Quantitative estimation of groundwater recharge ratio along the riparian of the Yellow River
Zhang Yan, Li Fadong, Li Jing, Liu Qiang and Zhao Guangshuai

ABSTRACT
Quantitative estimation of groundwater recharge is crucial for limited water resources management. A combination of isotopic and chemical indicators has been used to evaluate the relationship between surface water, groundwater, and rainfall around the riparian of the Yellow River in the North China Plain (NCP). The ion molar ratio of sodium to chloride in surface- and groundwater is 0.6 and 0.9, respectively, indicating cation exchange of Ca\(^{2+}\) and/or Mg\(^{2+}\) for Na\(^{+}\) in groundwater. The \(\delta\)D and \(\delta^{18}\)O values in rainfall varied from \(-64.4\) to \(-33.4\)‰ and from \(-8.39\) to \(-4.49\)‰. The groundwater samples have \(\delta\)D values in the range of \(-68.7\) to \(-58.0\)‰ and \(\delta^{18}\)O from \(-9.29\) to \(-6.85\)‰. The \(\delta^{18}\)O and \(\delta\)D in surface water varied from \(-8.51\) to \(-7.23\)‰ and from \(-64.42\) to \(-53.73\)‰. The average values of both \(\delta\)D and \(\delta^{18}\)O from surface water are 3.92‰ and 0.57‰, respectively, higher compared to groundwater. Isotopic composition indicated that the groundwater in the riparian area of the Yellow River was influenced by heavy rainfall events and seepage of surface water. The mass balance was applied for the first time to estimate the amount of recharge, which is probably 6% and 94% of the rainfall and surface water, respectively.

Key words | groundwater, rainfall, recharge, stable isotope, surface water

INTRODUCTION
The Yellow River is the second largest river in China, by length and basin area, and is the seventh largest in terms of discharge (Chen et al. 2003). The North China Plain (NCP), situated in the north of the Yellow River basin, is facing increasing water demands associated with population increase, industrial development and agricultural irrigation. Groundwater represents an important water resource in semi-arid and semi-humid areas in China and worldwide (Foster et al. 2004). Since many developing cities are located on the plain, increasing pumping of groundwater leads to water-shortage and poor water quality (Chen et al. 2005; Li et al. 2008). The diversion from the Yellow River provides annually about 70% of the total amount of the local water resource for agricultural irrigation. The groundwater in the Yellow River riparian area is influenced by the seepage and rainfall. Yellow River irrigation infiltration recharge accounts for about 20–40% of the total shallow groundwater resources (Qu et al. 2012). There are very important and practical implications for groundwater resource management in knowing the recharge ratio to groundwater in the Yellow River riparian area. However, information on quantifying groundwater recharge is limited (Scanlon et al. 2006). Therefore, recharge estimation has become a priority issue for groundwater management in this region.

In recent years, environmentally stable isotope (\(\delta^{18}\)O and \(\delta\)D) and chloride mass balance (CBM) have been commonly used to identify recharge percentage in groundwater (Subyani 2004; Stone & Edmunds 2012). Due to isotopic fractionation occurring during the evaporation of seawater and condensation during the advection of water vapour, information of the spatial variations in the isotopic composition of rainfall can be used for studying water cycle (Dotsika et al. 2010). The CBM is used for groundwater recharge because of its conservative nature. The combination of rainfall, surface water and groundwater can be used for studying regional hydrology or climatology (Sklash et al. 1976). Under favorable circumstances, hydrochemistry and isotopic compositions are very attractive tools for the identification of recharge and the quantitative...
evaluation of the time-varying contributions of these sources to groundwater.

In NCP, hydrogeochemical and isotopic methods have not only been used to determine the chemical evolution of groundwater, to evaluate groundwater’s past, current status and future, and to provide understanding for groundwater management (Chen et al. 2004, 2005), but have also been used to elaborate the interactions between surface water and groundwater (Li et al. 2008). However, these previous studies paid more attention to the spatial evolution, interconnection of individual aquifers, and vulnerability of surface water and groundwater from the piedmont, central plains, and littoral plain on a regional scale. Information about groundwater recharge in the riparian area is largely unknown and there is a need to quantitatively evaluate the recharge ratio to groundwater from rainfall and surface water along the riparian of the Yellow River. In this study, the presented hydrochemical data and stable isotope composition of local rainfall, surface water and groundwater at the side of the Yellow River were used to evaluate the relationship between surface water, groundwater, and rainfall, and to identify recharge ratio to groundwater from rainfall and surface water. This study utilizes rainfall, surface water and groundwater to provide baseline data on the more quantitative evaluations of recharge ratio for local hydrologic investigations and improve the accuracy of future groundwater management and development schemes.

METHODS

Study area

The study area is a part of the Yellow River basin in the west of the NCP, located in the eastern part of China between 36° and 40° N and between 114° and 118° E (Figure 1). The NCP is an important region of agriculture in China, with an area of about 13,600 km² and a population of around 112 million (Chen et al. 2004). Bounded by Taihang Mountain to the west and the Yellow River to the south, the study area is

Figure 1 | The sampling locations and hydrogeology. Note: ‘L,’ loose salts porous aquifer system (water-rich intensity gradually increasing from L1 to L3); ‘M,’ metamorphic rocks fractured aquifer rock group; ‘C,’ carbonate fissure salt dissolved water content of salt groups (water-rich intensity gradually increasing from C1 to C3); ‘S,’ broken nitrate aquifer system (water-rich intensity gradually increasing from S1 to S3).
on the terrain ladders III in China with a west-to-east elevation gradient of high to low. The alluvium thickness in the Piedmont area is less than 100 m; it thickens to more than 180 m toward the plain and in some areas reaches thicknesses of more than 400 m. Quaternary unconsolidated rock pore water is the main type of groundwater in the plain. Annual evaporation is between 900 and 1,400 mm/year with most falling during July to September. Since B 602, the Yellow River flowed toward the northeast along the east of Taihang Mountain across the south of Xinxiang, east of Anyang, west of Hengshui, and then converged with the Haihe River. The shallow groundwater table has declined significantly with a mean rate of approximately 1 m/year in this area over the past several decades (Yang et al. 2004). From 1974 to 2005, the water table in Xinxiang declined by 6 to 18 m with a depression cone area of 40 km² (Pan 2006). A general overview of the study site showing the sampling locations and hydrogeology is presented in Figure 1.

**Sampling sites and sampling frequency**

As shown in Figure 1, nine surface water samples were taken from the Yellow River and its main tributaries and were identified as S1–S9. Seventeen groundwater samples were collected from private, factory, and observation wells of locations around the lower reach of the Yellow River in July 2007. Groundwater samples are identified as G1–G17. The sampling for both surface water and groundwater was carried out at the same irrigation periods. Because of the flat terrain of the sampling locations and slow evolution of surface water and groundwater, the chemical characteristics of the collected samples could not be influenced by sampling time in a short-term period. In addition, twelve rainfall samples were taken for isotope analysis after storm events from July to September 2007. They are signified as P1–P12. All the water samples were collected using high-density polyethylene (HDPE) bottles for isotopic analyses.

**Analytical methods**

The electrical conductivity (EC) and pH-value were measured in situ using a portable pH and EC meter (Compact Meter, Horiba, Japan) and verified in the laboratory using a higher precision meter (D23, Horiba, Japan). The hydrochemistry and isotope analyses were carried out at the laboratories of the Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing, P. R. China. Each water sample was filtered through a 0.45 μm cellulose acetate filter membrane before using an ion chromatograph (Shimadzu, Japan) to determine the concentration (in mg/L) of Cl⁻, K⁺, Mg²⁺, Ca²⁺, SO₄²⁻ and Na⁺. Bicarbonate (as mg/L of HCO₃⁻) was measured by titration using 0.005 mol/L H₂SO₄. The chemical results were implemented when the charge balance error was within ±5%. The isotopic compositions of oxygen (δ¹⁸O) and deuterium (δD) in water samples were determined using an isotope ratio mass spectrometer (Finnigan MAT-253) with a TC/EA interface. The results of δ¹⁸O and δD analyses were expressed in per mil units, using the Vienna Standard Mean Ocean Water standard, as shown in Equation (1). The δ¹⁸O and δD measurements were reproducible to within ±0.2‰ and ±1.0‰, respectively.

$$\delta = \left( \frac{R_{sample}}{R_{standard}} - 1 \right) \times 1000$$  

(1)

where $R_{sample}$ and $R_{standard}$ are the measured isotopic ratios for the sample and for the standard, respectively.

**RESULTS AND DISCUSSION**

**The results of pH, EC and major ions analysis**

The values of EC and pH for surface water and groundwater samples in the study area are shown in Table 1. The pH-value ranged from 6.62 to 7.45 in rainfall, from 7.36 to 7.74 in surface water, and from 7.74 to 8.06 in groundwater (Table 1). The pH-value of rainfall is lower than that of both surface water and groundwater, and pH-values of surface water samples are slightly lower than those of groundwater samples. In NCP, the common pH-value of rainfall ranged from 6.5 to 7.5, indicating neutral nature. Carbonate rock is the main lithology in the current study area (Tong et al. 2005). The dissolution of carbonate rock leads to more alkaline HCO₃⁻ and CO₃²⁻ entering into the surface- and groundwater. The mean value of EC in groundwater and surface water was 1,195 μS/cm and 743 μS/cm, respectively. The groundwater had higher EC than surface water, maybe because of lixiviation (Amiaz et al. 2011). Ca²⁺ and HCO₃⁻ are the dominant cation and anion, respectively. The order of relative abundance of major cations in the studied waters is Ca²⁺ > Na⁺ > Mg²⁺ > K⁺ (on mg/L basis) while that of anions is HCO₃⁻ > SO₄²⁻ > Cl⁻ (Table 1).

The range of Cl⁻ values varied from 5.94 to 95.80 mg/L in groundwater and from 30.07 to 81.90 mg/L in surface water samples. Na⁺ values range from 23.77 to 367.26 mg/L in groundwater, and from 24.77 to 51.50 mg/L
in surface water (Table 1). G16 and G17 have higher concentration of Na\textsuperscript{+}, indicating ion exchange in groundwater. The ion molar ratio of sodium to chloride in surface water and in groundwater is 0.6 and 0.9, respectively (Figure 2). The regression equation shows that the Na/Cl ratio of groundwater is higher than of surface water, which indicates that ion exchange occurred between Ca\textsuperscript{2+} or Mg\textsuperscript{2+} and Na\textsuperscript{+} in groundwater. Calcite, dolomite, gypsum and anhydrite are the most likely additional sources from which Ca\textsuperscript{2+} and Mg\textsuperscript{2+} could enter the natural water — next to cation exchange. Na\textsuperscript{+} can be released into solution during weathering of Na-rich plagioclase and by cation exchange with Ca\textsuperscript{2+}, which is attached to the surface of newly formed clay minerals (Iwatsuki & Yoshida 1999).
The $\delta D$-$\delta^{18}O$ relationship

The isotope ratios of hydrogen ($\delta D$) and oxygen ($\delta^{18}O$) can provide useful information about the sources of groundwater and the water cycle. The isotope data of rainfall, surface water and groundwater are shown in Table 1 and Figure 3. The $\delta D$ values in rainfall varied from $-64.4$ to $-33.4\%$ with a mean value of $-53.6\%$, and $\delta^{18}O$ ranged from $-8.39$ to $-4.49\%$ with a mean value of $-7.4\%$, respectively. The groundwater samples have $\delta D$ values in the range of $-68.7$ to $-58.0\%$ and $\delta^{18}O$ values from $-9.29$ to $-6.85\%$. The average values of $\delta D$ and $\delta^{18}O$ in groundwater are $-63.1\%$ and $-8.3\%$, respectively. The $\delta^{18}O$ and $\delta D$ in surface water varied from $-8.51$ to $-7.23\%$ with a mean value of $-7.73\%$, and from $-64.42$ to $-53.73\%$ with a mean value of $-59.18\%$, respectively. The abundance of $\delta D$ and $\delta^{18}O$ in surface water is higher than those in groundwater. In the NCP, much of the groundwater is probably thousands of years old. This paleo groundwater is often characterized by depleted $\delta^{18}O$ and $\delta D$ with respect to modern recharge because it was recharged during a colder climate in the Pleistocene (Chen et al. 2005).

The results of the $\delta^{18}O$ and $\delta D$ analyses are plotted in Figure 3. A regression line drawn in $\delta D$-$\delta^{18}O$ space for the global precipitation defines the global meteoric water line (GMWL), termed as $\delta D = 8\delta^{18}O + 10$ (Rozanski et al. 1993). Precisely, the slope of the regression line between $\delta^{18}O$ and $\delta D$ composition of rainfall is different from one region to another depending on the local climatic conditions (Hoefs 2009). In this study, $\delta^{18}O$ and $\delta D$ of the twelve rainfall samples defined the best-fit line of $\delta D = 7.24\delta^{18}O - 0.22$ (Figure 3). This relationship has a correlation coefficient of $R^2 = 0.87$. This line closely resembles the GMWL and was used as the Local Meteoric Water Line (LMWL) shown in Figure 3. All of the points fall below the GMWL, commonly suggesting the effects of evaporation. In comparison to LMWL, most of the surface waters from the Yellow River fall below the LMWL, indicating the effect of evaporation on surface water. The majority of groundwater samples fall below the LMWL, while the rest of them were close to the LMWL, which indicates the recharge sources derived from modern meteoric water. The isotopic composition of groundwater samples at the riparian of the Yellow River is close to the surface water, which indicates that the groundwaters are affected by the seepage of the Yellow River. The average values of $\delta^{18}O$ and $\delta D$ of shallow groundwater are significantly lower than the average values of $\delta^{18}O$ and $\delta D$ of rainfall in this area, which indicates recharge of groundwater by rainfall with depleted stable isotopes in heavy rainfall events.

The shift of the isotopic composition of groundwater can be determined from the values of deuterium excess ($d$-values) listed in Table 1. The mean $d$-values of surface water and groundwater are 2.66‰ and 2.94‰, respectively. The average $d$-value of precipitation is 7.63‰. Based on a mass-balance of $d$-values, the relative contribution ratios of rainfall and surface water to the groundwater recharge can be estimated as the following equation:

$$d_{\text{groundwater}} = Xd_{\text{surface water}} + (1 - X)d_{\text{rainfall}}$$

where $X$ and $(1 - X)$ are the proportion of surface water and rainfall, respectively.

The calculated results indicate that the proportions of surface water and rain water as the main sources for groundwater are 94.37 to 5.63%, respectively. The value for the rain water fraction is in line with the average values (0.1–5%) for the contribution of rain water to groundwater in semiarid and arid regions (Scanlon et al. 2006).

Estimation of recharge ratio to groundwater based on Cl mass balance

The chloride ion can be used to estimate recharge ratios because of the conservative behavior of chloride in natural water. In comparison to other ions, the chloride ion neither leaches from nor is absorbed by aquifer sediments, and it does not participate in any chemical reaction (Scanlon 2000; Subyani 2004). By using the chloride ion mass balance method (Leaney & Herczeg 1995) it is possible to estimate the contribution of precipitation to groundwater. This method assumed: (1) chloride as the conservative ion; (2) rain water as the only source of chloride; and (3) evaporation as the main route for loss of water in the basin. The
rain water contribution $R$ (%) to groundwater can be calculated as follows:

$$R(\%) = \frac{C_{Cl(P)}}{C_{Cl(GW)}}$$  \hspace{1cm} (3)

where $C_{Cl(P)}$ is average chloride concentration of rain water (mg/L), $C_{Cl(GW)}$ is average chloride concentration of groundwater (mg/L).

The main lithology in the study area consists of carbonate rock (Tong et al. 2005), so chloride is mainly derived from atmospheric precipitation. Chloride concentrations in rain water and groundwater are 2.8 and 48.12 mg/L, respectively. Equation (1) is employed to calculate the recharge ratio to groundwater. The contribution of rain water to groundwater is 5.82%. Two main types of recharge sources are recognized: rain water through the unsaturated zone to groundwater and Yellow River water seepage to groundwater. Therefore, the other 94.18% of groundwater comes from seepage of Yellow River water. Based on CBM technique, Ruifen and Keqin (2001) reported that 9–12% of long-term average annual precipitation recharges groundwater along the middle reaches of the Yellow River. This may be related to uncertainty in chloride concentrations in precipitation, caused by a limited number of data (July to September 2007). The high recharge ratio of 18% is related to a chloride concentration of 10.2 mg/L in rain water, which is much higher than the value used in this study (2.8 mg/L). If the former value were used, the recharge ratio would be higher. Using the mass-balance of $^{18}$O-values, Miao (2010) also reported that the proportion of Yellow River water varies with the distance away from the Yellow River. In total, Yellow River water and rainfall accounts for approximately 20 and 80%, respectively in the north of our current study area. These results indicate seepage of Yellow River water is the main groundwater recharge source in the riparian area of the lower Yellow River.

**CONCLUSIONS**

In the riparian area of the Yellow River, Ca$^{2+}$ and HCO$_3^-$ are the dominant cations and anions in both surface water and groundwater. $\delta^{18}$O values range from $-8.39$ to $-4.49\%o$ in rain water, from $-9.29$ to $-6.85\%o$ in groundwater and from $-8.51$ to $-7.23\%o$ in surface water, while $\delta$D values vary from $-64.4$ to $-33.4\%o$ in rain water, from $-68.7$ to $-58.0\%o$ in groundwater and from $-64.42$ to $-53.73\%o$ in surface water. The average values of $\delta^{18}$O and $\delta$D of groundwater are significantly lower than that of rain water and surface water. Preliminary isotopic data indicate that the groundwater is recharged by rain water and seepage of Yellow River water. The calculation results of the mass-balance of $d$-values and chloride showed that approximately 6 and 94% of groundwater is derived from rain and surface water, respectively.

**ACKNOWLEDGEMENT**

This study was financially supported by the 100-Talent Project of Chinese Academy of Sciences and the National Natural Science Foundation of China 41271047 and the Chinese Academy of Sciences for Key Topics in Innovation Engineering (Grant No. KZCX2-EW-310-03).

**REFERENCES**


Li, F. D., Pan, G. Y., Tang, C. Y., Zhang, Q. Y. & Yu, J. J. 2008 Recharge source and hydrogeochemical evolution of...


First received 30 January 2013; accepted in revised form 31 July 2013. Available online 22 October 2013.