Environ Earth Sci (2012) 67:2141–2153
DOI 10.1007/s12665-012-1654-7

ORIGINAL ARTICLE

A hydrochemical framework and water quality assessment of river water in the upper reaches of the Huai River Basin, China

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Received: 17 March 2011 / Accepted: 15 March 2012 / Published online: 31 March 2012

Abstract This study characterizes the major ion chemistry for river water in the upper reaches of Bengbu Sluice in the Huai River Basin in wet and dry seasons, and assessed the suitability of water quality for irrigation and human consumption. It is found that sodium and calcium are the dominant cations and bicarbonate is the dominant anion in most river water samples. River water in Zhoukou of the Ying River and Bozhou of the Guo River is characterized as a Na–Cl water type, whereas river water from the upper reaches and the lower reaches of the two cities is characterized as a Na-HCO_3 water type, which may be attributed by anthropogenic influences in these cities. The river water types vary from the upstream to the downstream of the Fuyang sluice, which indicates that the sluices play a critical role in determining the water type. The water chemistry of these rivers clearly shows that the second group of rivers is affected more severely by waste effluent than is the first group. Calculated values of sodium adsorption ratio, %Na, and residual sodium carbonate indicate that, in general, most of the river water is of acceptable irrigation quality. The river water in Zhoukou section of the Ying River and the Bozhou section of the Guo River cannot be used as drinking water; pollution control should be further improved and enhanced across the river.

Keywords Hydrochemistry · Water quality · River water · Huai River Basin

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Introduction

The Huai River Basin (HRB) is a predominately developing area in China. The total gross domestic product (GDP) for the entire river basin in 2004 was 1.05 trillion yuan, which increased by 148 % with reference to the GDP in 1994 (at current prices; Ma 2006). The industry over the basin has been developing at an accelerated rate, encompassing food processing, paper making, textiles, and coal chemical production. Agricultural activities are relatively intensive. Grain is an important aspect of agricultural production that is based mainly on wheat, rice, corn, soybean, and cotton. Major cities including Zhenghou, Luohe, Zhoukou, and Bengbu, are located along Huai River systems. Water project constructions (dams and sluices) are of the major activities in infrastructure developments. To control floods and relieve droughts, more than 5,700 reservoirs and 5,000 sluices were constructed (Zhang et al. 2010).

Like many major river systems in the world, the Huai River and some of its tributaries are extensively used as both a prime water resource and disposal of waste discharged by industrial, agricultural, and domestic activities. Industrial processing is considered to be the main anthropogenic sources of metal and organic pollutants. Agriculture may be the main cause of pollution by the generation of chemical wastes from fertilized land. Effluents from domestic activities are a major cause of pollution of river waters due to large volumes of untreated sewage in some cities (Goudie 2006). More than 8.6 billion m^3 of sewage was eventually discharged into the Huai River in 2009, and 78 % of the Huai River did not meet designated standards for concentration of chemical oxygen demand (COD) and that of ammonia nitrogen (NH_3-N) in drinking water (Huai River Commission 2009). Serious pollution of river water has been expanding without being effectively controlled. Nearly 200 serious water pollution events occurred across the river basin (Huang et al. 2004; Wang et al. 2006; Hu et al. 2008; Zhang et al. 2010).

Previous work showed that organic pollution prevailed in the Jialu River (Zhang et al. 2009) and the Jiangsu section of the Huai River (Ma et al. 2005; Wang et al. 2006, 2009). However, few published studies focused on the effects of hydrochemistry of the Huai River introduced by human activities. Zhang et al. (2011) analyzed the control mechanisms of ion chemistry in the Huai River; however, they did not seem to provide detailed data of major ions chemistry in dry season. To that end, another sampling campaign was carried out in May 2009 (in dry season), aiming at investigating the hydrochemistry in the upper reaches of Bengbu Sluice in HRB. The main objectives of this study were to (1) characterize temporal and spatial variations in the river water hydrochemistry and (2) assess the suitability of river water for irrigation activities and human consumption in wet and dry seasons in the upper reaches of Bengbu Sluice.

Study area

The study area extends from 30°55′N to 34°56′N and 111°55′E to 117°30′E, which encompasses the upper reaches of Bengbu Sluice, including the Ying River, Guo River, Shi River, Feng River, Pi River, and the main stream of the Huai River (Fig. 1). The Huai River originates from the Tongbai Mountain in Henan Province, flows easterly through southern Henan, northern Hubei, northern Anhui, and northern Jiangsu, finally into the Yangtze River at Jiangdu, Yangzhou. The largest tributary of the study area is Ying River and the second is Guo River. The former originates from the Funiu Mountain in western Henan Province. It has a length of 1,078 km and a drainage area of 36,728 km^2. The latter is 380 km long, with a contributing area of 15,900 km^2.

Elevation of the study area ranges from about 23 m to 2,153 m. Variations in elevation are indicative of different land-use patterns and climatological changes. The west portion of study area is more hilly, while the east part is relatively level. Soils investigated include brown soil, cinnamon soil, yellow brown soil in the mountainous area, and yellow moist soil in the plain. They are developed under natural vegetations of coniferous broadleaved forest in the west and fruit forest, robinia and poplar in the east. Over 50 % of the study area is cultivated land. The chief enterprises are cloth, chemical pesticides in Zhengzhou, food processing, textiles, alcoholic beverages in Zhoukou, and wine, yarn in Bozhou, Fuyang, and Bengbu. The major urban areas are the metropolitan area of Zhoukou, Fuyang on the Ying River, Bozhou on the Guo River, and Bengbu on the Huai River (Anhui Provincial Bureau of Statistics, NBS Survey Office in Anhui 2010; Henan Provincial Bureau of Statistics, Henan Survey Office of NBS 2010). The climate throughout the study area varies from northern semi-tropics to sub-humid with warm, moist summers and cool, dry winters. The average temperature in study area is about 11.8—16 °C; the temperature often reaches 28 °C in summer and drops below freezing in winter when occasional cold fronts move through the area. The mean annual precipitation was 600–1,400 mm per year and most of the precipitation falls in the form of rain during the four-month period from June through September, i.e., the flood season of the river basin (Wang et al. 2001). Monthly variations in the water discharge of the Huai River main channel show an appreciable seasonal variability, with low discharges in dry season (October–May) and high values in wet season (June–September). The average discharge in July in Bengbu accounts for about 30 % of annual discharge (Zhang et al. 2011).

Bengbu Sluice, constructed in 1959 and located on the middle reach of the Huai River, is the only dam on the main stream of the river in Bengbu City, Anhui Province (Hu et al. 2008). The mean annual stream flow at the Bengbu station is about 30.5 billion m^3.

The geology of the study area is relatively complex (Fig. 2). The study area is one of the transitional areas between the mountains in the west and the plain in the east. The Pi River flows from granite, gneiss, schist, clasolite, and Quaternary alluvium. The lithology of Feng River is dominated by Quaternary alluvium. The Shi River and Huai River flow from granite, gneiss, schist, clasolite, Quaternary lacustrine-alluvium, and Quaternary alluvium-diluvium. The Ying River originating from the northwestern HRB drains primarily granite, andesite, carbonate, schist, clasolite, and Quaternary lacustrine-alluvium and Quaternary alluvium-diluvium. The Guo River flows initially through Quaternary aeolian, then through lacustrine-alluvium and Quaternary alluvium.

Sampling and analytical methods

A total of 41 water samples were collected at various locations along the main river and tributaries for two different periods of time, i.e., July 2008 (wet season, Zhang

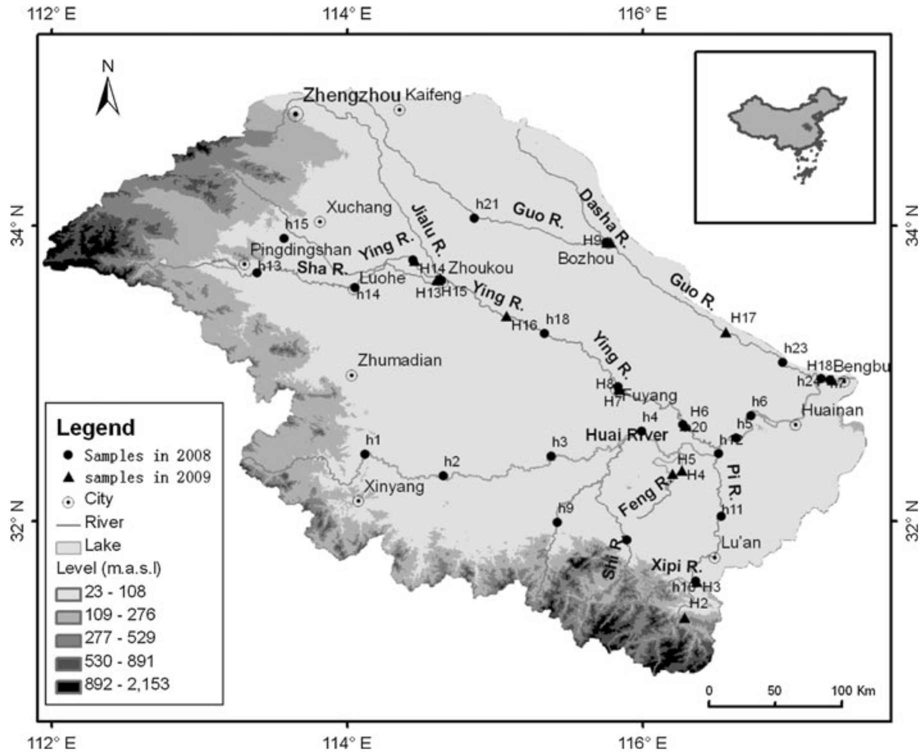


Fig. 1 Map of the study area and sampling locations

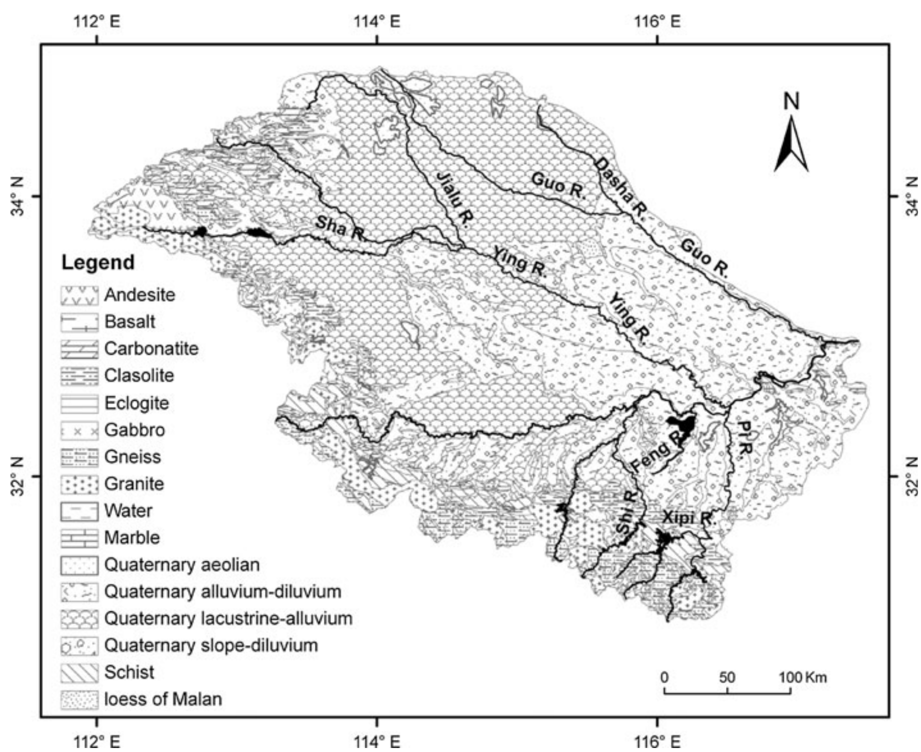


Fig. 2 Study area and its major geological formation

et al. 2011) and May 2009 (dry season, Fig. 1). Sampling sites for July 2008 were in the Shi River, Pi River, Huai River, Ying River, and Guo River (Table 1). Sampling sites for May 2009 were in the Feng River, Pi River, Huai River, Ying River, and Guo River (Table 2).

Collected and analysis methods of river samples in July 2008 are based on that in Zhang et al. (2011). River samples in May 2009 were typically collected off bridges at the mid-stream at a depth of about 30 cm using a weighted polyethylene water collector. Temperature, pH value, and specific

Table 1 Chemical characteristics of river water in study area in wet season (July 2008; Zhang et al. 2011)

Name	River	Location description	EC (μS/cm)	pH	T (°C)	HCO_3^{2-} (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Ca^{2+} (mg/L)	K^+ (mg/L)	Mg^{2+} (mg/L)	Na^+ (mg/L)	TDS (mg/L)	%Na (%)	SAR	RSC (meq/L)
h1	Huai River	Mid-channel at Minggang	129	6.8	28.9	100.8	35.5	BDL	24.5	18.8	3.3	10.4	43.6	236.9	50.2	2.00	−0.14
h2	Huai River	Mid-channel at Xi County	113	7	28.6	80	20.1	BDL	24.5	16.6	3.5	7.7	24.4	176.8	40.6	1.24	−0.15
h3	Huai River	Mid-channel at Huaibin	82	7.6	28.7	68.2	10.7	0.5	19.6	16.6	3.4	7.3	13.8	140.1	28.4	0.71	−0.31
h4	Huai River	Mid-channel at Nanzhao	85	7.5	28.2	62.2	10.2	2.6	18.6	25.2	3.3	8.2	12.4	142.7	21.1	0.55	−0.91
h5	Huai River	Mid-channel at Lutaizi	96	7.5	28.7	86	16.2	5.5	21.9	25.7	3.4	8.9	17.1	184.7	26.1	0.74	−0.60
h6	Huai River	Mid-channel at Huainan	99	7.5	28.7	73.1	15.1	3.4	20.3	27.1	3.3	8.9	16.6	167.8	25.0	0.71	−0.89
h7	Huai River	Mid-channel 100 m above Bengbu sluice	175	7.4	29.8	134.4	28	5.5	35.9	35.1	4.5	12.2	30.8	286.4	31.8	1.14	−0.55
h8	Shi River	Mid-channel of Shi River at Yeji	69	7.6	29.8	51.4	6.7	2.4	14.6	16.4	2.3	4.5	7	105.3	19.6	0.39	−0.35
h9	Shi River	Mid-channel of Guan River at Shangshiqiao	94	7.5	30.3	79	7.8	4.7	17.5	23.7	2.9	7.5	9.7	152.8	18.4	0.44	−0.50
h10	Pi River	Mid-channel 150 m below Hengpaitou sluice	55	7.7	26.7	47.4	5	2.7	14.9	13.9	2.2	3.4	5.3	94.8	18.3	0.33	−0.20
h11	Pi River	Mid-channel at Matou	60	7.6	30	39.5	6	3.9	14.2	13.7	2.3	3.7	5.8	89.1	19.4	0.36	−0.34
h12	Pi River	Mid-channel at Zhengyang	64	7.6	31.5	43.5	7.9	3.4	14.3	14.2	2.5	4.1	6.5	96.4	20.3	0.39	−0.33
h13	Ying river	Mid-channel of Sha River in Pingdingshan	181	7.7	29.8	142.3	19.2	4.9	55.9	49	2.6	13.2	112.6	399.7	57.7	3.69	−1.20
h14	Ying river	Mid-channel of Sha River in Luohe	413	7.8	29.9	135.6	205.1	1.5	103.5	23.5	4.9	14.4	148	636.5	72.2	5.93	−0.13
h15	Ying river	Mid-channel at Huahang	319	7.5	30	197.6	72.3	0.8	93.3	54.4	7.4	27.5	100.5	553.8	45.8	2.77	−1.74
h16	Ying river	Mid-channel at Huangqiao	421	7.4	29.8	201.6	109.7	BDL	129.5	22.3	9.6	33.7	110.6	617.0	53.8	3.45	−0.58
h17	Ying river	Mid-channel in Zhoukou	567	7.6	29.7	209.3	266.8	8.8	124.9	51	6.7	21.9	191.5	880.9	64.8	5.65	−0.92
h18	Ying river	Mid-channel at Jieshou	435	7.4	30.1	217.4	131.5	21.3	110.3	69.7	7.1	25.2	111.6	694.1	45.8	2.91	−1.99
h19	Ying river	Mid-channel 200 m above Fuyang sluice	937	7.4	29.9	181.8	126.8	5.5	128.6	73	8.3	30.3	123.8	678.1	45.9	3.07	−3.16
h20	Ying river	Mid-channel 150 m above Yingshang sluice	435	7.4	30.2	249	93	14.7	105.8	61	8.7	28	127.4	687.6	49.9	3.39	−1.27
h21	Guo River	Mid-channel at Taikang	458	7.5	29.9	320.1	94.8	33.8	177.3	44.9	14.6	30.4	149.3	865.2	55.9	4.22	0.51
h22	Guo River	Mid-channel in Bozhou	1,278	7.3	30.1	202.8	184.9	36.2	243.6	70.6	12	39.8	191.5	981.4	54.0	4.52	−3.47
h23	Guo River	Mid-channel at Mengcheng	676	7.6	30.2	355.7	159.3	16.9	169.4	65.4	9	42.7	185.6	1,004.0	53.5	4.39	−0.95
h24	Guo River	Mid-channel at Huaiyuan	507	7.6	30.6	237.1	114.3	17.7	160.2	49.8	7.5	34.2	176.7	797.5	58.3	4.72	−1.41

BDL below detection limit

Table 2 Chemical characteristics of river water in study area in dry season (May 2009)

Name	River	Location description	EC (μS/cm)	pH	T (°C)	HCO_3^{2-} (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Ca^{2+} (mg/L)	K^+ (mg/L)	Mg^{2+} (mg/L)	Na^+ (mg/L)	TDS (mg/L)	%Na (%)	SAR	RSC (meq/L)
H18	Huai River	Mid-channel 300 m below Bengbu sluice	605	8.29	21.6	172.8	74.7	4.1	72.2	44.3	3.5	17.2	59.1	447.9	40.9	1.91	−0.79
H5	Feng River	From Yan'gang River bank at Huoqiu County	261	7.7	23.3	73.2	16.5	3.8	30.2	19.8	3.4	8.1	16.8	171.8	29.6	0.81	−0.45
H4	Feng River	From Chenxi Lake bank at Huoqiu County	193	7.87	21.8	70.3	20.3	3.9	21.7	18.1	1.3	7.5	11.3	154.4	23.9	0.56	−0.37
H2	Pi River	From Foziling Reservoir bank	95.4	8.1	21.3	35.1	4	BDL	12	10.3	1.2	2.8	4.3	69.7	19.4	0.31	−0.17
H3	Pi River	Mid-channel at Hengpaitou	126.8	8.05	16.5	43.9	8.2	3.5	11.5	14	2.1	3.4	5.5	92.1	19.0	0.35	−0.26
H14	Ying River	Mid-channel 50 m below Huangqiao sluice	1,053	8.15	21.6	257.7	103.5	26.4	104.9	66.7	5.1	22.7	116.4	703.4	48.7	3.14	−0.97
H13	Ying River	Mid-channel of Sha River 200 m above confluence of Sha River and Ying River	966	8.26	23.1	171.5	175.8	13.7	117.3	60.9	3	18	112.6	672.8	51.6	3.26	−1.71
H12	Ying River	Mid-channel of Ying River 200 m below confluence of Sha River and Ying River in Zhoukou	962	8.22	24.6	166.9	167.5	13.9	120.8	57.4	5.1	17.9	111.2	660.7	52.0	3.28	−1.60
H15	Ying River	Mid-channel 200 m above Zhoukou sluice in Jialu River	1,007	7.96	22.9	254.7	69.9	7.3	200.8	68.5	7.7	23.8	102	734.7	44.3	2.70	−1.20
H16	Ying River	Mid-channel 150 m above Huaidian sluice	1,164	7.87	21.4	301.6	93.1	11.8	190.6	74	8.5	29.7	121.5	830.8	45.4	3.02	−1.19
H7	Ying River	Mid-channel 200 m above Fuyang sluice	1,213	8.35	22.9	292.8	177.3	19.8	146.9	74	6.9	33.1	133.4	884.2	46.8	3.24	−1.61
H8	Ying River	Mid-channel 160 m below Fuyang sluice	1,217	8	24	285.1	164.8	19.9	183.9	74	8.1	33.1	131.1	900.0	46.3	3.18	−1.74
H6	Ying River	Mid-channel 300 m below Yingshang sluice	1,191	7.72	21.3	264.3	146.6	28.7	188.1	67.3	8.2	33.6	127.5	864.3	46.7	3.17	−1.79
H10	Guo River	Mid-channel of Dasha River 150 m above confluence of Dasha Rive and Guo River	1,528	8.04	24.1	314.8	118.8	36.5	221.6	49.9	8.3	41.4	189.9	981.2	57.5	4.81	−0.73
H9	Guo River	Mid-channel 300 m above confluence of Dasha Rive and Guo River in Bozhou City	1,782	7.86	22.9	275.5	243.2	11.6	319	71.4	7.1	39.9	221.5	1,189.2	57.8	5.21	−2.33
H11	Guo River	Mid-channel 200 m below confluence of Dasha Rive and Guo River in Bozhou in Bozhou City	1,732	7.86	22.6	275.2	257.5	16.5	278.2	71	7.3	41.3	223	1,170.0	57.7	5.21	−2.42
H17	Guo River	Mid-channel 300 m above Mengcheng sluice	1,386	8.02	21.6	336.7	182.9	BDL	203.7	56.8	5.6	46.5	183.2	1,015.4	53.9	4.37	−1.14

BDL below detection limit

conductance were determined at the time of collection with a WM-22EP handled electrical conductivity meter at the field sites. The field water quality parameters were monitored until the values stabilized. The 100 mL polyethylene bottles used to store the unfiltered stream samples were pre-rinsed with sample water three times before the final stream sample was acquired. All samples were sealed with adhesive tape to prevent evaporation. The global positioning system was used to locate the sampling sites.

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. 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 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 and total dissolved solid (TDS) was calculated by summing up all major ions.

Parameters such as the sodium adsorption ratio (SAR), percent sodium (%Na), and residual sodium carbonate (RSC) were estimated to assess the suitability of water from the study rivers for irrigation purposes.

Sodium adsorption ratio parameter versus EC is very important in classifying irrigation water. The SAR parameter evaluates the sodium hazard in relation to calcium and magnesium concentrations (Richards 1954). It can be calculated as:

$$\mathrm{SAR} = \frac{m_{\mathrm{Na^+}}}{\sqrt{(m_{\mathrm{Ca^{2+}}} + m_{\mathrm{Mg^{2+}}})}} \qquad (1)$$

where m_i represents the concentration of ion (in mmol/L).

The total concentration of soluble salts in irrigation water can be expressed for the purpose of classification of irrigation water as low (EC = <250 μS/cm), medium (250–750 μS/cm), high (750–2,250 μS/cm), and very high (2,250–5,000 μS/cm) salinity zone.

Wilcox (1955) uses sodium percent (%Na) and EC values for classifying irrigation water quality. %Na is calculated by the following formula:

$$\%\mathrm{Na}^+ = \frac{\mathrm{Na}^+}{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + \mathrm{K}^+ + \mathrm{Na}^+} \qquad (2)$$

where all the concentrations are expressed in meq/L.

To quantify the effects of carbonate and bicarbonate, an experimental parameter termed as RSC was used (Eaton 1950). The RSC has the following equation:

$$\mathrm{RSC} = (\mathrm{CO_3^{2-}} + \mathrm{HCO_3^-}) - (\mathrm{Ca^{2+}} + \mathrm{Mg^{2+}}) \qquad (3)$$

where all the concentrations are expressed in meq/L.

Results

Electrical conductivity

Electrical conductivity (EC) is directly related to the concentration of ions dissolved in the water. EC varies between 55 and 1,278 μS/cm in wet season and 95–1,782 μS/cm in dry season for the river water (Tables 1, 2). The measured EC in wet season samples is slightly less than that in dry season samples. Such differences in EC can be related to the variation in river flow. The general trend for average EC in an increasing order by river is: Pi River < Feng River (or Shi River) < Huai River < Ying River < Guo River (Tables 1, 2; Fig. 3). The three samples collected from the Guo River in dry season in Bozhou City had values greater than 1,500 μS/cm, which was the highest EC values in the study and was probably a mixture of untreated or lightly treated sewage wastes and river water.

pH

The Environmental Quality Standard for Surface Water in China calls for river water to have a pH between 6 and 9 (Ministry of Environmental Protection 2002). The measured values of pH were found to range from 6.8 to 7.8 in wet season, and 7.7 to 8.35 with a mean of 8.0 in dry season (Tables 1, 2).

Major element concentration

Solute concentrations in the study area vary over a broad range. The river water is characterized by a medium TDS concentration of 445 and 679 mg/L for wet and dry season, respectively. The median TDS concentration is 542 mg/L that is relatively high compared to major river systems throughout the world, more than seven times the global median of 65 mg/L (Hu et al. 1982; Meybeck and Helmer 1989; Chen et al. 2002). TDS concentrations range from a low value of 69.7 mg/L in the Pi River to as high as 1,189.2 mg/L in the Guo River. Low concentrations in the Pi River are representative of basins containing shallow soils and rocks that are not easily dissolved, while extremely high concentrations in Guo River can be ascribed to the anthropogenic input of ions.

The major anions constitute more than 65 % of the TDS except one sample in Pingdingshan of the Ying River (h13). Bicarbonate is the dominant dissolved ion, accounting for almost 46 % of the TDS in the Huai River, Shi River, Feng River, and Pi River (Tables 1, 2). Its concentration varies between 39.5 and 134.4 mg/L in wet season and 35.1 and 172.8 mg/L in the dry season. Bicarbonate is followed by $SO_4{}^{2-}$, which accounts for 14 % of

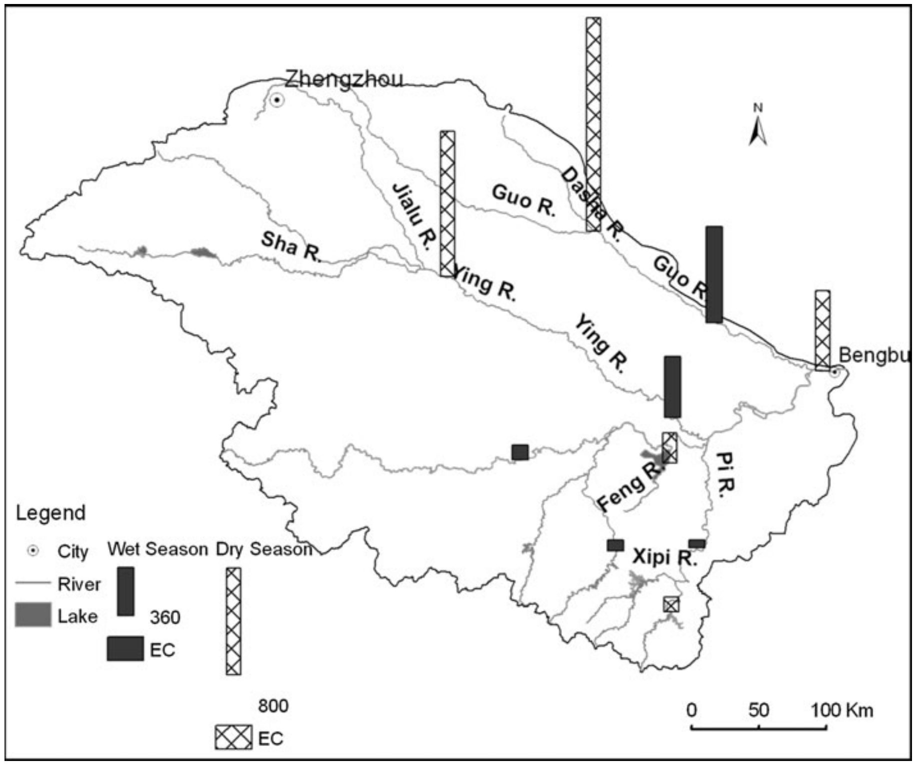


Fig. 3 Spatial distribution of the average electrical conductivity (EC) of rivers in dry and wet season

the total anion, with its concentration varying between 14.2–35.9 and 11.5–72.2 mg/L in wet and dry season, respectively. Sulfate and chloride are the two equivalent ions in most sites of the Ying River, occupying about 18 % of the TDS. The concentrations of bicarbonate, sulfate and chloride are nearly equal in most samples of the Guo River (H9, H11, and h22). The concentration of NO_3^- are relatively low in all rivers, showing a small contribution (<6 %) to the total anionic budget.

The major cations constitute around 29 % of the TDS. Sodium and calcium are the dominant cations accounting for 14 and 10 % of the TDS, respectively (Tables 1, 2). Sodium concentration ranges from 5.3 to 191.5 mg/L in wet season and 4.3 to 223.0 mg/L in the dry season, respectively. The average concentration of calcium in wet and dry season was found to be 36.7 (ranging between 13.7 and 73.0 mg/L) and 52.8 mg/L (ranging between 10.3 and 74.0 mg/L), respectively. The concentration of other two cations, i.e., Mg^{2+} and K^+, range between 3.4–42.7 and 2.2–14.6 mg/L in wet season and 2.8–46.5 and 1.2–8.5 mg/L in dry season, respectively.

Seasonal and spatial variation in the major ions

Seasonal data on the major ion chemistry of different river water show that the average EC is minimum (323 μS/cm) in the high-flow season and maximum (970 μS/cm) in low-flow season. This pattern indicates a decreased concentration of major ions in wet season. The decrease in ionic concentrations in flood season may be due to dilution (Chen et al. 2002; Quan et al. 2011). Sulfate, calcium, sodium, magnesium, and TDS show a similar trend as EC except in the Pi River, with the lowest concentration during wet season and highest during dry season. EC in Pi River is higher in dry season than that in wet season, while the concentration of ions is lower in dry season, which could be attributable to the lack of NH_4^+ or PO_4^{3-} measurements in water samples. Bicarbonate also has a relatively high percentage contribution to the total anions in wet season. Chloride, nitrate, and potassium do not show any systematic seasonal variations.

Figure 4 shows seasonal and spatial variations in concentration of measured parameters in different rivers of the study area. The six rivers under investigation can be conceptually divided into two groups on the basis of different lithologies and anthropogenic activities:

1. The first group includes the rivers—the southern rivers (the Shi River, Feng River, and Pi River) and the Huai River main channel, characterized by low ionic concentration. The catchments of these rivers consist of most part of a few reactive crystalline rocks of granites and granitic gneisses and of little any waste water discharge, explaining the low conductivity.
2. The second group includes the Ying River and Guo River characterized by high ionic concentration. The high concentration of dissolved ions in these rivers

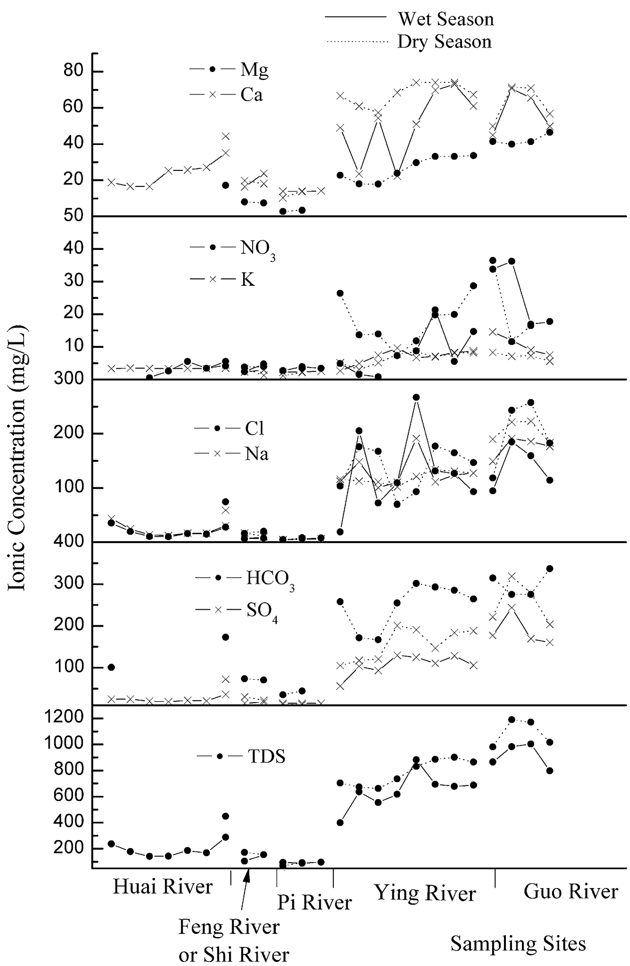


Fig. 4 Seasonal and spatial variations in the concentration of dissolved ions

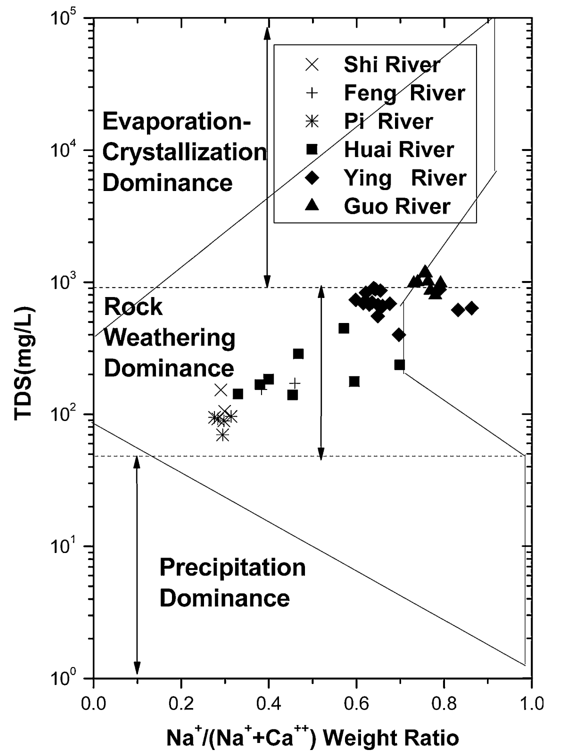


Fig. 5 A Gibbs diagram showing the most likely process responsible for hydrochemistry of the rivers under investigation (after Gibbs 1970)

may be attributed to the anthropogenic contribution from rich industrial and human settlement cities (e.g., Fuyang and Bozhou). The two rivers received a high domestic and industrial discharge load in the middle reaches, which shows a relatively high concentration of chloride and sulfate.

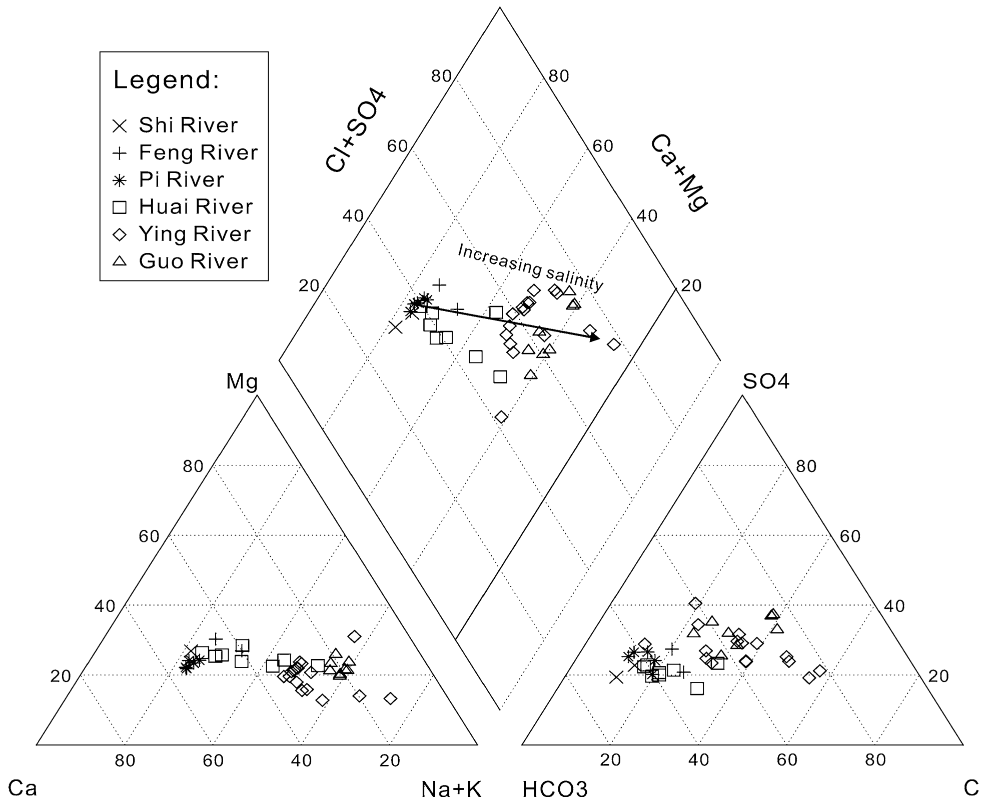
Discussion

Mechanism controlling water chemistry

Gibbs (1970) suggested that a simple plot of TDS versus the weight ratio of Na/(Na + Ca) would provide meaningful information on the relative importance of three major natural mechanisms controlling surface water chemistry: (1) atmospheric precipitation dominance, (2) rock weathering dominance, and (3) evaporation and fractional crystallization dominance. Although Gibbs' method seems to be controversial for rivers with high $Na^+/(Na^+ + Ca^{2+})$ (Feth and Gibbs 1971; Stallard and Edmond 1983), it indeed provides a simple tool to identify rivers that are dominated by precipitation or rock weathering or evaporation-crystallization. Most of points in the scatter in Fig. 5 fall between the regions, which indicate rock weathering.

Results of chemical analyses of river water samples are shown in the Piper diagram (Fig. 6). The major ion chemistry results show that calcium is the dominant cation and bicarbonate is the dominant anion in the river water samples from the Pi River and Feng River. Sodium and calcium are the dominant cations with a lower proportion of magnesium in the Huai River water. River water from H13, H12, and h17 about Zhoukou City is sodium and chloride dominant, characterized as a Na–Cl water type, whereas site H16 in the downstream of Zhoukou is sodium and bicarbonate dominant, characterized as a $Na\text{-}HCO_3$ water type in wet and dry season. Although a floodgate is open, the river water types are different between the upstream of Fuyang sluice (H7, h19) and the downstream of Fuyang sluice (H8). This indicates that the sluices play a critical role in determining the water type. River water (H9, H11, h22) from Bozhou City in the Guo River is sodium and chloride dominant, characterized as a Na–Cl water type, whereas the downstream of Bozhou City is sodium and bicarbonate dominant, characterized as a $Na\text{-}HCO_3$

Fig. 6 Piper diagram of major ion chemistry for river water in the study area



water type. This is similar with the Zhoukou section of the Ying River. The results may be attributed by anthropogenic influences in these cities.

Anthropogenic impact on hydrochemistry

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

The main parts of the first group are dominated by natural vegetation, which represent rural basin. Therefore, the anthropogenic contribution to their major ion budget is unlikely to be of importance.

The main parts of the second group are affected more significantly by human activities than the first group. 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. 7) for the two indicator ions (sodium and chloride) show the pronounced effects of urbanization on the major ion chemistry of the Ying River and Guo River. Concentration of chloride is below 110 mg/L in the upstream of Zhoukou, then increases by a factor 0.6–1.4 in the urban region, and becomes rapidly diluted over the downstream of the city in wet and dry seasons. Trends in chloride and sodium in the Fuyang section of the Ying River are the same as that of chloride in the Zhoukou section in wet and dry seasons. Among the dissolved solutes, Cl^-, NO_3^-, and SO_4^{2-} show maximum concentrations in Bozhou City in the upstream of the Guo River. Given all the chemical features are shown in the upstream (Bozhou) and middle stream (Mengcheng), it can be concluded that the Guo River (Bozhou Section) is a chemically active river with the secondary inputs from anthropogenic sources. The concentrations of chloride and sodium in the Bozhou section of the Guo River are higher than the upstream and downstream of Bozhou in wet and dry seasons, which is the same as those in the Fuyang section in the Ying River. However, there are insufficient inputs from basins downstream of cities to return chloride and sodium to their upstream levels. The high level chemical ions in wet and dry seasons are all in cities, which is due to the discharge of a large amount of sewage (0.12 million ton/day and 0.27 million ton/day in Fuyang (Huai River Water Resources Protection Bureau 2008), and 0.14 million ton/day and 0.20 million ton/day in wet and dry

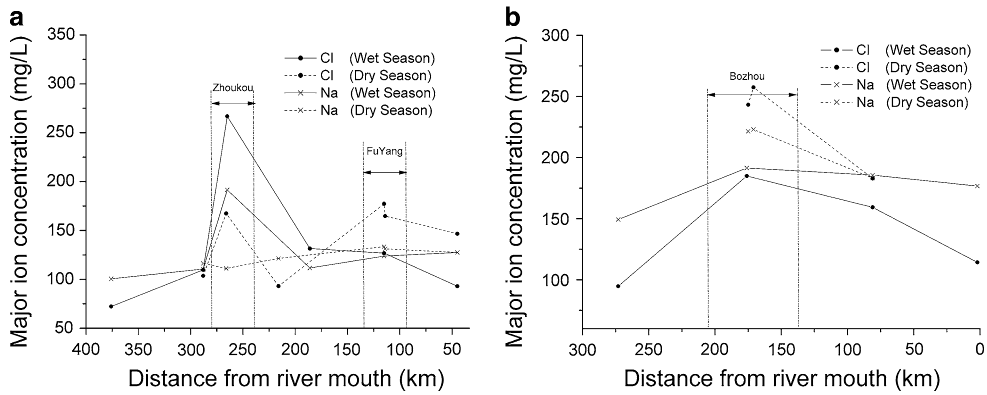


Fig. 7 Major ion concentration/distance from river mouth profiles for chloride and sodium in the main stream of the Ying River (**a**) and Guo River (**b**)

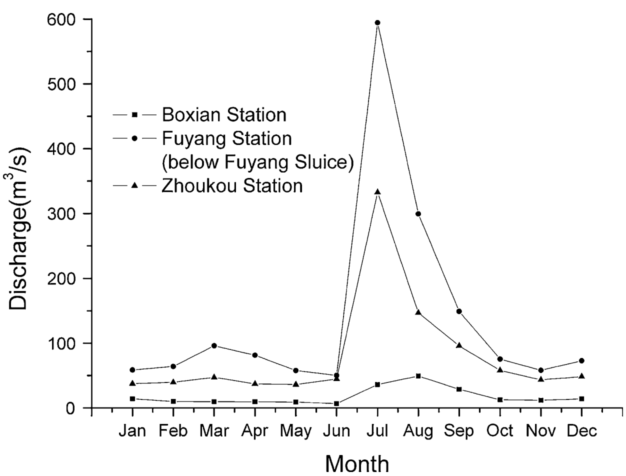


Fig. 8 Monthly variations in the water discharge at the Zhoukou Station and Fuyang Station (below Fuyang Sluice) in the Ying River and Boxian Station in the Guo River (average for the period 2006–2008)

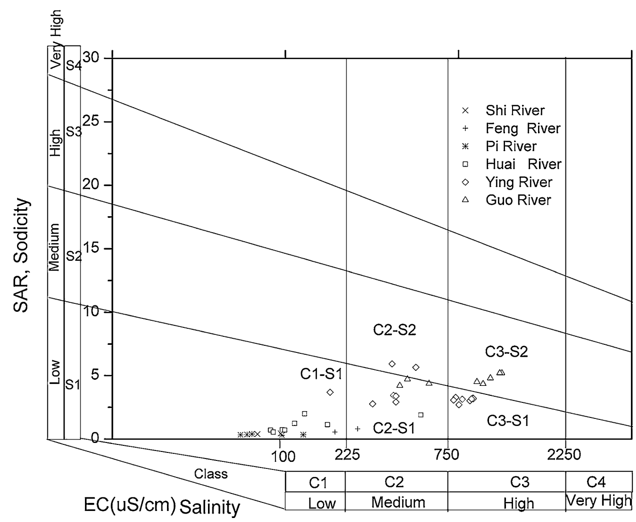


Fig. 9 The relationship between SAR and EC characterizing the irrigation quality of river water

seasons (Huai River Water Resources Protection Bureau 2009), respectively; 0.30 million ton/day in dry season in Zhoukou (Huai River Water Resources Protection Bureau 2010). Although the discharge of waste sewage of Bozhou City is smaller than that of Zhoukou City and same as that of Fuyang City, the annual runoff in the Boxian station is 21 and 12 % of that in the Zhoukou Station and Fuyang Station (below Fuyang Sluice) in the Ying River (Fig. 8). In this case, the pollution in Bozhou is more severe than that in Fuyang, while the concentrations in ions in Zhoukou are equal to that in Bozhou.

Water quality for irrigation

Sodium adsorption ratio

Figure 9 shows sodicity measured by the SAR against salinity. Both axes are divided into four major sections, i.e., S1–S4, from low to very high sodicity, and C1–C4 from low to very high EC, respectively. The calculated values of SAR in the study area range from 0.33 to 5.93 in the wet season and 0.31–5.21 in dry season. It is obvious that for data from the first group in wet and dry seasons shown in plot in the C1–S1 and C2–S2, most of data from the Ying River in the C1–S1 and C3–S1 and data from the Guo River in the C2–S1 and C3–S2. Replacement of sodium by absorbing calcium and magnesium is a hazard as it can lead to significant damages to the soil structure. Water of high sodium content and low calcium and magnesium concentrations can make the soil become compact and impervious. According to the Richards (1954), the low to medium SAR of rivers makes it suitable for irrigation of most crops with little danger of development of exchangeable sodium and salinity, although few of hard water can have high EC in the Ying River and Guo River.

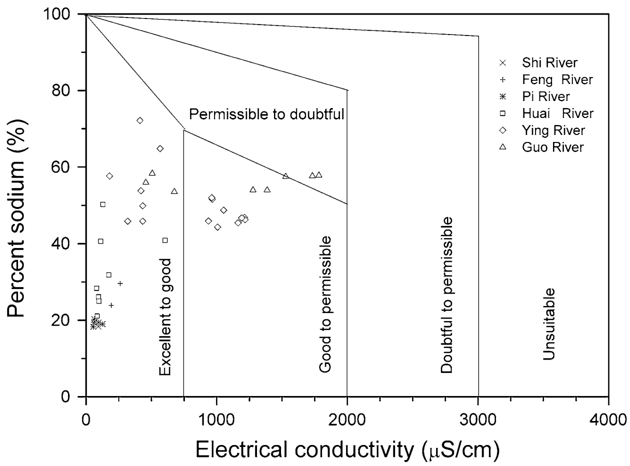


Fig. 10 Plot of sodium percent vs electrical conductivity (after Wilcox 1955)

%Na (sodium percent)

A plot of analytical data on the Wilcox (1955) diagram relating EC and sodium percent shows that most of water is excellent to good quality or good to permissible quality (Fig. 10).

Residual sodium carbonate

A high value of RSC in water value leads to an increase in the adsorption of sodium on soil. Irrigation water having RSC values greater than 5 has been considered harmful to the growth of plants, water with RSC values above 2.5 is not considered suitable for irrigation purpose, and water with RSC values less than 1.25 is considered safe. The RSC values of the study area river water samples are <1.25 in wet and dry season (Tables 1, 2), indicating that the water is safe for irrigation purpose.

Water quality for human consumption

The World Health Organization (WHO 2008) and the Environmental Quality Standard for Surface Water in China (Ministry of Environmental Protection 2002) explains the criteria of chemical parameters in drinking water (Table 3). A few samples exceed one or more of these criteria: Na^+ (H9 and H11), SO_4^{2-} (H9 and H11), and Cl^- (h17, H11).

Table 3 The guideline values of chemicals for drinking water in WHO and China (unit: mg/L)

Chemicals	WHO	China
Na^+	200	
SO_4^{2-}	250	250
Cl^-	250	250
NO_3^-	50	10 (as N)

There are no potential health effects related to elevated Na^+ and Cl^- levels, in addition to affecting the taste of the water (De Villiers 2005; WHO 2008).

The level of sulfate in most river water is low, i.e., <250 mg/L. Sulfate occurs at higher levels, which can exceed 300 mg/L, in the Guo River, particularly in Bozhou City in dry season. People unaccustomed to drinking water with elevated levels of sulfate can experience diarrhea and dehydration. If sulfate in water exceeds 250 mg/L, a bitter of medicinal taste may render the water unpleasant to drink. Infants are often more sensitive to sulfate than adults. As a precaution, water with a sulfate level exceeding 400 mg/L should not be used in the preparation of infant formula (Chien et al. 1968).

Nitrate is an acute contaminant, which means that a single exposure can affect the health of people. High levels of NO_3^- result in rare instances of methaemoglobinemia in infants (Fraser and Chilvers 1981) and cause hypertrophy of the thyroid (van Maanen et al. 1994) and childhood diabetes mellitus (Parslow et al. 1997). All the water samples have higher NO_3^- levels, but less than the 10 mg/L limit calculated as N. These sample locations all receive runoff from agricultural areas and fertilization is the most likely the origin of the presence of high NO_3^-.

These high level concentrations of ions suggest that the Zhoukou section of the Ying River and Bozhou section of the Guo River in the study area are not suitable for use as drinking water sources. To that end, pollution control should be improved and enhanced in the two rivers.

Conclusions

Chemical variables of river water in the upper reaches of Bengbu Sluice in the HRB were evaluated using a comparative approach in order to enhance an understanding of the most significant processes which impact the hydrochemical variations. The water quality was also assessed with respect to its suitability for irrigation activities and human consumption. Major conclusions of this study are drawn as follows:

1. Bicarbonate is the dominant anions and sodium and calcium are the dominant cations in most river samples. Ions and TDS displayed clear spatial patterns with lower concentrations in the south (the first group) and are higher in the north of the basin (the second group). The rivers are dominated by rock weathering according to the Gibbs diagram. The river water type ($Na-HCO_3$) in the upstream and downstream of the Zhoukou and Bozhou is different from that (Na–Cl) in the two cities. Although a floodgate of Fuyang Sluice is open, the river water type is different between the upstream and downstream of the sluice.

2. The main parts of the second group are affected more significantly by human activities than the first group. The main chemical composition of the second group may result from waste effluent.
3. Physicochemical parameters were used to evaluate the quality of river water for determining its suitability for irrigation purposes and human consumption. Calculated values of SAR, %Na, and RSC indicate that most of river water is suitable for irrigation of most crops. It is not recommended as drinking water sources in Zhoukou section of the Ying River and in the Bozhou section of the Guo River.

Acknowledgments The authors are grateful to the Major Science and Technology Program for Water Pollution Control and Treatment (Grant No. 2009ZX07210-006) and National Natural Science Foundation of China (No. 41101031) for financially supporting the study. Lihu Yang is also thankful to Dr. Di Long, who is currently with the Bureau of Economic Geology, Jackson School of Geosciences, The University of Texas at Austin, U.S., and was previously with the Department of Biological and Agricultural Engineering, Texas A&M University, U.S., for improving the writing of the original manuscript.

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