

This article was downloaded by: [Institute of Geographic Sciences & Natural Resources Research]

On: 19 March 2014, At: 00:16

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Human and Ecological Risk Assessment: An International Journal

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/bher20>

Impacts of Yellow River Irrigation Practices on Trace Metals in Surface Water: A Case Study of the Henan-Liaocheng Irrigation Area, China

Jing Li ^a, Fadong Li ^a, Qiang Liu ^a, Shuai Song ^a, Yan Zhang ^a & Guangshuai Zhao ^a

^a Key Laboratory of Ecosystem Network Observation and Modeling, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Chaoyang District, Beijing, China
Accepted author version posted online: 13 May 2013. Published online: 06 Feb 2014.

To cite this article: Jing Li, Fadong Li, Qiang Liu, Shuai Song, Yan Zhang & Guangshuai Zhao (2014) Impacts of Yellow River Irrigation Practices on Trace Metals in Surface Water: A Case Study of the Henan-Liaocheng Irrigation Area, China, *Human and Ecological Risk Assessment: An International Journal*, 20:4, 1042-1057, DOI: [10.1080/10807039.2013.802618](https://doi.org/10.1080/10807039.2013.802618)

To link to this article: <http://dx.doi.org/10.1080/10807039.2013.802618>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Impacts of Yellow River Irrigation Practices on Trace Metals in Surface Water: A Case Study of the Henan-Liaocheng Irrigation Area, China

Jing Li, Fadong Li, Qiang Liu, Shuai Song, Yan Zhang, and Guangshuai Zhao
Key Laboratory of Ecosystem Network Observation and Modeling, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Chaoyang District, Beijing, China

ABSTRACT

Large-scale irrigation practices may disturb local hydrologic cycles and distribute trace metals throughout the environment. Reported here is the spatial pattern of trace metals and associated health risks in an agricultural area of China, which has a long history of irrigation with water from the Yellow River. Multivariate statistical analyses and a risk-assessment model were employed to interpret the environmental data. It indicated that Zn, Se, B, Ba, Fe, Mn, Mo, Ni, V, Al, Li, Sr, Be, Cd, Cr, Cu, and Pb were all detected in the surface waters. Compared to drinking water guidelines, the primary trace metal pollution components (Al, Fe, Se, B, Mn, and Zn) exceeded drinking water standards by 40.7%, 14.8%, 29.6%, 25.9%, 11.1%, and 14.8%, respectively. Except for one site that exhibited anomalous metal concentrations, landscape features of trace metals identified a uniform distribution of trace metals for all sample sites. The calculated mean value of Hazard Quotients (HQs) exceeded the USEPA's recommendations by a factor of 2.9 times the threshold value. Primary sources of trace metals were associated with natural deposition, industrial and agrochemical processes, and a mixed source of both geogenic and anthropogenic origins.

Key Words: trace metal, HQs, water pollutant, spatial distribution.

INTRODUCTION

Metals are ubiquitous in the environment and may be found in water sources utilized for agriculture and human consumption. In the last decades, with the rapid economic development in China, environmental pollution caused by heavy metals has been identified in several important agricultural areas, for example, the Yellow

Received 5 February 2013; revised manuscript accepted 25 April 2013.

Address correspondence to Fadong Li, Key Laboratory of Ecosystem Network Observation and Modeling, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, 11A Datun Road, Chaoyang District, Beijing 100101, China. E-mail: lifadong@igsnr.ac.cn

Trace Metal Pollution in the Yellow River Irrigation Area

River Delta (Song *et al.* 2013), Han River Delta (Li *et al.* 2010; Bu *et al.* 2009) and the Yangtze River Delta (Yang *et al.* 2009). Li *et al.* (2010) indicated that the concentrations of dissolved heavy metals were significantly different in sampling sites. Except for Fe, Sr, and As, all dissolved heavy metals meet World Health Organization (WHO) recommendations and the Chinese standard for drinking water quality (GB 5749–2006) in the Han River. Bu *et al.* (2009) found that all dissolved heavy metals exceeded the background values in the upper Han River and the source area of the Yangtze River except for Mn. Additionally, Song *et al.* (2013) reported that the HQ value of trace metals indicated potential deleterious health effects for residents in the Yellow River Delta and required special attention. Although natural background levels of heavy metals in China are low (Cheng 2007), concentrations of trace metals in water in the region have been increasing over time (Pan and Wang 2012).

Trace metals in water may originate from industrial wastes, agricultural sources, urban runoff, atmospheric deposition, and automobile emissions (Taebi and Droste 2004) and pose critical public health problems that impact human mortality and cause other adverse health outcomes (Loska and Wiechula 2003). Therefore, identification of the sources and evaluation of the ecosystem risk of trace metal contamination of water sources is critical to manage these resources and limit harmful consequences.

Water diversion to the Henan-Liaocheng Irrigation Area (HLIA) from the Yellow River has been ongoing for more than 50 years. Researchers have recently assessed and forecasted the water resources in the HLIA (Sun *et al.* 2005; Wu and Yuan 2012). Wu *et al.* (2009) discussed the problems and countermeasures concerning sustainable utilization of water resources for the Yellow River in Henan. Sun *et al.* (2005) performed an evaluation and balance analysis between supply and requirement of water sources in Liaocheng city. But, it is not clear how the transfer of trace metals is impacted by irrigation projects. Moreover, the extent of environmental risk associated with trace metals has not yet been evaluated.

Here we use multivariate statistical analysis to tease apart complex biogeochemical processes that influence migration of trace metals through the environment. In particular, multivariate analysis reveals weighted relationships and interdependency among variables (De Bartolomeo *et al.* 2004). Correlation analysis can also be used to group objects of similar composition (Varol and Sen 2009), while principal component analysis (PCA) can be employed to reduce a large set of environmental factors, or a combination of factors, to a smaller set that explains most of the observed variation (Wang *et al.* 2011). This information can thus be used to infer the primary sources of variability (Krishna *et al.* 2009).

Probabilistic risk assessment involves characterization of variability (*i.e.*, natural sources of variation) and uncertainty (*i.e.*, lack of knowledge) in risk-management decisions (Oberg and Bergback 2005). Variability and uncertainty in the input parameters (variables or constants) are described by probability distributions, and the output (risk or exposure) is likewise presented as probability distributions (USEPA 1991a). For example, some people have studied the Pb, Mn and polycyclic aromatic hydrocarbons (PAHs) risk by the probabilistic risk assessment method (Mari *et al.* 2009; Zeng *et al.* 2009).

A combination of field surveys and laboratory analysis of samples was used in the present study to: (1) quantify the hydro-chemical and trace metal characteristics

of Yellow River water and surface water; (2) determine the spatial distribution of trace metals and map their concentrations; (3) ascertain the influence of ongoing irrigation projects on trace metal transfer; (4) identify the environmental risk caused by trace metals and establish origins of metals in the irrigation area.

METHODS AND MATERIALS

Study Area

The northern section of the Henan-Liaocheng Irrigation Area (HLIA, 113.938°–117.076° E and 34.982°–37.391° N) is part of the North China Plain (NCP) and spans eastern Henan province and western Shandong province. The HLIA is on the terrain ladders III in China with a west-to-east elevation gradient of high to low. The total area of the HLIA is approximately 28,500 km², including the Anyang, Hebi, Puyang, and Liaocheng districts. Extensive diversion of irrigation water from the Yellow River began with the opening of the People's Victory canal in 1952. Rivers in the area include the Yellow River (367.8 km), Wei River (184.3 km), Majia River (258.9 km), and Tuhai River (216.7 km) and their main tributaries. Climate in the HLIA is warm-temperate with an annual average air temperature of 14–15°C and total annual sunshine hours of 2200–2300 h. Wheat, rice, cotton, and corn are the main crops in the area. Annual average precipitation is about 600 mm with most falling during the June to September monsoon. The irrigated water for this area is mainly from the Yellow River. The effective irrigated area in the Henan Province is 2.1×10^4 km² and consists of 1.6×10^4 km² of arable land. The design capability of the Liaocheng irrigation area is 445 m³/s, effective irrigated area covers the whole city, real irrigation area is approximately 0.4×10^4 km², accounting for 66% of the city's total arable land.

HLIA is an important grain and vegetable production base in northern China, and the amount of fertilization and agro-chemicals developed extremely rapidly after the 1970s (Ju *et al.* 2009). Additionally, with the development of urbanization and industrialization, environmental and health risks deteriorated. Although there are stringent rules in China for treatment of industrial wastes, disposal of untreated wastewater into drains and subsequently into the rivers is very common.

Water Sampling

Surface water samples of 100 mL were collected from July 23–30, 2010 at each of 27 sites in the study area. Selected sites were distributed among the old channels, irrigation ditches, reservoirs, and around cities, towns, and locations with stream or branch afflux. The sampling was performed during irrigation periods. Surface water samples were collected manually at <1 m depth in the center of the river. Five samples were collected and composited for each location. The composite was homogenized and immediately filtered through acid-treated millipore filters (0.45 μm mesh, disposable not reusable) into pre-cleaned polyethylene-terephthalate (PET) bottles. The filtered samples were acidified to pH <2 with ultra-purified 6M HNO₃, stored at 4°C in the field, and then analyzed once we returned to the laboratory.

Trace Metal Pollution in the Yellow River Irrigation Area

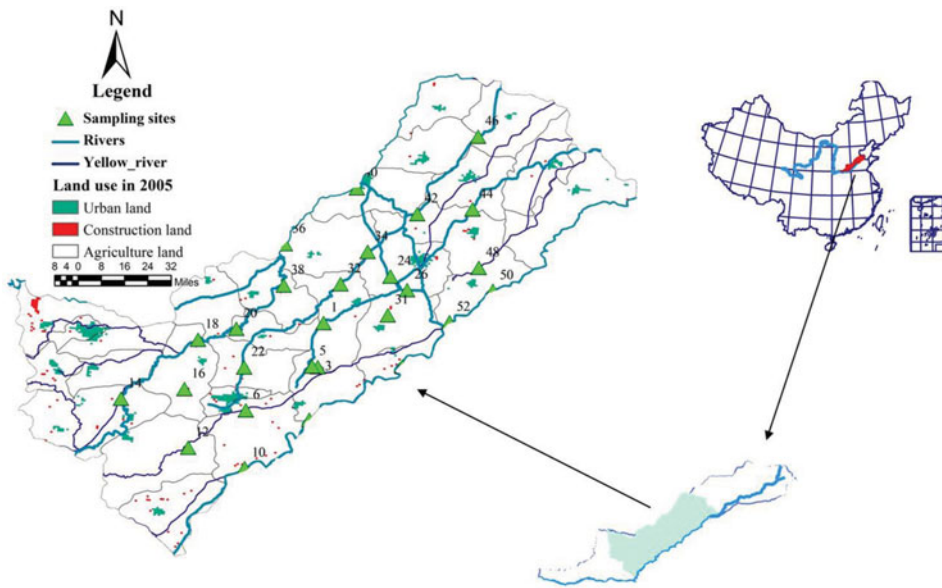


Figure 1. Map of sampling sites within the HLIA. (Color figure available online.)

A general overview of the study site showing the geology and the sampling locations is presented in Figure 1.

Experimental Analysis

Electrical conductivity (EC) and pH were measured by a portable pH and EC meter (Compact meter, Horiba, Japan) *in situ* and later corroborated in the laboratory with a high precision meter (D23, Horiba, Japan). All samples were filtered through a $0.45\ \mu\text{m}$ cellulose acetate filter membrane before using ion chromatograph (ICS 900, Shimadzu, Japan) to analyze Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , SO_4^{2-} , and HCO_3^- . HCO_3^- was measured by titration using $0.01\text{N H}_2\text{SO}_4$. The chemical results were only accepted when the charge balance error was within $\pm 5\%$.

Total concentrations of Zn, Se, B, Ba, Fe, Mn, Mo, Ni, V, Al, Li, Sr, Be, Cd, Cr, Cu, and Pb were analyzed using an Inductively Coupled Plasma–Optical Emission Spectrometer (ICP-OES, PerkinElmer Co. Ltd., USA). The detection limits for each element were $0.0001\ \text{mg/L}$ for Zn, Ba, Fe, Mn, Mo, Ni, V, Al, Li, Sr, Be, Cd, Cr, and Cu, and $0.001\ \text{mg/L}$ for Se, B, and Pb. The calibration curves were made after measuring a set of samples and evaluated against quality control standards. Reagent, procedural blanks, and samples were measured six times in parallel with the average of the last three values reported herein.

Data Treatment and Statistical Analyses

In this study, frequency distributions of concentrations of trace metals were investigated by calculating coefficients of skewness and kurtosis. Correlation analysis was performed to identify the sources of elements in terms of the correlation coefficients

Table 1. Descriptive statistics of chemical constituents in the surface water and Yellow River water.

Indexes	Surface water					Yellow River water				
	n	Min.	Max.	Mean	SD	n	Min.	Max.	Mean	SD
EC($\mu\text{S}/\text{cm}$)	27	329.0	3200.0	1133.5	617.8	4	471.0	892.0	767.5	199.8
pH	27	7.6	9.6	8.2	0.5	4	7.9	8.2	8.1	0.1
Ca ²⁺ (mg/L)	27	3.9	212.9	80.1	43.4	4	6.7	92.1	60.2	37.3
K ⁺ (mg/L)	27	0.2	14.4	7.7	4.0	4	0.4	6.7	4.1	2.6
Mg ²⁺ (mg/L)	27	1.3	139.2	40.9	25.9	4	2.2	27.9	21.3	12.7
Na ⁺ (mg/L)	27	2.7	676.6	150.8	131.2	4	4.5	77.1	57.0	35.1
SO ₄ ²⁻ (mg/L)	27	2.6	680.6	224.2	152.2	4	6.0	143.6	105.8	66.6
HCO ₃ ⁻ (mg/L)	27	76.3	433.1	216.9	69.1	4	146.4	189.1	170.8	18.5
Cl ⁻ (mg/L)	27	142.0	1218.0	279.1	207.1	4	173.0	212.0	190.5	20.0

among elements in water samples. PCA was used to compare patterns of relative concentrations of trace metals. Samples were grouped using varimax rotation and the identification of Principal component (PC) that exhibited eigenvalues >1 . Variables with similar characteristics were grouped into factors. Geostatistic methods were employed to analyze the horizontal distribution of trace metals and spatial maps were generated by use of geographic information system (GIS) software version 9.0 for Windows (Esri China, Limited).

Most values of Ni, Li, Be, Cd, Cr, Cu, and Pb were less than the detection limits in most samples. The distributions of Al, B, Ba, Fe, Mn, Mo, Se, Sr, V, and Zn were further analyzed by multivariate statistical methods to identify the influence of possible sources. All the metals were used to evaluate correlated health risks. All mathematical and statistical computations were made using SPSS 17.0 for Windows.

RESULTS AND DISCUSSION

Hydrochemical Characteristics of Surface Waters

Electrical conductivity values of surface water ranged from 329 $\mu\text{S}/\text{cm}$ to 3200 $\mu\text{S}/\text{cm}$, with a mean value of 1133.52 $\mu\text{S}/\text{cm}$ (Table 1). No significant spatial variations in pH were observed, and most of the surface water was weakly alkaline (7.58–9.56). The order of relative abundance of major cations in the surface water was $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ (on mg/L basis), while the order of anions was $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^-$. Overall, Na^+ and Cl^- were, respectively, the abundant cation and anion in surface water, and also several water samples contained high Ca^{2+} , Mg^{2+} , SO_4^{2-} , and HCO_3^- concentrations. A piper diagram revealed that the surface waters belonged to complex types, including Na-Cl, Na•Ca-Cl, Ca•Na-Cl, Ca•Na-HCO₃•Cl, Na•Ca-SO₄•Cl, and Na-Cl•HCO₃ (Figure 2). The background water type in the study area controlled by sediment mineralogy was Na-SO₄ (Li *et al.* 2008). Therefore, it can be deduced that there are other rivers or point water sources that converge in the surface water.

Trace Metal Pollution in the Yellow River Irrigation Area

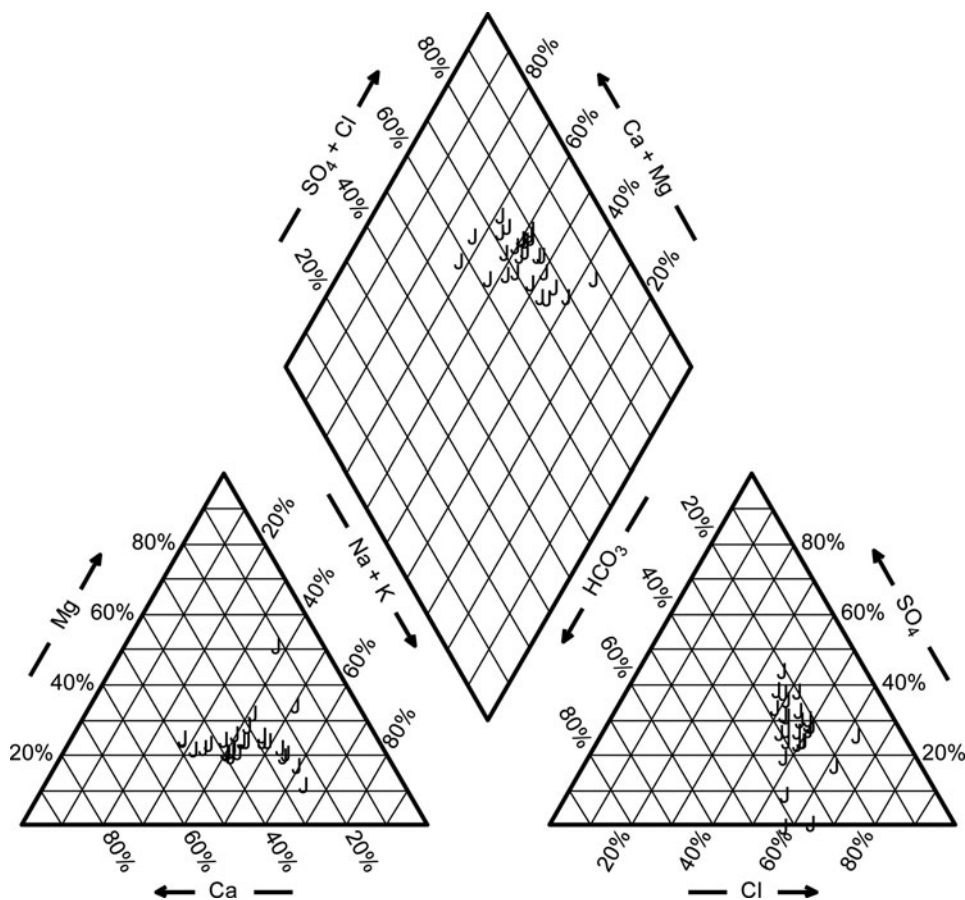
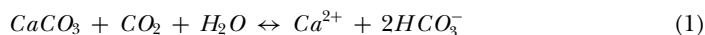


Figure 2. Piper diagram of surface water in the study area.

Correlation analysis and PCA can be used to identify the sources of elements in terms of the correlation coefficients among elements and to compare patterns of relative concentrations of ions in groundwater samples (Song *et al.* 2013). Three principal components with eigenvalues >1 were deduced and together accounted for 94.1% of the variance in the dataset. The first PC accounts for 39.4% of the total variance and has high loadings of Ca^{2+} , Na^+ , SO_4^{2-} and Cl^- , which is indicative of geogenic and anthropogenic inputs. Na^+ was strongly correlated with SO_4^{2-} ($R = 0.90$, $p < .01$), which coincides with the local background water type that is largely controlled by sediment mineralogy (Li *et al.* 2008). Sources of SO_4^{2-} include rainfall, chemical fertilizers such as $[(\text{NH}_4)_2\text{SO}_4]$ that have been used for the past 10 years, manure, and the dissolution of sulfide minerals present in lacustrine sediments (Jin *et al.* 2012). Ca^{2+} could also come from the fertilizer $(\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O})$. Cl^- can be derived from pollution sources, including domestic wastewater, septic effluent, chemical fertilizers, and manure (Jeong 2001). The second PC accounts for 29.1% of the total variance and exhibits positive loadings of Mg^{2+} and HCO_3^- ($R = 0.80$, $p < .01$). Natural processes, such as the dissolution of carbonate minerals and of

atmospheric and soil CO₂ gases could be the mechanisms that supply HCO₃⁻ to groundwater (Chen *et al.* 2010). The mechanism can be explained as follows:



The third PC, accounting for 20.4% of the total variance, is only influenced by K⁺. The high K⁺ concentration in the groundwater samples of paddy fields during the cultivation period and that of the vegetables fields could be attributed to the use of chemical fertilizers such as the nitrogenous, phosphorus, and potassic compound fertilizer. This component may be attributable to the fertilizer application.

Electrical conductivity (EC) values of Yellow River water ranged from 471.00 μS/cm to 892.00 μS/cm, which showed relatively low EC values compared with that in the whole surface water. Estimates of EC could be used as an index of water quality in the areas unaffected by seawater; thus, low Yellow River water EC in the study area indicates better water quality than other surface waters (Jin *et al.* 2012). From Table 1 it is observed that the order of relative abundance of major cations in the Yellow River water is Ca²⁺ > K⁺ > Mg²⁺ > Na⁺ (mean value, on mg/L basis), while the order of anions is Cl⁻ > HCO₃⁻ > SO₄²⁻. Ca²⁺, and Cl⁻ are the abundant cation and anion in Yellow River, and also several water samples contained high K⁺, Mg²⁺, HCO₃⁻, and SO₄²⁻ concentrations. A plot on a piper diagram revealed that the surface waters belonged to Ca•K-Cl•HCO₃ and K•Ca-HCO₃•Cl types.

Spatial Distribution of Trace Metals and Comparison of Contents with Background Values

Trace metals were detected in all surface water samples. The distribution parameters of dissolved trace metals in surface water of the HLIA are given in Table 2. Aluminum was quantifiable in 48.1% of the samples; Mn and Se were quantifiable in 85.2% of samples; Mo and V in 92.6%; Fe was in 96.3% of samples, while each of the remaining elements were quantifiable in all samples. The metals exhibited the decreasing concentration order: Sr > Zn > B > Al > Ba = Fe > Mn = V > Mo = Se.

Concentrations of trace metals in Yellow River samples are less than in other surface water samples except for Al, Fe, and Mo which showed relatively high concentrations. V showed the equivalence concentration. In addition to the Yellow River, the rivers Majia, Tuhai, and Wei are the three main rivers in the HLIA. Five sites were located in the Majia river (Nos. 22, 32, 34, 42, and 46), 4 sites in the Tuhai river (Nos. 31, 5, 1, and 44), and 6 sites in the Wei river (Nos. 14, 18, 20, 38, 36, and 40) (Figure 1). Al, Fe, Mn, Se, and Zn varied greatly in spatial distribution with coefficients of variation (CV) of 165%, 205%, 185%, 103%, and 240%, respectively. The concentrations of dissolved trace metals in surface waters of the three rivers fluctuated irregularly and did not exhibit a distinct spatial variance. Some sites exhibited elevated levels for some elements but showed no trend according to distance along the river. Al, Fe, Mn, and Se exhibited very high anomalies at site 52 in the Yellow River, while B, Fe, and V exhibited high anomalies at site 46 in the Majia River, and Al, Mn, and Zn exhibited high anomalies at site 36 in the Wei River. Those three abnormal sites are primarily attributable to intensified agricultural and urban industrial practices (Smail *et al.* 2012; Zeng *et al.* 2009).

Table 2. Concentrations of dissolved trace metals in surface water and the Yellow River water (mg/L).

n	Statistic description				Standards				Reported studies				
	Min.	Max.	Mean in		China Drinking water ^a	USEPA		WHO for drinking water ^c	Background concentrations world average ^d		Chang Jiang ^e	Rhine River ^d	Danjiangkou Reservoir ^g
			surface water	Yellow River		MCLG ^b	MCL ^b						
Al	27	nd	1.59	0.27	0.41	0.2		0.01		0.974	0.002	0.203	
B	27	0.05	0.83	0.40	0.28	0.5						0.219	
Ba	27	nd	0.28	0.13	0.11	0.7	2	0.7				0.019	
Fe	27	nd	1.09	0.13	0.28	0.3		0.3				0.006	
Mn	27	nd	0.34	0.04	0.03	0.1		0.4	0.006	0.003	0.011		
Mo	27	nd	0.06	0.01	0.03	0.07				0.0007	0.0004		
Se	27	nd	0.04	0.01	0.00	0.01	0.05	0.01		0.001		0.015	
Sr	27	0.02	2.07	0.95	0.69								
V	27	nd	0.06	0.04	0.04					0.0002		0.071	
Zn	27	0.02	10.02	0.88	0.23	1			0.01	0.018	0.033	0.002	

^aStandard (GB5749–2006) values indicate the maximum levels of various substances in drinking water in order to meet the health quality requirements of human beings (MEP 2006).

^bUSEPA (2006) Drinking Water Standards. MCLG: Maximum contaminant level goal; MCL: maximum contaminant level (USEPA 2006a).

^cWHO Drinking Water Standards (WHO 2006).

^dKlavins *et al.* (2000).

^eWang *et al.* (2011).

^fLi *et al.* (2008).

nd = not detected.

The detected levels of Al, Mn, Mo, Se, V, and Zn in surface waters of the HLIA are generally greater than observed at other locations around the world (Klavins *et al.* 2000). Indeed, values reported here for the HLIA are greater than for other rivers in China and abroad that have been impacted by agriculture (*e.g.*, the rivers Rhine, Changjiang, and Han, and the reservoir at Danjiangkou) (Klavins *et al.* 2000; Li and Zhang 2010; Buschmann *et al.* 2008; Pan and Wang 2012). The water in the studied area of the river is used for both irrigation and drinking. Standards of drinking water quality established by the WHO (2006), U.S. Environmental Agency (USEPA 2006a), and China (GB5749–2006) (MEP 2006) were used to assess water quality of the HLIA. On average, the ratios of concentrations of Al, Fe, Se, B, Mn, and Zn in the HLIA, relative to the drinking water sanitary standards, were 40.7%, 14.8%, 29.6%, 25.9%, 11.1%, and 14.8% greater, respectively. The highest concentrations of Al, Fe, Se, B, Mn, and Zn were observed at site 52 in the Yellow, sites 42 and 46 in the Majia, and site 36 in the Wei. The concentrations of these same elements at site 28 in the Yellow were greater than the standard by factors of 7.9, 3.6, 4.0, 1.6, 3.4, and 10.0, respectively. Sites 52 and 28 are situated along the Yellow River and may be affected by geochemical source. Site 36 is located at the intersection of two rivers. Sites 42 and 46 are located at the relative downstream sites, they are significantly impacted by human activities and receive pollution mostly from domestic wastewater and industrial effluents located in city areas (Smail *et al.* 2012). Concentrations of Sr, Ba, V, and Mo were each observed in all samples at concentrations less than the levels set by the drinking water sanitary standards.

Risk Assessment

Potential exposure to trace metals through surface water was assessed by use of the USEPA residential scenario (USEPA 2002). Under residential land use, exposure to trace metals through surface waters is assumed to be due to ingestion and absorption through the skin (*i.e.*, dermal absorption) (Song *et al.* 2013; Karim *et al.* 2013). Considering these two pathways, HQs associated with corresponding metals were evaluated via a risk-assessment model. The exposure dose and HQs are calculated using Eqs. (1)–(3) that are adapted from the USEPA models (Wu *et al.* 2009; Karim 2011):

$$D_{\text{ingestion}} = \frac{C_w \times IRW \times EF \times ED}{BW \times AT} \quad (3)$$

$$D_{\text{dermal}} = \frac{C_w \times SA \times K_p \times ABS \times ET \times EF \times ED \times CF}{BW \times AT} \quad (4)$$

$$HQs = D/RfD \quad (5)$$

where D is the exposure dose (mg/kg/day) contacted through ingestion of water ($D_{\text{ingestion}}$) and through dermal absorption (D_{dermal}); C_w is the average concentration of trace metal (mg/L) in water; IRW is the rate of ingestion of drinking water ingestion (2 L/day); EF is the exposure frequency (350 days/year) (USEPA 1991b); ED is the exposure duration in years, triangular type (50%: 9; 90%: 30) (Batchelor *et al.* 1998); BW is the average bodyweight (kg), as lognormal type (mean: 60.2, s.d.: 2.9) (Li *et al.* 2010); AT is the averaging time for non-carcinogens and carcinogens (30 yrs) (Zabin *et al.* 2008); SA is the assumed exposed skin area (2,800 cm²);

Trace Metal Pollution in the Yellow River Irrigation Area

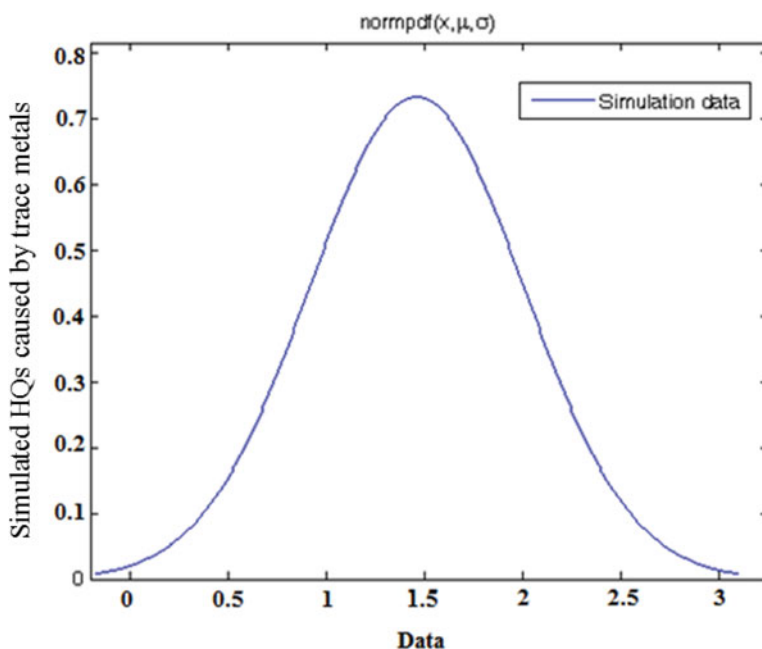


Figure 3. Distribution of HQ and probability of exceedance to risk level. (Color figure available online.)

K_p are the Dermal Permeability Constants (cm/hr); of Co (0.0004), Ni (0.0002), Zn (0.0006), and all other metals (0.001); ABS is the dermal absorption factor (0.001); ET is exposure time (0.6 h/day); CF is a unit conversion factor for water (1 L/1,000 cm³); RfD is the reference dose for different analytes, expressed in $\mu\text{g}/\text{kg}/\text{day}$ and is based on U.S. risk-based assessments (USEPA 2006b).

A Monte Carlo analysis was conducted on the probability distributions for each parameter. The output of HQ was presented as a normal distribution (Figure 3), and the probability of exceedance of the specified effect was calculated. The HQs of trace metals for local residents through oral and dermal pathways are summarized in Table 3. Ingestion of water was the predominant pathway of exposure to trace metals' residues in surface water. In fact, dermal exposure of trace metals was such a minor pathway of exposure that its effects can be disregarded.

The chemical-specific HQ for the 10 kinds of trace metals, Al, B, Ba, Fe, Mn, Mo, Se, Sr, V, and Zn as well as the sum of the 10 HQ values, ΣHQ , based on intake from water over two exposure routes are reported in Table 3. Mean ΣHQ s was estimated to be 1.46 for local residents. That value exceeded the generally acceptable risk level recommended by the USEPA for HQs > 1 (Karim 2011). Additionally, the maximum of HQ was 2.9, which was greater than the acceptable range. In fact, only 11% of surface water in the study area had a risk for HQs from trace metals that were less than 1, a result that indicates that the absorption of trace metals may have little or no consequences for human health for this portion of the study area.

Table 3. Reference dose and HQ for each element.

Element	RfD _{ingestion} ($\mu\text{g}/\text{kg}/\text{day}$)	RfD _{dermal} ($\mu\text{g}/\text{kg}/\text{day}$)	HQ _{ingestion}	HQ _{dermal}	$\Sigma\text{HQ}_s =$ (a) + (b)
Al	1.0E + 03	1.0E + 02	2.00E - 01	1.76E - 05	2.01E - 01
B	2.0E + 02	1.8E + 02	1.46E + 00	1.42E - 06	1.46E + 00
Ba	7.0E + 01	1.4E + 01	1.41E + 00	6.17E - 06	1.41E + 00
Fe	3.0E + 02	4.5E + 01	3.18E - 01	1.86E - 06	3.18E - 01
Mn	2.0E + 01	8.0E - 01	1.58E - 01	3.47E - 05	1.58E - 01
Mo	5.0E + 00	1.2E + 02	2.04E + 00	4.71E - 06	2.04E + 00
Se	5.0E + 00	1.0E - 02	1.09E + 00	2.17E - 06	1.09E + 00
Sr	6.0E + 02	6.0E + 01	1.17E + 00	5.10E - 06	1.17E + 00
V	1.0E + 00	1.9E + 00	2.94E + 01	2.58E - 03	2.94E + 01
Zn	3.0E + 02	5.4 E + 00	2.18E + 00	5.72E - 06	2.18E + 00
Total	—	—	3.95E + 01	2.66E - 03	3.95E + 01

RfD is based on U.S. risk-based assessments (USEPA 2006b).

Conversely, approximately 89% of the water in the remaining area could possibly have deleterious effects on the health of residents (Karim 2011).

Among the 10 trace metals, due to the greater concentrations, the proportion contributed by V to the ΣHQ was greatest (75%). The oxide and some other salts of V have moderate toxicity (Hosokawa and Yoshida 1989). Although V compounds are poorly absorbed through the gastrointestinal system, high doses of V by oral ingestion may affect blood conditions or cause liver or kidney damage (Hosokawa and Yoshida 1989). Due to the smaller RfD factors and greater concentrations, the contribution of Zn (5.5%) and Mo (5.2%) to the ΣHQ were larger than others, suggesting these elements also could pose a mild hazard to local residents. The relative contributions of each residue to the ΣHQ in surface water of the HLIA are shown Figure 4.

It is worth noting that the results of the risk assessment are based on the uncertain assumption that future concentrations will be the same as those at present. In reality, concentrations of metals will not be constant over time because of hydrologic and geochemical processes as well as massive production and by-production (Li *et al.* 2010). Thus, further investigation is necessary and measures should be taken to remedy hot spots to minimize risks of excess HQ in these areas.

Source Identification of Trace Metals

Concentrations of metals in the HLIA were several folds greater than uncontaminated surface water sampled from distant locations. The concentrations of Mn, Mo, Se, V, and Zn in the surface water in the HLIA were 13-, 14-, 10-, 200-, and 49-fold, respectively, that of the background value of Changjiang River, which is hundreds of kilometers away (Table 2). Thus we inferred that anthropogenic activities were affecting the water in the HLIA (Li *et al.* 2013). Further confirmation of this hypothesis was suggested with multivariate methods (De Bartolomeo *et al.*

Trace Metal Pollution in the Yellow River Irrigation Area

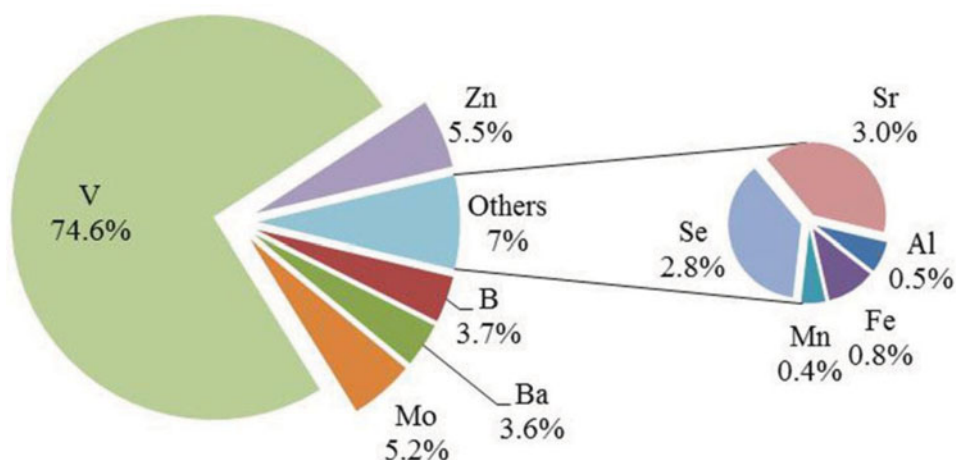


Figure 4. HQ proportions of trace metals in study area. (Color figure available online.)

2004). Accordingly, three principal components with eigenvalues >1 accounted for 73.9% of the variance in the dataset (Table 4).

Previous studies reported comprehensive sources for trace metals. For instance, Al and Fe are abundant in the earth while Ba and Mn are contributed from weathering of parent material and subsequent pedogenesis (Nriagu 1989). In contrast, the sources of V include urban and industrial activities such as energy production, mining, metal smelting and refining, manufacturing processes, vehicle exhaust, and waste incineration (Huang *et al.* 2007). Our results demonstrate that the first PC accounts for 29.7% of the total variance and has high loadings of Al, Fe, and Mn, which is indicative of a natural source. This interpretation is further confirmed by their strong pairwise geochemical correlations (Al and Fe, $R = 0.92$, $P < .01$; Al and Mn, $R = 0.67$, $P < .01$; Fe and Mn, $R = 0.62$, $P < .01$).

The second PC with 22.1% variance showed greater loadings for B, Ba, Mo, and V. Although B is not abundant in the Earth's crust, previous studies reported that concentrations of boride could be unusually enriched in oilfield brines (Song *et al.* 2013). Significant spatial differences of B (sites 46 and 42; Table 4) indicated an anthropogenic source. High Ba concentrations are primarily derived from geological processes (Krishna *et al.* 2009). Concentrations of V have been shown to be greatly influenced by anthropogenic activities such as mining and agricultural processes (Li *et al.* 2008). Therefore, the second PC can be identified as industrial and agrochemical processes (Yalcin and Ilhan 2008).

The third PC was mainly influenced by Se, Sr, and Zn. Depending on prevailing pedogenic processes, Zn can have a lithogenic source as it forms a number of soluble salts or insoluble salts (Pan and Wang 2012). However, Zn and its salts are also used to manufacture goods (*e.g.*, paints, automobile tires, and electrical apparatus) and are added to agricultural fertilizers. Therefore, this component may be attributable to a mixed source of both geogenic and anthropogenic origin.

Table 4. Total variance explained and component matrices of PCA.

Total variance explained											
Initial eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings					
Components	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance
1	4.075	40.752	40.752	4.075	40.752	40.752	2.975	29.749	29.749	2.975	29.749
2	2.094	20.942	61.694	2.094	20.942	61.694	2.212	22.123	51.872	2.212	22.123
3	1.221	12.215	73.909	1.221	12.215	73.909	2.204	22.037	73.909	2.204	22.037

Variables	Component matrix			Rotated component matrix		
	F1	F2	F3	F1	F2	F3
Al	.824	-.372	.347	.951	.086	.162
B	.795	.300	.300	.579	.641	.255
Ba	.191	.767	.480	-.008	.904	-.194
Fe	.785	-.355	.267	.876	.058	.206
Mn	.555	-.471	.250	.755	-.127	.073
Mo	.181	.507	-.008	-.118	.498	.166
Se	.731	.097	-.509	.252	.150	.846
Sr	.657	.284	-.541	.091	.275	.849
V	.561	.667	-.036	.070	.757	.427
Zn	.701	-.372	-.307	.553	-.193	.616

Extraction method: principal component analysis. Rotation method: varimax with Kaiser normalization. Rotation converged in 5 iterations. The biggest loading of trace metals on each PC are indicated in bold.

PERSPECTIVE

In China, the Yellow River Irrigation Area is mostly composed of arid and semi-arid areas. Other than precipitation, the Yellow River has been the only source of surface water in the HLLA since water diversion projects were first implemented in 1952. Surface water is the major source of water for drinking and for domestic, industrial, and agricultural sectors in the HLLA. Trace metals from different sources can impact surface waters, which, in turn, influence the aquatic life, crop production, and human health. Therefore, protecting surface water in this region has important implications for both food safety and human health. We showed here that trace metals' pollution was a serious problem and that distribution and sources of trace metals are not only impacted by the geogenic origin, but also by agriculture and industrial activities. The most severe outcome is that this kind of pollution is covert, long-term, and non-reversible. Nevertheless, removing heavy metals from the environment in order to prevent entrance into the food chain is important for protecting the health of animals and humans. An understanding of the status of heavy metal pollution is thus a fundamental prerequisite for remediating pollution. Therefore, it is urgent to devise guidelines for efficient management of the surface water in this region, including techniques to reduce the migration of heavy metals in water and their bio-availability, and to adopt management measures to control the origin of heavy metals, such as to change the land use type, to control non-point pollution sources, and to construct the sewage treatment plants.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support provided by the 100 Talents Program of Chinese Academy of Sciences, and the National Science Foundation (grant No. 41271047 and No. 41201514).

REFERENCES

- Batchelor B, Valdes J, and Araganth V. 1998. Stochastic risk assessment of sites contaminated by hazardous wastes. *J Environ Eng-Asce* 124(4):380–8
- Bu HM, Tan X, and Zhang QF. 2009. Dissolved heavy metals analysis and pollution sources recognition in the Jinshui River, Shaanxi. *Environ Chem* 28(1):107–12
- Buschmann J, Berg M, Stengel C, *et al.* 2008. Contamination of drinking water resources in the Mekong delta floodplains: Arsenic and other trace metals pose serious health risks to population. *Environ Int* 34(6):756–64
- Chen SF, Wu WL, Hu KL, *et al.* 2010. The effects of land use change and irrigation water resource on nitrate contamination in shallow groundwater at county scale. *Ecol Complex* 7(2):131–8
- Cheng S. 2007. Heavy metal pollution in China: Origin, pattern and control - a state-of-the-art report with special reference to literature published in Chinese journals. *Environ Sci Pollut R* 14(7):489–9
- De Bartolomeo A, Poletti L, Sanchini G, *et al.* 2004. Relationship among parameters of lake polluted sediments evaluated by multivariate statistical analysis. *Chemosphere* 55(10):1323–9

- Hosokawa S and Yoshida O. 1989. Vanadium in patients undergoing chronic haemodialysis. *Nephrol Dial Transpl* 4:282–4
- Huang SS, Liao QL, Hua M, *et al.* 2007. Survey of heavy metal pollution and assessment of agricultural soil in Yangzhong district, Jiangsu Province, China. *Chemosphere* 67(11): 2148–55
- Jeong CH. 2001. Effect of land use and urbanization on hydrochemistry and contamination of groundwater from Taejon area, Korea. *J Hydrol* 253(1–4):194–210
- Jin ZF, Pan ZY, Jin MT, *et al.* 2012. Determination of nitrate contamination sources using isotopic and chemical indicators in an agricultural region in China. *Agr Ecosyst Environ* 155:78–86
- Ju XT, Xing GX, Chen XP, *et al.* 2009. Reducing environmental risk by improving N management in intensive Chinese agricultural systems. *Proc Natl Acad Sci USA* 106(9):3041–6
- Karim Z. 2011. Risk assessment of dissolved trace metals in drinking water of Karachi, Pakistan. *Bull Environ Contam Toxicol* 86(6):676–8
- Karim Z, Qureshi BA, and Ghouri I. 2013. Spatial analysis of human health risk associated with trihalomethanes in drinking water: A case study of Karachi, Pakistan. *J Chem* <http://dx.doi.org/10.1155/2013/805682>
- Klavins M, Briede A, Rodinov V, *et al.* 2000. Heavy metals in rivers of Latvia. *Sci Total Environ* 262(1–2):175–83
- Krishna AK, Satyanarayanan M, and Govil PK. 2009. Assessment of heavy metal pollution in water using multivariate statistical techniques in an industrial area: A case study from Patancheru, Medak District, Andhra Pradesh, India. *J Hazard Mater* 167(1–3): 366–73
- Li F, Tang C, Zhang Q, *et al.* 2008. Surface water-groundwater interactions in a Yellow River alluvial fan. IAHS-AISH publication:189–96
- Li J, Lu YL, Wang G, *et al.* 2010. Evaluation and spatial diffusion of health risk of persistent organic pollutants (pops) in soils surrounding chemical industrial parks in China. *Hum Ecol Risk Assess* 16(5):989–1006
- Li J, Li FD, Liu Q, *et al.* 2013. Spatial distribution and sources of dissolved trace metals in surface water of the Wei River, China. *Water Sci Technol* 67(4):817–24
- Li S and Zhang Q. 2010. Spatial characterization of dissolved trace elements and heavy metals in the upper Han River (China) using multivariate statistical techniques. *J Hazard Mater* 176(1–3):579–88
- Loska K and Wiechula D. 2003. Application of principal component analysis for the estimation of source of heavy metal contamination in surface sediments from the Rybnik Reservoir. *Chemosphere* 51(8):723–33
- Mari M, Nadal M, Schuhmacher M, *et al.* 2009. Exposure to heavy metals and PCDD/Fs by the population living in the vicinity of a hazardous waste landfill in Catalonia, Spain: Health risk assessment. *Environ Int* 35(7):1034–9
- MEP (Ministry of Environmental Protection, the People's Republic of China). 2006. Standard of Drinking Water Quality (GB 5749–2006). Ministry of Health of the People's Republic of China. Beijing, China
- Nriagu JO. 1989. A global assessment of natural sources of atmospheric trace metals. *Nature* 338(6210):47–9
- Oberg T and Bergback B. 2005. A review of probabilistic risk assessment of contaminated land. *J Soil Sediment* 5(4):213–24
- Pan K and Wang WX. 2012. Trace metal contamination in estuarine and coastal environments in China. *Sci Total Environ* 421:3–16
- Smail EA, Webb EA, Franks RP, *et al.* 2012. Status of metal contamination in surface waters of the coastal ocean off Los Angeles, California since the Implementation of the Clean Water Act. *Environ Sci Technol* 46(8):4304–11

Trace Metal Pollution in the Yellow River Irrigation Area

- Song S, Li F, Li J, *et al.* 2013. Distribution and contamination risk assessment of dissolved trace metals in Surface waters in the Yellow River Delta. *Hum Ecol Risk Assess.* doi:10.1080/10807039.2012.708254
- Sun ZL, Feng SY, and Li QZ. 2005. On the issues of water resources sustainable utilization in Liaocheng city. *Journal of Water Resources & Water Engineering* 16(2):78–80
- Taebi A and Droste RL. 2004. Pollution loads in urban runoff and sanitary wastewater. *Sci Total Environ* 327(1–3):175–84
- USEPA (US Environmental Protection Agency). 1991a. Risk Assessment Guidance for Superfund: Volume III–Part A, Process for Conducting Probabilistic Risk Assessment. EPA/540/R-02/002. Washington, DC, USA
- USEPA. 1991b. Risk assessment Guidance for Superfund, Volume 1. Human Health Evaluation Manual (part b), Development of Risk-Based Preliminary Goals. EPA/540/R-92/003 Publication 92587–01B. Washington, DC, USA
- USEPA. 2002. Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites OSWER 93554–24. Washington, DC, USA
- USEPA. 2006a. Risk-based Concentration Table. Available at <http://www.epa.gov/reg3hwmd/risk/human/rbc/rbc1006.pdf> (accessed December 20, 2011)
- USEPA. 2006b. U.S. Environmental Protection Agency, Edition of the Drinking Water Standards and Health Advisories. Washington, DC, USA
- Varol M and Sen B. 2009. Assessment of surface water quality using multivariate statistical techniques: A case study of Behrimaz Stream, Turkey. *Environ Monit Assess* 159(1):543–53
- Wang L, Wang Y, Xu C, *et al.* 2011. Analysis and evaluation of the source of heavy metals in water of the River Changjiang. *Environ Monit Assess* 173(1):301–13
- WHO (World Health Organization). 2006. Guidelines for Drinking Water Quality, 3rd edition. Geneva, Switzerland
- Wu B, Zhao D, Jia H, *et al.* 2009. Preliminary risk assessment of trace metal pollution in surface water from Yangtze River in Nanjing Section, China. *Bull Environ Contam Toxicol* 82(4):405–9
- Wu XT and Yuan XL. 2012. Discussion on problems and countermeasures about water resources sustainable utilization of the Yellow River in Henan. *Yellow River* 34(9):50–3
- Yalcin M and Ilhan S. 2008. Multivariate analyses to determine the origin of potentially harmful heavy metals in beach and dune sediments from Kizkalesi Coast (Mersin), Turkey. *Bull Environ Contam Toxicol* 81(1):57–68
- Yang Z, Wang Y, Shen Z, *et al.* 2009. Distribution and speciation of heavy metals in sediments from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan, China. *J Hazard Mater* 166:1186–94
- Zabin S, Foaad MA, and Al-Ghamdi A. 2008. Non-carcinogenic risk assessment of heavy metals and fluoride in some water wells in the Al-Baha Region, Saudi Arabia. *Hum Ecol Risk Assess* 14(6):1306–17
- Zeng GM, Liang J, Guo SL, *et al.* 2009. Spatial analysis of human health risk associated with ingesting manganese in Huangxing Town, Middle China. *Chemosphere* 77(3):368–75