Characteristics and source identification of dissolved trace elements in the Jinshui River of the South Qinling Mts., China

Hongmei Bu¹ · Weibo Wang² · Xianfang Song¹ · Quanfa Zhang²

Received: 2 June 2014 / Accepted: 4 May 2015 / Published online: 15 May 2015
© Springer-Verlag Berlin Heidelberg 2015

Abstract Dissolved trace elements and physiochemical parameters were analyzed to investigate their physicochemical characteristics and identify their sources at 12 sampling sites of the Jinshui River in the South Qinling Mts., China from October 2006 to November 2008. The two-factor ANOVA indicated significant temporal variations of the dissolved Cu, Fe, Sr, Si, and V ($p < 0.001$ or $p < 0.05$). With the exception of Sr ($p < 0.001$), no significant spatial variations were found. Distributions and concentrations of the dissolved trace elements displayed that dissolved Cu, Fe, Sr, Si, V, and Cr were originated from chemical weathering and leaching from the soil and bedrock. Dissolved Cu, Fe, Sr, As, and Si were also from anthropogenic inputs (farming and domestic effluents). Correlation and regression analysis showed that the chemical and physical processes of dissolved Cu was influenced by water temperature and dissolved oxygen (DO) to some degree. Dissolved Fe and Sr were affected by colloid destabilization or sedimentary inputs. Concentrations of dissolved Si were slightly controlled by biological uptake. Principal component analysis confirmed that Fe, Sr, and V resulted from

domestic effluents, agricultural runoff, and confluence, whereas As, Cu, and Si were from agricultural activities, and Cr and Zn through natural processes. The research results provide a reference for ecological restoration and protection of the river environment in the Qinling Mts., China.

Keywords Jinshui River · Dissolved trace elements · South Qinling Mts. · Spatiotemporal distribution · Statistical analysis · Source identification

Introduction

Trace elements in the natural environment are one of the primary pollutants due to their toxicity, persistence, and bioaccumulation problems (Morales et al. 1999; Pekey et al. 2004). More specifically, the presences of dissolved trace elements in many rivers present a threat to human health on a global level. The source of dissolved trace elements in rivers may be natural and occurs through events such as rock weathering, water erosion, and surface runoff (Martin et al. 1993; Pekey et al. 2004). Alternately, dissolved trace elements may originate from anthropogenic sources such as domestic sewage, agricultural runoff, industrial effluents, etc. (Caccia and Millero 2003; Mendiguchía et al. 2007).

There have been many studies that have investigated the geochemical processes of dissolved trace elements (Shiller and Boyle 1985, 1987; Neal et al. 1997; Zwolsman et al. 1997; Ramessur et al. 2001; Ravichandran 2003; Chaudry and Zwolsman 2008) as well as the sources of the pollution (Morales et al. 1999; Hatje et al. 2003; Pekey et al. 2004; Kuppusamy and Giridhar 2006; Mendiguchía et al. 2007; Zhou et al. 2007). These complex physicochemical processes are controlled by many factors, such as riverine input, precipitation, pH, temperature, oxygen, nutrients, chemical sorption–desorption, and

Responsible editor: Céline Guéguen

✉ Hongmei Bu
buhm2004@163.com

✉ Quanfa Zhang
qzhang@wbcas.cn

¹ Key Laboratory of Water Cycle and Related Land Surface Processes, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Datun Road, A 11, Beijing 100101, People's Republic of China

² Key Laboratory of Aquatic Botany and Watershed Ecology, Wuhan Botanical Garden, Chinese Academy of Sciences, Wuhan 430074, People's Republic of China

redox conditions (Zwolsman et al. 1997; Zhou et al. 2003; Caccia and Millero 2003; Hatje et al. 2003; Chaudry and Zwolsman 2008), which determine the addition and removal of dissolved trace elements in the riverine systems. It is essential that we fully understand these processes in order to remediate the contamination of dissolved trace elements in rivers (Martin et al. 1993; Elbaz-Poulichet et al. 2006).

The Qinling Mts. form the boundary between the Yellow River and the Yangtze River basins and are a natural barrier between North and South China. The Han River, a major tributary of the Yangtze River, is the water source of the middle line of the south-to-north water diversion project in the South Qinling Mts. (Zhang et al. 2009). In recent years, the water quality of the Han River has deteriorated by dissolved trace elements and

Fig. 1 The location and 12 sampling sites of the Jinshui River in the South Qinling Mts., China

heavy metals due to increased economic development and the corresponding intensive human activities. This has been the subject of an environmental monitoring program for water and soil conservation in the Han River basin since 2004 (Zhang et al. 2009). In this study, we chose a major tributary of the Han River, the Jinshui River, to further investigate the environmental effects of trace elements in this region. Specifically, this study aims to 1) investigate the spatiotemporal distributions and concentrations of dissolved trace elements, 2) recognize the relationships among dissolved trace elements and physicochemical parameters, and 3) identify the sources of the dissolved trace elements.

Materials and methods

Study area

The Jinshui River (33° 16′–33° 45′ N, 107° 40′–108° 10′ E) of the upper Han River is located in the South Qinling Mts. in Shaanxi Province of China. It drains an area of 730 km² with a total length of 87 km and includes four major tributaries, i.e., Xi River, Xindianzi River, Dong River, and Lvguan River (Fig. 1). The river's flow velocity changes over different seasons. The mean flow velocity in the river is about 0.5 m³/s in the mean-flow period, 0.4 m³/s in the low-flow period, and 0.8 m³/s in the high-flow period.

The river basin is in a humid monsoon climate zone. The annual average temperature in the catchment is approximately 11.5 °C, while the highest is 21.9 °C in summer and the lowest −0.3 °C in winter. The rainfall varies between 924 and 1240 mm per year, and most of the rainfall occurs from June to August. The soil types include paddy soil, yellow cinnamon soil, yellow brown soil, brown soil, and dark brown forest soil along elevational gradients.

The Jinshui River basin is a typical mountainous catchment in the South Qinling Mts. with intensive forest cover (96.4 % of the drainage area) (Shen et al. 2006). Upstream of the river lies in the Foping National Nature Reserve, which with a forest cover of 97.47 %, has been established primarily for giant panda conservation. Forest and shrubland are the major land use types and arable land is scattered in the midstream of the river. Of the total populations of 19.21 thousand, 51.39 % of the total populations (19.21 thousand) and 94.06 % of the agricultural lands in the catchment are distributed in the lower reaches of the river, especially in Jinshui Town. However, no industrial activities exist in the basin.

Sampling

Water samplings have been conducted nine times between October 2006 and November 2008. Three of these samplings were carried out during the high-flow period (October 2006, August 2007, and August 2008), three in the low-flow period

(December 2006, March 2007, and March 2008), and the other three in the mean-flow period (May and November 2007 and November 2008). There were 12 sampling sites along the river (Fig. 1), of which, sites 1–5, sites 6–9, and sites 10–12 are located in the upper, middle, and lower river, respectively. Site 10 is located close to Jinshui Town where there is a population of 9,837. Meanwhile, site 12 is the confluence of the two rivers between the Jinshui River and the Han River. Approximately, 108 water samples were obtained during the sampling periods.

Physicochemical parameters including water temperature (Temp), dissolved oxygen (DO), pH, total dissolved solids (TDS), and nitrate nitrogen (NO₃-N) were measured in situ using multiparameter water quality monitoring instrument (YSI Incorporated, Yellow Springs, OH, USA). Calibration of sensors was performed before every survey. For analysis of dissolved trace elements and dissolved phosphate (DP), water samples were filtrated through cellulose nitrate membrane filters with pore size of 0.45 μm (Millipore, USA) and then stored for further analysis in acid-cleaned polyethylene bottles that were acidified to pH<2 with high-purity nitric acid.

Analytical methods

Dissolved trace elements and DP were quantified by inductively coupled plasma atomic emission spectrometer (ICP-AES) (IRIS Intrepid II XSP DUO, USA). Method accuracy and quality control were verified by triplicate analysis of standard reference material (SRM, SPEX CertiPrep, Inc., USA). A good agreement was observed between the data analyzed and those certified by the SRM (Table 1). Concentrations of Cd, Co, Ni, Mo, and Mn were below the detection limits and not shown here. Thus, dissolved trace

Table 1 Quality control data of SRM analysis and detection limits for the dissolved trace elements and DP using ICP-AES

Analyzed parameter	Detection limit (μg/l)	SRM certified (μg/l)	SRM analyzed (μg/l)	% recovery
DP	4	1.0	0.998	99.80
As	2	1.0	1.030	103.00
Cu	3	0.5	0.513	102.60
Fe	10	4.0	4.102	102.55
Cr	5	1.0	1.046	104.60
Sr	5	2.0	2.088	104.40
Si	20	5.0	5.272	105.44
V	5	1.0	1.023	102.30
Zn	2	2.0	2.106	105.30
Cd	5	0.8	0.801	100.13
Co	5	1.0	1.002	100.20
Ni	3	2.0	2.026	101.30
Mo	10	2.0	2.002	100.10
Mn	5	2.0	2.054	102.70

elements of As, Cu, Fe, Cr, Sr, Si, V, and Zn were selected for further analyses.

Statistical analysis

The two-factor ANOVA was performed to examine the influence of different sampling sites and flow periods on dissolved trace elements, physicochemical parameters, and their interaction effects (Hatje et al. 2003; Mendiguchía et al. 2007). Normality and homogeneity of variances were evaluated using the one-sample Kolmogorov–Smirnov and Levene’s tests, respectively. Logarithmic transformations were required for TDS, NO₃-N, DP, As, Fe, Cr, and Sr. For abnormally distributed or unequal variance variables ($p < 0.05$), the non-parametric Dunnett’s test was used (Bu et al., 2010, 2014). Multiple comparisons were conducted using Student–Newman–Keuls (SNK). Correlation and

regression analyses were used to explore the relationships among the variables (Zhou et al. 2003). In order to identify the sources of pollutants, principal component analysis (PCA) was operated by using Varimax Kaiser Normalization, only eigenvalues greater than or equal to 1 were considered as possible sources of variance (Kowalkowski et al. 2006). All statistical analyses were all performed by using SPSS 13.0.

Results and discussions

Spatiotemporal distributions and concentrations of the physicochemical parameters

Spatiotemporal distributions of physicochemical parameters are plotted in Fig. 2, and show no significant spatial

Fig. 2 Spatiotemporal series of physicochemical parameter concentrations associated with dissolved trace elements in the Jinshui River, China

variabilities except TDS ($p < 0.001$; Table 2). Water temperature, TDS, and $\text{NO}_3\text{-N}$ present significant seasonal variations ($p < 0.001$, Table 2) during the sampling periods. Water temperature ranges from 6.55 to 25.78 °C in the mean-flow period, from 3.50 to 16.33 °C in the low-flow period, and from 13.62 to 27.36 °C in the high-flow period. The TDS concentrations display large ranges of 35–225 mg/l during the mean-flow period in the Jinshui River. The $\text{NO}_3\text{-N}$ has significant high concentrations in the low-flow period with values ranging from 0.034 to 22.490 mg/l. Dissolved oxygen, pH, and DP also have significant seasonal variations at $p < 0.05$ level (Table 2) during the sampling periods. The mean concentration of DO in the Jinshui River is 9.40 ± 3.05 mg/l (mean $\pm$ S.D.), showing a high value. Values for pH range from slightly acid (6.7) during mean-flow and low-flow periods to alkaline (9.1) during high-flow period. The mean DP concentrations show relatively high values (0.031 ± 0.019 mg/l) during mean-flow period.

However, none of the physicochemical parameters have interaction effects between different sampling sites and flow periods. Large changes in pH values (6.7–9.1) occur among the different sampling sites during the sampling periods. Mean concentrations of TDS at sites 10 (174.33 ± 33.83 mg/l) and 12 (181.25 ± 35.98 mg/l) are much higher than those in other sampling sites. The peak value of $\text{NO}_3\text{-N}$ (22.490 mg/l) appears at site 7 during the low-flow period, while the maximum mean concentration of $\text{NO}_3\text{-N}$ (3.753 ± 5.593 mg/l) occurs at site 12. Dissolved phosphate displays the same trend as $\text{NO}_3\text{-N}$

N at different sampling sites; however, its concentrations is highest at site 12 (0.113 mg/l) during mean-flow period.

Spatiotemporal distributions and concentrations of the dissolved trace elements

The spatiotemporal variations of dissolved trace elements are shown in Fig. 3. Dissolved trace elements demonstrate no significant spatial patterns except in the case of Sr ($p < 0.001$). However, dissolved Cu, Fe, Sr, Si, and V show significant temporal trends ($p < 0.001$ or $p < 0.05$; Table 2), showing common origin from chemical weathering and leaching from the soil and bedrock. Dissolved Cu and Fe have much higher values in the low-flow period than in the mean-flow and high-flow periods, with mean values of 15.6 and 117 $\mu\text{g/l}$, respectively. Additionally, dissolved Sr has a significant interaction effect ($p < 0.05$) between different sampling sites and sampling periods, showing its multiple sources in the river. High mean concentrations of dissolved Si (7.05 ± 2.77 mg/l) and V (116 ± 118 $\mu\text{g/l}$) are all found in high-flow period, indicating their some sources from soil erosion during rainy season (Wang et al. 2009).

Dissolved trace elements still display some spatial characteristics although they have no significant spatial variations with the exception of Sr. Peak values of dissolved As and Si (22 $\mu\text{g/l}$ and 11.24 mg/l) occur at sites 6 and 10, respectively. The results are due to anthropogenic inputs, such as farming crops and releasing domestic effluents (Mendiguchia et al.

Table 2 Summary of two-factor ANOVA on the spatiotemporal variations of physicochemical parameters and dissolved trace elements in the Jinshui River, China

Source of variation	df	Temp			DO			pH			TDS			$\text{NO}_3\text{-N}$		
		MS	F	p	MS	F	p	MS	F	p	MS	F	p	MS	F	p
Periods (Pr)	2	1241.070	29.461	**	71.179	6.459	*	0.701	3.632	*	0.004	14.140	**	168.624	10.119	**
Sites (St)	11	10.227	0.243	ns	3.104	0.282	ns	0.249	1.288	ns	0.012	44.961	**	3.246	0.195	ns
Pr $\times$ St	22	2.775	0.066	ns	2.373	0.215	ns	0.101	0.521	ns	0.000	1.093	ns	2.645	0.159	ns
Residual	70	42.125			11.020			0.193			0.000			16.663		
Source of variation	df	DP			As			Cu			Fe			Cr		
		MS	F	p	MS	F	p	MS	F	p	MS	F	p	MS	F	p
Periods (Pr)	2	0.003	6.764	*	97.737	3.225	ns	638.301	13.635	**	69,379.480	5.847	*	608.954	2.780	ns
Sites (St)	11	0.000	0.917	ns	30.211	0.997	ns	13.903	0.297	ns	11,261.188	0.949	ns	51.819	0.237	ns
Pr $\times$ St	22	0.000	0.093	ns	16.922	0.558	ns	18.262	0.390	ns	13,174.353	1.110	ns	49.682	0.227	ns
Residual	70	0.000			30.307			46.813			11,865.606			219.034		
Source of variation	df	Sr			Si			V			Zn					
		MS	F	p	MS	F	p	MS	F	p	MS	F	p			
Periods (Pr)	2	896.946	5.047	*	98.744	14.327	**	90,495.007	11.725	**	326.586	2.144	ns			
Sites (St)	11	18,445.117	103.794	**	3.181	0.528	ns	402.194	0.052	ns	88.038	0.578	ns			
Pr $\times$ St	22	456.632	2.570	*	0.775	0.145	ns	231.429	0.030	ns	65.299	0.429	ns			
Residual	70	177.709			6.658			7717.871			152.329					

df degrees of freedom, MS mean square, ns not significant

*Represents significance at $p \leq 0.05$

**Represents significance at $p \leq 0.001$

Fig. 3 Spatiotemporal series of dissolved trace element concentrations in the Jinshui River, China

2007). The maximum values of dissolved Cu (23 µg/l), Fe (913 µg/l), and Sr (241 µg/l) are observed at site 10 closing to Jinshui Town (Fig. 1) in the low-flow period, suggesting their common origin from anthropogenic sources (Martin et al. 1993; Kumaresan and Riyazuddin 2008). Dissolved Cr, however, has the maximum (38 µg/l) at site 9 in the

high-flow period, affected by soil erosion (Crosa et al. 2006). During the three sampling periods, the maximum levels of dissolved V occur at site 12, revealing the hydrological and chemical differences may be due to the confluence of the Jinshui River and Han River (Ravichandran 2003).

The concentrations of dissolved Cu, Fe, Cr, and Zn (Fig. 3) are all below WHO recommendations (2004) for drinking water (2000, 2000, 50, and 3000 $\mu\text{g/l}$ for Cu, Fe, Cr, and Zn, respectively). Similarly, these concentrations with the exception of Fe, generally fall within the Chinese standards (2006) for drinking water (1000, 300, 50, and 1000 $\mu\text{g/l}$ for Cu, Fe, Cr, and Zn, respectively). The concentrations of dissolved As in most sampling sites, have high values and are higher than 10 $\mu\text{g/l}$ in the high-flow period, which exceed the WHO recommendations and Chinese standards for drinking water. Thus, the dissolved As may be introduced into the river by soil erosion in the rainy season (Crosa et al. 2006). The mean concentrations of dissolved Sr from site 9 to site 12 exceed levels observed in sites 1–8 by one order of magnitude, indicating that the sources of Sr are not only from atmospheric and weathering endmembers but also from anthropogenic activities.

Relationships among dissolved trace elements, physicochemical parameters, and inorganic nutrients

Correlations between dissolved trace elements and physicochemical variables are presented in Table 3. Dissolved Cu and V are significantly correlated with water temperature ($p<0.01$). This may suggest a temperature effect on a series of chemical and physical processes including adsorption (Fedoseyeva 1995; Shiller 1997), formation of complexes, and ion exchange (Morales et al. 1999; Kuppasamy and Giridhar 2006) in the rivers. Dissolved Cu is also negatively correlated to DO ($r=-0.454$, $p<0.01$); thus, its concentrations may be determined by oxidation–reduction processes due to its oxidability (Hatje et al. 2003). Since pH values in the river

vary over a relatively large range, the dissolved trace elements do not show any significant pH-related change (Shiller and Boyle 1987; Shiller 1997). Dissolved Fe and Sr are positively correlated to TDS concentrations ($p<0.01$), respectively. The correlations indicate that the dissolved trace elements in the Jinshui River are affected by colloid destabilization (Wang et al. 2009) or sedimentary inputs (Shiller and Boyle 1985). Dissolved Sr concentrations are strongly bound by TDS contents and linearly increase with them ($r^2=0.854$, $p<0.001$; Fig. 4a), suggesting a relationship of regulation effect.

The relationships among dissolved trace elements and nutrients are shown in Table 3. Dissolved Cu and Fe are positively associated with concentrations of $\text{NO}_3\text{-N}$ ($p<0.01$) since they display similar temporal patterns with $\text{NO}_3\text{-N}$ (Figs. 2 and 3), indicating part of the same sources from domestic effluents in low-flow period. Dissolved Cu also displays a quadratic trend with $\text{NO}_3\text{-N}$ ($r^2=0.392$, $p<0.001$; Fig. 4b). This could be explained by the influences of redox chemistry since nitrate is a fair measure of the redox condition in the river (anoxic) water column (Zwolsman et al. 1997). The inverse relationship between Si and $\text{NO}_3\text{-N}$ ($p<0.01$) indicates that Si is also possibly affected by biological uptake (Wang et al. 2009), such as floating algae (Ramessur et al. 2001), particularly by diatoms, since 194 taxa of benthic diatoms from 31 genera were identified in the upper Han River (Tan et al. 2013).

Dissolved As and Cu have strong negative affiliations with the DP values ($p<0.01$). Additionally, they follow a quadratic decrease ($r^2=0.570$, $p<0.001$; Fig. 4c) and a cubic trend ($r^2=0.613$, $p<0.001$; Fig. 4d) with DP, respectively, displaying removal trends for uptake of phytoplankton as substitutes for DP in the growing periods (Elbaz-Poulichet et al. 2006),

Table 3 Correlations among the dissolved trace elements and physicochemical parameters

	Temp	DO	pH	TDS	$\text{NO}_3\text{-N}$	DP	As	Cu	Fe	Cr	Sr	Si	V	Zn
Temp	1													
DO	-0.256^*	1												
pH	0.361^{**}	0.059	1											
TDS	-0.025	0.123	-0.082	1										
$\text{NO}_3\text{-N}$	-0.560^{**}	-0.403^{**}	-0.327^{**}	0.178	1									
DP	-0.273^{**}	0.456^{**}	-0.142	0.348^{**}	-0.079	1								
As	0.221	-0.298	0.112	0.166	0.171	-0.673^{**}	1							
Cu	-0.448^{**}	-0.454^{**}	-0.011	-0.021	0.596^{**}	-0.575^{**}	0.893^{**}	1						
Fe	-0.214	-0.023	-0.066	0.412^{**}	0.314^{**}	-0.083	-0.211	0.272	1					
Cr	0.012	0.151	0.178	-0.123	-0.304^*	0.164	-0.165	-0.169	-0.139	1				
Sr	0.136	-0.024	0.041	0.924^{**}	0.140	0.261^*	0.164	-0.004	0.469^{**}	0.049	1			
Si	0.170	0.215^*	0.027	0.059	-0.294^{**}	0.347^{**}	-0.020	-0.792^{**}	-0.309^{**}	0.641^{**}	0.083	1		
V	0.341^{**}	-0.061	0.085	-0.084	-0.191	0.208	-0.103	-0.550^{**}	-0.195	0.705^{**}	0.064	0.659^{**}	1	
Zn	-0.248	-0.115	-0.050	-0.064	0.162	0.312^*	-0.311	0.384^*	-0.019	-0.387^*	-0.070	-0.017	-0.221	1

*Correlation is significant at the 0.05 level (two-tailed)

**Correlation is significant at the 0.01 level (two-tailed)

Fig. 4 a–d Regression analyses of TDS with dissolved Sr and nutrient elements with dissolved Cu and As

especially in May of the mean-flow period. Meanwhile, Dissolved Si, Sr, and Zn are positively related to DP ($p < 0.01$ or $p < 0.05$), indicating their similarities in chemical properties and origin (Caccia and Millero 2003).

Dissolved As and Cu are significantly correlated ($r = 0.893$, $p < 0.01$) with each other (Table 3), suggesting a common origin from anthropogenic sources (Kumaresan and Riyazuddin 2008), such as agricultural activities. Most likely, dissolved Cu and Fe concentrations are determined by the local redox rate. However, the silicate input can change this condition, leading to the precipitation of Cu-Fe oxides (Elbaz-Poulitchet et al. 2006). Therefore, significant negative correlations are observed between the two elements and dissolved Si ($p < 0.01$). Dissolved V is correlated to the studied trace elements of Cu, Cr, and Si ($p < 0.01$; Table 3), which implies that these related elements are likely driven by similar hydrologic and geochemical processes (Neal et al. 1997; Zhou et al. 2003). In addition, dissolved Zn demonstrates significant correlations with positive Cu and negative Cr ($p < 0.05$; Table 3), since it is prone to be adsorbed and oxidized in rivers (Shiller and Boyle 1985).

Source identification of the dissolved trace elements

PCA is carried out for dissolved trace elements in river water to explore their sources (Zhou et al. 2007). The Kaiser–Meyer–Olkin (KMO) and Bartlett’s test of sphericity were used to detect the sampling adequacy and examine the validity of PCA. The results of KMO and Bartlett’s test were 0.198 and

60.229 ($df = 28$, $p < 0.01$), respectively, implying that PCA would be effective in reducing dimensionality. Four principal components (PCs) were extracted (eigenvalues > 1), explaining 88.39 % of the total variance. Afterwards, four varifactors (VFs) were obtained by the four rotated PCs.

In order to identify the source apportionment, the scores of sampling sites and loadings of variables associated with VF1 and VF2 were plotted on a plane graph (Fig. 5). The sampling sites could be divided into three groups which are consistent with the four VFs. The first group is correlated with sampling

Fig. 5 Plane graph on scores of sampling sites and loadings of variables defined by the first two rotated factors (S1–12 represents sampling sites 1–12)

sites 10 and 12, located in the lower reaches of the river. The relevant variables in the first group are Fe, Sr, and V, which may originate from domestic effluents, agricultural runoff, and confluence with the Han River. The second group includes sites 2 and 6, corresponding to As, Cu, and Si, confirming their anthropogenic sources due to agricultural activities. Sites 1, 3–5, 7–9, and 11 comprise the third group, where the observed levels of dissolved Cr and Zn are from natural sources, such as erosion and weathering of rock (Martin et al. 1993).

Conclusions

Dissolved Cu, Fe, Sr, Si, and V display significant temporal trends rather than spatial patterns in the Jinshui River, with an exception of dissolved Sr. Additionally, the relationships between the dissolved trace elements and associated parameters demonstrate their chemical and physical processes. Furthermore, four groups of source apportionment are identified, reflecting origins from anthropogenic (domestic effluents, agricultural runoff, and confluence with the Han River) and natural (erosion and weathering) sources. The analytical results for the Jinshui River provide an important basis for the ecological restoration and protection of the river system in the South Qinling Mts. Moreover, this study provides useful information on the hydrology and water quality of river environment for the middle line of the south-to-north water diversion project.

Acknowledgments This research is supported by the National Natural Science Foundation of China (Grant No. 41103069) and the Open Funding Project of the Key Laboratory of Aquatic Botany and Watershed Ecology, Chinese Academy of Sciences. The authors express sincere gratitude to Cen Wang and Mingyong Zhu for their assistance during the fieldwork.

References

- Bu H, Tan X, Li S, Zhang Q (2010) Temporal and spatial variations of water quality in the Jinshui River of the South Qinling Mts., China. *Ecotoxicol Environ Saf* 73:907–913
- Bu H, Meng W, Zhang Y (2014) Spatial and seasonal characteristics of river water chemistry in the Taizi River in Northeast China. *Environ Monit Assess* 186:3619–3632
- Caccia VG, Millero FJ (2003) The distribution and seasonal variation of dissolved trace metals in Florida Bay and adjacent waters. *Aquat Geochem* 9:111–144
- Chaudry MA, Zwolsman JJG (2008) Seasonal dynamics of dissolved trace metals in the Scheldt estuary: relationship with redox conditions and phytoplankton activity. *Estuaries Coasts: J CERF* 31:430–443
- Crosa G, Froebrich J, Nikolayenko V, Stefani F, Gallid P, Calamari D (2006) Spatial and seasonal variations in the water quality of the Amu Darya River (Central Asia). *Water Res* 40:2237–2245
- Elbaz-Poulichet F, Seidel JL, Casiot C, Tusseau-Vuillemin MH (2006) Short-term variability of dissolved trace element concentrations in the Mame and Seine rivers near Paris. *Sci Total Environ* 367:278–287
- Fedoseyeva VI (1995) Effects of pH and temperature on the adsorption of molybdenum on certain oxides and clays. *Geochem Int* 32:95–100
- Hatje V, Apte SC, Hales LT, Birch GF (2003) Dissolved trace metal distributions in Port Jackson estuary (Sydney Harbour), Australia. *Mar Pollut Bull* 46:719–730
- Kowalkowski T, Zbytniewski R, Szejna J, Buszewski B (2006) Application of chemometrics in river water classification. *Water Res* 40:744–752
- Kumaresan M, Riyazuddin P (2008) Factor analysis and linear regression model (LRM) of metal speciation and physico-chemical characters of groundwater samples. *Environ Monit Assess* 138:65–79
- Kuppusamy MR, Giridhar VV (2006) Factor analysis of water quality characteristics including trace metal speciation in the coastal environmental system of Chennai Ennore. *Environ Int* 32: 174–179
- Martin JM, Guan DM, Elbaz-Poulichet F, Thomas AJ, Gordeev VV (1993) Preliminary assessment of the distribution of some trace elements (As, Cd, Cu, Fe, Ni, Pb and Zn) in a pristine aquatic environment: the Lena River estuary (Russia). *Mar Chem* 43:185–199
- Mendiguchia C, Moreno C, García-Vargas M (2007) Evaluation of natural and anthropogenic influences on the Guadalquivir River (Spain) by dissolved heavy metals and nutrients. *Chemosphere* 69:1509–1517
- Morales MM, Marti P, Llopies A, Campos L, Sagrado S (1999) An environmental study by factor analysis of surface seawaters in the Gulf of Valencia (Western Mediterranean). *Anal Chim Acta* 394: 109–117
- Neal C, Robson AJ, Jeffery HA, Harrow ML et al (1997) Trace element inter-relationships for the Humber Rivers: inferences for hydrological and chemical controls. *Sci Total Environ* 194(195):321–343
- Pekey H, Karakaş D, Bakoğlu M (2004) Source apportionment of trace metals in surface waters of a polluted stream using multivariate statistical analyses. *Mar Pollut Bull* 49:809–818
- Ramessur RT, Parry SJ, Ramjeawon T (2001) The relationship of dissolved Pb to some dissolved trace metals (Al, Cr, Mn, and Zn) and to dissolved nitrate and phosphate in a freshwater aquatic system in Mauritius. *Environ Int* 26:223–230
- Ravichandran S (2003) Hydrological influences on the water quality trends in Tamiraparani Basin, South India. *Environ Monit Assess* 87:293–309
- Shen Z, Zhang Q, Yue C et al (2006) The spatial pattern of land use/land cover in the water supplying area of the Middle-Route of the South-to-North Water Diversion (MR-SNWD) Project. *Acta Geograph Sin* 61:633–644 (in Chinese)
- Shiller AM (1997) Dissolved trace elements in the Mississippi River: seasonal, interannual, and decadal variability. *Geochim Cosmochim Acta* 61:21–30
- Shiller AM, Boyle EA (1985) Dissolved zinc in rivers. *Nature* 317:49–52
- Shiller AM, Boyle EA (1987) Dissolved vanadium in rivers and estuaries. *Earth Planet Sci Lett* 56:214–224
- Tan X, Sheldon F, Bunn SE, Zhang Q (2013) Using diatom indices for water quality assessment in a subtropical river, China. *Environ Sci Pollut Res* 20:4164–4175
- Wang R, You C, Chu H, Huang J (2009) Seasonal variability of dissolved major and trace elements in the Gaoping (Kaoping) River Estuary, Southwestern Taiwan. *J Mar Syst* 76:444–456
- Zhang Q, Shen Z, Xu Z, Liu G, Wang S (2009) The Han River Watershed Management Initiative for the South-to-North Water Transfer Project (Middle Route) of China. *Environ Monit Assess* 148: 369–377

- Zhou J, Liu Y, Abrahams PW (2003) Trace metal behaviour in the Conwy estuary, North Wales. *Chemosphere* 51:429–440
- Zhou F, Guo H, Liu L (2007) Quantitative identification and source apportionment of anthropogenic heavy metals in marine sediment of Hong Kong. *Environ Geol* 53:295–305
- Zwolsman J, Van Eck B, Van Der Weijden C (1997) Geochemistry of dissolved trace metals (cadmium, copper, zinc) in the Scheldt estuary, southwestern Netherlands: impact of seasonal variability. *Geochim Cosmochim Acta* 61:1635–1652