Tracing groundwater recharge sources beneath a reservoir on a mountain-front plain using hydrochemistry and stable isotopes
Xue Li, Siyuan Ye, Liheng Wang and Jiangyi Zhang

ABSTRACT

Mountain-front recharge, including mountain block recharge and stream seepage, is important for basin aquifers. With the construction of reservoirs in mountainous areas and the recurrent seepage problems of dams, reservoir seepage might become another type of mountain-front recharge. This study identified the recharge sources of groundwater beneath Huangbizhuang Reservoir on the North China Plain (NCP). Hydrochemical data and the stable isotopic compositions ($\delta^{18}$O and $\delta^D$) of water were employed to determine the occurrence of Huangbizhuang Reservoir seepage recharge to groundwater in the mountain-front area. Then, the relative percentages of ‘reservoir seepage’ to total recharge were quantified using end-member mixing analysis (EMMA). The results suggest that the recharge sources beneath the reservoir are mountain block recharge, local precipitation and reservoir seepage. Using D and $\delta^{18}$O values, EMMA revealed that the mean contribution ratio of reservoir seepage to groundwater beneath the reservoir is 36% ± 4%, while that of mountain block recharge is 33% ± 11% in consideration of the uncertainty. Reservoir seepage accounts for a large proportion of mountain-front recharge and should be included in the calculations of mountain-front recharge on the NCP, which is currently ignored.

Key words | hydrochemistry, mountain-front recharge, North China Plain, reservoir seepage, stable isotope

INTRODUCTION

In semi-arid regions, a significant component of recharge to basin aquifers occurs along the mountain front and is called ‘mountain-front recharge’. The two components of mountain-front recharge are mountain block recharge and stream seepage (Manning & Solomon 2003; Wilson & Guan 2004). Studies have demonstrated that stream seepage is an important recharge source for groundwater in mountain-front plains, and a growing number of studies have focused on quantifying exchanges between groundwater and streams (Niswonger et al. 2005; Kuraś et al. 2008). However, for example, to use the energy and irrigation potential of some rivers, a series of reservoirs in mountainous areas were designed, and some reservoirs worldwide have suffered from water seepage by gradual development of channels and openings that were formerly filled with fine sediments (Ertunç 1999). Reservoir seepage can thus dramatically change mountain-front recharge and might become another recharge source for the basin aquifers.

The North China Plain (NCP) is one of the most important social, economic, and agricultural regions in China, and groundwater resources provide about 70% of the water supply in this region. However, many urban and irrigated areas on the NCP have experienced regular water shortages, with the water table declining at an average rate of...
0.3 m year$^{-1}$ (Cao et al. 2013). One important reason for the groundwater level decline is that 81.8% of runoff downstream is not available due to reservoirs that have been built upstream since 1960. Although the construction of reservoirs has decreased river seepage downstream, it remains unclear if reservoir seepage is recharging groundwater. If it is, reservoir seepage becomes another component of mountain-front recharge. In that case, the quantity of recharge beneath the reservoir becomes the focus.

Hydrochemistry and isotope tracer approaches have been widely used to determine the origins of recharged groundwater (De Vries & Simmers 2002). Stable isotopes are particularly useful for determining whether recharge originates from direct rainwater infiltration or from surface water (Peng et al. 2016). Furthermore, stable isotopic approaches can be used in quantitative analyses of groundwater mixing from the local scale to the whole watershed scale, including the mixing of different recharge sources or different aquifers and even different systems (Clark & Fritz 1997; Carucci et al. 2012; Kong et al. 2015). Hydrochemical data can be used to identify groundwater flow paths and to complement isotopic information (Liu & Yamanaka 2012).

We present a case study of groundwater recharge beneath Huangbizhuang Reservoir on the NCP using hydrochemistry and stable isotopes. This study has two objectives which assisted with identifying the recharge sources of groundwater beneath the reservoir. The first was to determine the occurrence of Huangbizhuang Reservoir seepage recharge to groundwater in the mountain-front area on the NCP. The second objective was to quantify the relative percentages of the ‘reservoir seepage’ to total recharge, for the Huangbizhuang Reservoir, using end-member mixing analysis (EMMA).

**STUDY AREA**

Huangbizhuang Reservoir is located on the Hutuo River, 30 km to the northwest of Shijiazhuang City. It is one of the most important reservoirs on the NCP, with 12.1 billion m$^3$ of total storage, which is the water supply for more than seven million people and irrigates more than 80 thousand km$^2$ of cultivated lands (Fei et al. 1997; He 2009).

The study area located beneath Huangbizhuang Reservoir on the mountain-front plain was the focus of this study. It is bordered to the northeast by the Hutuo River, to the west by the junction of the mountain and plain, and to the southeast by the border of the groundwater cone of Shijiazhuang city (Fei et al. 1997) (Figure 1(a)). The elevation ranges from 110 m in the northwest to 60 m in the east (Figure 1(a)). This region has a semi-arid continental monsoon climate, with an annual mean temperature of 13 °C and annual average precipitation of 549.4 mm, 70%–80% of which occurs from June to August. The annual water surface evaporation ranges from 900 to 1,200 mm.

Precambrian, Cambrian, and Ordovician rocks (marble, limestone, dolomite, slate, phyllite and gneiss) and Quaternary alluvial deposits are distributed in the mountainous area. The type of groundwater is fissure karst water. This indicated mountain block recharge between mountainous area and plain area.

The geology of the dam area is comprised of Precambrian rocks (phyllite, marble, and silica limestone), Tertiary (R) red clay with gravel, middle Pleistocene (Q2) clay and upper Pleistocene (Q3) deposits. Q3 of sand with gravel is the main aquifer, and it is connected with the aquifers downstream (Fei et al. 1997)). The plain area beneath the reservoir is overlain by Quaternary sediments, which are predominantly loose gravel and sand (Figure 1(b)). The clay has a lenticular distribution; thus, good hydraulic connectivity exists among aquifers, which are single-layer hydrogeological structures (Zhang et al. 1997). Groundwater flows from the west and northwest to the east and southeast. This indicated the possibility of the occurrence of reservoir leakage.

**METHODS**

**Sampling and analysis**

Field surveys were carried out three times: in May 2012, September 2012 and May 2013. Considering the seasonal variation of hydrochemistry and isotopes, we chose May as the sampling month to stand for the dry season, and
Figure 1 | (a) Map of the study area and sampling points and (b) schematic hydrogeological cross-section A-B of the study area (drawn based on a previous study, Fei et al. 1997).
September to stand for the wet season. Overall, 16 samples were collected from groundwater (GW1–GW16 in Figure 1(a)), and two samples were collected from Huangbizhuang Reservoir (RE1–RE2 in Figure 1(a)) covering the entire study area. The groundwater samples were taken directly from shallow and deep wells that were water-supplying wells, after 10 minutes of pumping. The reservoir samples were collected in different areas.

The pH and total dissolved solids (TDS) were measured in situ. The chemical compositions of water samples were analysed in the Key Laboratory of Shale Gas and Geoenineering, Institute of Geology and Geophysics, Chinese Academy of Sciences (CAS). The accuracies of the hydrochemical analyses were checked using an electrical balance. Samples whose results gave relative errors greater than 5% were reanalysed. The hydrogen and oxygen stable isotopic compositions of water samples were analysed in the Key Laboratory of Water Cycle and Related Land Surface Processes, CAS. The isotopic ratios of $^{18}$O and D were expressed as $\delta^{18}$O and $\delta$D, respectively, relative to Vienna Standard Mean Ocean Water. The analytical errors were 0.1‰ for $\delta^{18}$O and 2‰ for $\delta$D.

RESULTS AND DISCUSSION

The chemical characteristics and stable isotopic compositions of samples from the study area are shown in Table 1.

Hydrochemical characteristics

The pH values of groundwater ranged from 7.05 to 7.50. The minimum value was observed in mountain block groundwater (GW16) and the maximum value was observed in GW2. The pH value of the reservoir water was higher than that of the groundwater (Figure 2(a)), and this might have some relationship with the pH of the soil and dissolved CO$_2$ (Lang et al. 2005).

Groundwater was variable, with TDS contents of 421.0 to 722.1 mg/L. The minimum value was observed at GW7 (32 m), and the maximum was observed at GW4 (155 m) (Figure 2(b)). The value of reservoir sample RE2 was higher than that of RE1. This might be caused by the location of RE2, which was near the shore and potentially affected by human activities. Furthermore, the TDS value of the groundwater became larger along the flow paths (Figure 2(c)), reflecting flow paths that had been proposed in other studies (Afshin 1997; Edmunds et al. 2002; Moya et al. 2014).

NO$_3$ was detected in all samples. The concentration ranged from 0.36 to 23.16 mg/L, and the lowest value was observed adjacent to the reservoir in GW2 and the maximum was observed in GW12. The nitrate is largely from anthropogenic activities that influence the aquifers (Elisante & Muzuka 2015). Considering the land use in this area, the application of nitrogenous fertilizer in agriculture might have contributed NO$_3$ to groundwater (Liu & Chen 2009). The value became higher along the flow paths (Figure 2(d)). This suggests that anthropogenic activities get more intense downstream (Singh et al. 1979).

The piper diagram suggests that Ca-HCO$_3$ is the dominant hydrochemical type in the study area (Figure 2(e)), which represents the recharge water. This is the same water type as observed in the Taihang Mountains on the NCP (Zhang et al. 1997). Groundwater samples adjacent and close to the reservoir (GW1–GW13, except GW7 and GW12) had relatively high SO$_4^{2-}$ content in their total anions, while the reservoir water was dominated by SO$_4^{2-}$. This might indicate interactions between groundwater and reservoir water, that is to say, reservoir leakage might be a recharge source for groundwater.

Isotopic signatures

Stable $\delta$D and $\delta^{18}$O isotopes are ideal tracers for estimating the recharge areas and flow paths of groundwater because they are sensitive to physical processes such as mixing and evaporation (Coplen 1995). The meteoric water line was acquired from the Shijiazhuang station via the GNIP/IAEA database (http://isohis.iaea.org), with $\delta$D (‰) = 6.07 $\delta^{18}$O−5.80 ($R^2 = 0.86$). Shijiazhuang station is located 24 km from the reservoir and monitored isotopic data in precipitation from January 1985 to December 2003. The average value of $\delta^{18}$O got by long-term weighted means from this dataset is $-7.62$‰, while $\delta$D is $-51.9$‰.

Figure 3(a) shows that the isotopes of groundwater samples are below the meteoric water line, indicating that groundwater has been affected by evaporation or mixing.
<table>
<thead>
<tr>
<th>Water group</th>
<th>No.</th>
<th>Sample ID</th>
<th>Location</th>
<th>Depth (m)</th>
<th>pH</th>
<th>TDS (mg/L)</th>
<th>Na⁺ (mg/L)</th>
<th>K⁺ (mg/L)</th>
<th>Ca²⁺ (mg/L)</th>
<th>Mg²⁺ (mg/L)</th>
<th>Cl⁻ (mg/L)</th>
<th>SO₄²⁻ (mg/L)</th>
<th>HCO₃⁻ (mg/L)</th>
<th>NO₃⁻ (mg/L)</th>
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processes. $\text{Cl}^- \text{ vs } \delta^{18}O$ is not linear (Figure 5(b)) because the kinetic fractionation causes the $\delta^{18}O$ to increase in a different magnitude to that of Cl. Considering hydrogeological conditions, the groundwater recharge sources are not only precipitation but also other sources such as mountain block recharge and reservoir water recharge. This is a mixing process and the trend line of groundwater is a mixing line instead of an evaporation line.
Mountain block water sample GW16 is the most enriched in the $^{18}$O stable isotope (−6.50‰) compared with values of other groundwater samples, indicating a relatively long flow path and residence time (Rodgers et al. 2005). The most depleted in $^{18}$O is sample GW4 (−8.30‰).

The stable isotopic compositions of reservoir waters change greatly, suggesting that reservoir waters are more susceptible to environmental influences than groundwater. Based on other studies of Huangbizhuang Reservoir (Chen et al. 2004; Zhang et al. 2008; Wei 2012), although the values of stable isotopic compositions are variable, their distributions plot along a linear line with a slope of 5.3 (Figure 3(c)). The data points are located below the LMWL, which indicates water experiences the process of evaporation (Yi et al. 2008; Li et al. 2015; Kong et al. 2016). This line represents the evaporation line of reservoir water.

EMMA

Based on a previous analysis, the groundwater beneath the reservoir is the mixing product of many sources. Therefore, EMMA based on mass balances of tracers was used to determine the contributions of each source to the groundwater beneath Huangbizhuang Reservoir.

Based on the hydrogeological analysis, the groundwater beneath the reservoir has at least two sources: precipitation and mountain block recharge. Although the dam has done with seepage treatment, whether reservoir seepage occurs or not is our concern. The stable isotopic compositions of groundwater, reservoir water and precipitation are shown in Figure 4. Data for all groundwater samples plot within a triangle. Mountain block water is clearly one end-member.
(GW16). Local precipitation has large average values of stable isotopic data and, therefore, is the second end-member. The third end-member has lower $^{18}$O and D values. The groundwater sample GW4, located near the reservoir, exhibited a high value of TDS (722.1 mg/L) that was similar to that of the mountain block water (686 mg/L), but the stable isotopic composition clearly differed. GW4 is more depleted $^{18}$O ($-8.30\%$) than both local precipitation ($-7.62\%$) and mountain block water ($-6.50\%$). This indicates that the groundwater has been recharged by a source with more depleted $^{18}$O relative to the local precipitation. Thus, the source could be reservoir water. Reservoir water comes from runoff from mountainous areas, exhibiting a more depleted value than local precipitation because of elevation effects (Craig et al. 1961). Therefore, the reservoir water from previous studies acts as the third end-member ($-8.82\%$).

The groundwater $\delta$ values can be used for EMMA, assuming three end-members: mountain block groundwater, local precipitation and reservoir water. A mixing computation was performed to establish the proportional ratios in the groundwater. The contribution ratio ($r$) from each of the potential sources was estimated using the following equations:

$$(\delta D)_g = r_1(\delta D)_1 + r_2(\delta D)_2 + r_3(\delta D)_3$$  \hspace{1cm} (1)

$$(\delta^{18}O)_g = r_1(\delta^{18}O)_1 + r_2(\delta^{18}O)_2 + r_3(\delta^{18}O)_3$$  \hspace{1cm} (2)

$$r_1 + r_2 + r_3 = 1$$  \hspace{1cm} (3)

where $(\delta D)_g$ and $(\delta^{18}O)_g$ are the stable isotopic compositions of each groundwater sample; $(\delta D)_1$, $(\delta D)_2$, $(\delta D)_3$, $(\delta^{18}O)_1$, $(\delta^{18}O)_2$, and $(\delta^{18}O)_3$ are the stable isotopic compositions of each potential source; and $r_1$, $r_2$, and $r_3$ are the contribution ratios of each potential source.

The estimated contribution ratios and calculated mean standard errors (SE) (Phillips & Gregg 2001) are shown in Table 2. The resulting $\delta^{18}$O and D values of mountain block recharge, local precipitation and reservoir water accounted for 33%, 31%, and 36%, respectively, of groundwater beneath the reservoir. The mean SE values of these sources were 11%, 12%, and 4%. These suggest that the results of EMMA were $33\% \pm 11\%$, $31\% \pm 12\%$ and $36\% \pm 4\%$ in consideration of the uncertainty, which should always be used.

The contribution ratios of reservoir water ranged from 15% to 63%. From the general characteristics of the spatial distribution (Figure 5(a)), the smallest values are found at GW1 and GW2 (16%, 15%), which are located adjacent to the reservoir. This suggests that reservoir seepage has little effect on the location, and the contribution of the reservoir is smallest. Relatively large contribution ratios, as high as 30%, are observed at GW3–GW13 near the reservoir, except at GW11 (29%). The reservoir has experienced see page prevention and been reinforced many times since operation, especially via the anti-seepage reinforcement of the secondary dam in 2003. In that project, an impervious corewall was constructed, considerably affecting groundwater downstream (He 2009; Liu & Hou 2013). The results from EMMA suggest that reservoir seepage still occurs. Furthermore, it contributes substantially to groundwater recharge near the reservoir. Relatively small values (below 20%) are found at GW14 and locations further from the reservoir (GW15). These findings suggest that the contribution of reservoir water decreases with increasing distance from the reservoir.

The contribution ratios of mountain block recharge ranged from 3% to 82%. Relatively large contribution

<table>
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<th>Table 2</th>
<th>The contribution ratios (%) and mean SE values of each source in groundwater samples</th>
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</table>
ratios were observed at GW1 and GW2 (49%) adjacent to the reservoir. The ratio distribution is uneven near the reservoir, ranging from 3% to 59% (Figure 5(b)). The main source of groundwater samples GW14 and GW15, which were located far away from the reservoir, was mountain block recharge, accounting for 82% and 47%, respectively.

The contribution ratios of precipitation ranged from 1% to 48%. They do not differ greatly in all samples, with ratios between 22% and 48%, except at GW7 and GW14 (Figure 5(c)), and the variance is the smallest among the three sources. The small contributions of precipitation at GW7 and GW14 indicate the influence of a large amount of other sources, such as mountain block recharge, which were decided by geological conditions. Where they located were underlying limestone and dolomite, and kept good hydraulic relations with the mountainous area.

Overall, reservoir seepage recharges groundwater beneath the reservoir. He (2009) also proposed that seepage occurred based on the groundwater dynamics beneath the reservoir. Moreover, the contribution ratios are large and cannot be ignored in the calculation of mountain-front recharge.

CONCLUSIONS

Isotope and hydrochemistry analyses indicated that precipitation, mountain block recharge and reservoir seepage are the three main recharge sources beneath Huangbizhuang Reservoir on the mountain-front plain. Thus, the occurrence of reservoir seepage as a groundwater input was determined.

EMMA can be used to estimate the contribution ratios of different recharge sources. It was used to quantitatively
evaluate the contribution of ‘reservoir seepage’ to groundwater on the mountain-front plain with acceptable error. The results demonstrate that reservoir seepage contributes a considerable amount of water to aquifers, with the mean contribution ratio reaching 36% in the aquifers. Reservoir seepage accounted for 52% of the mountain-front recharge. Although the reservoir has caused groundwater recharge via runoff to decrease, seepage has become another recharge source for the basin aquifers and should be emphasized in calculations of mountain-front recharge. In a previous study, the calculations of mountain-front recharge did not include reservoir leakage in the NCP and caused a large error in evaluating groundwater resources of NCP.

This paper highlights the importance of reservoir leakage, which has implications for the calculation of mountain-front recharge on the entire NCP. Although this study of hydrochemical data and stable isotopes improved the understanding of many processes, some results may be one-sided because of limited sampling. To verify and further increase the reliability of the calculated results, other methods, such as numerical simulations, are necessary.

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