Surface Water–Groundwater Interaction in the Guanzhong Section of the Weihe River Basin, China

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Abstract

As a crucial agricultural and economic development zone since the Qin Dynasty (221 to 206 BC), the Guanzhong section of the Weihe River basin is facing serious water resource shortages due to population growth and regional development. Its water resource amount per capita is only 361 m³, about 1/6 of the average in China and less than 1/20 of the average in the world. Surface water and groundwater (SW-GW) interaction, having a significant influence on the spatiotemporal distribution of water resources, was qualitatively and quantitatively investigated during a wet year based on stable isotopes and hydrochemistry. The results show that the recharge pattern in the north part varies with season, that is, 40% of the surface water recharge comes from groundwater in the dry season, but 93% of the groundwater recharge comes from surface water in the rainy season. In the south part, groundwater is always recharged by surface water, with contributions of 47% and 61% in the rainy and dry seasons, respectively. For the main stream, the recharge pattern is complicated and varies with season and site. This study will provide useful information about SW-GW interaction at basin scale. Integrated management of groundwater and surface water could improve the efficiency of regional water resources utilization and promote accurate and sustainable water management in the semi-arid basin.

Introduction

Despite its abundance on the Earth, water does not always occur at the time, in the place or in the form desired (Sophocleous 2002a). The uneven distribution of water resources seasonally and spatially is the primary cause of water shortages which have been a bottleneck restricting the economic and social development, especially in semi-arid regions (Oki and Kanae 2006; Liu et al. 2013). Additionally, the non-uniformity of water resources strongly affects water exchange and hydrological cycle (Oki and Kanae 2006). Surface water and groundwater are not isolated components of the hydrological system.
(Kumar et al. 2009) but are viewed as linked components of hydrologic processes (Simplicio 2002a; Kumar et al. 2009; Guzmán et al. 2016). Surface water bodies, such as streams, lakes and reservoirs, interact with groundwater in different ways and at different sites, and their interaction is of great importance in the hydrologic processes of river basins (Song et al. 2006; Allen et al. 2010; Guzmán et al. 2016). Thus, the water quality and quantity in hydrological zones will be significantly affected by their interactions, because the development of one is bound to have an influence on the other (Kalbus et al. 2006; Kumar et al. 2009). Moreover, both surface water and groundwater are critical water sources for agricultural irrigation and drinking water in semi-arid areas, both in China and worldwide (Zhang et al. 2013c). Therefore, integrated management of groundwater and surface water will help decision-makers take scientific and reasonable measures to avoid problems that arise from managing one resource at the expense of the other or allocating the same water twice.

The Guanzhong section of the Weihe River basin is located in a semi-arid area in Shaanxi Province, China, and it has supported significant agriculture since the Qin Dynasty. Today, this area is still designated as a state key economic development zone and has a significant influence on the economic development of its surrounding areas (Du and Shi 2012). However, natural factors and human activities have led to many environmental problems over the past 50 years, such as the shortage of water resources, the aggravation of water pollution, and the degradation of vegetation (Zuo et al. 2014). Water shortages are especially noted problems, which have become a major social and economic challenge to sustainable development of the basin (Song et al. 2006; Du and Shi 2012; Zhao et al. 2015). Meanwhile, with the dramatic increase of human activities in recent years, both patterns and fluxes of surface water-groundwater (SW-GW) interaction have undergone considerable changes, such as an increase in water pollution and a decline in groundwater levels (Li et al. 2013). The Weihe River has experienced runoff declines as large as 35% in the last century (Chang et al. 2015). Moreover, some tributaries, such as the Hengshui River, have experienced flow cutoff in recent years. Due to the increase in population and agricultural activities, the increasing demand for water intensifies the conflict between the population and the watershed with 444 persons/km² (Du and Shi 2012; Chang et al. 2015). Approximately 85% of the water supply for the Guanzhong section, with a population of 22 million, is derived from the Weihe River, and agricultural irrigation is the largest water consumer, representing 60% of the total amount of water consumption, which is withdrawn from the river and aquifer (Song et al. 2015). The chemical properties of water change, and contaminants spread, because of SW-GW interaction. Due to the vital importance of water, especially in economic, cultural and environmental contexts, SW-GW interaction has a critical role in determining rational water resource utilization schemes and regional sustainable development (Kumar et al. 2009).

A wide range of approaches, such as isotopic tracer methods (Lambs 2004; Paces and Wurster 2014), hydrochemical methods (Malcolm et al. 2005), thermal methods (Kalbus et al. 2006; Guzmán et al. 2016), Darcy’s law methods (Song et al. 2016), and multivariate statistical techniques (Kumar et al. 2009), have been developed to study the SW-GW interaction at various spatial and temporal scales. Hydrochemical parameters such as major ions (Ca²⁺, Na⁺, K⁺, Mg²⁺, CO₃²⁻, HCO₃⁻, SO₄²⁻, Cl⁻) and electric conductivity (EC), have been well-used as tracers to determine the relationship between surface water and groundwater (Song et al. 2006). As a significant tracer, EC is closely related to the concentration of dissolved ions and is widely used to investigate hydrochemical features and even to trace hydrological processes because conductivity differs among water sources (Peng et al. 2014; Khalil et al. 2015). Surface waters and local ground waters commonly differ substantially with respect to their ionic strength (Harvey et al. 1997). Groundwater typically has greater total dissolved solids than surface water and has greater ionic strengths and higher EC, because groundwater experiences more intensive water-rock interactions and thus dissolves more ions in groundwater flow (Lee and Dal Bianco 1994). Moreover, on the basis of the conservative behavior in water and the large variability of their isotopic ratios ^2H/^1H and ^18O/^16O (Mook and Rozanski 2000), the stable hydrogen and oxygen isotopes of waters are commonly used as natural tracers to study the hydrological cycle (Gat et al. 1994; Telmer and Veizer 2000; Gibson and Edwards 2001; Mills et al. 2011), especially with respect to SW-GW interaction (Negrel et al. 2011; Wassenaar et al. 2011; Qin et al. 2011a; Paces and Wurster 2014). Each of the methods has advantages and drawbacks, so multiple approaches combining different techniques are recommended to reduce their individual uncertainties (Kalbus et al. 2006; Allen et al. 2010; Guzmán et al. 2016). The integration of hydrochemical and isotopic methods is useful to understand complex hydrological processes (Abid et al. 2012; Bagheri et al. 2014; Li et al. 2015; Sun et al. 2016) and has been chosen to elucidate the SW-GW interaction in this study.

A large number of studies in hydrology and water resources have been performed in the Weihe River basin (Ma et al. 2007; Zhao et al. 2015; Yu et al. 2016). However, there are notably few specific and explicit studies of SW-GW interaction, especially for the quantitative evaluation of the SW-GW interaction in the Guanzhong section of the Weihe River basin. In addition, this study is focused on the basin scale, not just a single tributary. The objectives of this study are to integrate hydrochemical and isotopic methods to (1) characterize the seasonal and spatial signatures of hydrochemistry and isotopes of surface water and groundwater and (2) qualitatively and quantitatively investigate the spatiotemporal patterns of SW-GW interaction. Thus, this study will provide basic...
information about the more quantitative evaluation of SW-GW interaction for local hydrologic research at the basin scale that can improve the accuracy of regional water resource utilization and promote sustainable water management in semi-arid basin.

**Study Area**

The study area is located at approximately 32.77°–36.09°N and 105.86°–111.55°E in the middle of Shaanxi Province, China (Figure 1). This region experiences a temperate continental monsoon climate with an annual average rainfall of 573 mm (Du and Shi 2012). Approximately 78% of the rainfall is concentrated from May to October. The annual average temperature is approximately 13.3 °C (Song et al. 2015). The potential annual evapotranspiration ranges from 770 to 1100 mm (Zhao et al. 2013) and the actual annual evapotranspiration range from 491 to 571 mm in the Guanzhong area (Mei et al. 2012). Topographically, the study area is surrounded by the Tsinling Mountains to the south and the Loess Plateau to the north. The Loess Plateau is covered by Quaternary loess and loess-like deposits and is the main source of sediments in the river. The Tsinling Mountains contain massive water reserves and supply plentiful water resources to the Weihe River.

As the largest tributary of the Yellow River, the Weihe River flows for approximately 502.4 km with a drainage area of 6.71 × 10⁴ km² in the Shaanxi Province where the well-known Guanzhong Basin is located (Zhao et al. 2015). The values of the catchment area, annual runoff and annual sediment load of the Weihe River account for 17.9%, 16.5%, and 2.5% of the total amount of the Yellow River basin, respectively (Li et al. 2013). The temporal and spatial distribution of the runoff in this basin is uneven: more than 70% occurs in the southern tributaries and less than 30% occurs in the northern tributaries; approximately 75% of the total annual runoff is concentrated from May to October (Zhao et al. 2013). The Weihe River basin has an asymmetrical catchment with well-developed and high drainage density along the northern bank but low drainage density along the southern bank. Along the northern bank, tributaries flowing through the Loess Plateau have long channel lengths, shallow stream gradients, and high sediment concentrations due to heavy storms in the flood season, easily eroded loess soils and low vegetation cover. Numerous southern tributaries originate from the northern foot of the Tsinling Mountains, which is the natural boundary between south and north China. These tributaries carry a large quantity of sand and gravel or cobble into the Weihe River (Chen et al. 2014) and are characterized by straight channels, short lengths, steep gradients and large flow velocities.

**Materials and Methods**

A total of 31 sites were studied including nine sites in the main stream of the Weihe River, 11 sites in the south part (the southern bank of the Weihe River) and 11 sites in the north part (the northern bank of the Weihe River) (Figure 1). During each investigation, surface water samples were taken in the river, and groundwater samples were taken from irrigation or domestic wells in the vicinity of the surface water sampling sites. These were taken as the reference for the local groundwater. The depth of the wells and the elevation of the mouth of the well were also recorded as well (Table S1, Supporting Information). The groundwater table was calculated by subtracting the groundwater table depth from the elevation of the mouth of the well (Figure 1b). However, the set of groundwater table depth data is old (1979) and cannot represent the recent groundwater table. Therefore, SW-GW interaction was investigated by the stable isotopic method and hydrochemical method instead of using groundwater table data. A total of 124 water samples, including 62 surface water samples and 62 groundwater samples, were collected in October 2014 (autumn) and January 2015 (winter). In the Guanzhong section, 80% of the precipitation is concentrated from June to October (Chang et al. 2015). Thus, the samples collected in October and January were chosen to represent the rainy season and dry season. The annual precipitation amount of 682 mm in 2014 was calculated by averaging the annual precipitation values from all stations in the Guanzhong section (Bureau of Hydrology-Ministry of Water Resource 2015), and it is higher than the average annual precipitation in this region of 573 mm (Du and Shi 2012). Therefore, this study focuses on the GW-SW interaction in different parts of the Guanzhong section during the rainy and dry seasons of a wet year. The inverse distance weighted (IDW) interpolation method in ArcGIS 10.1 was used to produce the contour lines of annual water surface evaporation and annual precipitation in the study area for 2014 by interpolating the surface evaporation data from 19 stations and the precipitation values from 266 stations in the Guanzhong section of the Weihe River basin and its surrounding areas (Bureau of Hydrology-Ministry of Water Resource 2015).

A portable GPS was used to record the geographical locations and elevations of sampling sites. A HACH HQ40d portable multi-parameter water analyzer was used to measure EC, pH, dissolved oxygen (DO), and oxidation-reduction potential (ORP) (Table S1). Water samples were packaged in 2.5 L HDPE bottles, and they were taken back to the laboratory and stored in a refrigerator at 4 °C until they were analyzed. The major cations (Ca²⁺, Mg²⁺, Na⁺, and K⁺) in the water samples were analyzed with an inductively coupled plasma-optical emission spectrometer (PerkinElmer, ICP-OES 5300DV). The anions SO₄²⁻ and Cl⁻ were measured using an auto discrete analyzer (Clever Chem200). The HCO₃⁻ and CO₃²⁻ anions were determined by acid-base titration. The δD and δ¹⁸O values of all water samples were measured with a liquid water isotope analyzer (DLT-100, Los Gatos Research Inc., United States) in the Key Laboratory of Water Cycle and Related Land Surface Processes of the Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing, China.
Isotopic results were reported as delta values relative to the Vienna Standard Mean Ocean Water (V-SMOW) with a precision of ±0.2‰ for δ\(^{18}\)O and ±1.0‰ for δD. The isotopic and chemical data are presented in Table S2.

**Results and Discussion**

**Isotope Composition**

The relationship between δ\(^{18}\)O and δD is plotted in the δD/δ\(^{18}\)O diagram, with the global meteoric water line (GMWL) and local meteoric water line (LMWL) (Figure 2) being defined as δD = 8 δ\(^{18}\)O + 10 (Craig 1961) and δD = 7.49 δ\(^{18}\)O + 6.13 (\(R^2 = 0.92\)), respectively. The calculated LMWL is based on the isotope composition of meteoric waters from the Xi’an station (in the Guanzhong section of the Weihe River basin) of the Global Network for Isotopes in Precipitation (GNIP) of the International Atomic Energy Agency (IAEA/WMO, http://www-naweb.iaea.org/) from 1985 to 1993. Depending on the local climatic conditions, the slope of the regression line between the δ\(^{18}\)O and δD
Figure 2. The plot of δ\(^{18}\)O-δD of the SW (surface water) and GW (groundwater) of three parts (the north part, the south part, and the main river) in (a) autumn and (b) winter.

composition of precipitation varies with regions (Hoefs 2009; Zhang et al. 2013a). The slope of the LMWL is smaller than the GMWL, indicating the precipitation in the study area experiences strong evaporation. Most of the sampling points fall below the LMWL, although certain isotopic sample points of the surface water and groundwater fall close to the LMWL, suggesting that the waters in the study area experience strong evaporation after they are recharged by precipitation.

The mean isotope composition of precipitation in autumn is more enriched (in heavy isotopes) than in winter. The mean isotope composition of groundwater is close to that of precipitation and shows similar seasonal variation to precipitation. This indicates that groundwater is mainly recharged by precipitation, and the origin of seasonal variation of groundwater is close to the seasonal variations in precipitation (Table 1 and Figure 3). For surface water, the mean isotope composition of δ\(^{18}\)O and δD and the mean EC values in autumn are close to those in winter. (Table 1 and Figure 3). None seasonal variation of isotopic and EC values in surface water indicates the surface water in winter has limited water source recharge from precipitation. However, in winter, the isotopes of surface water are more enriched than groundwater, indicating surface water experiences strong evaporation. Therefore, for surface water in winter, evaporation has a more significant influence on the isotope composition than precipitation. In autumn, the isotope composition of surface water is closer to groundwater and more depleted than precipitation, and the EC value of surface water is lower than groundwater. Therefore, it can be deduced that groundwater is mainly recharged by surface water in autumn. These seasonal SW-GW recharge relationships described above are in accordance with research by Tian (2003).

Surface water samples, collected from three parts of the Guanzhong section of the Weihe River basin in two seasons, display positive isotope values in the north part, intermediate isotope values in the main stream and negative isotope values in the south part (Figure 2), indicating different recharge sources. For the north part, most of the surface water samples fall below the LMWL, indicating evaporation of the surface water. The isotope composition of surface water is more depleted than groundwater in autumn and is more enriched than groundwater in winter (Figure 2). The isotopic composition of surface water and groundwater samples in the south part and the main stream is distributed along the LMWL (Figure 2), and there is little difference between surface water and groundwater, suggesting that surface water has a close relationship with groundwater in the south part and the main stream. For the south part, the stable isotopes of surface water are more depleted than groundwater in both seasons (Figure 2), indicating the same recharge pattern in autumn and winter. For the main stream, the stable isotopes of surface water are more enriched than groundwater at sites T2, T6, and T9 but more depleted than groundwater at sites T1, T3, T5, and T8 in both autumn and winter. These results indicate the same recharge pattern at these sites during the two seasons. The stable isotopes of surface water in winter are more depleted than groundwater but more enriched than groundwater in autumn at site T4 (Figure 4d to 4e), indicating the opposite recharge pattern in autumn and winter.
Table 1: The Average Value of δ¹⁸O, δD, and EC in Autumn and Winter in the Guanzhong Section

<table>
<thead>
<tr>
<th>Water Type</th>
<th>Season</th>
<th>δ¹⁸O (‰)</th>
<th>δD (‰)</th>
<th>EC (µS/cm)</th>
<th>Season</th>
<th>δ¹⁸O (‰)</th>
<th>δD (‰)</th>
<th>EC (µS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface water</td>
<td>Autumn</td>
<td>−8.94</td>
<td>−63.60</td>
<td>945</td>
<td>Winter</td>
<td>−8.98</td>
<td>−64.59</td>
<td>1053</td>
</tr>
<tr>
<td>Groundwater</td>
<td>Autumn</td>
<td>−8.82</td>
<td>−63.61</td>
<td>1308</td>
<td>Winter</td>
<td>−9.49</td>
<td>−67.69</td>
<td>1060</td>
</tr>
<tr>
<td>Precipitation</td>
<td>Autumn</td>
<td>−8.51</td>
<td>−59.75</td>
<td></td>
<td>Winter</td>
<td>−9.47</td>
<td>−62.94</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3. The precipitation, water surface evaporation, and stable isotopes in the Guanzhong section.

A steady state with a moderate fluctuation of the isotope composition is maintained along the main stream (Figure 4d to 4e). Both surface water and groundwater isotope composition are increasingly depleted in the north part (Figure 4a to 4b) with significant fluctuations with the decrease in distance to the river mouth. In contrast, the isotope composition of surface water and groundwater is increasingly enriched in the south part (Figure 4h to 4i) with slight fluctuations with the decrease in distance to the river mouth. In addition, most of the groundwater parameters covary with those of surface water parameter in the north part and the south part, indicating intensive SW-GW interaction.

Three important factors can affect the spatial distribution of isotopes in the Guanzhong section of the Weihe River basin including climate features, such as the spatial variation of precipitation and evaporation, drainage characteristics of the Weihe River and human activities. Precipitation decreases, but evaporation increases from the south part to the north part of the basin (Figure 5). Thus, the surface water isotopes of the north part are more enriched than that of the south part and the main stream because of inadequate precipitation but higher evaporation in winter in the north part (Figure 5). Moreover, large differences in the drainage characteristics of the river exist between the north part and south part. The south tributaries flow out from the Tsinling Mountain area with a short flowpath and later drain into the main stream. The north tributaries flowing through the Loess Plateau are characterized by their long flowpath and large drainage density; thus, isotopes of water in the north part are more enriched than those in the south part due to experiencing more evaporation. Because there is a mixture of surface water from the north and south tributaries that has different isotopic compositions, the isotopic composition of surface water along the main stream is intermediate. Human activities are also an important factor impacting water isotopic compositions in the Weihe River basin. People use river water by establishing irrigation projects to meet their agricultural irrigation needs. To protect people and crops from flood hazards, reservoirs and dams are built to control the flow in different river reaches and seasons. All of these activities can directly or indirectly result in isotope composition variations in water.

Hydrochemistry

Table 2 summarizes the major chemical components of the surface water and groundwater during different seasons in the Guanzhong section. Statistical data such as minima, maxima, and means are presented in Table 2. The average pH of water in winter (7.88) is higher than that in autumn (7.78), and the average pH of surface water (7.89) is higher than that of groundwater (7.77). The groundwater has higher EC than surface water in autumn, which may be attributed to lixiviation (Zhang et al. 2013a). The mean EC value of groundwater (1060 µS/cm) in winter is close to that of surface water (1053 µS/cm) (Table 1), indicating a close relationship between the two in winter. In general, the water in this basin is fresh because most of the total dissolved solids (TDS) values are less than 1000 mg/L (Table 2).

The three major mechanisms controlling global surface water chemistry include atmospheric precipitation, rock dominance, and the evaporation-crystallization process (Gibbs 1970). The chemical composition of surface water and groundwater samples in three parts of the Guanzhong section are plotted in the Gibbs diagram (Figure 6). Most samples from the north tributaries and the main stream with high TDS and a Na/(Na + Ca) ratio greater than 0.5 predominantly fall within the evaporation-crystallization dominance area. This property can be illustrated by the strong evaporation in the main stream and north part, as presented in Figure 5. The south tributary samples, with low TDS and a Na/(Na + Ca) ratio less than 0.5, predominantly fall in the rock dominance area (Figure 6). The waters in the south tributaries flowing through the mountainous area experience rock-water interactions and the dissolved ions are controlled by rock weathering.
In the south part of the Guanzhong section, groundwater has the same dominant hydrochemical pattern of HCO₃⁻-Ca in autumn and HCO₃⁻•SO₄²⁻-Ca in winter with surface water (Figure 7a to 7d). The EC values of most groundwater samples are close to those of surface water samples, and the stable isotopes of surface water are more depleted than groundwater in both seasons. Therefore, groundwater recharge by surface water in the rainy and the dry seasons can be deduced in the south part. The groundwater in both seasons shows more SO₄²⁻ than surface water, which is mainly from the dissolution of gypsum and anhydrite (Sun et al. 2014), indicating the groundwater experiences water-rock interactions. Located in the northern piedmont of the Tsinling Mountains, the south part has abundant rainfall and the runoff in this area accounts for 70% of the total runoff of the Weihe River basin (Sun et al. 2013). The southern tributaries flow through metamorphic rock type fissured water-bearing formation, magmatic rock type fissure-karst water-bearing formation, and loose sediment type pore water-bearing formation (Figure 1). The first two water-bearing formations are characterized by laminar distributions, poor water-bearing properties and water permeability, while the third one consists of sand gravel and gravel-cobble of the Quaternary pluvial phase (Tian 2003), so groundwater can be directly recharged by precipitation and river seepage water at the same time. The hydrochemical patterns of samples S12, S13, S14, and S15 in autumn are similar to those in winter with similar patterns of HCO₃⁻•SO₄²⁻-Ca and SO₄²⁻•HCO₃⁻-Ca for S12 and S13, respectively, and similar patterns of HCO₃⁻-Ca•Na for S14 and S15 (Figure 7c to 7d). These patterns illustrate that the recharge pattern between surface water and groundwater at these sites may be the same in autumn and winter. The same hydrochemical patterns can be seen in groundwater samples S10, S11, S17, and S18 with HCO₃⁻-Ca in autumn and HCO₃⁻•SO₄²⁻-Ca in winter (Figure 7c to 7d). Site S20 is located in a stream where there is a nearby upstream poultry farm and the water runs slowly because of the lush aquatic vegetation on the riverbed and riverbank; therefore, duck feces can stagnate in the stream. Thus, salinity accumulates in the river water with higher chloride contents from fecal inputs (Figure 7a). However, in the groundwater at this site, the chloride content does not increase with that of the river water, and the calcium content is higher than the surface water in autumn (Figure 7a and 7c).

The north part can be divided into two smaller areas by different hydrochemical patterns: the western area (sites N21, N22, N23, N24, N25, N26, and N27) of the Jinghe River, and the eastern area (sites N28, N29, N30, and N31) of the Jinghe River. For the western area, HCO₃⁻-Na•Ca is the dominant hydrochemical pattern of surface
water and groundwater in autumn and winter (Figure 7a to 7d). For the eastern area, the surface water and groundwater in autumn are dominated by the hydrochemical pattern of $\text{HCO}_3$•$\text{SO}_4$-Na and $\text{SO}_4$-Na, respectively. The groundwater has the same dominant hydrochemical pattern of $\text{SO}_4$-Na as surface water in winter (Figure 7c to 7d). In addition, the isotope composition of surface water is more depleted than groundwater in autumn and is more enriched than groundwater in winter, indicating groundwater is recharged by surface water in autumn and surface water is recharged by groundwater in winter. The combination of the unobstructed surface water runoff and rough particle matter in the soil leads to high water permeability (Jiang 2002), which generates low mineralization water in the western area. The eastern area is characterized by low relief topography with a small groundwater hydraulic gradient and slow groundwater runoff in this loess platform and alluvial-pluvial fan region (Sun et al. 2014). There are continental evaporites in the eastern area such as carbonates, sulfates (He et al. 2014). $\text{SO}_4^{2-}$ is mainly from the dissolution of gypsum and anhydrite because of the increasing saturation index of the gypsum and anhydrite with the increase in $\text{SO}_4^{2-}$ concentration (Sun et al. 2014). The coal water in the northern bank of the Weihe River basin increases the sulfide in groundwater. According to the molar ratio of $r\text{Cl}/r\text{Na}$, most of the values are less than 1 (Table 2). If halite dissolution were responsible for the sodium, the $r\text{Cl}/r\text{Na}$ molar ratio should be approximately one. The lower $r\text{Cl}/r\text{Na}$ ratio indicates that the excess $\text{Na}^+$ is attributed to silicate weathering rather than halite (Tiwari and Singh 2014; Hussien and Faiyad 2016). Furthermore, fruits (apple, pear, and peach) and crop (winter wheat and corn) farming are the two main agricultural production patterns in the north part. A large quantity of manure and inorganic fertilizers, such as potassium chloride, ammonium chloride, potassium sulfate, and ammonium sulfate, is applied to fruit trees and crops. Then irrigation water and heavy rain dissolve the unabsorbed fertilizers and farmyard manure and transport them into the river, or they infiltrate into the groundwater, eventually leading to higher $\text{Na}^+$ and $\text{SO}_4^{2-}$ concentrations in the water.

The surface water and groundwater in the main stream are dominated by the hydrochemical patterns of $\text{HCO}_3$•$\text{SO}_4$-Na•Ca in autumn and $\text{SO}_4$•$\text{HCO}_3$-Na•Ca in winter (Figure 7a to 7d). Combining the features of stable isotopes revealed that surface water was recharged by groundwater at sites T2, T6, and T9 but that groundwater was recharged by surface water at sites T1, T3, T5, and T8 in both seasons. Furthermore, groundwater was
Table 2
Statistical Summary of Chemical Data of Surface Water (the First Part) and Groundwater (the Second Part) Samples in Guanzhong Section

<table>
<thead>
<tr>
<th>Season</th>
<th>Location</th>
<th>The North Part</th>
<th>The Main Stream</th>
<th>The South Part</th>
<th>The North Part</th>
<th>The Main Stream</th>
<th>The South Part</th>
<th>The North Part</th>
<th>The Main Stream</th>
<th>The South Part</th>
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<td></td>
<td>Parameters</td>
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<td>Mean</td>
<td>Range</td>
<td>Mean</td>
<td>Range</td>
<td>Mean</td>
<td>Range</td>
<td>Mean</td>
<td>Range</td>
</tr>
<tr>
<td></td>
<td>TDS (mg/L)</td>
<td>361–1562</td>
<td>926</td>
<td>605–876</td>
<td>768</td>
<td>125–694</td>
<td>412</td>
<td>434–1832</td>
<td>1211</td>
<td>598–1439</td>
</tr>
<tr>
<td></td>
<td>rCl/rNa</td>
<td>0.4–1.1</td>
<td>0.6</td>
<td>0.6–4.8</td>
<td>1.2</td>
<td>0.1–1.6</td>
<td>0.7</td>
<td>0.4–0.8</td>
<td>9.3</td>
<td>0.5–0.7</td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>7.7–8.3</td>
<td>8.0</td>
<td>7.7–8.1</td>
<td>7.8</td>
<td>7.2–8.3</td>
<td>7.8</td>
<td>3.2–9</td>
<td>7.7</td>
<td>7.1–8.9</td>
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<tr>
<td></td>
<td>δ¹⁸O (%)</td>
<td>−10.9 to −7.0</td>
<td>−8.45</td>
<td>−9.9 to −8.1</td>
<td>−9.0</td>
<td>−10.7 to −7.4</td>
<td>−9.4</td>
<td>−10.4 to −6.5</td>
<td>−8.5</td>
<td>−10.4 to −6.9</td>
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<tr>
<td></td>
<td>δD (%)</td>
<td>−69.2 to −49.2</td>
<td>−61.9</td>
<td>−69.2 to −61.4</td>
<td>−64.6</td>
<td>−70.4 to −55.9</td>
<td>−64.5</td>
<td>−72.5 to −80.0</td>
<td>−62.4</td>
<td>−73.2 to −56.9</td>
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<tr>
<td></td>
<td>DO (mg/L)</td>
<td>6.0–12.8</td>
<td>10.1</td>
<td>8.7–11.3</td>
<td>9.7</td>
<td>4.8–12.0</td>
<td>9.5</td>
<td>8.5–9.5</td>
<td>9.2</td>
<td>8.1–10.0</td>
</tr>
<tr>
<td></td>
<td>MTC (mV)</td>
<td>47.6–106.7</td>
<td>78.6</td>
<td>27.9–109.8</td>
<td>69.2</td>
<td>25.4–138.5</td>
<td>90.3</td>
<td>39.6–102.4</td>
<td>71.2</td>
<td>49.6–101.1</td>
</tr>
<tr>
<td></td>
<td>rCl/rNa</td>
<td>0.1–1.1</td>
<td>0.5</td>
<td>0.1–1.0</td>
<td>0.5</td>
<td>0.0–2.6</td>
<td>0.8</td>
<td>0.1–0.9</td>
<td>0.4</td>
<td>0.2–0.9</td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>7.4–8.1</td>
<td>7.82</td>
<td>7.3–7.9</td>
<td>7.74</td>
<td>6.7–7.9</td>
<td>7.51</td>
<td>7.25–9.55</td>
<td>8.23</td>
<td>6.7–8.6</td>
</tr>
<tr>
<td></td>
<td>δ¹⁸O (%)</td>
<td>−10.2 to −5.4</td>
<td>−8.4</td>
<td>−10.0 to −7.5</td>
<td>−9.0</td>
<td>−10.5 to −7.7</td>
<td>−9.6</td>
<td>−11.1 to −6.4</td>
<td>−9.5</td>
<td>−11.6 to −7.7</td>
</tr>
<tr>
<td></td>
<td>δD (%)</td>
<td>−70.5 to −48.5</td>
<td>−62.6</td>
<td>−70.1 to −57.9</td>
<td>−65.1</td>
<td>−71.9 to −56.9</td>
<td>−66.2</td>
<td>−83.2 to −52.1</td>
<td>−68.8</td>
<td>−78.4 to −58.3</td>
</tr>
<tr>
<td></td>
<td>DO (mg/L)</td>
<td>5.6–20.6</td>
<td>12.1</td>
<td>9.3–12.3</td>
<td>11.0</td>
<td>7.6–14.7</td>
<td>11.0</td>
<td>9.4–9.9</td>
<td>9.7</td>
<td>9.6–9.9</td>
</tr>
<tr>
<td></td>
<td>MTC (mV)</td>
<td>14.9–79.4</td>
<td>50.8</td>
<td>11.1–61.0</td>
<td>43.1</td>
<td>3.7–68.3</td>
<td>47.5</td>
<td>37.8–71.2</td>
<td>53.6</td>
<td>31.4–78.6</td>
</tr>
</tbody>
</table>
recharged by surface water in autumn, but surface water was recharged by groundwater in winter at site T4. The EC values and stable isotopes present intermediate values between the south part and the north part (Figure 4c and 4j) and the hydrochemical pattern is more complicated than it is in the south and north parts. In addition, the groundwater direction in the study area is similar to the flow direction of river water. Therefore, the surface water and groundwater in the north part and the south part make a combined contribution to the main stream.

Quantitative Analysis by Isotopic and Chloride Mass Balance

In problems related to the interaction of surface water with groundwater, one often address a mixture of two (or more) components having different isotopic signatures (Mook and Rozanski 2000). Therefore, the mass balance approach is used to identify and quantify the SW-GW interaction. This method is based on the assumption that any gain or loss of one water body can be related to the water sources (Kalbus et al. 2006). Therefore, the contribution ratios of different water bodies to the mixture of water can be easily derived by the following isotope mass balance equations:

\[ \delta_m = f_s \times \delta_s + f_p \times \delta_p, \]  

(1)

where \( \delta_s \) and \( \delta_p \) are two mixing components of the mixed water (\( \delta_m \)); \( f_s \) and \( f_p \) are the contribution ratios of the two mixing components to the mixed water. Both \( \delta^{18}O \) and \( \deltaD \) of precipitation (Table 1) are used in the parameter \( \delta_p \) (IAEA/WMO, http://www-naweb.iaea.org/).

For the north part, and the contribution rate of the surface water to groundwater is 93\% in autumn the contribution ratio of the groundwater to surface water is 40\% in winter. For the south part, the contribution ratio of the surface water to groundwater is 47\% in autumn and 61\% in winter. For the main channel, the contribution rate of the surface water to groundwater is 56\% in autumn and 69\% in winter, and the groundwater to surface water is 53\% in autumn and 37\% in winter.

The chloride ion can be used to estimate the contribution ratios of precipitation to groundwater because of its conservative behavior in natural water. We assume chloride is conservative and chloride in groundwater is not influenced by the Weihe River, and rain water is the only source of chloride. The precipitation contribution \( R \) (\%) to groundwater can be calculated by the Cl\(^-\) mass balance:

\[ R (\%) = \frac{C_{Cl(p)}}{C_{Cl(G)}}, \]  

(3)
where $C_{Cl(p)}$ is the average chloride concentration of precipitation (mg/L), and $C_{Cl(G)}$ is the average chloride concentration of groundwater (mg/L). The Cl$^-$ concentration of precipitation is 1.62 mg/L. In autumn, the Cl$^-$ concentrations of groundwater in the north part, the south part and the main stream are 236.9, 44.38, and 101.65 mg/L, respectively. In winter, the Cl$^-$ concentrations of groundwater in the north part, the south part and the main stream are 105.55, 22.93, and 98.7 mg/L, respectively.

The calculated results indicate that precipitation has a contribution rate of 3%, 20%, and 6% to groundwater in the north part, the south part and the main stream in autumn, respectively. The precipitation has a contribution rate of 3%, 18%, and 4% in the north part, the south part and the main stream in winter, respectively.

Both stable isotopic and chloride mass balance show that the surface water makes a more significant contribution to groundwater recharge in the north part and the main river than that in the south part.

**Conclusions**

Stable isotopes in association with hydrochemistry are used to investigate the complicated spatial and seasonal SW-GW interaction qualitatively and quantitatively in a semi-arid region of the Guanzhong section of the Weihe River basin, China.

Both stable isotopes composition and hydrochemical pattern show significant seasonal variation in the north part, but both seasonal and spatial variability are observed in the south part and the main stream of the study area. The mechanisms controlling the basin’s water chemistry is rock weathering in the south part and evaporation crystallization in the north part and the main stream. High quality of surface water and groundwater are found in the south part, with hydrochemical patterns of HCO$_3$-Ca in autumn and HCO$_3$•SO$_4$-Ca in winter. The water samples in the north part show the same dominant hydrochemical pattern in autumn with that in winter, with HCO$_3$-Ca-Na in the western area and HCO$_3$•SO$_4$-Na (surface water)
and SO$_4$-Na (groundwater) in the eastern area of the north part, respectively. The surface water and groundwater in the main stream are dominated by the hydrochemical patterns of HCO$_3$•SO$_4$-Na•Ca in autumn and SO$_4$•HCO$_3$-Na•Ca in winter. Thus, the hydrochemical patterns and distribution of major ions can provide information about whether these water resources can be used for production and in households directly, or if it needs to be treated first.

The recharge relationship in the Guanzhong section varies with season and site. Surface water makes a significant contribution to groundwater in the north part, and precipitation makes a more significant contribution to groundwater in the main river and the south part. The groundwater is mainly recharged by surface water in autumn and groundwater discharges into surface water in winter. In the north part, 40% of surface water recharge comes from groundwater in the dry season, but 93% of groundwater recharge comes from surface water in the rainy season. In the south part, 47% and 61% of groundwater recharge are contributed by surface water in the rainy season and dry season, respectively. The surface water has intensive interactions with groundwater in the main stream in both seasons, with surface water mainly recharged by groundwater at sites T2, T6, and T9 but groundwater mainly recharged by surface water at sites T1, T3, T5, and T8.

Identification of the spatiotemporal recharge relationship and recharge rate between surface water and groundwater is conducted to the calculation of the water recharge-discharge fluxes in a basin. Then, based on the seasonal and spatial distribution and dynamic changes in the total amount of water resources, combined with the variation of climatic features and the underlying surface, future dynamic changes of regional water resources can be simulated and predicted. This will provide scientific guidance for decision-makers to make scientific and effective regulation and to better utilize water resources to decrease the stress of regional water shortages.

Acknowledgments

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Authors’ Note

The authors do not have any conflicts of interest or financial disclosures to report.

Supporting Information

Additional supporting information may be found online in the Supporting Information section at the end of the article. Supporting Information is generally not peer reviewed.

Table S1. Field data of surface water and groundwater samples of the Guanzhong section of the Weihe River basin in autumn and winter, respectively.

Table S2. Isotopic and chemical data of surface water and groundwater samples of the Guanzhong section of the Weihe River basin in autumn and winter, respectively.

References


