Response of redox zonation to recharge in a riverbank filtration system: a case study of the Second Songhua river, NE China

Xiaosi Su, Yaoxuan Chen, Hang Lyu, Yakun Shi, Yuyu Wan and Yiwu Zhang

ABSTRACT

Bank filtration induced by groundwater pumping results in redox zonation along the groundwater flow path. Besides the river water, recharge from other sources can change local redox conditions; therefore, redox zonation is likely to be complex within the riverbank filtration (RBF) system. In this study, hydrodynamics, hydrogeochemistry, and environmental stable isotopes were combined together to identify the redox conditions at an RBF site. The recharge characteristics and redox processes were revealed by monitoring the variations of water level, $\delta^2$H and $\delta^{18}$O, and redox indexes along shallow and deep flow paths. The results show that local groundwater is recharged from river, regional groundwater, and precipitation. The responses of redox zonation are sensitive to different sources. In the river water recharge zone near shore, $O_2$, $NO_3^-$, Mn(IV), Fe(III), and $SO_4^{2-}$ are reduced in sequence, the ranges of each reaction are wider in deep groundwater because of the high-velocity deep flow. In the precipitation vertical recharge zone, precipitation intermittently drives $O_2$, $NO_3^-$, and organic carbon to migrate through vadose zone, thereby decreasing the groundwater reducibility. In the regional groundwater lateral recharge zone in the depression cone, the reductive regional groundwater is continuously recharging local groundwater, leading to the cyclic reduction of Mn(IV) and Fe(II).

Key words | hydrodynamics, hydrogeochemistry, recharge characteristics, redox zonation, riverbank filtration system, stable isotope

HIGHLIGHTS

- Hydrodynamics, hydrogeochemistry, and environmental stable isotopes were combined to explore the redox zonation in an RBF system.
- Redox zones and sequential redox processes involved were identified and partitioned.
- Analysis of the redox zonation response to flow regime and recharge of river, precipitation, and regional groundwater.

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INTRODUCTION

Riverbank filtration (RBF) involves water extraction by pumping wells at riverside fields to enhance water supply by stimulating river recharge to groundwater. This can attenuate or degrade pollutants, such as suspended solids, inorganic or organic substances, poisonous heavy metals, pathogenic viruses, and bacteria; hence, it is considered an efficient and natural treatment technology for water quality improvement (Hiscock & Grischek 2002; Tufenkji et al. 2002; Trauth et al. 2017; Muz et al. 2019). Rivers are rich in O₂ and organic matter; driven by Gibbs free energy, the organic matter supplies electrons to the lowest unoccupied molecular orbital locations during river filtration; therefore, O₂, NO₃⁻, Mn(IV), Fe(III), and SO₄²⁻ are reduced in sequence (Kedziorek & Bourg 2009; Farnsworth & Hering 2011). However, this process can also cause incomplete removal of organic carbon, suspended solids, and inorganic pollutants, and release of heavy metals, such as Fe, Mn, and As, from sediment or the aquifer medium to groundwater (Gandy et al. 2007; Su et al. 2018).

Bank filtration controlled by groundwater pumping results in a relatively stable redox zonation along the groundwater flow path and previous research has mostly focused on the spatial distribution of the redox environment (Greskowiak et al. 2006; Kumar & Riyazuddin 2012). Many factors affecting the formation of redox zonation, such as fluctuations in river stage and groundwater level, intensity of pumping, lithology and structure of aquifer medium, and water temperature, have all been considered in previous studies, yet the influence of recharge conditions of local groundwater, such as water from precipitation and regional groundwater conditions have been neglected (Burt et al. 2002; Massmann et al. 2008; Kohfahl et al. 2009; Wang et al. 2009). In addition to river water, groundwater recharge from other sources can also change the local redox conditions, and hence, redox zonation is likely to be more complex within the RBF system (Kedziorek & Bourg 2009; Buzek et al. 2012).

The Kaladian well field, located in northeastern China, is characterized by regional groundwater rich in Fe and Mn with Mn²⁺ and Fe²⁺ contents of over 6 and 10 mg/L, respectively. The local groundwater in recent 3 years has concentrations of NH₄⁺, Mn²⁺, and Fe²⁺ at 0.98–3.62 N mg/L, 4.71–6.82 mg/L, and 8.54–12.74 mg/L, respectively, which exceed the WHO guideline limits of 0.50 N mg/L, 0.40 mg/L, and 2.00 mg/L, respectively. (WHO 2011). Therefore, an appraisal of the characteristics of the redox environment and biogeochemical behavior of the sensitive components during bank filtration under different sources of recharge should be undertaken to gain a deeper understanding of the complex biogeochemical processes.

This study aims to: (1) carry out survey and analysis of the hydrodynamics of the river and groundwater around the Kaladian well field by combining δ³H and δ¹⁸O analyses to identify the spatial distribution characteristics of recharge; (2) survey the spatial distribution of the redox environment, sensitive components in river water and groundwater, and the soluble N and C components in the aquifer medium, as well as analyze their relationships with hydrodynamic conditions; and (3) partition the redox zonation along the groundwater flow path based on the spatial distribution of recharge and redox conditions, as well as clarify the hydrogeochemical processes within each zone.

MATERIALS AND METHODS

Study area

The Kaladian riverside well field, located on the alluvial–proluvial plain of the Second Songhua River in northeastern China, is characterized by flat topography with elevations varying from 124 to 129 m above sea level. The unconfined aquifer is mainly composed of sand with the thickness of 17–20 m, and a continuous and stable clay-laminated layer of ~24 m thickness forms the impervious base of the unconfined aquifer. The upper and lower parts of the unconfined aquifer consist of fine sand and medium sand with a thin layer of silty-clay in the middle, respectively. The long-term pumping wells (C1–C8) operating intermittently at a total pumping rate of 6,000–10,000 m³/day have formed a stable groundwater depression cone centered around well C5 and C6.
The well field is located in a cold temperate zone that experiences a continental semi-arid monsoon climate with a dry and windy spring, hot and rainy summer, cool autumn with early frost, and a cold and long winter. Monthly average temperatures in January and July can reach −17.5 and 23.3 °C, respectively, while the annual average temperature is 4.7 °C. Annual mean precipitation is 425.7 mm, of which more than 70% is concentrated from June to August, while the annual mean evaporation is 1,689.8 mm, with the maximum in May at 316.5 mm. The Second Songhua River, flowing from southeast to northwest, is controlled by climate and upstream water conservancy projects and has an annual average runoff, river surface width, and depth of 476.0 m³/s, 400–450 m, and 3–7 m, respectively.

Herein, 22 long-term monitoring wells with a depth of 6–9 m were constructed to monitor the groundwater level and quality since December 2015. Based on the monitoring results, a dense monitoring section from the river to the depression cone center was constructed in August 2018, as shown in Figure 1. The hydrodynamic and environmental conditions are susceptible to change within 30 m of the shore; therefore, six near-shore monitoring points NS1, NS2, NS3, NS4, NS5, and NS6 were established at 0, 2, 5, 8, 14, and 30 m from the shore, respectively. Furthermore, six far-shore monitoring points FS1, FS2, FS3, FS4, FS5, and FS6 were located at 80, 200, 420, 700, 850, and 1,110 m from the shore. Each monitoring point has a shallow (7.5 m) and deep (14 m) well with a screen interval of 6–7.5 and 12.5–14 m, respectively. Furthermore, two regional groundwater monitoring wells, RG1 and RG2, are located at 2,100 and 2,700 m, respectively, from the shore.

**Sampling**

**River and groundwater sampling**

River water and groundwater samples were collected in September 2018. River water was collected 0.5 m below the surface. Groundwater was pumped at a rate <5 L/min from the wells, and the samples were collected after flushing the volume of the well pipe three times. Sampling bottles were filled to the brim and then sealed. Samples for SO₄²⁻, NO₃⁻, and NH₄⁺ were stored in polyethylene bottles, while concentrated sulfuric acid was added to the samples for NH₄⁺ to

![Figure 1](http://iwaponline.com/hr/article-pdf/51/5/1104/775805/nh0511104.pdf)
generate a pH <2. Samples for Mn$^{2+}$ were packed in brown glass bottles with diluted hydrochloric acid to generate a pH <2. Samples for DO were stored in brown glass bottles and concentrated sulfuric acid was added to generate a pH <2. Samples for testing stable isotopes were collected in 500 mL polyethylene bottles and stored at –4 °C.

A Hach HQ40d portable meter (Hach Company, USA) was used to test pH, Eh, and dissolved oxygen (DO) content in water, while a Hach DR1900 was used to test Fe$^{2+}$ and HS$^{-}$ on site. An atomic absorption analyzer (Scientific iCE 3300, Thermo, Germany) was used to analyze Mn$^{2+}$ content, and an ion chromatograph (881 Compact IC pro, Metrohm, Switzerland) was used to test SO$^{2-}_4$ content at the Institute of Water Resources and Environment, Jilin University (Changchun, China). A continuous flow analyzer (San++, Skalar, Netherlands) was used to measure NO$_3$ and NH$_4^+$ contents, and a TOC analyzer (TOC-L CPH Shimadzu, Japan) was used to test DOC at the Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences (Changchun, China). The δ$^18$H and δ$^13$C values were tested using a laser isotope meter (L2140-i, Picarro, USA) at the Third Institute of Oceanography, Ministry of Natural Resources (Xiamen, China), with accuracies of ±0.50 and ±0.20‰, respectively.

Aquifer medium sampling

Sample sites of the vadose zone and aquifer medium were located in the vicinity of point NS1, FS1, and FS3 and samples were collected using percussion drills in September 2018. The collection horizons were 0–0.5, 1.0–1.5, 2.0–2.5, and 6.5–7.5 m below the land surface. Samples were stored in 500 mL glass bottles and were immediately transported to the laboratory at –20 °C for testing total nitrogen (TN), soil organic carbon (SOC), and ion exchange forms of NO$_3^{-}$/NH$_4^+$ (IEF-NO$_3^{-}$/NH$_4^+$).

TN content was tested at 120–124 °C in an alkaline substrate using K$_2$S$_2$O$_8$ to oxidize all forms of nitrogen in the medium to NO$_3^{-}$, then tested using a continuous flow analyzer. The loss-on-ignition method was used to obtain the organic matter content, and then by using the Van Bemmelen factor of 1.724, was converted to the SOC content. The IEF-NO$_3^{-}$/NH$_4^+$ in the 2 mol/L KCl extraction medium was tested using a continuous flow analyzer.

In situ permeability test for riverbed sediment

The standpipe falling head test method, also known as the tube test, was used to determine the permeability of the riverbed sediments; four test points R1, R2, R3, and R4 were arranged, respectively, at 5, 30, 150, and 300 m from point NS1, as shown in Figure 1. The length of the standpipe was 1.50 or 2.80 m for different river depths, with an inner diameter of 0.04 m. After being inserted into the depth $L_v$ of the riverbed sediment, the water head change process in the tube was recorded after adding water from the upper end, and the calculation was carried out by Equation (1) (Chen 2000),

$$K_v = \frac{L_v}{t_2 - t_1} \ln \left(\frac{h_1}{h_2}\right), \quad (1)$$

where $K_v$ is the vertical hydraulic conductivity of riverbed sediments, m/day; $L_v$ is the length of the riverbed sediments in the test tube, m; $t_1$ and $t_2$ are the instantaneous moments at the beginning and end of the test days; and $h_1$ and $h_2$ correspond to the water level in the test tube, m.

RESULTS

River stage and groundwater level dynamics

The river stage and groundwater level dynamics from January 2016 to October 2018 are shown in Figure 2. Annual variations in the river stage ranged between 1.0 and 3.2 m, and the river stage was high during July–September and relatively low during October–March of the following year. The surface of the river was frozen from December–March of the following year with the frozen layer thickness being 1 m. The trend of regional groundwater level changes was consistent with that of the river stage, and the annual change was generally less than 1.5 m. The local groundwater level of the well field was lower than the river level throughout the year, indicating year-round river filtration.

In point NS1–NS6 near the shore, the groundwater level could quickly respond to the change in the river level, showing an annual variation of 2.8–3.0 m. In point FS1–FS4 far from shore, the annual variation in the groundwater level
was low, at 0.9–1.8 m. During winter when the pumping intensity was high, variations in the water levels in point FS3 and FS4, located within the depression cone, were relatively large, indicating that the far-shore groundwater level was less affected by the fluctuations in the river level and was instead mainly affected by pumping.

According to the above-mentioned water level dynamics of the river and groundwater, the NS1–FS4 monitoring section was divided into three hydrodynamic zones as follows: (1) river filtration zone (RFZ) (River-NS6); (2) groundwater runoff zone (GRZ) (NS6–FS3); and (3) depression cone zone (DCZ) (FS3–FS4).

**Spatial distribution of $\delta^2$H and $\delta^{18}$O in river water and groundwater**

River water and regional groundwater are two stable lateral recharge sources, and two major end members of the groundwater in the well field. The Second Songhua River originates in the Changbai Mountains (elevation 2,750 m), and the elevation difference with respect to the well field is more than 2,000 m, leading to lower $\delta^2$H and $\delta^{18}$O values in the river water. The western part of Jilin, where the well field features low terrain and shallow groundwater depth, is easily affected by evaporation; hence, the $\delta^2$H and $\delta^{18}$O values of the regional groundwater are relatively high.

In the NS1–FS4 monitoring section, the distribution ranges and average of $\delta^2$H and $\delta^{18}$O values for shallow and deep groundwater lie between those for the river water and regional groundwater, as shown in Figure 3(a) and 3(b). In the horizontal dimension, the groundwater $\delta^2$H and $\delta^{18}$O values at the RFZ are closer to those of the river end members, along the direction of the groundwater runoff, whereas the groundwater $\delta^2$H and $\delta^{18}$O values at the GRZ and DCZ increase gradually, and are close to the values of the regional groundwater end member. In the vertical dimension, the shallow and deep groundwater $\delta^2$H and $\delta^{18}$O values show no obvious difference in the RFZ and GRZ within 200 m from the shore, while the shallow groundwater $\delta^2$H and $\delta^{18}$O values are obviously closer to those of the regional groundwater end member than deep groundwater in the DCZ, which is 420–700 m from the shore.

**Spatial distribution characteristics of redox-sensitive indexes**

**Redox indexes in river water and shallow groundwater**

$\text{Eh}/\text{DO}$. The Eh values and DO contents of the river water were high at 152.25 mV and 8.205 mg/L, respectively, as shown in Figure 4(a) and 4(b), indicating an oxidizing environment. During river filtration, shallow groundwater Eh and DO at the RFZ rapidly dropped to below $-150.00$ mV and 1.0 mg/L, respectively, gradually making the environment in this zone reducing in nature. Regional groundwater Eh and DO were $-151.62$ mV and 0.68 mg/L, respectively, indicating a reducing environment. Average shallow groundwater Eh and DO at the GRZ and DCZ were $-126.25$ mV and 1.18 mg/L, respectively, which were higher than those of the shallow groundwater at the RFZ and regional groundwater, with a tendency of increasing along the direction of flow until reaching their highest values at the DCZ.
Figure 3 | Spatial distribution of $\delta^{2}H$ and $\delta^{18}O$ values in river water and groundwater along the groundwater flow path in the monitoring section.

Figure 4 | Spatial distribution of environmental and hydrochemical indexes in shallow groundwater along the groundwater flow path in the monitoring section.
**pH.** The pH value of the river water was 7.72 as shown in Figure 4(c). During river filtration, pH continuously decreased to 7.28 in well NS1-1, then slowly increased along the direction of flow, while the average shallow groundwater pH in the RFZ was 7.64. Average regional groundwater pH was 7.18. Average shallow groundwater pH at both the GRZ and DCZ was 7.31, which is between the shallow groundwater at the RFZ and regional groundwater, with a tendency of decreasing along the direction of flow; the lowest pH was recorded in the DCZ.

\[ NO_3^-/NH_4^+ \]. The contents of NO\(_3^-\) and NH\(_4^+\) in river water were 2.274 and 0.124 N mg/L as shown in Figure 4(d) and 4(e), respectively. During river filtration, the shallow groundwater NO\(_3^-\) decreased rapidly, while NH\(_4^+\) increased rapidly, until in well NS1-1 at the shore, where NO\(_3^-\) then dropped to 0.762 N mg/L, having been consumed up to approximately 70%. Meanwhile, NH\(_4^+\) increased to 0.613 N mg/L, a 4-fold increase, until in well NS4-1 that is 8 m from shore, where NO\(_3^-\) dropped below the detection limit, while NH\(_4^+\) was 0.865 N mg/L. Regional groundwater NO\(_3^-\) was very low, mostly below the detection limit, while average NH\(_4^+\) was relatively high at 1.881 N mg/L. In the shallow groundwater of the GRZ and the DCZ, average NO\(_3^-\) was 0.759 N mg/L, which was higher than the shallow groundwater at the RFZ and regional groundwater, while average NH\(_4^+\) was 1.188 N mg/L, which was between that of the shallow groundwater at RFZ and regional groundwater.

**Mn\(^{2+}/Fe\(^{2+}\).** The contents of Mn\(^{2+}\) and Fe\(^{2+}\) in the river water were extremely low as shown in Figure 4(g) and 4(h). During river filtration, shallow groundwater Mn\(^{2+}\) and Fe\(^{2+}\) began to increase until reaching well NS1-1; with Mn\(^{2+}\) peaking at 1.12 mg/L in well NS3-1, which is 5 m from the shore. Fe\(^{2+}\) peaked at 3.42 mg/L in well NS6-1, which is 30 m from the shore. Both Mn\(^{2+}\) and Fe\(^{2+}\) began to decrease after peaking until they dropped to a minimum value in well FS1-1, which is 80 m from the shore. Average regional groundwater Mn\(^{2+}\) and Fe\(^{2+}\) were 5.98 and 12.21 mg/L, respectively. Average shallow groundwater Mn\(^{2+}\) and Fe\(^{2+}\) at the GRZ and DCZ were 3.79 and 6.38 mg/L, respectively, ranging between the shallow groundwater at the RFZ and the regional groundwater. Meanwhile, Mn\(^{2+}\) and Fe\(^{2+}\) at the DCZ were closer to that of the regional groundwater.

**SO\(_4^{2-}\).** The SO\(_4^{2-}\) content in the river water was 29.72 mg/L as shown in Figure 4(f). Average shallow groundwater SO\(_4^{2-}\) in well NS1-1–NS4-1 that is within 14 m from shore was 29.98 mg/L without obvious change. In well NS5-1, which is 30 m from shore, SO\(_4^{2-}\) began to decrease, reaching its lowest value of 8.97 mg/L in well FS1-1, which is 200 m from shore at the GRZ. Average regional groundwater SO\(_4^{2-}\) was 58.36 mg/L. Average shallow groundwater SO\(_4^{2-}\) at the DCZ was 62.29 mg/L, which is higher than the shallow groundwater at the RFZ, GRZ, and regional groundwater. Meanwhile, the content of HS\(^-\) was relatively low at all monitoring wells and was maintained below the detection limit.

**DOC.** The DOC content of the river water was 23.14 C mg/L as shown in Figure 4(i). During river filtration, at the RFZ and GRZ within 80 m from the shore, average shallow groundwater DOC of well FS1-1–FS4-1 gradually decreased along the direction of flow with a value of 9.33 C mg/L on average, which is approximately 60% less than that of the river water. The average regional groundwater DOC was 16.38 C mg/L. At the GRZ and DCZ within 80–700 m from the shore, the average shallow groundwater DOC of well FS1-1–FS4-1 was 17.75 C mg/L, which is higher than that of the shallow groundwater at the RFZ and regional groundwater.

**Redox indexes in deep groundwater**

**Eh/DO.** The Eh values and DO contents of deep groundwater were relatively stable as shown in Figure 5(a) and 5(b), respectively. Average deep groundwater Eh and DO in well NS1-2–NS6-2 that are within 30 m from shore at the RFZ were –125.32 mV and 0.63 mg/L respectively, indicating a reducing environment. Deep groundwater Eh and DO in well FS1-2–FS4-2 that are 80–700 m from shore at the GRZ and DCZ were –129.49 mV and 0.74 mg/L, respectively, and there was no significant change when compared with the deep groundwater at the RFZ.

**pH.** The pH value was relatively stable in deep groundwater as shown in Figure 5(c) along the direction of flow. Average deep groundwater pH in well NS1-2–FS2-2 within 420 m
from shore at the RFZ and GRZ was 7.39. The average deep groundwater pH in well FS3-2–FS4-2 at the DCZ was 7.21, which was closer to that of the regional groundwater.

$NO_2^-/NH_4^+$. Compared with the shallow groundwater, the deep groundwater had lower $NO_2^-$ content and higher $NH_4^+$ content as shown in Figure 5(d) and 5(e), respectively. Average deep groundwater $NO_2^-$ and $NH_4^+$ in well NS1-2–NS6-2, which are within 30 m from shore at the RFZ, were 0.394 and 2.081 N mg/L, respectively. Average $NO_2^-$ and $NH_4^+$ in well FS1-2–FS4-2, which are 80–700 m from shore at the GRZ and DCZ, were 0.452 and 2.230 N mg/L, respectively, which are higher than those of deep groundwater at the RFZ and regional groundwater.

$Mn^{2+}/Fe^{2+}$. As shown in Figure 5(g) and 5(h), the contents of $Mn^{2+}$ and $Fe^{2+}$ in deep groundwater at the RFZ and GRZ began to increase in well NS1-2, with $Mn^{2+}$ in well NS6-2, which is 30 m away from the shore, peaking at 1.18 mg/L, and average $Fe^{2+}$ in well FS1-2 and FS2-2, which are 80–200 m from shore peaking at 3.76 mg/L. After peaking, $Mn^{2+}$ began to decrease in well FS1-2, which is 80 m from shore, while $Fe^{2+}$ did not show a significant decline, and both average $Mn^{2+}$ and $Fe^{2+}$ gradually increased in well
FS2-2–FS3-2, which are at the junction of the GRZ and DCZ with values of 3.79 and 6.18 mg/L, respectively. The Mn$^{2+}$ and Fe$^{2+}$ contents were closer to those in the regional groundwater than to the water near the depression cone center.

SO$_4^{2-}$. The SO$_4^{2-}$ content in deep groundwater of well NS1-2–FS1-2, which are within 80 m from shore at the RFZ and GRZ, remained relatively stable with an average value of 24.53 mg/L as seen in Figure 5(f). Deep groundwater SO$_4^{2-}$ in well FS1-2 and FS2-2, which are 80–200 m from shore, decreased for a short interval, and then continued to increase along the direction of flow to reach 32.43 mg/L in well FS3-2 and FS4-2, which are 420 and 700 m from shore, respectively. Concentrations of HS$^-$ were the same as those for shallow groundwater, with relatively low concentrations.

DOC. The content of DOC in deep groundwater was higher than that in the shallow groundwater as shown in Figure 5(i). In deep groundwater, average DOC in well NS1-2–NS6-2, which is within 30 m from shore at the RFZ, was 24.75 C mg/L. Average DOC in well FS1-2–FS4-2, which are 80–700 m from shore at the GRZ and DCZ, was 25.85 C mg/L, which is higher than the value recorded for the deep groundwater at the RFZ and the regional groundwater; DOC at the GRZ increased significantly.

Spatial distribution characteristics of carbon and nitrogen in aquifer

Vertical distributions of N and C contents in the vadose zone and aquifer medium are shown in Figure 6. The points NS5, FS2, and FS4 are 14, 200, and 700 m from the shore and are located in the RFZ, GRZ, and DCZ, respectively.

In the vertical profile, the surface medium of the vadose zone of each hole had a high content of fine particles, as the surface is mostly covered by trees and crops; the surface medium forms an important growth and metabolism area for plants and microorganisms where organic life and humus are abundant, as well as fertilizers. The average contents of TN and SOC were 0.262 N and 6.273 C g/kg, respectively, and the average C:N value was 14.217, indicating that nitrogen assimilation and mineralization might be prevalent (Dhondt et al. 2005; Evans et al. 2011). The content of coarse particles in the lower part of the vadose zone and aquifer medium increased, while contents of TN and SOC were lower with an average of 0.144 N g/kg and 1.495 C g/kg, respectively, and the average C:N ratio was 8.186. Although this C:N value indicates that ammonification could occur, the organic nitrogen content within the substrate was limited. Meanwhile, the spatial distribution characteristics of IEF-NH$_4^+$ and IEF-NO$_3^-$ in the medium were similar to those of TN and SOC, with a tendency to gradually decrease.
In the horizontal direction, the lithological composition and structure of pores in point NS5 and FS4 were similar, as well as the nitrogen and carbon indicators. In point FS2, the content of coarse particles in the vadose zone was significantly higher than those in point NS5 and FS4, indicating that the permeability of the vadose zone of point FS2 is relatively stronger. Meanwhile, the contents of TN, SOC, IEF-NH$_4^+$, and IEF-NO$_3^-$ in the medium of each layer in point FS2 were also lower than those of point NS5 and FS4.

DISCUSSION

Hydrodynamic exchange between river and groundwater

Flow path along the direction of filtration and runoff

The hydraulic gradient between the river and groundwater acts as a driving force, while gravity flow induces groundwater runoff from the river to the pumping wells (Su et al. 2017). As Figure 7 shows, the riverbed sediments near point NS1 were relatively denser and continuous, comprising of silty-clay mixed with fine sand with a thickness of 0.05–0.3 m, while for tube test points R1 and R2 located at this district, the results of $K_v$ varied from 4.82 to 6.39 m/day. Riverbed sediments in the middle of the river contained fine sand with low horizontal continuity and stratification, and the tube test points R3 and R4 showed that $K_v$ varied from 46.11 to 59.37 m/day. Otherwise, the vertical difference in lithology and permeability of the upper and lower aquifer was evident; the upper aquifer consisted of fine sand with a hydraulic conductivity ($K$) of 28.47 m/day, while the lower aquifer consisted of medium sand with a $K$ of 40.38 m/day.

The heterogeneity of the water-bearing medium affected the different hydraulic exchange characteristics between the river and groundwater, showing two flow paths from the river to the center of the depression cone, as shown in Figure 7. In shallow riverbed with lower permeability, flow occurred at a shallow depth (9 m) with lower velocity and was lateral. In deeper riverbed with higher permeability, flow occurred at a depth greater than 9 m (reaching 17–19 m at the bottom of the aquifer), had a higher velocity, and was vertical to the lateral flow.

Recharge of local groundwater

To more precisely clarify the recharge conditions along the direction of the two flows, the hydrogen and oxygen stable isotopes of the river water and groundwater were calculated and analyzed based on mass conservation. Relative contributions of the river water and regional groundwater could be estimated using an end member mixing model which can be determined using Equation (2),

$$\delta_1 n_1 + \delta_2 n_2 = \delta(n_1 + n_2)$$
$$n_1 + n_2 = 1$$

where $\delta_1$, $\delta_2$, and $\delta$ are the isotope values for river water, regional groundwater, and local groundwater, respectively; and $n_1$ and $n_2$ are the proportions of river and regional groundwater, respectively.
In this study, δ18O was used for this calculation. The contribution rates of the river at the RFZ, GRZ, and DCZ were 84.37–93.56%, 72.80–74.82%, and 26.08–50.42%, respectively, at the shallow depths; the contribution rates of the river at the three zones were 78.45–89.80%, 59.93–64.82%, and 52.23–55.03%, respectively, at deeper depths. Thus, it can be concluded that the contribution rate of the river to deep local groundwater is greater than that of the shallow groundwater, indicating a closer relationship between the river and deep groundwater. Meanwhile, along the direction of groundwater flow, with increasing distance away from the river, the contribution rate of the river to both shallow and deep groundwater continuously decreased, especially at the DCZ, where the contribution of the regional groundwater was quite high.

The amplitude of the contribution rate of the river at shallow flow was higher than that at deep flow, indicating that the recharge condition was more complex for shallow groundwater. In point FS2 at the GRZ, where the permeability of the vadose zone is greater than that in point NS5 and FS4, precipitation could more easily pass through the vadose zone to recharge the shallow groundwater. In points FS1 and FS2 at the GRZ, the δ18O values of shallow groundwater are lower than that of deep groundwater, as shown in Figure 3, which implies that the shallow groundwater at the GRZ could be affected by precipitation.

### Redox zonation of RBF

#### Principle and identification processes

River water is the most important recharge component of the RBF system. During river filtration, the main sequence of reduction processes indicates DOC as the electron donor, as shown in Table 1. Generally, −ΔG° (W) values of aerobic respiration and denitrification are higher and closer, leading to in situ overlapping of their ranges (Korom 1992; Rivett et al. 2008). The reactions of Mn(IV) and Fe(III) reduction with lower −ΔG° (W) values could occur sequentially with a clear boundary. However, when the Eh values become low, SO42− reduction and methane fermentation can occur simultaneously (Champ et al. 1979; Stumm & Morgan 1995). In this study, as the redox environmental indexes and sensitive components along the direction of flow varied, O2, NOx, Mn(IV), Fe(III), and SO42− were reduced sequentially, as shown in Figure 8(a) and 8(b), until reaching well FS1-1, which is 80 m from the shore at shallow flow, and well FS2-2, which is 200 m from the shore at deep flow.

Based on this, regional groundwater makes the second highest contribution toward the quantity of recharge, which is continuous and stable, and shows spatial variability. The variations in Mn2+ and Fe2+ contents in groundwater might reflect the influence of regional groundwater lateral recharge in cases when: (1) the regional groundwater has high concentrations of Mn2+ and Fe2+; (2) the Mn2+ and Fe2+ contents in groundwater at well FS1-1, which is 80 m away from shore, are lowest because of the sequential redox processes; and (3) mixing of groundwater with two different reducibilities suggests a new environment wherein the concentrations of Mn2+ and Fe2+ in the far-shore groundwater are influenced by groundwater mixing and reaction.

Precipitation recharge may also contribute to the quantity of groundwater. However, variations in NH4+, NO3-, and DOC contents in groundwater might reflect the influence of the vertical recharge of precipitation, in cases

<table>
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<th>Reaction</th>
<th>Equation</th>
<th>ΔG° (W) kJ/eq</th>
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<tr>
<td>Aerobic respiration</td>
<td>CH2O + O2 = CO2 + H2O</td>
<td>−125.1</td>
</tr>
<tr>
<td>Denitrification</td>
<td>CH3O + 4/5NO3− + 4/5H+ = CO2 + 2/5N2 + 7/5H2O</td>
<td>−118.8</td>
</tr>
<tr>
<td>Mn(IV) reduction</td>
<td>CH2O + 2MnO2 + 4H+ = CO2 + 2Mn2+ + 3H2O</td>
<td>−81.8</td>
</tr>
<tr>
<td>Fe(III) reduction</td>
<td>CH2O + 4Fe(OH)3 + 8H+ = CO2 + 4Fe2+ + 11H2O</td>
<td>−28.9</td>
</tr>
<tr>
<td>Sulfate reduction</td>
<td>CH2O + 1/2SO4− + 1/2H+ = CO2 + 1/2HS− + 2H2O</td>
<td>−25.3</td>
</tr>
<tr>
<td>Methane fermentation</td>
<td>CH2O = 1/2CH4 + 1/2H2O</td>
<td>−23.2</td>
</tr>
</tbody>
</table>
when: (1) contents of TN and SOC are quite low which inhibits the release of $\text{NH}_4^+$ and DOC to the groundwater; (2) contents of TN, $\text{NH}_4^+$, NO$_3^-$, and SOC of the vadose zone medium are abundant, especially at the upper region of the aquifer; and (3) increasing $\text{NH}_4^+$ and SOC contents are positively correlated with the particle contents of the vadose zone medium.

Therefore, along the directions of both shallow and deep flows, the increasing rates of $\text{NH}_4^+$, NO$_3^-$, and DOC contents were greater than those of the Mn$^{2+}$ and Fe$^{2+}$ contents between points FS1 and FS3, while the trend was opposite between points FS3 and FS4, as shown in Figure 8(a) and 8(b). Thus, by adjusting the hydrodynamic zonation to partition the redox zonation, the range of the river water recharge zone (RWZ) was inferred as 0–80 m in shallow flow and 0–200 m in deep flow. The range of the precipitation vertical recharge zone (PVZ) was 80–420 m in shallow flow and 200–420 m in deep flow. The range of the regional groundwater lateral recharge zone (RGZ) was 420–700 m at both the shallow and deep flows.

**Range of sequential redox reactions in the river water recharge zone**

Precise partitions of the RWZ were carried out and the results are shown below. Vertical differences in the
permeability of aquifer medium are known to lead to the differences in flow velocity, which in turn, influence water retention time, nutrient flux, microbial community structure, acid–base condition, and redox condition between the river water and groundwater (Massmann et al. 2008; Su et al. 2018), leading to sequential reduction reactions that have wider distribution ranges in deep groundwater. Meanwhile, this zone is the most important for producing NH$_4^+$ by ammonification (Dhondt et al. 2003; Evans et al. 2011).

**Aerobic respiration and denitrification zone**

Microorganism-induced aerobic respiration and denitrification occurred preferentially and overlapped; they occurred within point NS2, less than 2 m from shore. As denitrification was catalyzed by denitrifying bacteria, the facultative anaerobic bacteria could reduce NO$_3^-$ to N$_2$ under a relatively O$_2$-rich environment and a DO content of up to 2–4 mg/L (Rivett et al. 2008). However, aerobic respiration occurred within ~0.1–1.5 m beneath the riverbed surface, as previously reported (Revsbech et al. 2005; Kumar & Riyazuddin 2012; Su et al. 2018).

**Mn(IV) reduction zone**

When the Eh values of groundwater dropped to a desired range, manganese minerals in the riverbed sediment and aquifer medium were released into the groundwater by organic complexation or reductive dissolution, as symbolized by the variation in Mn$^{2+}$ content, which increased slowly to reach a peak value along the flow direction and then decreased because of oxidation and precipitation (Greskowiak et al. 2006; Kedziorek & Bourg 2009). Hence, the range of this zone could be assigned as well NS2-1–NS4-1, 2–8 m from shore for shallow flow and well NS2-2–FS1-2, 2–80 m from shore for deep flow.

**Fe(III) reduction zone**

Similar to Mn(IV) reduction, under favorable Eh values of groundwater, ferrous minerals in the riverbed sediment and aquifer medium were released into the groundwater by organic complexation or reductive dissolution, as symbolized by the variation in Fe$^{2+}$ content similar to that in Mn$^{2+}$ content. However, this range of this zone could be assigned in well NS4-1–NS6-1, 8–30 m from the shore for shallow groundwater and well FS1-2–FS2-2, 80–200 m from the shore for deep groundwater.

**SO$_4^{2-}$ reduction zone**

This zone is symbolized by an obvious decrease in SO$_4^{2-}$ contents, as shown in Table 1; the $-\Delta G_f$ (W) values of Fe(III) and SO$_4^{2-}$ reduction were relatively similar, leading to a non-definite boundary. The HS$^-$ produced by SO$_4^{2-}$ reduction would precipitate upon reaction with Fe$^{2+}$, which is one of the reasons for the decreasing levels of Fe$^{2+}$ and low concentrations of monitored HS$^-$ as mentioned above. The ranges could be assigned in well NS6-1–FS2-1, 30–200 m from the shore for the shallow groundwater, and well FS2-2, ~200 m from the shore for the deep groundwater.

**Redox conditions within the PVZ**

The contents of Mn$^{2+}$ and Fe$^{2+}$ reduced, but stable values were observed between well NS6-1 and FS1-1 for shallow groundwater during RBF with a relatively little influence of precipitation and regional groundwater as shown in Figure 8(a); therefore, shallow groundwater in well FS1-1 and the regional groundwater were determined to be the two Mn$^{2+}$ and Fe$^{2+}$ mixing end members for far-shore groundwater. By using the end member mixing model as shown in Equation (2), the mixing ratio of water using $\delta^{18}$O was calculated; then, the Mn$^{2+}$ and Fe$^{2+}$ mixed lines for the shallow and deep flows were obtained. Results are shown in Figure 9(a) and 9(b).

The redox background at the PVZ, which is represented by point FS2, was the SO$_4^{2-}$ reduction environment. The measured Fe$^{2+}$ concentration was lower than that in the Fe$^{2+}$ mixed line for both the shallow and deep flows, indicating the occurrence of reactions that consume Fe$^{2+}$. Possible reasons for this might be (1) Fe$^{2+}$ combined with HS$^-$ produced by SO$_4^{2-}$ reduction and (2) oxidizing by O$_2$ recharge occurred vertically through the vadose zone as Fe$^{2+}$ was readily oxidized, except for DOC and HS$^-$ as shown in Table 2. However, in the shallow groundwater, HS$^-$ was consumed almost completely in well FS2-1 and DO content was still relatively high as seen in Figure 4(a), thus O$_2$ would act
on the consumption. In the deep groundwater, SO$_2^-$ began to reduce in well FS2-2, while DO content was maintained at low levels as seen in Figure 5(a); thus, it is inferred that HS$^-$/CO$_4^-$ and O$_2$ contributed to the decreasing of Fe$^{2+}$. Unlike Fe$^{2+}$, the measured Mn$^{2+}$ concentration was obviously higher than the Mn$^{2+}$ mixed lines of both shallow and deep groundwater, indicating high Mn(IV) reduction. The redox environment was still reductive despite an increase of Eh in comparison with the SO$_2^-$/CO$_4^-$ reduction zone. Therefore, it is inferred that the actual lowest Eh values in shallow and deep groundwater should be located between the controlling values of Mn(IV) and Fe(III) reduction. Under this relatively weak reductive condition, nitrification would hardly occur in the presence of HS$^-$/CO and Fe$^{2+}$. Therefore, NO$_3^-$ could be recharged and accompany O$_2$ vertically, and both would be reduced before Fe(III) and SO$_2^-$ reduction. This shows that the vertical recharge affected the sequential redox zonation mainly because of the recharge of electron accepters with higher Gibbs free energy and electron donors.

### Table 2  Redox processes in an open system (modified after Stumm & Morgan 1995; Champ et al. 1979)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
<th>$\Delta G$ (W) kJ/eq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic respiration</td>
<td>CH$_2$O + O$_2$ = CO$_2$ + H$_2$O</td>
<td>-125.1</td>
</tr>
<tr>
<td>Sulfide oxidation</td>
<td>1/2HS$^-$/CO + O$_2$ = 1/2SO$_4^{2-}$ + 1/2H$^+$</td>
<td>-99.8</td>
</tr>
<tr>
<td>Fe(II) oxidation</td>
<td>4Fe$^{2+}$ + O$_2$ + 10H$_2$O = 4Fe(OH)$_3$ + 8H$^+$</td>
<td>-96.2</td>
</tr>
<tr>
<td>Nitrification</td>
<td>1/2NH$_4^+$ + O$_2$ = 1/2NO$_3^-$ + H$^+$ + 1/2H$_2$O</td>
<td>-43.3</td>
</tr>
<tr>
<td>Mn(II) oxidation</td>
<td>2Mn$^{2+}$ + O$_2$ + 2H$_2$O = 2MnO$_2$ + 4H$^+$</td>
<td>-40.3</td>
</tr>
</tbody>
</table>

### Redox conditions within the regional groundwater lateral recharge zone

At this zone, under conditions where NH$_4^+$, NO$_3^-$, and DOC along the flow direction did not increase, (NH$_4$)$_2$SO$_4$ fertilizer used at the surface caused significant accumulation of SO$_2^-$ in both shallow and deep groundwater as shown in Figures 4(f) and 5(f), indicating that vertical recharge is significant but still less than the lateral recharge. The Eh values and DO contents along the flow direction at points FS3 and FS4 increased, where they were located within the depression cone, and except for direct vertical recharge, the intermittent state of pumping would promote groundwater fluctuation leading to O$_2$ dissolution by air trap and diffusion (Massmann et al. 2008; Kohfahl et al. 2009).

The points FS3 and FS4 represent the groundwater of RGZ, where the measured Mn$^{2+}$ and Fe$^{2+}$ concentrations were obviously higher than the mixed lines at both shallow and deep groundwater as shown in Figure 9(a) and 9(b), indicating that Mn(IV) and Fe(III) reduction were both
active. The actual lowest Eh values in shallow and deep groundwater should be located at the controlling values of Fe(III) reduction, which was lower than that of the PVZ, owing to continuous lateral recharge of the high Fe\(^{2+}\) reductive regional groundwater.

Similar to the PVZ, under relatively reductive conditions, oxidation of HS\(^{-}\), Fe\(^{2+}\), NH\(^{4+}\), and Mn\(^{2+}\) would barely occur, and small quantities of O\(_2\) and NO\(_3\) were recharged vertically would be rapidly reduced. In summary, at the RGZ and PVZ, O\(_2\), NO\(_3\), Mn(IV), and Fe(III) would be reduced in sequence again, which is affected by vertical and lateral recharge including: (1) depression of groundwater reduction in different degrees; (2) recharge intensity of electron donors; and (3) recharge intensity of electron accepters with higher Gibbs free energy.

### CONCLUSIONS

With a background of high ferrous and manganese content in regional groundwater, river filtration and groundwater runoff toward the groundwater depression cone in the RBF system have two different groundwater flow paths (shallow and deep) due to the variation in permeability of riverbed sediments at different intervals of the river. Meanwhile, recharge intensities of the river water, regional groundwater, and precipitation showed differences in the spatial distribution along the groundwater path from the river to the depression cone, influencing the redox conditions. At the RWZ with a high river recharge contribution, O\(_2\), NO\(_3\), Mn(IV), Fe(III), and SO\(_4^{2-}\) were reduced in sequence meaning the DOC, as the electron donor, formed a strong reducing environment accompanied by an increase in NH\(^{4+}\) through ammonification. However, lateral recharge from reductive regional groundwater with high Fe\(^{2+}\) and Mn\(^{2+}\) concentrations and vertical recharge from oxidative precipitation with high O\(_2\), NO\(_3\), SO\(_4^{2-}\), and DOC concentrations change the redox conditions of the local groundwater from RBF. At the PVZ, the influence of vertical precipitation recharge was more significant than that of the lateral recharge, which led to higher Eh values in groundwater in the PVZ than that in the RGZ. These redox conditions provided an opportunity for Mn(IV) reduction at the PVZ and for both Mn(IV) and Fe(III) reduction at the RGZ; therefore, the aquifer medium would consistently release more Mn\(^{2+}\) and Fe\(^{2+}\) into the groundwater.

### ACKNOWLEDGEMENTS

The authors would like to thank the editors of Hydrology Research and the reviewers for their thoughtful and constructive comments, which helped improve the manuscript.

### FUNDING INFORMATION

This work was supported by the National Natural Science Foundation of China (Grant numbers: 41877178, 41372238).

### DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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First received 30 July 2020; accepted in revised form 27 August 2020. Available online 14 September 2020.