Hydrogeochemical characterization of groundwater flow systems in the discharge area of a river basin

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S U M M A R Y

The lowest reaches of a large-scale basin could be the discharge area of local, intermediate and regional groundwater flow systems with different travel distances and travel times. However, little research has been devoted to identify the flow systems in such a site. In this study, 44 groundwater samples were collected from wells with different depths in the discharge area of the Dosit River Watershed in the Ordos Cretaceous Basin. Using the major ions and pH as the input, hierarchical cluster analysis was conducted, which leads to five clusters (from C1 to C5) with distinct geochemical compositions. The relationship between CSV and δ18O shows that clusters C1 and C2 were recharged during the cold time while clusters C3, C4 and C5 were recharged recently. According to the Gibbs scheme, groundwater samples in all clusters except for C5 were controlled by rock–water interaction. Both hydraulic and geochemical perspectives were considered to identify the mechanisms of groundwater evolution. Both hydrochemistry and isotopes versus depth show a three-part structure with boundaries around depths of 200 m and 600–750 m, which were assumed to be associated with the circulation depths of local and intermediate flow systems. After excluding C4 with highly variable water-types, three geochemical indicators (Cl/C0, SO4/C0, and the slope of (Ca2++Mg2+)−(Na+–Cl−)) imply that the processes of water–rock interaction for clusters C1, C2 and C3 include dissolution of halite and gypsum, weathering of feldspar, and ion-exchange. Moreover, it was found that C3 from local flow system, C1 from intermediate flow system, and C2 from regional flow system has increasingly higher concentrations of Cl− and lower values of Chloro-Alkaline index, which indicate increasingly higher degrees of dissolution and ion-exchange. This study not only reveals the mechanisms of groundwater evolution in the study area, but also provides a method to identify nested flow systems using hydrochemistry and isotopes.

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1. Introduction

Groundwater circulation, which is an important component of the hydrological cycle, is extremely complicated in a large-scale groundwater basin. Tóth (1963) found that basin-scale groundwater circulation has a hierarchically nested structure, i.e., local, intermediate, and regional flow systems could develop. Each flow system has its own recharge area, discharge area and circulation depth. The hierarchically nested flow systems have been found to be related to many geological, chemical and biological processes (Batelaan et al., 2003; Cardenas, 2007; Gleeson and Manning, 2008; Marchetti and Carrillo-Rivera, 2014; Tóth, 1999) because of the interaction between groundwater and its ambient environment.

The geochemical composition of groundwater is mainly controlled by such processes as weathering, dissolution, ion exchange, and evaporation (Appelo and Postma, 2005; Denning, 2002; Freeze and Cherry, 1979; Hiscock and Bense, 2014). Therefore, lithology and climate generally determine the water type. Even if lithology is similar, the travel distance and travel time determine the degree of water–rock interaction, thus the geochemical composition. Therefore, hydrochemistry provides an excellent indicator to identify the sources of groundwater from different aquifers (Adomako et al., 2011; Barth, 2000; Clouter et al., 2008; Currell et al., 2010; Demlie et al., 2007; Edmunds et al., 1982; Elliot et al., 1999; Fagundo-Castillo et al., 2008; Han et al., 2010; Kimbín, 1995; Montcoudiol et al., 2014; Portugal et al., 2005; Zhu et al., 2007) or the flow path from a recharge area to its corresponding discharge area (Adomako et al., 2011; Aji et al., 2008; Alconada-Magliano et al., 2011; Cartwright et al., 2004; Chen et al., 2004; Edmunds et al., 2006; Han et al., 2009; Herczeg et al., 1991; Mahlknecht et al., 2006; Montcoudiol et al., 2014).

According to Tóth's (1963) classic model, the lower reaches of a groundwater basin could be the discharge area of local,
In this study, the hydrochemistry of groundwater from wells with different depths in the discharge area are examined, and the depth-dependent characteristics of hydrochemistry are related to the different groundwater flow systems, which have different travel times, travel distances and circulation depths.

2. The study area

The Dosit River Watershed is a sub-basin of the Ordos Basin in Northwestern China. Its longitude is from 106°54′E to 108°16′E and its latitude is from 38°18′21″ to 39°36′06″N, occupying an area of 10,924 km² (Fig. 2). The elevation of the Dosit River Watershed decreases from 1300 to 1400 m above the sea level in the east to 1000–1100 m in the west. The watershed has a semi-arid to arid climate. The precipitation decreases from 340 mm/year in the southeast to 220 mm/year in the northwest, while the potential evaporation increases from 2400 mm/year in the southeast to 2700 mm/year in the northwest (Jiang et al., 2014; Yin et al., 2011).

The main aquifer of the watershed is the poorly consolidated Cretaceous sandstone with a thickness of 700–1000 m, which is overlain locally by Tertiary mudstones and extensively by thin unconsolidated Quaternary sediments. The Jurassic mudstone with coal mines, which underlies the Cretaceous sandstone, is generally assumed to be an aquiclude. The Cretaceous sandstone and the Quaternary sediments constitute the main aquifer system, which is a thick unconfined aquifer. Quartz, albite and feldspars are the main minerals in the Cretaceous sandstone, while gypsum, halite,
calcite, and dolomite also exist in minor quantities (Dong, 2005; Sun, 2010).

The Dosit River, which develops in the low-lying area of the watershed and flows from the east to the west, is mainly recharged by groundwater. In the discharge area of the upper reaches of the Dosit River, there are numerous wells operated by local residents for irrigation and drinking. Some shallow dug wells tap the Quaternary sediments and/or the shallow Cretaceous sandstone, with depths smaller than 10 m. Other wells were drilled into the Cretaceous sandstone and only cased in the shallow part, with maximum well depths ranging between tens of meters and several hundred meters. Many deep wells are flowing artesian wells, i.e., could flow out at the ground surface, at least seasonally.

3. Methods

3.1. Sampling and analysis

44 groundwater samples were collected from the wells in the upper reaches of the Dosit River in the summers of 2012 and 2013. The maximum depths of most wells without well records were told by local residents. Before sampling, electrical conductivity (EC), temperature, and pH were measured in the field. Hydrogeochemical components, Na⁺, K⁺, Mg²⁺, and Ca²⁺ were analyzed by inductively coupled plasma (ICP-900, Thermo), while Cl⁻, SO₄²⁻, and NO₃⁻ by ion chromatography (ICS-900, Dionex), CO₂⁻ and HCO₃⁻ by titration. All samples have been found to have a charge balance error within 10%. Stable isotopes of ¹⁸O and D were measured by isotopic liquid and vapor analyzer (L2120-L, Picarro) and were expressed in δ values with respect to the Vienna Standard Mean Ocean Water value.

3.2. Data treatment for multivariate statistical analysis

Multivariate statistical analysis of hydrogeochemical measurements has been widely used to classify groundwater and interpret evolution of groundwater (Clark and Fritz, 1997). The δD and δ¹⁸O of groundwater are mainly determined by the meteoric process, therefore, they can serve as a natural tracer for the origin of groundwater. However, both δD and δ¹⁸O vary regionally and over time because they could be influenced by temperature, which controls evaporation and condensation processes (Craig, 1961; Epstein and Mayeda, 1953).

The scatter plot of δD versus δ¹⁸O of groundwater samples from different clusters, whose shape displays the relative proportions major ions and whose size indicates the total concentrations, clearly shows the differences and similarities among clusters (Fig. 3b). C1 and C2 are quite similar on the cation side, with a domination of Na⁺ + K⁺, but differ in the anion side due to the much higher concentration of SO₄²⁻ in C2. The anion is dominated by HCO₃⁻, in C1, and by SO₄²⁻ in C2. According to Back (1966), C1 implies an early stage of groundwater evolution while C2 indicates a later stage.

C3 and C4 have a similar shape on the cation side, but a different shape on the anion side. Although C3 and C4 have nearly the same concentration of HCO₃⁻, C4 has much higher concentrations of SO₄²⁻ and Cl⁻, which are quite close to that of HCO₃⁻. Based on the trends of TDS, HCO₃⁻ and Cl⁻, C4 has a later stage of groundwater evolution than C3. It is difficult to relate C5, which has the highest concentrations of major ions, to other clusters. To sum up, based on the Stiff Diagram of different clusters, we find C1 has an earlier stage of groundwater evolution than C2, while C3 has an earlier stage of groundwater evolution than C4.

4.2. Deuterium and oxygen isotopes of different clusters

Environmental isotopes are increasing widely applied in hydrogeology (Clark and Fritz, 1997). The δD and δ¹⁸O of groundwater are mainly determined by the meteoric process, therefore, they can serve as a natural tracer for the origin of groundwater. However, both δD and δ¹⁸O vary regionally and over time because they could be influenced by temperature, which controls evaporation and condensation processes (Craig, 1961; Epstein and Mayeda, 1953).

The scatter plot of δD versus δ¹⁸O of groundwater is shown in Fig. 4. Note that the LMWL is calculated based on the rain data of cities nearest to the watershed given by Yin et al. (2011), not from the whole Ordos Plateau. Both G1 (including C1 and C2) and G2 (including C3, C4 and C5) are below the LMWL with G1 in the bottom left of the plot and G2 in the top right. The slope of G2 is 8.77, which is close to that of the LMWL with a slope of 7.81. This indicates that groundwater in G2 has close relation to recent precipitation.

Compared with G2, G1 is depleted in δD and δ¹⁸O. The slope of G1 is only 2.69, which is much smaller than that of the LMWL. In this case, the cross point of the fitted line of G1 and the LMWL indicates the isotopic composition of infiltrated rainwater (Clark and Fritz, 1997; Petrides et al., 2006). We infer that groundwater in G1 might be recharged during the cold climate and have undergone evaporation. The inference on the recharge time of G1 is supported by age measurements in borehole B2 (Fig. 2c) drilled especially for geological and hydrogeological exploration, which belongs to C2. The ages of groundwater sampled in the middle (297–773 m) and deep (777–954 m) sections of borehole B2 were measured to be 26,060 and 21,400 years (Jiang et al., 2012), which corresponds to the fourth glacial period.

Based on the relationship between δD and δ¹⁸O, we have inferred that groundwater in C1 and C2 was recharged much earlier than that in C3, C4 and C5. This is in accordance with the depths of wells. C1 and C2 are both from flowing artesian wells with deep depths, while C3, C4 and C5 are from non-artesian wells with shallow depths. Based on the water type and ratios of cations and anions, we had already found the relative evolution stages between C1 and C2, and between C3 and C4. Therefore, up to now, we can order the evolution stages of the four clusters, C1 through C4.
4.3. Mechanism of groundwater evolution

The Gibbs scheme (Gibbs, 1970), which shows the ratios of Na+/\text{(Na}+ \text{Ca}^{2+}) and Cl-/\text{(Cl}^- + \text{HCO}_3^-) against TDS, is an effective way to identify the mechanisms controlling water chemistry of a region, such as precipitation, rock, and evaporation. As shown in Fig. 5, nearly all groundwater samples are located in the rock dominance section. The only exception is the two samples in C5 with high TDS (1569.9 and 2334.8 mg/L, respectively), which is located in the evaporation dominance. However, the isotopic information of C5 does not support the possible mechanism of evaporation. Note that the two wells of C5 are both shallow dug well with depths of 4 m and 10 m. In the current study, C5 is considered to be abnormal and is not discussed.

In this sub-section, the mechanisms controlling groundwater chemistry in C1, C2, C3 and C4 are discussed from the hydraulic and geochemical perspectives.

4.3.1. Circulation depths of different flow systems

In the hydraulic view, the degree of water–rock interaction is dependent on the residence time of groundwater. Jiang et al. (2010, 2012) modeled the spatial distribution of groundwater age (similar to residence time) in basins and established the relationship between flow systems and groundwater age. In the lower reaches, groundwater is young in local flow systems with shallow circulation depth, and is old in regional flow system with deep circulation depth. Therefore, circulation depth, which is closely related to groundwater age, could be considered as an indicator of the degree of water–rock interaction.

The plot of hydrochemistry versus depth is effective in characterizing depth-dependent hydrochemistry (Carrillo-Rivera et al., 2007). TDS and pH are two comprehensive indicators of
hydrochemistry. Although wide ranges of pH and TDS are shown, with pH ranging from 7.3 to 9.3 and TDS ranging between 204.91 and 1029.58 mg/L, we noticed a three-part vertical structure with boundaries around depths of 200 and 600 m (Fig. 6). The mean values of TDS in the shallow (<200 m), middle (between 200 and 600 m) and deep (>750 m) parts are 674.2 mg/L, 316.7 mg/L, and 623.2 mg/L, respectively. The mean values of pH in the three parts are 8.0, 8.9 and 8.8, respectively. Therefore, the middle part has the lowest TDS and the highest pH.

Moreover, there are different trends in different parts. For TDS, it decreases with depth in the shallow part, keeps almost constant with depth in the middle part and increases with depth in the deep part. All cation and anion, except for HCO$_3^-$ and Mg$^{2+}$ in the deep part, have similar trends. HCO$_3^-$ in the deep part has a trend of depth-decreasing, while Mg$^{2+}$ in the deep part changes little with depth (Fig. 6).

A three-part structure could also be observed when plotting $\delta^{18}$O and $\delta$ D versus depth (Fig. 7). For $\delta^{18}$O, it varies between $-9.35\%$ and $-6.98\%$ in the shallow part, between $-11.44\%$ and $-9.56\%$ in the middle part, and between $-11.32\%$ and $-10.56\%$ in the deep part. The mean values of $\delta^{18}$O in the shallow, middle and deep parts are $-8.46\%$, $-9.89\%$ and $-10.88\%$, respectively. For $\delta$ D, it changes between $-78.74\%$ and $-52.88\%$ in the shallow part, between $-87.50\%$ and $-79.3\%$ in the middle part, and between $-86.30\%$ and $-84.54\%$ in the deep part. The mean values of $\delta$ D in the three parts are $-67.79\%$, $-80.99\%$ and $-85.45\%$, respectively. Both $\delta^{18}$O and $\delta$ D show a depth-decreasing trend.

As shown in Figs. 6 and 7, the three-part structure of both hydrochemistry and isotopes is closely related to the results of hierarchical cluster analysis. We found C3 and C4 are located in the shallow part, C1 is mainly located in the middle part, and C2 is located in the deep part. Due to the circulation depths of different flow systems, we infer that the depth 200 m represents the maximum circulation depth of local flow systems in the discharge area, and the depth range 600–750 m represents the maximum circulation depth of intermediate flow systems in the discharge area. Therefore, samples in C2 are mainly from regional flow systems, in C1 are mainly from intermediate flow systems, while in C3 and C4 are mainly from local flow systems.

### 4.3.2. Chemical indicators of water–rock interaction

In the geochemical view, the processes or degree of water–rock interaction can be represented by the water type or the concentrations of specific ions. Here, we first use the water type to exclude C4, whose mechanism of evolution is different from that of C1, C2 and C3, then use three indicators to identify the processes and degrees of water–rock interaction in C1, C2 and C3.

Although C3 and C4 are both located in the shallow part, and their mean concentrations of HCO$_3^-$ are close enough, they differ greatly in water type. C3 is dominated by HCO$_3^-$, while C4 is dominated by Cl$^-$, and 3 are dominated by SO$_4^{2-}$, showing variable water types. The TDS, as well as Cl$^-$ and SO$_4^{2-}$ of C4 are much higher than those of C3. The high Cl$^-$ and SO$_4^{2-}$ could be resulted from dissolution of halite and sulfate minerals in the shallow part, which is quite common in the shallow parts in arid areas due to high evaporation (Schwartz and Zhang, 2003).

In strata with siltstone and shale, where Cl$^-$ is present in soluble minerals occurring in only trace amounts, flowing groundwater could gain Cl$^-$ along the flow path (Freeze and Cherry, 1979). Moreover, chloride is as an inert element and seldom took part in geochemical reactions. Therefore, the increases in Cl$^-$ along the flow path could be recognized as an indicator of groundwater residence time (Hiscock and Bense, 2014). The mean concentrations of Cl$^-$ in C3, C1, and C2 are 41.8 mg/L, 47.0 mg/L, and 66.3 mg/L, which well corresponds to the increasingly longer flow distances and residence times in local, intermediate and regional flow systems. Moreover, there is a clear trend of increasing Cl$^-$ with depth in C2, which belongs to regional flow systems. C2 also shows a depth-increasing trend of SO$_4^{2-}$ and Ca$^{2+}$, which might be a result of dissolution of trace gypsum in the deep part of the sandstone aquifer.

The plot of (Ca$^{2+}$ + Mg$^{2+}$) – (SO$_4^{2-}$ + HCO$_3^-$) against (Na$^+$ – Cl$^-$) could be employed to evaluate the role of water–rock interaction on hydrochemistry (Ma et al., 2014). If the relation between these
two parameters is linear with a slope of $-1.0$, silicate mineral weathering and ion exchange are significant in controlling geochemical composition. In our study area, the slope is found to be $-1.03$ (Fig. 8), which is very close to $-1.0$. Therefore, groundwater in C1, C2 and C3 could have been influenced by weathering of silicate minerals and ion exchange.

The degree of ion exchange, which is an important process influencing groundwater chemistry, can be quantified by the Chloro-Alkaline (CA) indices (Schoeller, 1965). CAI-1 is defined as the ratio of $[\text{Cl}^- - (\text{Na}^+ + \text{K}^+)]$ to $\text{Cl}^-$. A negative CAI-1 indicates that the ion-exchange takes place between $\text{Ca}^{2+}$ or $\text{Mg}^{2+}$ in the groundwater and $\text{Na}^+$ in the aquifer medium, while a positive CAI-1 indicates that the ion-exchange occurs between $\text{Na}^+$ in the groundwater and $\text{Ca}^{2+}$ or $\text{Mg}^{2+}$ in the aquifer medium. Moreover, the larger the absolute value of CAI-1, the higher the degree of ion-exchange. We found CAI-1 is below zero in all groundwater.

Fig. 6. The depth-dependent hydrochemistry. (a) TDS; (b) pH; (c) Cl$^-$; (d) HCO$_3^-$; (e) SO$_4^{2-}$; (f) Na$^+$; (g) K$^+$; (h) Ca$^{2+}$; and (i) Mg$^{2+}$.
samples in C1, C2 and C3 (Fig. 9), indicating that Na\(^+\) is released from the aquifer medium through the process of ion-exchange. The mean values of CAI-1 in C3, C1 and C2 are found to be \(/C_0\) 1.34, \(/C_0\) 1.57 and \(/C_0\) 1.98. This trend shows an increasingly stronger degree of ion-exchange in C3, C1 and C2, which corresponds to local, intermediate and regional flow systems.

5. Conclusion

Using hierarchical cluster analysis, 44 groundwater samples collected from wells with different depths in the discharge area of a river basin were classified into five clusters. The relationship between \(\delta\) D and \(\delta^{18}O\) shows that C1 and C2 were recharged during the cold climate, while C3, C4 and C5 were recharged recently. The characteristics of hydrochemistry and relative evolution stages were examined using the Stiff Diagram.

Based on the Gibbs scheme, four clusters were found to be caused by water–rock interaction. From the hydraulic perspective, the different characteristics were caused by the differences in travel time and travel distance among flow systems, which determine
the degree of water–rock interaction. Based on the three-part vertical structure of hydrochemistry and isotopes, C3 and C4 were assumed to be from local flow systems with circulation depths within 200 m; C1 was assumed to be from intermediate flow systems with circulation depths ranging between 200 m and 600–750 m; while C2 was assumed to be from regional flow systems with circulation depths greater than 750 m. The geochemical processes and degree of water–rock interaction of each cluster were also examined. Based on the highly variable water type in C4, it was assumed that the high Cl− and SO42− in C4 were resulted from dissolution of halite and sulfate minerals in the shallow part caused by high evaporation. After excluding C4, such indicators as Cl−, SO42−, the slope of (Ca2+ + Mg2+) / (SO42− + HCO3−) versus (Na+ − Cl−) imply that the geochemical processes for clusters C1, C2 and C3 include dissolution of halite and gypsum, weathering of feldspar, and ion-exchange. The increasingly higher concentrations of Cl− and lower values of CAI-1 in C3, C1 and C2, which indicate the increasingly stronger degree of water–rock interaction, are in accordance with the increasingly longer travel times from the order of local, intermediate and regional flow systems in the discharge area. This study enhances the understanding on the pattern of groundwater circulation and geochemical evolution in the study area. Moreover, the methodology used in the current study is fundamental to interpret the complicated distribution of hydrochemistry and isotopes, C3 and C4 were the shallow part caused by high evaporation. After excluding C4, the increasingly stronger degree of water–rock interaction, are in accordance with the increasingly longer travel times from the order of local, intermediate and regional flow systems in the discharge area.

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References


