	15.89	28.80
F-group 3	Mean	7.49	713	379	34.88	12.87	35.51	2.33	183.46	22.70	27.78	17.81
	SD	0.25	196	92	17.72	4.20	34.53	1.23	60.89	18.32	42.55	28.39
Total	Min	6.66	417	247	18.46	5.08	4.17	1.04	88.62	2.73	1.53	0.98
	Max	8.63	2848	1410	238.71	79.06	226.42	12.62	851.69	177.99	165.93	461.09
	Mean	7.65	880	445	76.80	23.16	50.90	3.12	355.82	42.34	25.64	35.36
	SD	0.52	485	241	51.46	15.69	51.15	2.35	170.3	50.79	36.69	80.34
<i>Dry Season (27 samples)</i>												
D-group 1	Mean	7.51	2030	1015	33.13	61.67	1213.50	2.03	2960.39	316.35	78.50	114.35

	SD	-	-	-	-	-	-	-	-	-	-	-
D-group 2	Mean	7.66	888	444	55.29	30.13	90.43	2.45	380.32	77.78	20.69	38.39
	SD	0.31	360	180	28.78	11.01	65.18	0.72	168.85	56.42	28.00	24.45
D-group 3	Mean	7.60	538	269	22.52	13.63	38.84	1.43	206.72	10.12	10.11	7.98
	SD	0.24	99	49	10.42	4.73	27.43	0.37	100.21	6.66	5.31	2.97
Total	Min	7.20	440	220	7.06	9.44	6.85	0.88	38.34	3.48	3.56	5.00
	Max	8.13	2030	1015	116.01	61.67	1213.50	3.84	2960.39	316.35	118.11	114.35
	Mean	7.63	801	400	42.33	25.19	112.92	2.06	411.59	61.56	18.91	29.94
	SD	0.27	409	205	27.80	13.97	227.42	0.77	535.28	74.35	25.11	29.18

231 The unit of EC is $\mu\text{S}/\text{cm}$; pH is dimensionless. Other parameters have unit of mg/L .

232 In the dry season, the pH value varied from 7.20 to 8.13 with a mean of 7.63, which
233 indicates an alkaline environment. TDS concentration ranged from 220 to 1015 mg/L
234 with an average of 400 mg/L . The dominant cation was Na^+ (average 112.92 mg/L),
235 followed by Ca^{2+} (average 42.33 mg/L), Mg^{2+} (average 25.19 mg/L), and K^+ (average
236 2.06 mg/L). The abundance of anions was that HCO_3^- (average 411.59 mg/L) > SO_4^{2-}
237 (average 61.56 mg/L) > Cl^- (average 29.94 mg/L) > NO_3^- (average 18.91 mg/L), which
238 is the same as the order of anion concentration in the flood season. As shown in Table
239 2, the standard deviation of major cations and anions was highly dispersive, indicating
240 that the chemical composition of groundwater exhibited a large spatial difference. Fig.
241 3 showed the Wilcoxon test results of major ions content in different seasons. As shown
242 in Fig. 3, the difference of most ions was not significant ($p>0.05$) except for Ca^{2+}
243 ($p=0.0078$) and Na^+ ($p=0.033$), which implied the contents of Ca^{2+} and Na^+ in
244 groundwater changed significantly in the two seasons. This is the reason why the order
245 of abundance of major cations is different in the flood season and the dry season.

Fig. 3 Box plots showing variations of major cations (a) and anions (b) concentrations in groundwater in two different seasons ($p < 0.05$ means significant difference).

3.2 Hydrochemical facies

By using HCA, three clusters were identified for both the flood season (F-Group 1, 2 and 3) and the dry season (D-Group 1, 2 and 3) based on hydrochemical parameters (Table 1 and Fig. 4a). F-Group1, consisting of samples F28 and F30 (6% of total samples), was characterized by the highest average concentrations of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , Cl^- , NO_3^- , and TDS and the lowest pH value. The dominant hydrochemical type was $\text{Ca}\cdot\text{Na}\text{-}\text{HCO}_3\cdot\text{Cl}$. As shown in Fig. 4b, the samples of F-Group1 were mainly distributed in Yan'an City in northern Shaanxi, where there were a lot of petroleum industry, and the increase in salinization observed in this system may be potentially related to petroleum production. Approximately 62% of the samples ($n = 23$) were clustered into F-Group2, which was characterized by the higher mean contents of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , Cl^- , TDS, and pH and the lowest mean concentrations of NO_3^- , and the hydrochemical type of which was dominated by $\text{Ca}\text{-}\text{HCO}_3$. These samples were mainly distributed in loess tablelands with thick loess and large groundwater storage in the southeast of Gansu Province and the southwest of Shaanxi Province. About 32% of the samples ($n = 12$) were classified as F-Group3,

which was characterized by the lowest contents of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , Cl^- , and TDS and the higher contents of NO_3^- and pH values, and distributed in the southern junction of Gansu and Ningxia. $\text{Ca}\cdot\text{Mg}\cdot\text{HCO}_3$ was the dominant hydrochemical type for F-Group3.

D-Group 1 consisted of only one groundwater sample (sample D13) with the highest concentrations of Mg^{2+} , Na^+ , HCO_3^- , SO_4^{2-} , Cl^- , NO_3^- , and TDS, which was located in Pucheng County in Southern Shaanxi, and the hydrochemical type of which was $\text{Na}\cdot\text{HCO}_3$. This may be related to the massive use of mirabilite in the local pyrotechnic manufacturing industry. Thus, D-Group 1 was regarded as an indicator of human activities. Nearly 70% of the samples ($n = 16$) were classified as D-Group 2, which was characterized by the higher mean concentrations of Mg^{2+} , Na^+ , HCO_3^- , SO_4^{2-} , Cl^- , NO_3^- , and TDS and the highest mean concentrations of Ca^{2+} , K^+ , and pH,. The dominant hydrochemical type was $\text{Na}\cdot\text{Ca}\cdot\text{HCO}_3\cdot\text{SO}_4$. About 37% of groundwater samples ($n = 10$) were clustered into D-Group 3, which was characterized by the lowest mean contents of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , Cl^- , and NO_3^- , and the hydrochemical type of which was dominated by $\text{Na}\cdot\text{HCO}_3$.

Fig. 4 Spatial distribution (a) and ternary diagrams (b) of the six clusters (F-Group 1-3, D-Group1-3) in the study area.

3.3 Groundwater quality for domestic purpose

Table 3 listed the statistics and weight assignment of the chemical composition of

groundwater exceeding acceptable limits in the flood and dry season. Obviously, Mg^{2+} and SO_4^{2-} concentrations in the flood season and Mg^{2+} , Cl^- and K^+ concentrations in the dry season were within the allowable limits of drinking water set by the WHO. However, the concentration of other water quality parameters exceeded their respective acceptable limits. In the flood season, approximately 43%, 3%, 6%, 14%, 3%, and 3% of groundwater samples had Ca^{2+} , Na^+ , K^+ , NO_3^- , Cl^- , and TDS exceeding the acceptable limits, respectively. In the dry season, 11%, 4%, 7%, 4%, and 4% of the samples exhibited Ca^{2+} , Na^+ , NO_3^- , SO_4^{2-} , and TDS exceeding the acceptable limits, respectively.

Table 3 Statistics and weight assignment of the chemical composition of groundwater exceeding acceptable limits in the flood season and the dry season.

Parameter	Unit	WHO (2011)	2018 Flood season (N = 37)		2019 Dry season (N = 27)		Parameters for WQI calculation	
			NSEL	% of SEL	NSEL	% of SEL	w_i	W_i
TDS	$mg \cdot L^{-1}$	1000	F28	3	D13	4	5	0.15
SO_4^{2-}	$mg \cdot L^{-1}$	250		0	D13	4	5	0.15
NO_3^-	$mg \cdot L^{-1}$	50	F14,17,21,28,30	14	D13,20	7	5	0.15
Cl^-	$mg \cdot L^{-1}$	250	F28	3		0	5	0.15
Ca^{2+}	$mg \cdot L^{-1}$	75	F2,9,14-17,19,27-30, 33-34,36-37,40	43	D1,20,27	11	3	0.09
Mg^{2+}	$mg \cdot L^{-1}$	100		0		0	3	0.09
Na^+	$mg \cdot L^{-1}$	200	F28	3	D13	4	4	0.12
K^+	$mg \cdot L^{-1}$	10	F29,36	5		0	3	0.09

Note: NSEL = number of samples exceeding acceptable limit; % of SEL = % of samples exceeding acceptable limit.

The WQI values ranged from 12 to 132 (average 36) and from 11 to 149 (average 33) in the flood season and the dry season, respectively (Table 1). Slight differences in groundwater quality for domestic purpose were found in the two seasons. In the flood season, about 81%, 14% and 5% of the samples were classified as excellent, good and poor quality, respectively. Compared with the flood season, the percentage of excellent quality water (89%) increased, while the percentage of good (7%) and poor quality (4%)

decreased in the dry season.

3.4 Groundwater quality for irrigation purpose

As shown in Table 1, the SAR values ranged between 0.14 and 5.44 (average 1.40) and between 0.16 and 28.62 (average 3.20) in the flood season and the dry season, respectively. Obviously, groundwater in the flood season was suitable for irrigation, while only one sample (sample D13) was unsuitable for irrigation in the dry season. %Na values varied from 4.19 to 72.70 with an average 27.37 in the flood season, which was lower than those in the dry season (from 5.10 to 88.60, average 41.73). Approximately 5.4% of the flood season samples and 11.1% of the dry season samples had Na% values greater than 60, indicating that these groundwater were unsuitable for irrigation. EC values ranged between 417 and 2848 $\mu\text{S}/\text{cm}$ (average 880 $\mu\text{S}/\text{cm}$) and between 440 and 2030 $\mu\text{S}/\text{cm}$ (average 801 $\mu\text{S}/\text{cm}$) in the flood season and the dry season, respectively. Most of the groundwater samples (except sample F28) in both seasons were classified as good quality ($250 < \text{EC} < 750 \mu\text{S}/\text{cm}$) or permissible quality ($250\text{--}750 \mu\text{S}/\text{cm}$) for irrigation.

The diagrams developed by the USSS (1954) and Wilcox (1948) have been widely applied to evaluate the groundwater quality for irrigation (Loh et al. 2019). As shown in Fig. 5a, 35 samples (19 collected from the flood season and 16 collected from the dry season) were plotted in the C2-S1 zone, showing good quality for irrigation; 17 flood samples and 10 dry samples were plotted in the C3-S1 zone, indicating moderate quality for irrigation. Moreover, samples D13 and F28 were plotted in C3-S4 and S1-C3 zones, respectively, signifying unsuitable for irrigation owing to high salinity or high sodium hazard. The Wilcox diagram (Fig. 5b) showed that 89% of the samples were suitable for irrigation; 5 samples (2 collected from the flood season and 3 collected from the dry season) were plotted in the “doubtful to permissible” zone because of

high %Na values; only 2 samples (F28, D13) were unsuitable for irrigation due to sodium hazard or salinity hazard.

Fig. 5 USSL diagram (a) and Wilcox diagram (b) to investigate the quality of irrigation water.

4 Discussion

4.1 Spatiotemporal variations in the hydrochemical characteristics

To investigate the spatiotemporal variations in the hydrochemical characteristics, we calculated the concentration differences of different indices (ΔTDS , ΔCa^{2+} , ΔNa^{+} and ΔNO_3^{-}) between the dry season and the flood season (Fig. 6). For example, $\Delta\text{TDS} = \text{TDS}_{\text{dry season}} - \text{TDS}_{\text{wet season}}$. A positive value indicated that the concentration of hydrochemical indices increase from the flood season to the dry season, while a negative value suggests that the concentration decreases. In previous studies, the groundwater level near the river was relatively shallow, and it was susceptible to the dilution effect of precipitation and flash flood event during the flood season, making the concentration of groundwater ions in the flood season lower than that in the dry season (Guo et al. 2019; Masoud et al. 2018). However, in this study, the average contents of TDS, Ca^{2+} and NO_3^{-} were lower in the dry season (Table 2), which was related to the generally deeper groundwater level in the vadose zone. As shown in Fig.

6a-d, most of the groundwater, especially in the central and southeast, showed negative ΔTDS , ΔCa^{2+} and ΔNO_3^- values. The areas with negative values of ΔTDS , ΔCa^{2+} and ΔNO_3^- accounted for 79%, 83%, and 88% of the study area, respectively, indicating that the contents of TDS, Ca^{2+} and NO_3^- were generally higher in the flood season.

The Na^+ concentrations increased in most areas from the flood season to the dry season. Especially, the largest increase of Na^+ concentrations ($\Delta\text{Na}^+ = 1185.0 \text{ mg/L}$) occurred in Pucheng County, Shaanxi Province (sample D13) (Fig. 6c). ΔNO_3^- was used to determine the effect of anthropogenic activities on the spatiotemporal evolution (Fig. 6d). As shown in Fig. 6d, groundwater with increased NO_3^- concentration was mainly distributed in areas where farmland was the main land use type (samples D13 and D20), indicating that anthropogenic activities played a significant role in groundwater chemistry in these areas. Figs. 6e and 6f showed the spatial distribution of WQI values in the flood season and the dry season, respectively. The WQI values of groundwater were higher in the northern Loess Plateau, which may be related to higher salt contents of groundwater caused by strong evaporation and sparse rainfall in the north. In addition, local groundwater quality may also be affected by anthropogenic activities. For example, in the dry season, the WQI value in a limited region in the south around sample D13 was higher than other regions, which was possibly caused by anthropogenic inputs from firework factories.

Fig. 6 Spatial patterns in the seasonal difference of TDS (a), Ca^{2+} (b), Na^{+} (c), NO_3^{-} (d), and WQI in the flood season (e) and the dry season (f).

4.2 Qualitative analysis of ion sources

Gibbs plots (Gibbs, 1970) was used to illustrate three significant natural factors controlling groundwater chemistry by plotting $\text{Na}^{+} / (\text{Na}^{+} + \text{Ca}^{2+})$ or $\text{Cl}^{-} / (\text{Cl}^{-} + \text{HCO}_3^{-})$ versus TDS (Fig. 7). Fig. 7 showed that 97.3% of samples in the flood season and 96.3% in the dry season fell into the rock weathering dominance zone, suggesting that water-rock interactions and rock weathering were the predominantly factors controlling the chemical composition. Moreover, two samples (F28 and D13) were plotted in the evaporation dominance zone, which indicated that evaporation also had a certain effect on groundwater chemistry.

Fig. 7 Scatterplots of (a) TDS versus $\text{Na}/(\text{Na} + \text{Ca})$ and (b) TDS versus $\text{Cl}/(\text{Cl} + \text{HCO}_3)$ to illustrate the dominant processes that control dissolved solutes.

The Na-normalized molar ratios (Gaillardet et al., 1995) was used to explore the effect of rock weathering on groundwater chemistry by dividing solute sources into evaporite dissolution, silicate and carbonate rock weathering (Fig. 8). As shown in Fig. 8, most of the samples in the flood season were distributed in the middle and upper right areas, which indicated that the dissolved solutes in the flood season were mainly controlled by silicate and carbonate weathering. The samples in the dry season were mainly located in the middle and left lower areas, indicating the dominance of silicate weathering and evaporite dissolution in the formation of groundwater chemistry.

Fig. 8 Scatterplots of Na^+ -normalized Ca^{2+} versus $\text{Mg}^{2+}/\text{Na}^+$ (a) and HCO_3^- (b) to investigate the processes that control groundwater chemistry.

The bivariate diagrams of ion concentrations were used to further discriminate the different processes of water-rock interactions (Yong-Hong et al., 2007). HCO_3^- was the main ionic component of each group (Fig. 3) since it can be naturally introduced by dissolved CO_2 in rainwater or carbonate weathering (Marcé et al., 2015). The proportion of dissolved ions is generally determined by the reaction of calcite (Eq. 5) and dolomite (Eq. 6). The molar ratio of $\text{HCO}_3^-/\text{Ca}^{2+}$ in groundwater is 2 or 4 for exclusive control of calcite or dolomite dissolution, respectively (Liu et al., 2020). Approximately 56.8% of the flood season samples and 25.9% of the dry season samples were located between the calcite dissolution line (Fig. 9a, $y = 2x$) and dolomite dissolution line ($y = 4x$), implying the weathering of calcite and dolomite contributed of the most HCO_3^- in these groundwater samples. The significant positive correlation between Mg^{2+} and Ca^{2+} ($r=0.643$) in the flood season further confirmed the importance of calcite and dolomite dissolution in groundwater chemistry (Table 4). However, about

32.4% of the flood season samples and 66.7% of the dry season samples were plotted above the dolomite dissolution line, which may be related to cation exchange or silicate dissolution.

Fig. 9 Bivariate diagrams of HCO_3^- versus Ca^{2+} (a) to explore the contribution of carbonate to groundwater chemistry; $1/2\text{HCO}_3^- + \text{SO}_4^{2-}$ versus $\text{Ca}^{2+} + \text{Mg}^{2+}$ (b) to examine gypsum dissolution; HCO_3^- versus Na^+ (c) to investigate the silicate weathering; SO_4^{2-} versus Na^+ (d) to verify the dissolution of evaporite.

In the flood season, a significant correlation existed between Ca^{2+} and SO_4^{2-} ($r=0.5$), indicating gypsum dissolution may have a certain impact on groundwater chemistry. (Eq.7). However, the concentration of SO_4^{2-} was too low to match Ca^{2+} . Therefore, gypsum dissolution may contribute little in the flood season (Yong-Hong et al. 2007).

If Ca^{2+} , Mg^{2+} , SO_4^{2-} and HCO_3^- are derived from the dissolution of calcite, dolomite and gypsum, the charge balance is expressed as $(1/2 [\text{HCO}_3^- + \text{SO}_4^{2-}]) / (\text{Ca}^{2+} + \text{Mg}^{2+}) = 1$ (Liu et al. 2020). However, most samples (83.8% collected in the rainy season and 96.3% collected in the dry season) were located above the 1:1 equilibrium line (Fig. 9b), which indicated insufficient Ca^{2+} and Mg^{2+} or excessive HCO_3^- and SO_4^{2-} . Excessive SO_4^{2-} and HCO_3^- ions was subsequently equalized by Na^+ , i.e. the conversion of albite to kaolinite releases HCO_3^- and Na^+ (Eq. 8). In the dry season, HCO_3^- was significantly correlated with Na^+ ($r = 0.981$) and Mg^{2+} ($r = 0.716$), and most of the dry season samples were close to the albite dissolution line (Fig. 9c). Thus, the silicate weathering played an important role in the groundwater chemistry in the flood season and the dry season (Yong-Hong et al. 2007).

The contribution of halite and mirabilite dissolution can be confirmed by the scatterplot of $(2\text{SO}_4^{2-} + \text{Cl}^-)$ versus Na^+ (Sarin et al., 1989) (Fig. 9d). As shown in Fig. 9d, approximately 75.7% of the samples in the flood season and 81.5% in the dry season fell below the $y = x$ line, signifying that Na^+ in groundwater may have other sources such as cation exchange or silicate dissolution in addition to evaporite dissolution.

Table 4 Pearson correlation matrix between hydrochemical parameters of groundwater samples in the flood season (the right upper part) and in the dry season (the left lower part)

	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	NO_3^-	Cl^-	TDS
Ca^{2+}		0.634**	0.191	0.161	0.737**	0.5**	0.426**	0.462**	0.389**
Mg^{2+}	0.328		0.614**	0.089	0.711**	0.585**	0.527**	0.661**	0.647**
Na^+	-0.076	0.651**		0.101	0.385**	0.676**	0.372**	0.733**	0.806**
K^+	0.609**	0.52**	0.098		0.213	0.017	0.057	0.078	0.071
HCO_3^-	0.05	0.716**	0.981**	0.204		0.264	0.269	0.214	0.308*
SO_4^{2-}	0.208	0.759**	0.786**	0.25	0.755**		0.36**	0.734**	0.771**
NO_3^-	0.355*	0.247	0.413**	0.147	0.416**	0.248		0.412**	0.425**

Cl ⁻	0.154	0.62**	0.67**	0.249	0.599**	0.824**	0.521**	0.828**
TDS	-0.034	0.57**	0.713**	0.094	0.627**	0.868**	0.215	0.889**

*: Correlation is significant at p < 0.05 level (2-tailed).

** : Correlation is significant at p < 0.01 level (2-tailed).

Cation exchange was considered a significant process to control groundwater chemistry (Schoeller 1967). The chloro-alkaline indices (i.e., CAI1 and CAI2) were used to interpret the occurrence of cation exchange in groundwater (Eq.11 and Eq.12) (Yong-Hong et al. 2007):

$$CAI1 = \frac{Cl^{-} - (Na^{+} + K^{+})}{Cl^{-}} \quad (11)$$

$$CAI2 = \frac{Cl^{-} - (Na^{+} + K^{+})}{SO_4^{2-} + HCO_3^{-} + CO_3^{2-} + NO_3^{-}} \quad (12)$$

where all the ionic units are meq/L. Approximately 94.6% of the flood season samples in and 96.3% of the dry season samples exhibited negative CAI1 and CAI2 values, which suggested that cation exchange between Ca²⁺ and Mg²⁺ in groundwater and Na⁺ and K⁺ in aquifers was prevalent in the study area. Again, this indicated that cation exchange played an important role for source of Na⁺ in groundwater.

4.3 Quantification of source contributions to dissolved solutes

The calculation results of the contribution of different sources to the dissolved solutes in groundwater in the two seasons were shown in Table 5.

Table 5 Contributions of different sources to the dissolved solutes in groundwater.

		Atmospheric	Anthropogenic	Evaporite	Silicate	Carbonate
		Input (%)	Input (%)	Dissolution (%)	Weathering (%)	Weathering (%)
Flood season	Min	0.50	0.27	0.33	0.52	0.00
	Max	9.26	39.40	88.96	92.82	71.77
	Mean ± SD	2.3±1.5	5.0±7.1	19.3±21.4	42.8±27.3	30.6±27.1
Dry season	Min	0.60	0.00	2.24	1.28	0.00
	Max	25.05	26.33	69.59	87.19	53.50
	Mean ± SD	9.1±6.4	3.4±5.2	20.3±15.9	56.6±23.2	10.7±15.4

Mean of all samples	5.2±5.5	4.3±6.1	19.7±19.1	48.6±26.4	22.2±24.8
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458 The contribution of atmospheric inputs to solutes in groundwater was measured by the
459 Cl^- content in rainwater (Noh et al. 2009). With reference to the East Asia Acid Rain
460 Network, the average concentration of Cl^- in rainwater was 0.81 and 2.15 mg/L in the
461 dry season and the flood season, respectively. The mean contribution of atmospheric
462 inputs to dissolved solutes in the dry season was $9.1\% \pm 6.4\%$, which was significantly
463 higher than that in the flood season ($2.3\% \pm 1.5\%$). This result was consistent with
464 previous studies in arid areas (Li et al. 2019b; Xiao et al. 2015). This phenomenon can
465 be explained by two potential reasons: (i) compared with the flood season, the rainwater
466 in the dry season had a higher ion concentration, which dominated the contribution of
467 atmospheric inputs to the solutes; (ii) the flux of atmospheric inputs was larger in the
468 flood season, but it may have time lag to reach the aquifer because of the thick vadose
469 zone (Li et al. 2017). However, more frequent sampling is required to clarify this.

470 **Table 6** Chemical composition of rainwater (Data from East Asia Acid Rain Network).

	Ion concentration (mg/L)						
	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}
Flood season	2.50	0.79	0.81	0.45	0.47	1.72	0.24
Dry season	4.12	3.85	2.15	0.99	0.69	8.44	1.64

471 The anthropogenic impacts on groundwater chemistry can be characterized by the
472 concentration of NO_3^- and H_2PO_4^- in the water (Xiao 2016). In this study, H_2PO_4^- was
473 not considered because its concentration was below detection limit. The average
474 contribution of anthropogenic inputs to solutes in groundwater was $5.0\% \pm 7.1\%$ and
475 $3.4\% \pm 5.2\%$ in the flood season and the dry season, respectively. Although the overall
476 contribution of anthropogenic inputs to groundwater was minor, it is the dominant
477 source of solutes for some groundwater. For example, for sample F14 with NO_3^-
478 concentration up to 165.9 mg/L, the average contribution value of anthropogenic inputs

reached 39%. The groundwater nitrate from human activities may include NO_3^- fertilizer, NH_4^+ fertilizer, manure and septic waste (Zhang et al. 2018). Due to excessive fertilizer application in most regions, the storage of NO_3^- is large in the soil and rocks (Fewtrell and Lorna 2004). As such, precipitation had insignificant dilution effect on NO_3^- in groundwater (Table 2), and even increased the groundwater NO_3^- contents in the flood season (Ji et al. 2020).

The contributions of evaporite dissolution, silicate and carbonate weathering to dissolved solutes were calculated according to the flowchart in Fig.2. For evaporite, we only considered the contributions of gypsum and halite dissolution to solutes because of no evidence for the existence of pyrite (Larssen et al. 1999; Li et al. 2019b) and rare sulfuric acid in precipitation on the Loess plateau (Table 5). The average contribution of evaporite dissolution was $19.7\% \pm 19.1\%$ in the flood season, which was slightly lower than that in the dry season.

The contribution of silicate weathering to dissolved solutes varied from 1% to 93% (average $42.8\% \pm 27.3\%$) and from 1.28 to 87.19 (average $56.6\% \pm 23.2\%$) in the flood season and the dry season, respectively, while for carbonate, the corresponding values were in the range of $30.6\% \pm 27.1\%$ and $10.7\% \pm 15.4\%$, respectively.

The order of the contribution of different sources to solutes in the flood season was silicate > carbonate > evaporite > anthropogenic input > atmospheric input, while the contribution in the dry season was silicate > evaporite > carbonate > atmospheric input > anthropogenic input. Obviously, silicate weathering was the major contributor to dissolved solutes in groundwater in the Loess Plateau. This finding was consistent with the results obtained by (Hua et al. 2019) and (Kou et al. 2019) in studying the source of groundwater solutes in the Loess Plateau. However, compared with other regions, the predominant source of groundwater chemistry was different due to different geological

factors and climatic conditions. For instance, carbonate weathering was the main source of solutes in the groundwater of the Bishuiyan subterranean basin in Guangxi (Jiang et al. 2020), while evaporite dissolution contributed most in the Tarim River Basin (Xiao et al. 2015).

5 Conclusions

Water quality is an important indicator for ensuring biological growth and socio-economic development, especially in arid regions such as the Chinese Loess Plateau. In this study, the hydrochemical characteristics of dissolved major elements in groundwater collected from the Loess Plateau were studied. The contents of Na^+ , Mg^{2+} , HCO_3^- , and SO_4^{2-} in groundwater during the dry season were greater than those during the flood season, while the contents of K^+ , Ca^{2+} , Cl^- , and NO_3^- were lower than those during the flood season. HCA and correlation analysis coupled with conventional hydrochemical plots suggests that minerals dissolution and cation exchange are the key factors in controlling groundwater chemistry. Moreover, anthropogenic activities (e.g., agricultural activities) also have a certain impact on the formation of dissolved solutes in groundwater, especially during the flood season. Most of the groundwater (95% in the flood season and 96% in the dry season) was suitable for drinking, and overall water quality was acceptable for irrigation. The calculation results based on the forward model showed that the order of the contribution of different sources to dissolved solutes in the flood season was silicate > carbonate > evaporite > anthropogenic input > atmospheric input, while in the dry season was silicate > evaporite > carbonate > atmospheric input > anthropogenic input.

Data availability

The datasets used and/or analyzed during this study are included in this published article.

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Authors' contributions

Shujian Li: Conceptualization, Methodology, Software, Investigation, Formal analysis, Writing - Original Draft. **He Su:** Writing - Review & Editing, Funding acquisition. **Zhi Li:** Conceptualization, Methodology, Resources, Writing-Review & Editing, Data Curation, Validation, Supervision, Funding acquisition.

Ethics declarations

Conflict of interests

676 The authors claim no conflicts of interest.

677 **Ethical approval**

678 Not applicable

679 **Consent to participate**

680 Not applicable

681 **Consent to publish**

682 Not applicable

Figures

Figure 1

(a) Geographical location of the Loess Plateau and groundwater sampling sites. (b) Land use of the Loess Plateau. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal

status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

Figure 2

Overall framework of forward model for quantification of source contribution to dissolved solutes in groundwater.

Figure 3

Box plots showing variations of major cations (a) and anions (b) concentrations in groundwater in two different seasons ($p < 0.05$ means significant difference).

Figure 4

Spatial distribution (a) and ternary diagrams (b) of the six clusters (F-Group 1-3, D-Group 1-3) in the study area. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

Figure 5

USSL diagram (a) and Wilcox diagram (b) to investigate the quality of irrigation water.

Figure 6

Spatial patterns in the seasonal difference of TDS (a), Ca^{2+} (b), Na^{+} (c), NO_3^{-} (d), and WQI in the flood season (e) and the dry season (f). Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

Figure 7

Scatterplots of (a) TDS versus $\text{Na}/(\text{Na} + \text{Ca})$ and (b) TDS versus $\text{Cl}/(\text{Cl} + \text{HCO}_3)$ to illustrate the dominant processes that control dissolved solutes.

Figure 8

Scatterplots of Na⁺-normalized Ca²⁺ versus Mg²⁺/Na⁺ (a) and HCO₃⁻ (b) to investigate the processes that control groundwater chemistry.

Figure 9

Bivariate diagrams of HCO_3^- versus Ca^{2+} (a) to explore the contribution of carbonate to groundwater chemistry; $1/2\text{HCO}_3^- + \text{SO}_4^{2-}$ versus $\text{Ca}^{2+} + \text{Mg}^{2+}$ (b) to examine gypsum dissolution; HCO_3^- versus Na^+ (c) to investigate the silicate weathering; SO_4^{2-} versus Na^+ (d) to verify the dissolution of evaporite.