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Classification of Groundwater Contamination in Yuxi River Valley, Shaanxi Province, China

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Abstract This study investigated groundwater contamination in the Yuxi River Valley in northern Shaanxi Province, one of largest energy resource centers in China. Groundwater samples collected from 129 locations in the Yuxi River Valley area were analyzed and evaluated to establish the local groundwater quality zonings. Results indicate that groundwater in the Yuxi River Valley is contaminated, and the dominant contaminants in the groundwater are ammonium (NH_4^+) and nitrite (NO_2^-). Maximal concentration of NH_4^+ was detected at 0.019 and 3.50 mg/L in the samples collected up-gradient and down-gradient, respectively, of the segment of Yuxi River that flows through Yulin City. Concentration of NO_2^- was detected at 0.0015 and 1.522 mg/L, respectively from the same samples. Zones I through IV, from non-polluted to seriously polluted, were identified for groundwater quality in the Yuxi River Valley. We attribute the groundwater contamination in the Yuxi River valley to sources in the Yulin township, presumably its wastewater discharge.

Keywords Groundwater contamination · Nitrite · Shaanxi · Yulin · Yuxi River Valley

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Yuxi River Valley covers approximately 4940 km^2 in Shaanxi Province, China, as shown in Fig. 1. This region is characterized as inland, semiarid, continental monsoon climate with scarce precipitation. Groundwater in Yuxi River Valley consists of the pore water of alluvial-lacustrine deposits in the Salawusu formation in sandy region, pore-fissure water of aeolian deposit in loess region, and pore water in sandy gravel in river valley region. In the desert pool region, aeolian sand and the Salawusu formation below make up a uniform aquifer (Yunfeng Li et al. 2005). Groundwater is the main supply of water to meet municipal, industrial and agriculture usages. Yulin City is the only urban center located within Yuxi River Valley. It is one of the major coal, oil and natural gas basins in China. Many energy, utility, and chemical industries have been established in this region since late 1990s. These industries aggravate the concern on potential contamination to groundwater in the Yuxi River Valley. Prior to this study, groundwater quality data was lacking; zoning information of the local groundwater quality was deemed critical to sustain the regional environmental management and economic growth. The objective of this study was to conduct the first comprehensive groundwater survey in the Yuxi River Valley, and use the data to identify the distribution of the existing contamination in groundwater to develop a regulatory guideline and achieve better management of the local water resources.

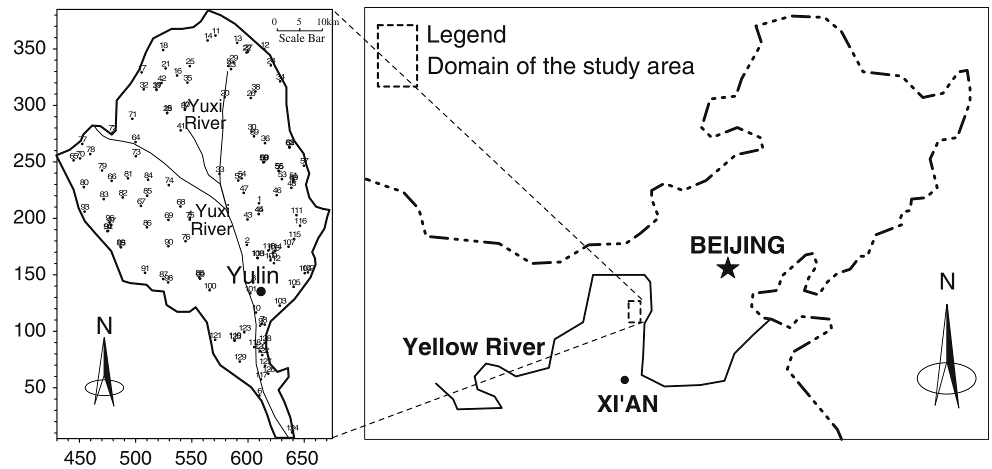

Fig. 1 Geographic and sampling map of Yuxi River Valley

Materials and Methods

Yuxi River a branch of Wuding River, which is further tracked upstream to the Yellow River. Yuxi River Valley occupies an area of 4938 km^2. It borders Inner Mongolia in the northwest, with the watershed of Yuxi River and Wuding River as its southwest boundary, and the watershed of Yuxi River, Tuwei River, and Jialu River as its east boundary. Groundwater samples were collected from 120 cropping-outs of the groundwater distributed throughout the Yuxi River Valley during September 2005 to December 2006, including groundwater monitoring wells, natural springs, and residential wells (Fig. 1). Collected groundwater samples were promptly packaged and shipped to the laboratory for analyses.

Groundwater samples were initially analyzed for potential contaminants based on the groundwater standards published by the Chinese government (1994). Detected parameters that exceeded the national standards included ammonium (NH_4^+), nitrite (NO_3^-), nitrite (NO_2^-), total manganese (Mn) and total iron (Fe). Standard methods specified by the Chinese government (GB7481-87, 1994) were used in the analysis. For example, NH_4^+ was detected by using the salicylic acid spectrophotometric method; NO_3^- was determined by ion chromatography. Total Mn and Fe were analyzed by using flame atomic absorption spectrophotometry.

The obtained data were comprised and evaluated. A series of mathematic methods were used to develop a classification system for groundwater quality, as described below:

A "pollution index" system was adopted from the Chinese Geological Survey Bureau (2005) to quantify the contamination level based on the concentrations of each individual constituent detected at different locations.

The pollution index PI_j ($j = 1, 2,\ldots, m$) of the jth water sample is calculated by single pollution indexes $I_{j,i}$ ($i = 1, 2,\ldots, n$) of each contamination component, the formula is:

$$PI_j = \sqrt{\frac{\bar{I}_{j,n}^2 + I_{j,n-\max}^2}{2}}$$

where PI_j indicates the pollution index of the jth water sample; $\bar{I}_{j,n}$ indicates the average value of a single component pollution index $I_{j,i}$ ($i = 1, 2,\ldots, n$) of n constituents in the jth water sample; $I_{j,n-\max}$ indicates the maximal value of a single component pollution index $I_{j,i}$ ($i = 1, 2,\ldots, n$) among n constituents of the jth water sample.

The formula of single component pollution index $I_{j,i}$ is:

$$I_{j,i} = \frac{a_{j,i}}{a_{j-0}}$$

where $a_{j,i}$ indicates the detected concentration of constituent i in the jth water sample (mg/L); a_{i-0} indicates the background value of constituent i (mg/L).

If the background value is a concentration range, the calculation formula is:

$$I_{j,i} = \frac{|a_{j,i} - a_{i-m}|}{a_{i-\max} - a_{i-m}}$$

where a_{i-m} indicates the medium value of background concentration range of the ith constituent (mg/L); $a_{i-\max}$ indicates the maximal value of background concentration range of the ith constituent (mg/L).

A system of four classifications was established based on pollution index PI_j. The classifications include "non-polluted zone with $PI_j \leq 1$, slightly polluted zone with $1 < PI_j \leq 2.5$, medium polluted zone with $2.5 < PI_j \leq 5$, and seriously polluted zone with $PI_j > 5$. These polluted zones were designated respectively as I, II, III and IV.

The background value of constituents is defined as groundwater quality under natural state in the region. Due to the fact that there was no groundwater quality survey that preceded this study, the background value for the detected parameters could not be established due to the preexisting contamination. According to the recommendation by the China Geological Survey, for regions lacking of background data, the parameter values of Class II water as specified in the "Chinese Quality Standard for Groundwater (GB/T 14848-93)" (1994) can be used as the background for water quality evaluation purpose. Therefore we used the values of Class II water as the background data in this study.

Pollution indices PI_j ($j = 1, 2, \ldots, 129$) of the 129 groundwater samples were summarized to plot the division map for groundwater in Yuxi River Valley, as shown in Fig. 2. Zones of different pollution levels (as categorized in "classes") were indicated by different lines.

Results and Discussion

As shown in the contamination zoning map (Fig. 2), majority area of the valley (approximately 60% total area) was categorized as non-polluted or slightly polluted zone, each accounting for about 30% of the whole valley. The medium polluted zone accounted for approximately 30% of the area, and seriously polluted zone accounted for approximately 10% of the whole area. The seriously polluted zone was located in the down-stream area of Yuxi River and the watershed area in the up-stream, indicating a link between the surface and groundwater water bodies in terms of water quality.

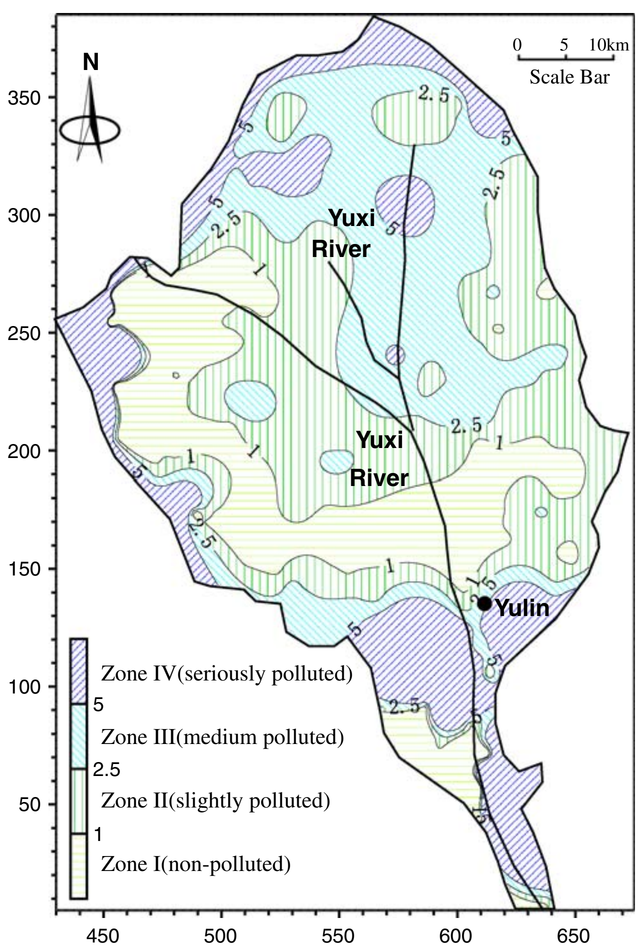

Fig. 2 Contamination zoning map of groundwater in Yuxi River Valley

Based on the aforementioned classification of groundwater, approximately 30% of the Yuxi River valley belongs to medium polluted zone and 10% of the valley belongs to seriously polluted zone. We analyzed the data to determine the dominant factor(s) contributing to such a result. Data from the water samples that were determined to be within the medium polluted zone (pollution indexes >2.5) were evaluated. Samples with the single constituent pollution indices $I_{j,i} > 2.5$ were listed in Table 1. There are 45 water samples with pollution index values above 2.5 (including Zone II and Zone III, the slightly polluted zone and medium polluted zone respectively). Among these 45 samples, individual constituents with pollution indexes $I_{j,i}$ above 2.5 included NH_4^+, NO_2^{1-}, NO_3^{1-}, total Mn and Fe. Distribution of the pollution indices shows 38 samples for NH_4^+, 7 samples for NO_2^{1-}, 7 samples for Mn, 4 samples for Fe and 3 samples for NO_3^{1-}. Obviously, NH_4^+ is the dominant factor of contamination in the groundwater surveyed.

From Table 1, we also found that there were 14 water samples with pollution indices above 5 (Zone IV, the seriously polluted zone). Among these 14 points, parameters with single constituent pollution index above 5 included NH^{4+} (10 samples), NO_2^{1-} (5 samples), and total Fe (2 samples). Among the 10 samples with detection of NH_4^+, 5 samples were also detected with NO_2^-. Among the rest 13 samples, 9 samples were due to the detection of NH_4^+ and 4 samples due to the detection of NO_2^-. In two samples with both Fe and NH_4^+ (sample points 20 and 42), the pollution index of NH_4^+ is 10 and Fe 6, indicating Fe is not but NH_4^+ is the dominant pollution factor. However, for sample point 42, the pollution index of NH_4^+ is 6 and Fe 10.5, indicating that Fe is the dominant pollution factor.

In general, groundwater contamination in Yuxi River Valley was mostly attributed to a few dominant constituents. Among 14 sample points with pollution indices above 5, 13 points were caused by NH_4^+ and NO_2^-, indicating that the dominant contamination constituent are NH_4^+ and NO_2^{1-}, especially NH_4^+, which presumably originated from the municipal and agricultural wastes.

This conclusion agrees with results from other studies of other areas of similar geopolitical features. High contents of NH_4^+ and NO_2^- in the groundwater were tracked to municipal wastewater and agricultural sources in the region (Xing et al. 2001; Hong 2002; Ren et al. 2006; Wang 2002; Xu and Zhang 2003; Han 2007; Yang et al. 2007). These

Table 1 Pollution index $I_{j,i}$ of water samples with pollution indexes $PI_j > 2.5$

Id	PI_j	$I_{j,i}$					Id	PI_j	$I_{j,i}$				
		NH^{4+}	NO_2^{1-}	NO_3^{1-}	Mn^{2+}	Fe			NH^{4+}	NO_2^{1-}	NO_3^{1-}	Mn^{2+}	Fe
65	345.80		487				54	3.92	5.5				
126	124.19	175					121	3.92	5.5				
123	107.96	4	152				105	3.70	3.5	5		4.8	
103	30.58	3.5	43				38	3.61	5				
12	17.81	25					15	3.57	5				
89	15.64	22					28	3.57	5				
19	13.20	18.5	6				40	3.57	5				
16	8.90	12.5					47	3.57	5				
20	7.22	10				8	32	3.46				4.8	
42	7.22	6				10.05	14	3.45				4.8	
122	7.17	5	10				1	3.38			4.66		
24	5.74	8				3.05	13	3.19	3.5			4.4	
33	5.70	8					107	2.99	4		3.79		3.7
31	5.02	7					98	2.90	4				
85	4.99	7					10	2.88	4				
17	4.64	6.5					36	2.88	4				
11	4.59				6.4		120	2.88	4				
25	4.31	3			6		51	2.87		4			
70	4.31	3			6		26	2.86	4				
53	4.28	6					125	2.65			3.61		
35	3.95	5.5					92	2.51	3.5				
75	3.94	5.5					118	2.51	3.5				
30	3.92	5.5											

Table 2 Analysis of groundwater contamination in areas up-stream and down-stream of Yulin City

	Id	PI_j		NH_4^+			N–NO_2		
		PI_j	Class	Content (mg/L)	$I_{i,j}$	Class	Content (mg/L)	$I_{i,j}$	Class
Upstream (North of Yulin)	2	0.77	I	0.0190	0.95	I	0.00609	0.6	I
	108	0.70	I	0.0190	0.95	I	0.00149	0.1	I
	110	0.70	I	0.0190	0.95	I	0.00149	0.1	I
	113	0.72	I	0.0190	0.95	I	0.00304	0.3	I
Downstream (South of Yulin)	103	30.58	IV	0.0700	3.5	III	0.42609	43	IV
	123	107.96	IV	0.0800	4	III	1.52174	152	IV
	126	124.19	IV	3.5000	175	IV	0.00304	0.3	I
Background value	C_0			0.02			0.01		

studies demonstrate that NH_4^+ is the dominant factor for groundwater contamination in these areas in China.

To further analyze the environmental factors contributing to the groundwater pollution in Yuxi River valley, we analyzed the data collected from up-stream and down-stream of Yulin City, the results were summarized in Table 2.

Results indicate that the content of NH_4^+ increased from 0.019 mg/L up-stream to 3.50 mg/L down-stream, and the content of NO_2^- increased from 0.0015 to 1.522 mg/L. The pollution classification shifted correspondingly from Zone I (non-polluted zone) to Zone IV (seriously polluted zone). This further supports our presumption that the source for groundwater contamination in Yuxi River valley is probably the city of Yulin.

Upon determination of the dominant pollutant NH_4^+ in the groundwater, the pollution zoning map of single constituent NH_4^+ was plotted in Fig. 3. The distribution of the

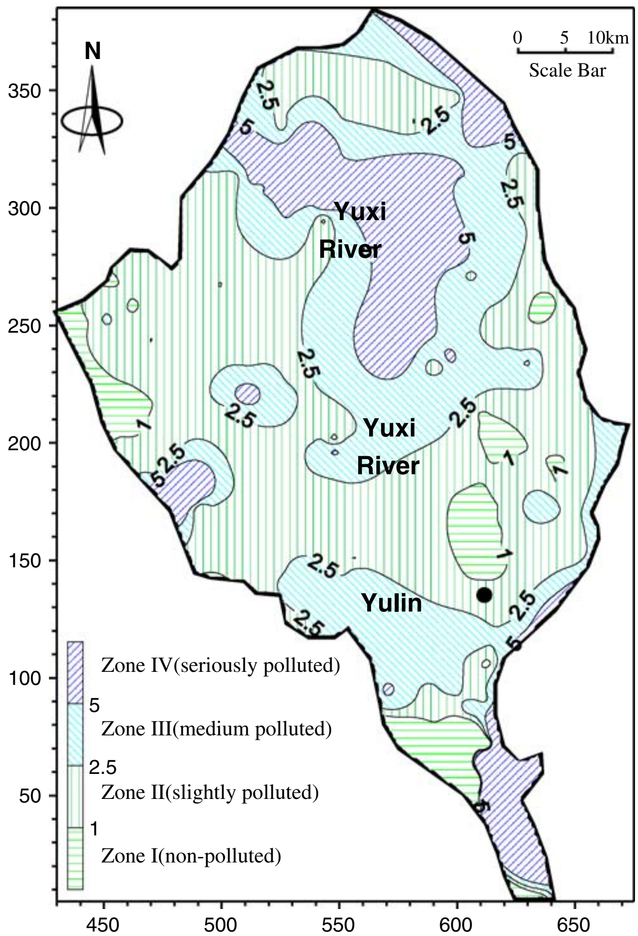

Fig. 3 Contamination zoning map of ammonium in groundwater in Yuxi River Valley

seriously polluted zone, as depicted by NH_4^+ single constituent index (above 5) in Fig. 3, is very similar to that for general pollution indices above 5 as shown in Fig. 2. This offers another piece of evidence that NH_4^+ is the dominant contamination factor in the Yuxi River Valley.

Among the 45 sample points ($I_{j,i} > 2.5$) belonging to medium polluted zone, 7 sample points are attributed to Mn and 4 points to Fe. Among the 14 sample points ($I_{j,i} > 2.5$) belonging to seriously polluted zone, 2 sample points were attributed to Fe, in which only one sample point was classified as from the seriously polluted zone because of an elevated pollution index for Fe. It is difficult to determine if the excessive content of Mn and Fe in the groundwater at these sampling locations were caused by the discharges from the industry (e.g., factories and mines), or if the background values of Mn and Fe are high in the background. Most industries in the region located nearby the river, which is downgradient from most groundwater flow. Therefore, it is less likely that the existing industries contributed significantly to the contamination in the local groundwater. Nevertheless, with the undergoing construction of the Shaanxi Energy Base in the area, great attention should be paid to the location of industries and engineering controls to eliminate contaminant discharge. Meanwhile, frequent and broad network of groundwater quality monitoring and database establishment should be implemented to protect the groundwater quality in the region.

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