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Characterizing interactions between surface water and groundwater in the Jialu River basin using major ion chemistry and stable isotopes

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Abstract

The Jialu River, a secondary tributary of the Huaihe River, has been severely contaminated for the major contaminant sources, such as a number of untreated or lightly treated sewage wastes in some cities. Groundwater along the river is not an isolated component of the hydrologic system, but instead connected with the surface water. This study aims to characterize the relationships between surface water (e.g. reservoirs, lakes and rivers) and groundwater near the river in the shallow Quaternary aquifer. The concentration of Cl^- in North Zhengzhou City increased prominently due to the discharge of a large amount of domestic water. Nitrate and potassium show maximum concentrations in groundwater in Fugou County. These high levels can be attributed to the use of a large quantity of fertilizer over this region. The regional well had water with a constant stable isotopic signature, which illustrates that the groundwater never or rarely receive recharge from surface water. However, the groundwater of transitional well (location SY3) seemed to be recharged by river water via bank infiltration in September 2010. Fractional contributions of river water to the groundwater were calculated based on isotopic and chemical data using a mass-balance approach. Results show that the groundwater was approximately composed of 60–70 % river water. These findings would be useful for a better understanding of hydrogeological processes at the river-aquifer interface and ultimately benefit water management in the future.

1 Introduction

The Jialu River (JR), the secondary tributary of the Huaihe River, is severely contaminated by a variety of contaminant sources such as a large number of trade wastes and the untreated or lightly treated sewage wastes in some cities (Zhang et al., 2009). These wastes have resulted in elevated concentrations of chemical oxygen (COD) and ammonia nitrogen (NH_3-N) in water within the Zhengzhou region (Lu et al., 2008) and the lower reaches in the Zhoukou region (Zhao et al., 2005; Xie et al., 2008). Zhang

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et al. (2009) reported that concentrations of alkylphenols in surface water were more enriched in the lower reaches compared with the upper stream, with the maximum enrichment taking place in the lower reaches of the Zhengzhou urban zone. Zhang et al. (2011) showed elevated concentrations of nonylphenol, octylphenol, and bisphenol A in the JR bed sediment. Some of the elevated concentrations were high enough to result in potential aquatic and human-health problems.

The Jialu River basin (JRB) aquifer is the primary source of drinking water for the rapidly growing population of Zhongmou, Weishi, Fugou, Xihua and nearby communities. Groundwater and surface water are not isolated components of the hydrologic system, but instead interact with each other across a variety of physiographic and climatic landscapes (Winter et al., 1998; Woessner, 2000; Winter, 2001; Sophocleous, 2002). Thus, there is a noteworthy concern that the trace elements in the water and sediment of JR could contaminate the JRB aquifer. Temporal variations in groundwater chemistry in response to changes in river chemistry and stream flow are also of great concern. An better understanding of the interactions between the two water bodies is a key for effective management of water resources over this region. However, the published studies did not seem to have adequately addressed these issues.

Two field campaigns for investigating the interaction between surface water and groundwater was conducted in July and September 2010, respectively. The former one was in flood processing, and the latter one was after flood period. The overall objective of this study was to characterize relationships between surface water and groundwater along the JR.

2 Study area

The JRB covers an area of of 2750 km^2, ranging in latitude between 33° 37′ 47″ and 34° 53′ 50″ N and in longitude betwen 113° 6′ 17″ and 114° 38′ 7″ E (Fig. 1). As a secondary tributary of the Huaihe River, the JR is 220 km long, originating from Shenshuiyu of Xinmi in Henan Province. In its source region, the river flows northeasterly

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in Xinmi and Zhengzhou. From Zhengzhou, the river has two abrupt turns, i.e. flowing eastwardly and then southeastwardly through Weishi, Fugou, Xihua, and lastly joining in the Yinghe River at Zhoukou. The main Jialu River channel is contributed by several tributaries. The main tributaries include the Suoxu River, Donfengqu and Shuangji River.

The climate throughout the study area is with warm, moist summers and cool, dry winters. The average annual temperature in Zhengzhou is 14.4 °C, and the maximum is observed in July with extreme value of 43 °C and minimum in February of −17.9 °C between 1951 and 2010. The mean annual precipitation in Zhengzhou was 641 mm per year from 1951 to 2010, with large interannual variability from minimum 381 mm to maximum 1041 mm. Most of the precipitation falls in the form of rain during the 4-month period from June through September, i.e. the flood season of the river basin, when precipitation accounts for more than 65 % of annual precipitation (Fig. 2; data from China Meteorological Data Sharing Service System, http://cdc.cma.gov.cn/).

The geology of this study area is relatively complex (Fig. 3). This study area pertains to one of the transitional areas between the mountains in the west and the plains in the east. The upper reaches of the JRB are dominated by Paleoproterozoic quartzite and schist and Cambrian sedimentary rocks (i.e. sandstone, limestone, shale, and mudstone). The lower reaches are composed mainly of Holocene alluvium, aeolian deposit and Pleistocene lacustrine-alluvium, alluvium-diluvium, and slope-diluvium sediments (clay, silt sand, fine sand, sand and gravel; data from National Geological Archives of China, http://www.ngac.cn).

3 Sampling and analytical methods

Two major sampling campaigns were carried out along the JR and surrounding JRB aquifer up to 1.5 km from the river in July and September 2010, respectively. The first campaign was in flooding processing. Water samples were taken in Xingyang and Zhengzhou on 18 July 2010 before the rainy event. It began to lightly rain in the evening

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of 18 July and became more intense after the midnight. The rainfall amount was up to 102 mm until 08:00 a.m. LT (local time). The JR rose quickly from a low flow stages to a high stage. River water (location J10, SY12, and SY15) had been sampled when flood peak passed. However, the river water SY9 and SY20 had been sampled when flood peak did not reach the locations. The second campaign was conduced from 8 to 10 September 2010. A 121.6 mm rainfall was observed between 5 and 7 September 2010, i.e. the second campaign was carried out during the post-flood period.

Surface water samples were collected at nine locations (Fig. 1). The groundwater samples were taken from 9 domestic wells in the quaternary aquifer (Table 3). The depths of the wells ranged between 9 m (location SY14 and SY16 in Fig. 1) in Fugou Qilijing and Xihua, and 50 m (location J5 in Fig. 1) in Xingyang, the northwestern part of the investigated area where the surface elevation is approximately 156 m with reference to the sea level.

Surface water samples were typically collected at bridges in the reaches at a depth of about 30 cm using a weighted polyethylene water collector. The existing village-supply wells were selected for sampling groundwater. The 100 ml polyethylene bottles used to store the unfiltered stream samples were pre-rinsed with sample water three times before the final water sample was acquired. All samples were sealed with adhesive tape so as to prevent evaporation. The global positioning system (GPS) was used to locate the sampling locations.

Temperature, pH value and electrical conductivity of each sample were measured in situ using a WM-22EP handled electrical conductivity meter. Oxygen concentration and redox potential were also determined using a Hach HQ30d Single-Input Multi-Parameter Digital Meter. The field water quality parameters were monitored until these values were stabilized.

The water quality was measured at the Center for Physical and Chemical Analysis of Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences (IGSNRR, CAS). All samples were analyzed for major ion composition, including Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-}, NO_3^{-}, and Cl^{-}. Major cations were determined

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using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES), while major anions were determined using ion chromatography (LC-10A, Shimadzu, Japan). HCO_3^- was measured by the diluted vitriol-methylic titration method using 0.0112 M H_2SO_4.

The Normalized Inorganic Charge Balance, NICB, defined as $(TZ^+ - TZ^-)/TZ^+$, represents the deviation extent between the total cations and total anions (Edmond et al., 1995; Huh et al., 1998). It was indicated by Huh et al. (1998) that the measured major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, NO_3^-, Cl^-, HCO_3^-) are generally in the charge balance. A few of these water samples showed a charge imbalance with a positive charge excess, or some inversely with a negative charge surplus. This positive charge excess could be related to the fact that no analysis of PO_4^{3-} was made and the negative charge surplus could be attributable to the lack of NH_4^+ measurements. However, the chemical analysis results were adopted when the charge-balance error was within ±10 % in the study.

Water isotopes (δD and δ^{18}O) were determined at IGSNRR, CAS using off axis integrated-cavity output laser spectroscopy (Model DLT-100; Los Gatos Research Inc.) and the method described in Lis et al. (2008). All samples were normalized to internal laboratory water standards that were previously calibrated relative to the Vienna Standard Mean Ocean Water (VSMOW) (0 ‰). Results were expressed as parts per thousand deviations from the VSMOW with analytical precisions of ±1 % (δD) and ±0.15 % (δ^{18}O).

4 Results

4.1 Stable isotopic composition in waters

Stable isotopic compositions in water can be considered conservative and hardly affected by water-rock reactions under normal temperatures (McCarthy et al., 1992; Gat, 1996). Therefore, isotopic variations may occur within the catchment as a consequence

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of concentration variations in the input such as rainfall and surface water (Kendall and McDonnell, 1998).

The δD and δ^{18}O values of the surface and groundwater samples collected in July and September 2010 were plotted in Fig. 4 with the local meteoric line (LML; precipitation in Zhengzhou; WMO/IAEA, 2010) giving accurate information on the input signal. These samples are well distributed along the LML, illustrating that surface and groundwater from the shallow Quaternary aquifer most probably originate from present-day precipitation.

The δ^{18}O values varied from −12.58‰ to −3.34‰, and the δD values changed from −91.33‰ to −35.48‰ in JR water (Tables 1–2 and 4–5). Moreover, heavier isotopes were enriched in river water in the upper reaches, which resulted mostly from evaporation form reservoirs where these samples were collected (Fig. 4).

The two tributaries of Suoxu River and Dongfengqu flow into the JR in north and east Zhengzhou, respectively, and the resulting water sampled downstream (J10) should reflect the mixture of the two channels.

The surface water samples obtained in the second sampling campaign present a wide range of stable isotopic signatures. Isotopic composition of river water was mostly negative. It could be due to precipitation with lighter isotope.

Signatures of all of these groundwater samples except the sample SY3 remained the same during the flood period and after the flood period, which indicates that the aquifer seems to be large enough to mask the seasonal isotopic variation caused by rainfall. Sample SY3 was depleted in lighter isotopes after the flood period, possibly indicating that the riverbank-aquifer water may originate from a mixing of original groundwater and river water with more depleted isotope values.

4.2 Main geochemical parameters

Electrical conductivity (EC) (Tables 1, 2) measured in surface water varied from 541 to 1637 µS cm^{-1} in July and 429–965 µS cm^{-1} in September 2010. The former EC reflected the pollutant migration process in the river channel. The high level of EC in

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location J9 and SY9 was primarily due to samples collected before rain and during the flood peak period. The levels of EC in location J10, SY12 and SY15 were lower than that in location SY9, which is because the flood peak carrying a large amount of pollutant passed. The latter EC values were significantly lower during post-rain conditions, which is likely due to a considerable amount of dilution of ions concentration resulting from heavy precipitation during this period. EC values in groundwater varied from 608 to 2280 $\mu S\,cm^{-1}$, with the highest values observed in groundwater from Fugou (sample J20). The water temperature measured in surface water varied from 25.5 to 29.1 °C in July and 22.5–24.5 °C in September 2010, which were much higher than the temperature measured in groundwater in both campaigns (16.8 to 21.3 °C. Most of the surface water showed pH values between 7.0 and 8.0, whereas groundwater pH varied between 6.83 and 7.52 with no obvious variation during the campaigns. DO concentrations of the surface water and groundwater ranged from 1.2 to 6.3 $mg\,l^{-1}$ with an averaged concentration of 3.04 $mg\,l^{-1}$ and 0.36–7.09 $mg\,l^{-1}$, respectively. Most part of this study area was found to be under oxidation conditions with Eh values ranging from −119 to 236 mV.

The total dissolved solids (TDS) represents the total mineralization (inorganic content) of water and was well correlated with EC ($R^2 = 0.86$), which also reflects the dissolved content in water. TDS values varied between 303.9 (surface water J3) and 1385.3 $mg\,l^{-1}$ (sample location J20, groundwater in the Fugou). Such high mineralization in a natural environment of groundwater generally occurs in water evaporite formations (Petelet-Giraud et al., 2007). The local geological environment is Pleistocene lacustrine-alluvium and contains no evaporate; therefore it is impossible that the layers studied are influenced by the deep saline groundwater (Han et al., 2002; Gao, 2008). The source of the high dissolved ions content can, therefore, be related to direct or indirect anthropogenic activities that have occurred in cities or counties along the river over the last few decades.

Results of chemical analyses of groundwater and surface water samples are shown in the Piper diagram (Fig. 5). In the upper stream waters (J3 and J8), SO_4^{2-} and Ca^{2+}

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are the predominant ions, with concentrations ranging from 132 to 172 mg l^{-1} and from 49.08 to 56.17 mg l^{-1} (Table 1), respectively. It is speculated that the source of SO_4^{2-} results from the oxidation of uncovered pyrite in headwater areas of the Suoxu River and JR, considering mining in the upstream mountain area (Pang, 1994). Because the reservoir retains river water, the concentration of SO_4^{2-} is accumulated. Chloride is the second anion after HCO_3^- over the lower reaches of reservoirs, with the highest concentration being measured in north Zhenghzou during the flood period (191 mg l^{-1}, July 2010). There are many possible sources of Cl^-, which may be related to untreated or inadequately treated sewage and industrial activities. Sodium is the dominant cation of the river water during the flood period, varying from 92 to 194 mg l^{-1}, whereas, Ca^{2+} is the dominant cation except for north Zhenghzou during the post-flood period, varying from 41 to 63 mg l^{-1}. It showed most variations in Cl^- and Na^+ content due to anthropogenic influences during the flood period compared to the post-flood period.

The chemical composition of groundwater at SY3 varied from Ca-Na-Cl-HCO_3 rich in July to Na-Ca-HCO_3 rich in September 2010. In contrast, the chemical composition of water from other wells did not change significantly during the study period, but the concentrations of major ions varied considerably from well to well. For example, groundwater from the area near the Chulou Reservoir is Ca^{2+} and HCO_3^- dominant and is characterized as Ca-Mg-HCO_3 water type, whereas groundwater in the lower reaches Zhengzhou (SY14) is Ca^{2+} and Cl^- dominant and is characterized as Ca-Mg-Cl-HCO_3 water type. In the groundwater of location J20, the concentration of K^+ was as high as 51.49 mg l^{-1}, which is 32 times higher than the averages of the other groundwater samples. Furthermore, clear anthropogenic inputs are indicated in groundwater of location SY14 and J20 (Fugou County) where high NO_3^- contents excess the World Health Organization Standard (WHO, 2008) and Chinese limitation value (10 mg l^{-1} calculated as N) for drinking water (Ministry of Environmental Protection, China, 2002).

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5 Discussion

5.1 Anthropogenic sources and impacts on surface water and groundwater

Human activity is one of the most important factors affecting hydrology and water quality. Water chemistry of rivers can reflect changes in watersheds, making rivers good indicators of land use (Meybeck and Helmer, 1989). Chemical alteration associated with human activity is related to development of city and intensification of agriculture, especially the discharge of untreated sewage wastes. Therefore, human activities driven by economic development, population growth, and urbanization jointly result in alterations of river water quality.

Chloride and sodium are major electrolytes in human urine (Kirchmann and Pettersson, 1995) and are therefore concentrated primarily in waste water. The concentration-river distance profiles (Fig. 6) for the two indicator ions (Cl^- and Na^+) show the pronounced effects of urbanization on the major ion chemistry of the JR. Concentration of Cl^- is below 30 $mg\,l^{-1}$ in the upper reaches of Zhengzhou, and then increases by a factor of 4.4 in the urban region of north Zhengzhou. It becomes rapidly diluted over the lower reaches of the city in July. The reason is that Zhengzhou is a big city with a population of $4.3 \cdot 10^6$ people, whereas the lower reaches of counties are relatively small with population of $0.5–0.8 \cdot 10^6$ people (Henan Provincial Bureau of Statistics, 2011). Trends in Cl^- and Na^+ during the post-flood period are the same as those during the flood period. However, the concentration during the post-flood period is lower than that during the flood period due to the precipitation.

Among the dissolved solutes, NO_3^- and K^+ show maximum concentrations in groundwater in Fugou County. These high nitrate levels can be attributed to agricultural practices in this region, especially artificial and manure fertilization (Zhang et al., 1996; Liu et al., 2005; Ma et al., 2009) and animals breeding. Fugou County is one of the top 10 counties growing vegetable in China. In 2009, Fugou had 361 000 rural employees, a total sown area of 144 730 ha, and 120 099 large animals (Henan Provincial Bureau of Statistics and Henan Survey Office of NBS, 2010). To increase crop yield

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and income, farmers are currently decreasing the use of organic fertilizer in favor of inorganic fertilizers with improper proportions of nitrogen, phosphorous, and potassium throughout agricultural regions of Fugou. This approach has led to losses of fertilizer into groundwater. Potassium concentration (J20) largely exceeds the mean potassium concentrations in drinking water, e.g. 2.5 mg l^{-1} in the UK (Powell et al., 1987) and up to 8 mg l^{-1} in Canada (Health Canada, 2008). Those results are probably caused by the use of a large amout of fertilizer.

5.2 Interactions between surface water and groundwater

By synthesizing various types of field data obtained in this study, it is possible to provide a picture of the surface water and groundwater interactions within the basin. Groundwater wells were generally categorized into two groups based on dissolved-solids concentrations and stable isotope values: (1) regional wells, in areas where ground water did not include water recently recharged from the river (all locations except the SY3 in the basin); and (2) transitional wells, in areas where ground water was possibly a composite of recharge from the river and water from regional systems during river high flow periods; and was only water from regional systems during river low flow periods (location SY3).

The regional wells ranged from 70 to 1190 m from the river and had water with a constant stable isotopic signature (δD, δ^{18}O) throughout the hydrological cycle, which did not reflect seasonal variations although the river water isotope varied greatly due to precipitation. This illustrates that the groundwater never or rarely received recharge from surface water.

The transitional well of SY3, 30 m from the river, seemed to be closely connected to the nearest river water as the groundwater had similar trends of stable isotope signatures and chloride content with the river. The salient features of the isotope and hydrochemistry of groundwater at SY3 are as follows. During the pre-flood (July 2010), the δD and δ^{18}O of water were −57.80 and −7.54, respectively. During the post-flood (September 2010), the δD and δ^{18}O was found to be depleted. In the same way, the

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Cl^- content in September 2010, was also diluted. That is because the recharge by river water via bank infiltration in September 2010, could be characterized by lower Cl^- and relatively depleted δD and δ^{18}O signatures.

The composition of groundwater at SY3 in September 2010 can be described by a mixture of two possible sources, including groundwater from the regional system, and river water. The river water and rainwater sources were combined in one as river water because river flood in September 2010 was mainly from the precipitation.

When these water sources are considered as end members to the groundwater at SY3, it is possible to estimate mixing proportions between the waters using a mass-balance approach (Christophersen and Hooper, 1992; Clark and Fritz, 1997; Kendall and Mcdonnell, 1998).

Assuming that groundwater at SY3 in September 2010 was a result of mixing original groundwater (GW) and river water (RW), the following equation could be used to assess the fractional contributions of river water to the groundwater:

$$f = \frac{C_s - C_{GW}}{C_{RW} - C_{GW}} \cdot 100\% \quad (1)$$

where C_s is the Cl^-, δD or δ^{18}O (mgl^{-1} or ‰) of the mixed water sample (location SY3 in September 2010); C_{RW} is the Cl^-, δD or δ^{18}O of river water (location J9 in September 2010); and C_{GW} is the Cl^-, δD or δ^{18}O of original groundwater in July 2010 that is not influenced by river recharge. Location SY3 in July 2010 was chosen as the original groundwater end-member because it has not recharged by the river.

The resulting fractional contrition percentages are 60 %, 61 % and 70 % using Cl^-, δD and δ^{18}O, respectively. Mixing calculations suggest that the groundwater at SY3 in September 2010 was composed of approximately 60–70 % river water, depending on the tracer employed. This result shows that more than half of water contamination of river water can be into the groundwater if the river water is severely polluted.

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6 Conclusions

The Jialu River basin is being faced with environmental pressures mainly coming from anthropogenic influences. Hence, it is important to systemically monitor the Jialu River and groundwater to provide detailed isotopic and hydrochemical information for a greater understanding of these impacts on the river and groundwater and effective manage of the basin in the future. The objective of this study was to investigate the relationships between surface water and groundwater in the Jialu River basin by studying the isotopes and major dissolved inorganic ions. Major findings are as follows.

1. The concentration of Cl^- in north Zhengzhou City significantly increased in river samples during two campaigns conducted due to discharge of a large amount of untreated or slightly treated waste water. Nitrate and potassium show maximum concentrations in groundwater in Fugou County. These high levels can be attributed to agricultural practices cross this region, especially artificial and manure fertilization and animals breeding.

2. The regional wells had water with a constant stable isotopic signature. This illustrates that the groundwater never or rarely receive recharge from surface water.

3. The transitional well of SY3 seemed to be recharged by river water via bank infiltration in September 2010. Fractional contributions of the river water to the groundwater were calculated based on isotopic and chemical data using a mass-balance approach. The groundwater (SY3 in September 2010) was approximately composed of 60–70 % river water. This finding demonstrates that more than half of water contamination of river water can be into the groundwater if the river water is severely polluted.

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Table 1. Major ions and stable isotope concentrations in surface water in July 2010.

Name	EC $\mu S\,cm^{-1}$	T °C	pH	DO $mg\,l^{-1}$	HCO_3 $mg\,l^{-1}$	Cl $mg\,l^{-1}$	NO_3 $mg\,l^{-1}$	SO_4 $mg\,l^{-1}$	Ca $mg\,l^{-1}$	K $mg\,l^{-1}$	Mg $mg\,l^{-1}$	Na $mg\,l^{-1}$	δD ‰	$\delta^{18}O$ ‰
J3	600	28.60	7.97	3.38	144.93	40.46	BDL	171.64	56.17	6.49	28.25	31.63	−38.10	−4.02
J8	541	28.60	8.34	4.91	109.58	35.20	BDL	159.25	49.08	7.38	24.62	27.18	−35.48	−3.34
J7	951	28.10	8.51	6.30	201.49	138.47	12.69	134.45	49.51	8.79	29.60	104.70	−54.25	−6.64
J9	1535	28.50	7.62	1.62	381.77	191.24	9.84	241.17	86.59	16.36	29.27	194.50	−62.48	−8.47
J10	967	25.50	7.54	1.29	265.12	134.22	8.14	111.00	72.19	11.80	22.21	92.28	−71.80	−9.68
SY9	1637	26.50	7.69	1.97	320.01	106.48	37.41	93.32	81.10	11.02	27.23	101.60	−62.78	−8.58
SY12	1023	26.10	7.64	1.45	353.50	113.08	17.47	95.09	77.12	11.25	27.66	99.55	−63.06	−8.54
SY15	1025	27.30	7.47	1.20	331.17	114.70	23.52	92.59	76.90	10.69	27.95	105.00	−62.36	−8.29
SY20	1063	29.10	7.52	1.48	312.56	122.26	18.58	111.01	73.07	11.19	29.30	111.10	−61.56	−8.36

BDL: below detection limit.

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Table 2. Major ions and stable isotope concentrations in surface water in September 2010.

Name	EC $\mu S\,cm^{-1}$	T °C	pH	DO $mg\,l^{-1}$	ORP MV	HCO_3 $mg\,l^{-1}$	Cl $mg\,l^{-1}$	NO_3 $mg\,l^{-1}$	SO_4 $mg\,l^{-1}$	Ca $mg\,l^{-1}$	K $mg\,l^{-1}$	Mg $mg\,l^{-1}$	Na $mg\,l^{-1}$	δD ‰	δ^{18}O ‰
J3	490	24.20	7.51	3.48	29.00	127.26	15.98	BDL	132.67	41.32	5.16	20.90	24.23	−54.08	−6.47
J8	511	24.50	8.02	6.02	142.50	126.51	15.88	BDL	150.33	45.35	6.91	21.52	25.46	−45.26	−4.96
J7	429	22.50	7.41	3.02	−105.90	156.28	33.42	2.26	47.88	44.87	8.50	8.14	25.66	−91.33	−12.37
J9	965	22.90	7.27	1.64	45.30	241.87	73.56	2.31	191.02	62.24	10.57	15.97	109.30	−83.12	−11.24
J10	720	22.90	7.46	2.66	173.00	226.98	66.23	6.95	97.30	63.06	10.04	17.56	58.85	−81.49	−11.61
SY9	604	23.00	7.41	2.57	165.20	226.98	32.67	3.31	86.01	63.16	9.91	15.90	46.33	−86.61	−11.93
SY12	525	22.50	7.37	4.06	167.40	186.05	20.61	BDL	84.46	56.56	8.25	14.68	35.72	−85.92	−12.58
SY15	532	22.80	7.39	4.02	180.20	208.38	31.24	9.98	71.06	54.31	8.28	15.10	38.85	−86.53	−12.07
SY20	565	23.20	7.45	3.65	137.40	183.82	58.32	BDL	76.29	50.93	8.22	15.62	42.49	−82.91	−11.52

BDL: below detection limit.

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Table 3. The information of groundwater wells.

Name	Approximate distance from river m	Depth of well m
J5	570	50
SY3	30	28
SY4	230	20
SY6	170	38
SY7	380	25
SY10	590	16
J20	310	14
SY14	1190	9
SY16	70	9

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Table 4. Major ions and stable isotope concentrations in groundwater in July 2010.

Name	EC $\mu S\,cm^{-1}$	T °C	PH	DO $mg\,l^{-1}$	HCO_3 $mg\,l^{-1}$	Cl $mg\,l^{-1}$	NO_3 $mg\,l^{-1}$	SO_4 $mg\,l^{-1}$	Ca $mg\,l^{-1}$	K $mg\,l^{-1}$	Mg $mg\,l^{-1}$	Na $mg\,l^{-1}$	δD ‰	δ^{18}O ‰
J5	646	17.50	7.11	3.16	335.82	38.71	12.68	18.69	93.13	0.81	22.21	18.68	−59.27	−8.15
SY3	1534	17.20	7.33	0.36	417.12	264.47	9.42	150.91	147.50	4.56	25.33	152.10	−57.80	−7.54
SY4	1274	20.20	7.00	1.47	487.82	131.27	13.16	154.71	139.60	1.86	29.14	103.60	−58.18	−7.63
SY6	1370	17.70	7.13	1.80	544.38	118.04	BDL	77.86	106.70	2.36	38.13	120.90	−61.26	−8.42
SY7	1018	17.30	7.52	3.68	439.08	115.80	6.05	14.32	83.53	1.32	54.80	59.51	−63.00	−8.76
SY10	1063	17.50	7.16	0.94	367.63	106.96	BDL	97.52	138.60	1.47	29.99	50.90	−51.53	−6.72
J20	2050	18.00	7.16	2.59	661.04	218.50	49.72	255.85	116.90	51.49	68.52	199.00	−55.43	−7.54
SY14	2130	16.80	6.83	1.11	427.73	363.39	122.62	117.01	224.90	0.24	77.89	75.21	−59.35	−8.39
SY16	1956	17.50	6.94	2.58	569.31	186.23	39.35	144.74	156.80	0.27	78.79	126.50	−58.95	−8.15

BDL: below detection limit.

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Table 5. Major ions and stable isotope concentrations in groundwater in September 2010.

Name	EC $\mu S\,cm^{-1}$	T °C	PH	DO $mg\,l^{-1}$	ORP MV	HCO_3 $mg\,l^{-1}$	Cl $mg\,l^{-1}$	NO_3 $mg\,l^{-1}$	SO_4 $mg\,l^{-1}$	Ca $mg\,l^{-1}$	K $mg\,l^{-1}$	Mg $mg\,l^{-1}$	Na $mg\,l^{-1}$	δD ‰	$\delta^{18}O$ ‰
J5	608	23.20	7.22	7.09	236.00	327.45	28.23	6.44	19.90	83.94	0.61	20.90	17.72	−59.82	−8.29
SY3	1317	18.30	7.16	2.25	193.60	502.34	150.22	16.95	105.74	114.30	4.69	18.56	162.00	−73.33	−10.12
SY6	1275	18.20	7.16	2.08	−119.90	513.50	113.74	BDL	91.14	112.40	2.14	33.45	110.30	−61.19	−8.08
SY7	980	21.30	7.34	4.34	138.40	476.29	90.07	BDL	15.72	79.05	1.25	51.63	56.55	−63.24	−8.38
SY10	1070	17.90	7.16	2.49	165.60	409.31	98.90	BDL	113.66	133.90	1.42	29.33	55.56	−51.75	−6.52
J20	2280	17.80	7.00	1.62	154.10	632.57	251.22	58.63	285.70	154.30	50.80	74.35	194.00	−56.93	−8.04
SY14	1913	17.20	6.90	1.73	158.80	420.47	338.26	72.14	155.42	228.70	0.36	70.05	68.24	−58.22	−8.77
SY16	2040	17.40	6.89	2.95	161.30	561.87	218.74	33.31	234.50	211.00	0.31	80.81	132.30	−57.67	−8.47

BDL: below detection limit.

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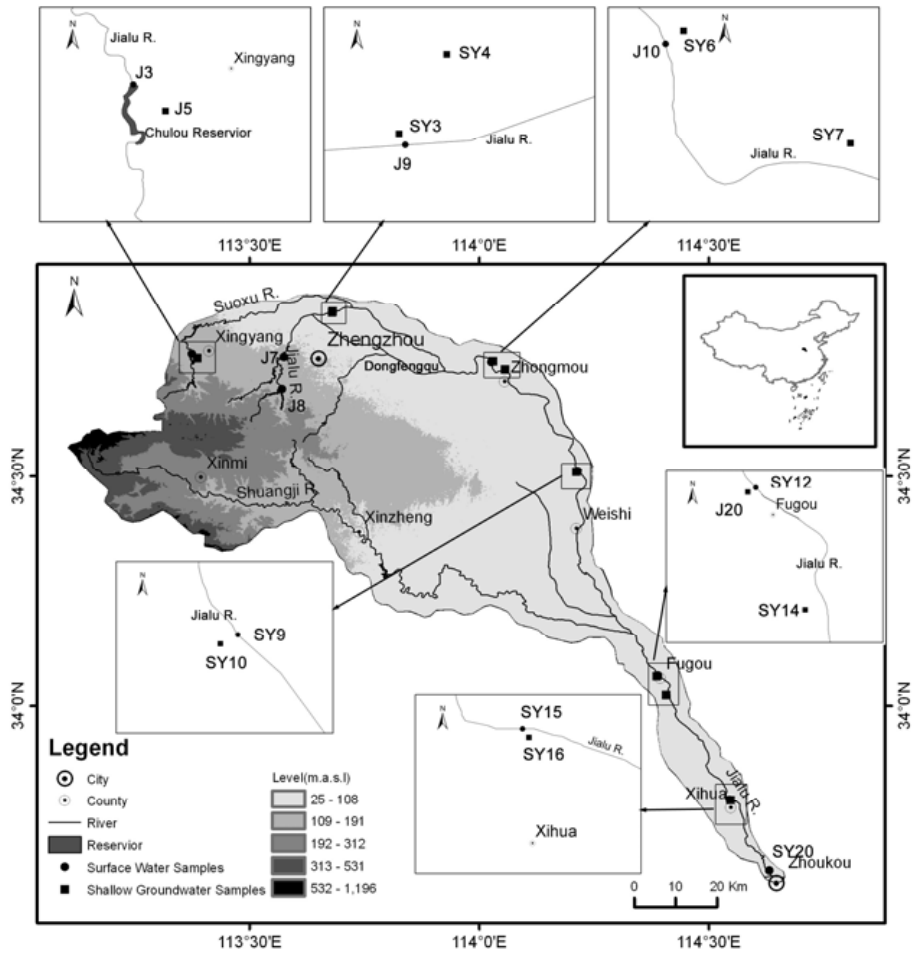

Fig. 1. Study area and relevant sampling locations.

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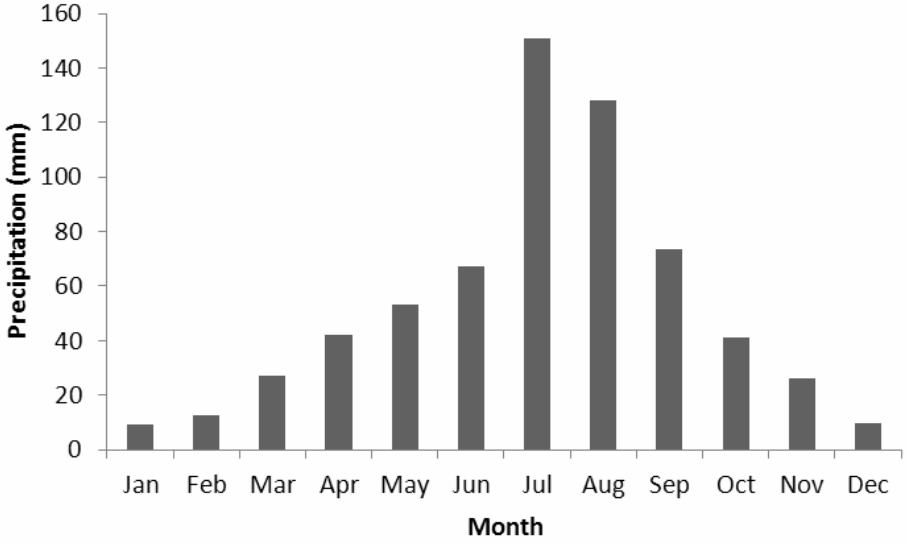

Fig. 2. Monthly precipitation in Zhengzhou.

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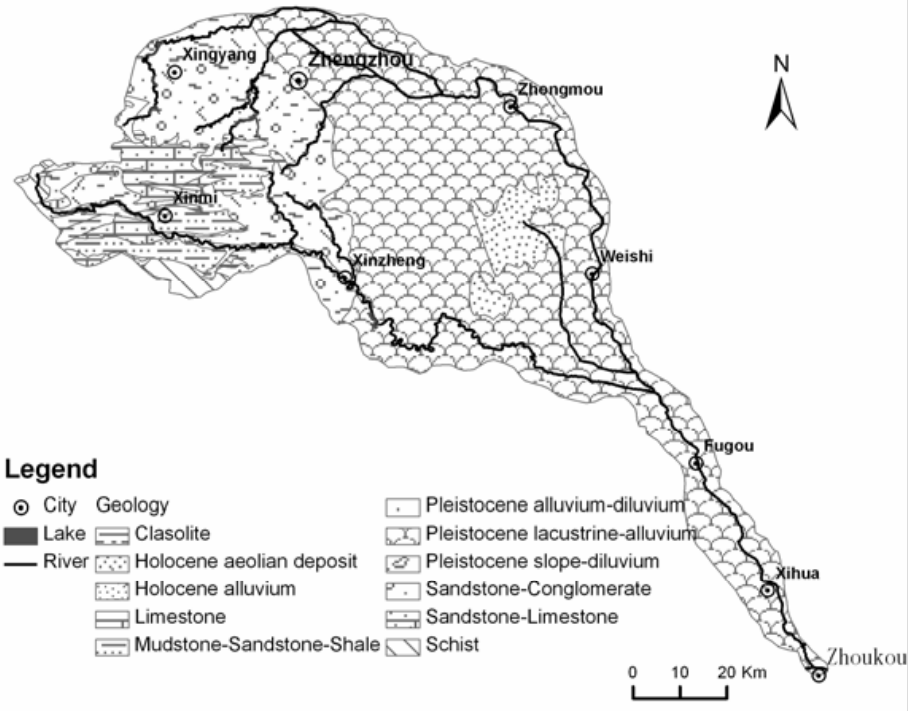

Fig. 3. Major geological formation of the study area (data source: http://www.ngac.cn).

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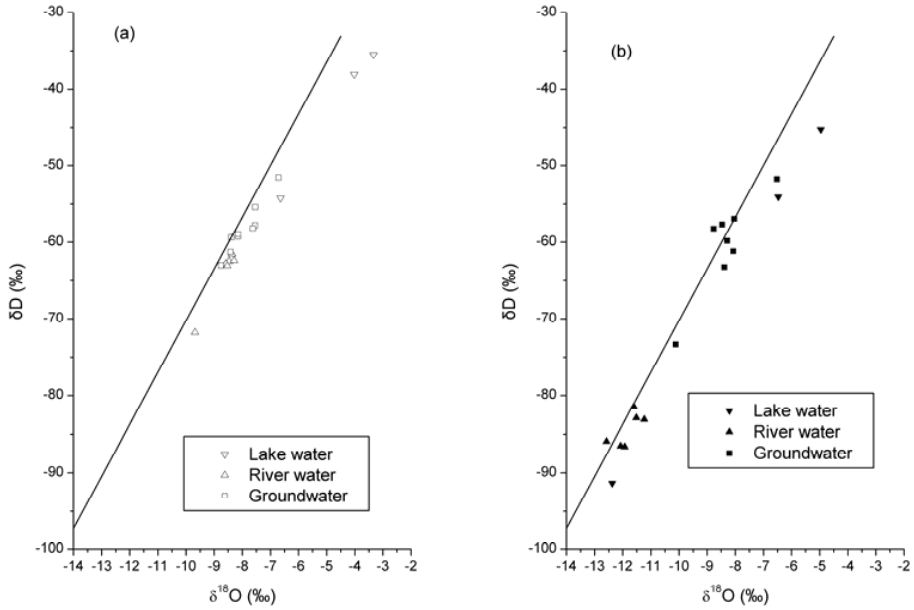

Fig. 4. Relationships between δD and δ^{18}O in water collected from JRB in **(a)** July and **(b)** September 2010.

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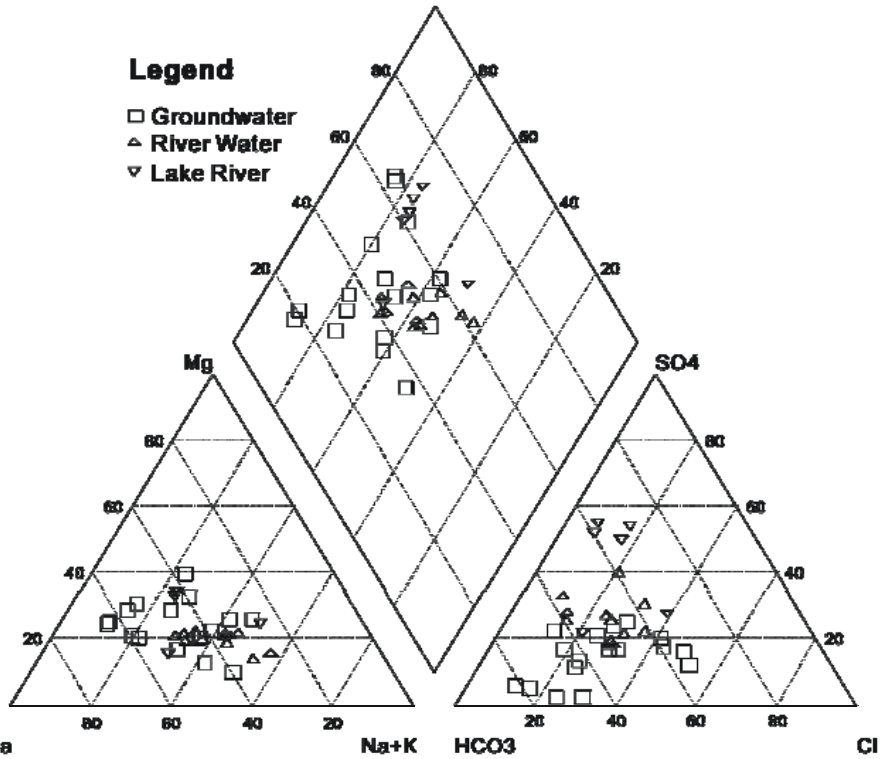

Fig. 5. Piper diagram of major ion chemistry for groundwater, river water and lake water in the study area.

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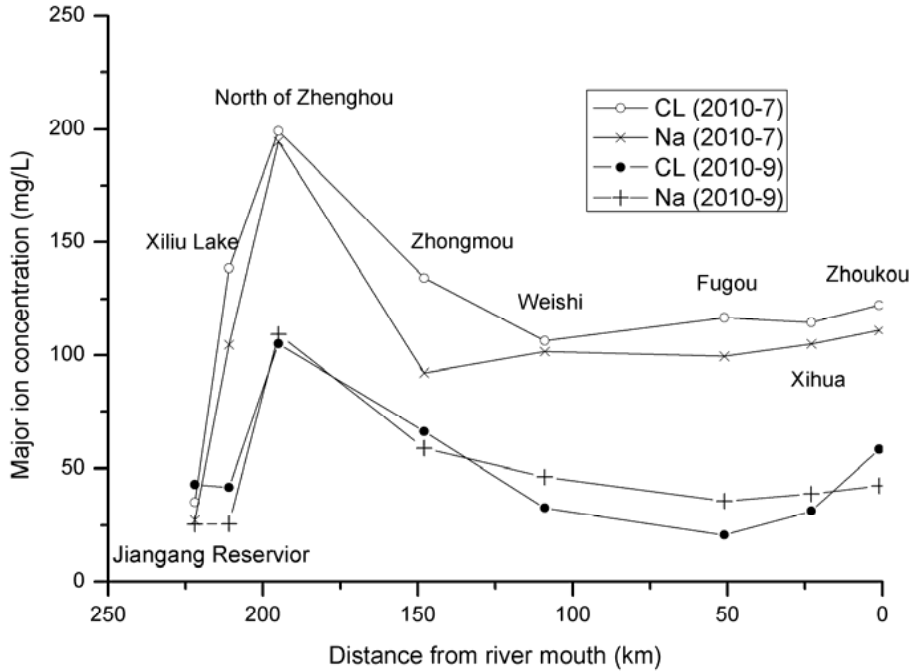

Fig. 6. Major ion concentration/distance from river mouth profiles for chloride and sodium in the main stream of the JR.

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