



Trace metal in surface water and groundwater and its transfer in a Yellow River alluvial fan: Evidence from isotopes and hydrochemistry



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HIGHLIGHTS

- Trace metal pollution in surface water was more serious than that in groundwater.
- Distribution of trace metal exhibited a certain relationship with water flow direction.
- Surface–groundwater interactions influence spatial distribution of trace metal.
- Agriculture and industrial activities contributed to increasing levels of trace metal pollution.

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ABSTRACT

Metals are ubiquitous in the environment. The aim of sustainable management of the agro-ecosystem includes ensuring that water continues to fulfill its function in agricultural production, cycling of elements, and as a habitat of numerous organisms. There is no doubt that the influence of large-scale irrigation projects has impacted the regional surface–groundwater interactions in the North China Plain (NCP). Given these concerns, the aim of this study is to evaluate the pollution, identify the sources of trace metals, analyze the influence of surface–groundwater interactions on trace metal distribution, and to propose urgent management strategies for trace metals in the agriculture area in China. Trace metals, hydrochemical indicators (EC, pH, concentrations of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , and HCO_3^-) and stable isotopic composition ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) were determined for surface water (SW) and groundwater (GW) samples. Trace metals were detected in all samples. Concentrations of Fe, Se, B, Mn, and Zn in SW exceeded drinking water standards by 14.8%, 29.6%, 25.9%, 11.1%, and 14.8% higher, respectively, and by 3.8%, 23.1%, 11.5%, 11.5%, and 7.7% in GW. The pollution of trace metals in surface water was more serious than that in groundwater, and was also higher than in common irrigation areas in NCP. Trace metals were found to have a combined origin of geogenic and agriculture and industrial activities. Their distribution varied greatly and exhibited a certain relationship with the water flow direction, with the exception of a number of singular sites. Hydrochemical and environmental isotopic evidence indicates surface–groundwater interactions influence the spatial distribution of trace metal in the study area. Facing the ongoing serious pollution, management practices for source control, improved control technologies, and the construction of a monitoring net to warn of increased risk are urgently needed.

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1. Introduction

The main objective of China's 11th Five-Year Plan for economic and social development (2005–2010) is an annual GDP growth rate of 7.5%, and a reduction of total emissions of major pollutants of 10%. Statistics over the last decade (National Bureau of Statistics and Ministry of Environmental Protection of China (MEP), 2002–2011) indicated China's GDP had grown at an average annual rate of 14% from 2001 to

2010 and 17% from 2005 to 2010, while the total volume of waste water discharged and total volume of soot discharged have decreased sharply, and the total volume of industrial solid waste discharged increased (Fig. A). There are large variations in the emission intensity (emissions of pollutants per unit of GDP) for different industries in China. The average pollutant emission intensity in western areas is about 3.5 times as large as in eastern areas (Chen, 2008). Rapid economic growth as well as lax environmental oversight has increased water pollution and caused increasing total sewage emissions in recent years. Although there is stringent regulation in China for treatment of industrial wastes, disposal of untreated wastewater into drains and subsequently into rivers is common (Liu et al., 2011). Additionally, trace metals from agricultural sources and atmospheric deposition are

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directly discharged into streams without treatment via surface runoff or rain water, posing potential health and environmental risks to people living in downstream areas (Smail et al., 2012).

In most countries of the world, groundwater and surface water in agricultural areas are at a serious risk of metal pollution, due to rapid industrialization and urbanization, and intensification of agriculture (Klavinš et al., 2000; Li and Zhang, 2010). In China, the geological background level of heavy metals is low, including for Fe (0.013 mg/L), Mn (0.003 mg/L), V (0.0002 mg/L), Zn (0.0007 mg/L), etc. (Cheng, 2007), but concentrations of trace metals in water have been increasing over recent years (Pan and Wang, 2012; Song et al., 2013). Rapid economic development in China over the last decades has resulted in environmental degradation, amongst others, with heavy metal pollution in several important agricultural areas, e.g., the Yellow River Delta (Song et al., 2013), Han River Delta (Bu et al., 2009; Li and Zhang, 2010) and the Yangtze River Delta (Yang et al., 2009). Li and Zhang (2010) indicated that concentrations of dissolved heavy metals differed significantly in different sampling sites. With the exception of Fe, Sr, and As, all dissolved heavy metals met World Health Organization (WHO) recommendations as well as the Chinese standard for drinking water quality (GB 5749-2006) (MEP, 2006). Bu et al. (2009) found that all dissolved heavy metals, except for Mn, exceeded the background values in the upper Han River and the source area of the Yangtze River. In addition, Song et al. (2013) reported that the hazard quotients (HQ) value of trace metals indicated potential deleterious health effects for residents in the Yellow River Delta and required special attention. Metals are of concern to both scientists and environmental quality managers or policy makers because of their persistence, bioaccumulation, toxicity, and long-range environmental transport ability (Göran, 1989; Buschmann et al., 2008; Bichet et al., 2013). In 2011, the MEP issued the “12th Five-Year Plan for National Environmental Monitoring and Opinions on Strengthening Environmental Monitoring of Heavy Metal Pollution” to improve metal management capacities.

Metals from industrial wastes, agricultural sources, urban runoff, atmospheric deposition, and automobile emissions could also disperse to the surface water via surface runoff or rain water (Smail et al., 2012). They could penetrate to deeper soil layers, and eventually reach groundwater (Bichet et al., 2013). Trace metals in waters are non-degradable and remain present for long periods of time and need to be carefully monitored (Buschmann et al., 2008). Therefore, the identification of sources and evaluation of ecosystem risk of trace metal contamination of the water body are critical for the management of these resources and limiting the potential for harmful consequences (Wu et al., 2009). However, due to difficulties in continuous metals monitoring with actual on-site sampling, especially in a wide range, there is an urgent need for suitable techniques and methods to identify the environmental behavior of metals, and to forecast their migration and distribution trends at a regional scale (Sadler et al., 2011). In order to meet the need of understanding metal pollution patterns and migration processes at the regional and landscape scale, new technologies, such as environmental modeling, GIS technology, and isotope tracing tools are increasingly being applied (Hoefs, 2009; Halder et al., 2013; Petrisic et al., 2013). For example, Oxygen-18 (^{18}O) and deuterium (^2H) isotopes could indicate water sources and recharge conditions (Hoefs, 2009), and have been widely used to trace the origin of groundwater salinity because of their limited transport in shallow aquifer settings (Gao et al., 2011).

Irrigation projects have diverted water from the lower reaches of the Yellow River for more than 50 years in China and are unique in the world. Researchers have recently assessed and forecasted the water resources in the Yellow River alluvial fan (Sun et al., 2005; Wu and Yuan, 2012). Wu and Yuan (2012) 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 demand of water sources in

Liaocheng City. F. Li et al. (2008) studied surface water–groundwater interactions in a Yellow River alluvial fan. However, it is not clear what the status of trace metal contamination and the extent of their environmental risk are. Moreover, it has not yet been evaluated how the transfer of trace metals from surface water and groundwater is impacted by irrigation projects.

Samples were collected during a field survey in order to (1) identify the hydrochemical characteristics and quantify trace metal content, (2) assess the potential risk posed by trace metals in the surface water and groundwater, (3) reveal the source of trace metals in the surface water and the influence of surface–groundwater interactions on trace metal distribution in the groundwater, and (4) propose management recommendations for trace metals in surface water and groundwater in agricultural areas in China.

2. Material and methods

2.1. Study area

The northern section of the Henan–Liaocheng Irrigated Area (HLIA, 113.938°–117.076° E and 34.982°–37.391° N), a typical agricultural region, spans eastern Henan Province and western Shandong Province, with a total area of approximately 28,500 km². In Liaocheng City, average annual GDP growth has been 18% from 2005 to 2010. The discharged volume of all key pollutants—waste water, soot, and industrial solid waste have increased continually, with a sharp increase in particular of soot discharge from 2004 to 2006 (Statistic bureau of Shandong Province, 2002–2011). The area is in a warm-temperate continental monsoon climate. Rivers include the Yellow River, Wei River, Majia River and Tuhai River, and their main tributaries. The annual average air temperature (14–15 °C) and annual sunshine hours (2200–2300 h) are suitable for wheat, rice, cotton, and corn production. Annual precipitation ranges from 600 to 1000 mm, with 2/3 of that available between June and September. The entry water mainly comes from the Yellow River water resources. The effective irrigated area in Henan Province was 21,430 km² with 16,070 km² of arable land. The design capacity of Liaocheng irrigation area is 445 m³/s, with the effective irrigated area covering the entire city. The source of groundwater is dominated by vertical fill rows, including lateral runoff recharge of atmospheric precipitation, and surface water supplies. Drainage ways are mainly for vertical evaporation, discharge to Majia, Tuhai and other rivers, and manual drainage. Groundwater flows slowly from southwest to northeast, along a hydraulic gradient of 0.1 to 0.4%. The shallow groundwater table has declined significantly, at a mean rate of approximately 1 m/year in this area over the past several decades (Yang et al., 2002).

2.2. Water sampling and analysis

Surface water samples of 100 mL were collected from July 23th to 30th, 2010 in the study area. Selected sites were distributed amongst 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. Groundwater samples were collected from private wells located nearby each surface water sampling site. Five samples were collected and mixed 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 6 M HNO₃, stored at 4 °C in the field, and then analyzed once we returned to the laboratory. A general overview of the study site showing the geology and the sampling locations is presented in Fig. 1.

Electrical conductivity (EC) and pH were measured by portable pH and EC meters (Compact meter, Horiba, Japan) in situ. All samples

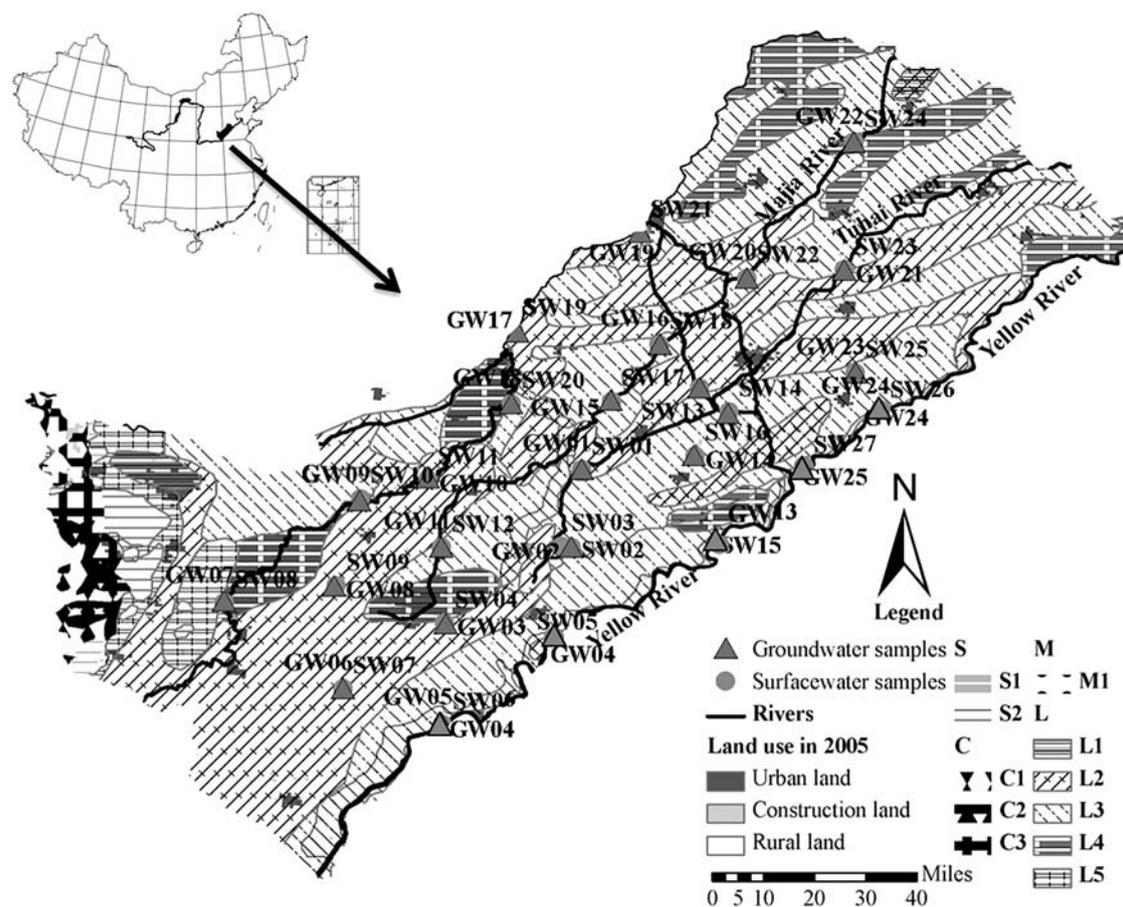


Fig. 1. Topography and location of the sample sites. Note: “L,” loose salts porous aquiferous group (saturation gradually increasing from L1 to L5); “M,” metamorphic rocks fractured aquifer rock group; “C,” carbonate fissure salt dissolved water content of salt groups (saturation gradually increasing from C1 to C3); and “S,” broken nitrate aquiferous group (saturation gradually increasing from S1 to S2).

were filtered through a 0.45 μm cellulose acetate filter membrane before using ion chromatography (Dionex China Ltd.) to analyze Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , and SO_4^{2-} . HCO_3^- was measured by titration using 0.01 N H_2SO_4 . The chemical results were only accepted when the charge balance error was within $\pm 5\%$. The isotopic composition of oxygen (^{18}O) and deuterium (D) in groundwater and surface water was examined using an Isotope Ratio Mass Spectrometer (LGR LWIA-V2(DLT-100)). The results of ^{18}O and D were expressed in per mil unit as delta-notation relative to the Vienna Standard Mean Ocean Water (VSMOW) standard. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ measurements were reproducible to $\pm 0.2\%$ and $\pm 1.0\%$, respectively. We analyzed total concentrations of Zn, Se, B, Ba, Fe, Mn, Mo, Ni, V, Al, Li, Sr, Be, Cd, Cr, Cu, and Pb, using an Inductively Coupled Plasma–Optical Emission Spectrometer (ICP–OES, PerkinElmer Co., Ltd., USA). Calibration curves were made after measuring a set of samples and evaluated according to quality control standards. Reagent, procedural blanks and samples were measured 3 times in parallel, with the average values reported in the Results section.

In this study, the frequency distributions of concentrations of trace metals were checked for skew and kurtosis. Principal component analysis (PCA) was used to compare patterns of relative concentrations of trace metals. Analysis of variance (ANOVA) was used to analyze differences of trace metals in surface water and groundwater where there was a strong hydraulic connection. Kriging was employed to analyze the horizontal distribution of trace metals using GIS software version 9.0 for Windows (Esri China (Beijing) Limited) (Saby et al., 2009). The values of Al, Ba, Ni, Li, Sr, Be, Cd, Cr, Cu, Mo, and Pb were small or below detection limits in most samples. The

distributions of B, Fe, Mn, Se, V and Zn were further analyzed by multivariate statistical methods to identify the influence of possible sources. All mathematical and statistical computations were made using SPSS 17.0 for Windows.

3. Results

3.1. Character of hydrochemical indicators and stable isotopes in surface water and groundwater

In the study area, groundwater samples were all relatively similar in pH (7.05–7.59), while those of surface water samples ranged from 7.58 to 9.56, indicating alkaline conditions (Table 1). EC values varied from 405 $\mu\text{S}/\text{cm}$ (GW14) to 3060 $\mu\text{S}/\text{cm}$ (GW22) in groundwater, while the range was 329 $\mu\text{S}/\text{cm}$ (SW13) to 3200 $\mu\text{S}/\text{cm}$ in surface water (SW09). Low EC values in surface water were found in the Yellow River water, whereas groundwater had higher EC because of leaching from soil or from the interaction of different sources of groundwater. 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 $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^-$. Correspondingly, the order of major cations in the groundwater was $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ (on mg/L basis), while the order of anions was $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$.

EC values in the Yellow River water ranged from 471 $\mu\text{S}/\text{cm}$ to 892 $\mu\text{S}/\text{cm}$, which is relatively low compared with that in other surface water. Estimates of EC can be used as an index of water quality in the areas unaffected by seawater; thus, the low EC value of the Yellow River water in the study area indicates better water quality than that

Table 1
Descriptive statistics of chemical constituents and stable isotopes in the surface water and groundwater.

Indexes	Surface water					Yellow River water					Groundwater				
	N	Min.	Max.	Mean	Std.	N	Min.	Max.	Mean	Std.	N	Min.	Max.	Mean	Std.
EC ($\mu\text{S}/\text{cm}$)	27	329	3200	1133.52	617.83	4	471	892	767.5	199.8	26	405	3060	1135.62	522.18
pH	27	7.58	9.56	8.2	0.53	4	7.92	8.16	8.06	0.10	26	7.05	7.59	7.31	0.13
$\delta^{18}\text{O}$ (‰)	27	-12.9	-8.0	-10.0	1.4	4	-9.2	-8.4	8.0	0.3	26	-10.1	-7.9	-8.9	0.6
$\delta^2\text{H}$ (‰)	27	-98	-62	-74	11	4	-65	-62	-63	1.0	26	-71	-57	-64	3
Ca^{2+} (mg/L)	27	3.9	212.9	80.1	43.4	4	6.7	92.1	60.2	37.3	26	0.0	226.7	69.8	48.8
K^+ (mg/L)	27	0.2	14.4	7.7	4.0	4	0.4	6.7	4.1	2.6	26	0.0	15.5	2.8	3.1
Mg^{2+} (mg/L)	27	1.3	139.2	40.9	25.9	4	2.2	27.9	21.3	12.7	26	0.0	155.1	66.9	29.6
Na^+ (mg/L)	27	2.7	676.6	150.8	131.2	4	4.5	77.1	57.0	35.1	26	0.1	354.1	131.4	84.2
SO_4^{2-} (mg/L)	27	2.6	680.6	224.2	152.2	4	6.0	143.6	105.8	66.6	26	1.0	390.6	139.5	97.6
HCO_3^- (mg/L)	27	76.3	433.1	216.9	69.1	4	146.4	189.1	170.8	18.5	26	326.4	957.7	534.7	149.8
Cl^- (mg/L)	27	142.0	1218.0	279.1	207.1	4	173.0	212.0	190.5	20.0	26	116.0	401.0	223.5	132.2

of other surface waters (Jin et al., 2012). Table 1 shows that the order of relative abundance of major cations in the Yellow River water is $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ (on mg/L basis), while the order of anions is $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$. Ca^{2+} and Cl^- are the abundant cation and anion in Yellow River, while several water samples also contained high Na^+ , Mg^{2+} , HCO_3^- and SO_4^{2-} concentrations. A plot on a Piper diagram revealed that the Yellow River waters belonged to Ca-Na-Cl, Na-Ca-Cl, and Ca-Cl- HCO_3 types.

δD values in groundwater varied from -71 to -57‰ with a mean value of -64‰, and $\delta^{18}\text{O}$ ranged from -10.1 to -7.9‰ with a mean value of -8.9‰. $\delta^2\text{H}$ values in surface water varied from -98 to -62‰ with a mean value of -74‰, and $\delta^{18}\text{O}$ varied from -12.9 to -8‰ with a mean value of -10‰.

3.2. Character of trace metal in surface water and groundwater

Trace metals were detected in all of the water samples. Coefficients for skew and kurtosis revealed that concentrations of trace metals were not normally distributed. Therefore, the median values of concentrations of B, Fe, Mn, Se, V and Zn were used instead of the mean values (Krishna et al., 2009). The distribution parameters of dissolved trace metals in surface water and groundwater of HLIA are presented as box and whisker plots with the bottom and top of the box representing the 25th and 75th centiles (Fig. 3). The pollution of trace metals in surface water was more serious than that in groundwater in the HLIA. Except for B, the median value of each element in surface water was greater than that in groundwater, the same goes for the maximum

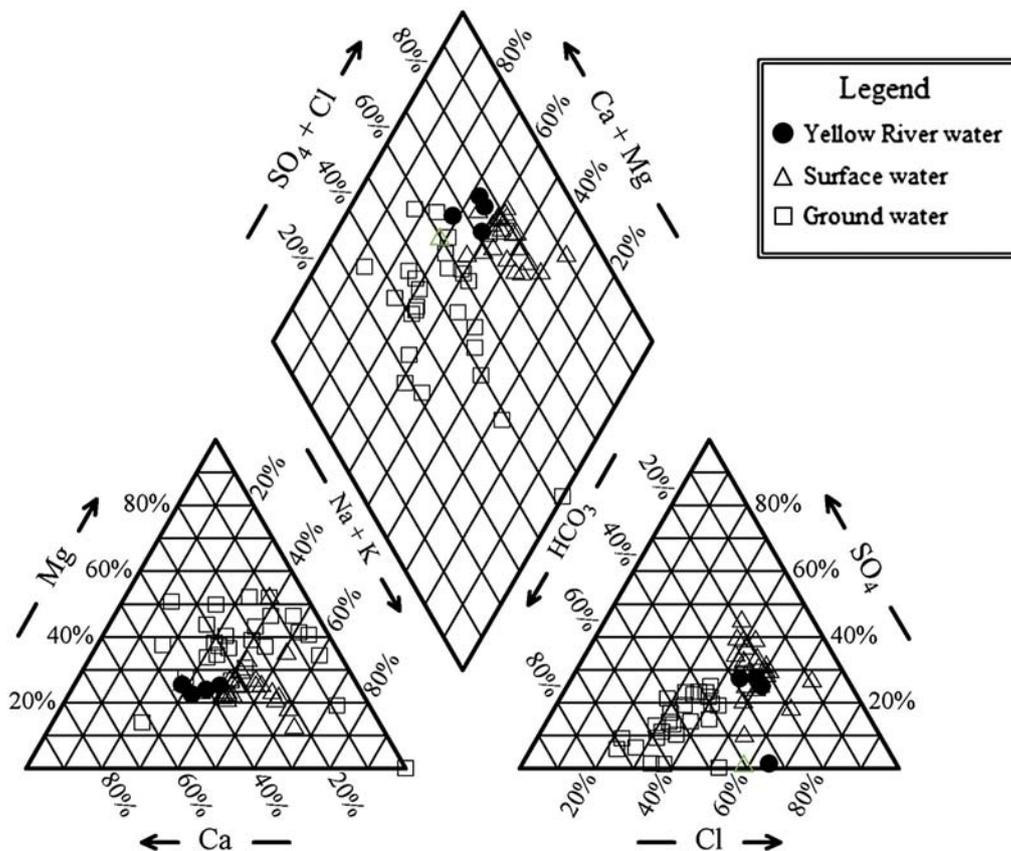


Fig. 2. Piper diagram of surface water and groundwater in HLIA.

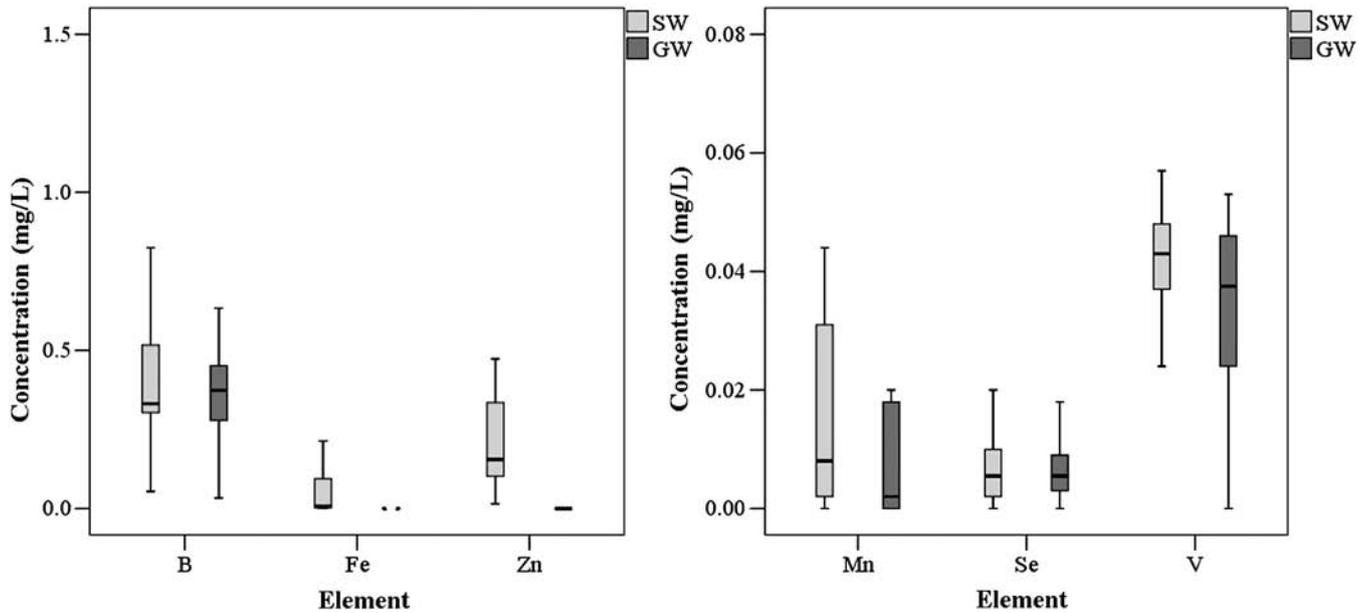


Fig. 3. Boxplot of dissolved trace metals in surface water and groundwater in the HLIA (mg/L).

value. Samples from the Yellow River had lower concentrations of trace metals than other surface water samples, with the exception of Fe, which showed relatively high concentrations.

B was quantifiable in 100% of water samples; the concentrations in surface water (0.05–0.83 mg/L, with median value of 0.33 mg/L) were higher than those in groundwater samples (0.03–0.63 mg/L, 0.37 mg/L). Fe was quantifiable in 96.3% of surface water samples and 46.2% of groundwater samples; the maximum value in surface water (1.09 mg/L) was 3.5 times that found in groundwater (0.31 mg/L). Zn was quantifiable in 100% of surface water samples and 96.2% of groundwater samples; the concentration of trace metals in surface water (0.02–10.02 mg/L, 0.16 mg/L) was higher than that in groundwater. However, there were two sites where groundwater exhibited anomalous concentrations (22.21 mg/L and 1.39 mg/L), indicating point source pollution; the concentrations at other sites were all below 0.10 mg/L. The concentration of Mn in surface water (range: not detected (nd)–0.34, median: 0.01, detected ratio: 85.2%) was slightly higher than that in groundwater (nd–0.33 mg/L, 0.002 mg/L, 73.1%), as was the case for Se (nd–0.04 mg/L, 0.01 mg/L, 85.2%; nd–0.02 mg/L, 0.01 mg/L, 96.2%), and V (nd–0.06 mg/L, 0.04 mg/L, 92.6%; nd–0.05 mg/L, 0.04 mg/L, 85.2%).

4. Discussion

4.1. Comparison with reported trace metal values and standards

Detected levels of dissolved trace metals in SW of HLIA were generally higher than estimated world averages (Klavinš et al., 2000), and higher than other rivers impacted by agriculture and urban pollution in China and abroad, such as the Congo, Niger, Rhine, Changjiang, Han River and Danjiangkou Reservoir (Gaillardet et al., 2003; Buschmann et al., 2008; S.Y. Li et al., 2008; Li and Zhang, 2010). Considering that the surface water and groundwater in this stretch are used for both irrigation and drinking, we summarized the standards of water quality established by WHO (2006), USEPA (2006) and China (MEP, 1992, 2006), including the purposes, contents, ranges, and applications, and found that the Surface Water Standard, Drinking Water Standard and Irrigation Water Standard are three common criteria to determine the pollution of river water and groundwater (Huang et al., 2007; Yang

et al., 2009; Aydin et al., 2013; Bichet et al., 2013). However, the Surface Water Standard contains several water quality levels corresponding to different function zoning of a water body. There is no unified Surface Water Standard that is globally adhered to. In China, there are five levels in the Surface Water Standard (GB 3838-2002) (level I is suitable for headwaters, level II for first-grade centralized drinking surface water, level III for second-grade centralized drinking surface water, level IV for general industrial water and level V for agricultural water and the landscape water). The level III of the Surface Water Standard has the same values as the Drinking Water Standard (GB5749-2006) in China (MEP, 2006), which has often been used to judge surface water quality. The Irrigation Water Standard addresses irrigation water only, with high threshold values and greater tolerances (Table 2). To sum up, the Drinking Water Standard is the optimum choice. On average, concentrations of Fe, Se, B, Mn, and Zn in SW in the HLIA exceeded drinking water standards established by WHO (WHO, 2006), USEPA (USEPA, 2006), and China (MEP, 2006) by 14.8%, 29.6%, 25.9%, 11.1%, and 14.8%, respectively. Similarly, concentrations of B, Fe, Mn, Se, and Zn in GW in the HLIA exceeded drinking water standards by 11.5%, 3.8%, 11.5%, 23.1%, and 7.7%, respectively.

4.2. Source identification of trace metals in surface water

Concentrations of metals in the HLIA were several folds greater than uncontaminated surface water sampled from distant locations. The concentrations of Mn, Se, V, and Zn in the surface water in the HLIA were 13-, 10-, 200-, and 49-fold greater, respectively, than 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 (Tariq et al., 2008; Li et al., 2013). As individual metal concentrations were several times higher than background levels in uncontaminated ground water sampled from far-off locations, it was inferred that anthropogenic activities were affecting the water in the area. Further confirmation of this hypothesis was secured through multivariate methods of statistical analysis (Yalcin and Ilhan, 2008). Because concentrations of trace metals were not normally distributed, Box-Cox transformation was performed for calculating the profile likelihood function, using SPSS syntax. Accordingly, using Varimax normalized rotation, three principal components (PC) with eigenvalues > 1

Table 2
Trace metal content in standards and reported studies (mg/L).

		B	Fe	Mn	Se	V	Zn	References
Background concentrations	World average						0.01	Klavinš et al. (2000)
	Chang Jiang		0.013	0.003		0.0002	0.0007	Zhang et al. (1996)
	Sweden		0.1				0.003	Göran (1989)
Reported concentrations in agriculture area	Yellow River Delta	0.62	0.12	0.1		0.05	2.33	Song et al. (2013)
	Han River		0.056	0.011	0.0096	0.0009	0.004	Li and Zhang, (2010)
	Wei River	0.516	0.011	0.064	0.01	0.068	0.873	Li et al. (2013)
	Konya Closed Basin		0.27	0.001				Aydin et al. (2013)
Standards	China						1	MEP (2006)
	Drinking water ^a	0.5	0.3	0.1	0.01			MEP (1992)
	Irrigation water ^b	1					2	MEP (1992)
	USEPA					0.05		USEPA (2006)
	MCLG ^c					0.05		USEPA (2006)
WHO for drinking water		0.3	0.4	0.01			WHO (2006)	

^a This standard's (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).

^b This standard (GB5084-92) applies to water from national surface water, groundwater, treated urban sewage and industrial wastewater, etc., and would be used as irrigation water (MEP, 1992).

^c USEPA (2006) drinking water standards. Maximum Contaminant Level Goal (MCLG); Maximum Contaminant Level (MCL) (USEPA, 2006).

were extracted for trace metals in SW, accounting for 83.1% of variance in the dataset (Fig. 4). The first PC accounts for 37.3% of total variance and has high loadings of Zn, Fe, and Mn. The second PC with 32.3% variance showed greater loadings for B and V. The third PC explained 13.5% of the total variance and was associated with distributions of Se.

Previous studies reported comprehensive sources for trace metals. For instance, Fe is abundant in the earth while Mn originates 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 exhausts, and waste incineration (Huang et al., 2007). Concentrations of V have been shown to be greatly influenced by anthropogenic activities such as mining and agriculture (S.Y. Li et al., 2008). Concentrations of B can be unusually high in oilfield brines (Song et al., 2013). Significant spatial differences of B (SW 23, 24) suggested an anthropogenic source (Tan et al., 2011). Depending on prevailing pedogenic processes, Zn can have a lithogenic source as it forms a number of soluble or insoluble salts (Pan and Wang, 2012). Therefore, the first PC is indicative of a natural source, while the second PC can be identified as industrial and agrochemical processes (Yalcin and Ilhan, 2008).

4.3. Surface–groundwater interactions evidenced by hydrochemistry and stable isotopes and its influence on the occurrence of trace metals

A Piper diagram revealed that the surface waters belonged to complex types, including Na–Cl, Ca–Cl, Ca–HCO₃, Na–SO₄ and Mg–Cl types (Fig. 2), while the groundwaters belonged to Na–HCO₃, Mg–HCO₃, Ca–HCO₃, and Na–Cl types. The background water type in the study area determined 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 groundwater.

The relationship of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ composition of meteoric waters varied in a range that was close to the global meteoric water line (GMWL), defined as $\delta^2\text{H} = 8\delta^{18}\text{O} + 10$ (Rozanski et al., 1993). The relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ composition of rainfall is different from one region to the other and depends on local climatic conditions (Hoefs, 2009). $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of rainfall data from the Global Network for Isotopes in rainfall dataset (IAEA/WMO, 2004) was used as the Local Meteoric Water Line (LMWL, $\delta^2\text{H} = 6.7(\pm 0.3)\delta^{18}\text{O} - 3(\pm 2)$) (shown in Fig. 5). LMWL data are calculated by monthly accumulated rainfall on Zhengzhou City (113.65°E, 34.72°N, 110 m) from September 1985 to December 1992. Fig. 5 indicates that some isotopic data points fall close to the GMWL while most of the points fall below the GMWL, commonly suggesting that precipitation after evaporation was the main source of surface water in the study area, and the groundwater was recharged not only with atmospheric precipitation, but also via surface runoff. There was a heavy rainstorm in the study area 4 days prior to our sampling moment with 136.6 mm of rainfall and a $\delta^{18}\text{O}$ value of -14.4‰ . Obviously, the surface water points located in the left lower corner of Fig. 5 were impacted by this rainstorm. The points located in the right upper corner showed a strong hydraulic connection between the surface water and groundwater. The ANOVA results of trace metals in surface water and groundwater in this area supported the above hypothesis. There was no significant difference ($P > 0.05$) between trace metals in surface water and those in groundwater (Table 3). The relationship of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of the surface water (Eq. (1)) and the groundwater (Eq. (2)) was as follows:

$$\delta^2\text{H} = 7.69(\pm 0.34)\delta^{18}\text{O} + 2.31(\pm 3.40) \quad R^2 = 0.95 \quad (1)$$

$$\delta^2\text{H} = 6.51(\pm 0.60)\delta^{18}\text{O} - 5.84(\pm 5.36) \quad R^2 = 0.74 \quad (2)$$

The spatial distribution of Fe, Mn, and Zn in surface water varied greatly with coefficients of variation (CV) of 205%, 185%, and 240%, respectively. The same goes for those in groundwater, where CV were 477%, 236% and 465%, respectively. The concentration of B, Fe, Mn, Se, V, and Zn in surface water increased along the direction of water flow

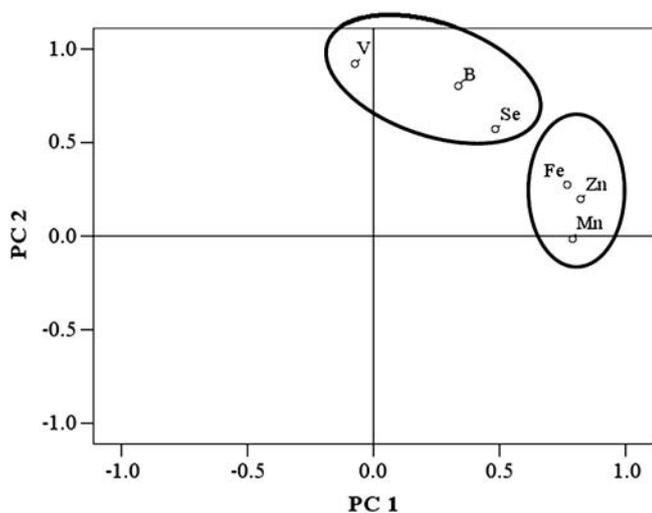


Fig. 4. Total variance explained and PCA component matrices. Note: Extraction method: principal component analysis. Rotation method: Varimax with Kaiser normalization. Rotation converged in 5 iterations.

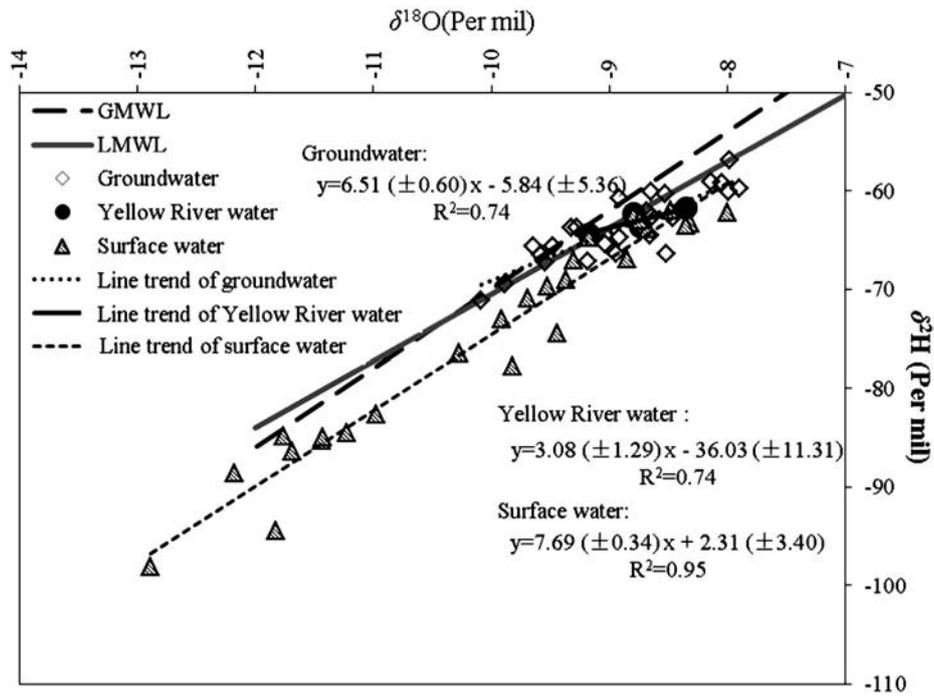


Fig. 5. Plot of relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in the study area.

of the Yellow River, except for separate sites with anomalous concentrations, which indicated point sources entry. The spatial distribution of trace metals in the groundwater showed a similar pattern with that in the surface water (Fig. B). Additionally, the concentration of B, Mn, Se, and V in surface water decreased from far to near the Yellow River, perpendicular to the direction of flow, indicating the rule of diffusion with water dilution. However, due to the time lag of surface water filtration into groundwater, the water dilution effect was not apparent in the groundwater.

$\delta^2\text{H}$ values in surface water of the Yellow River varied from -65 to -62‰ with a mean value of -63‰ , and $\delta^{18}\text{O}$ ranged from -9.2 to -8.4‰ with a mean value of -8.8‰ . These values were similar to those at Xiaolangdi hydrological station (Gao et al., 2011). Comparing the ratio of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ compositions in surface water of the Yellow River with LMWL, all points are close to the LMWL except at one site, which reflects the apparent evaporation characteristics and makes it clearly different from the precipitation lines. The Yellow River's tributaries are mainly concentrated in the upper and mid reaches, with less water supply from other rivers in the downstream (Chen et al., 2007). Experiencing strong evaporation and less supply, the isotopic composition becomes more fractionated and enriched along the Yellow River (Fig. 5). The majority of surface water samples from the Yellow River fell below the LMWL and the slope of a linear equation of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ decreased to 3.08, reflecting the apparent evaporation characteristics that differ from the precipitation lines.

In addition to the Yellow River, the rivers Majia, Tuhai, and Wei are the three main rivers in the HLIA. We took samples from five sites located in the Majia river (No. SW 12, 17, 18, 22, and 24), 4 sites in the Tuhai river (No. SW 16, 3, 1, and 23), and 6 sites in the Wei river (No. SW 08, 10, 11, 20, 19, and 21) (Fig. B). 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. Fe and Mn exhibited very high anomalies at site SW 27 in the Yellow River, while B, Fe, and V exhibited high anomalies at site SW 24 in the Majia River, and Mn, and Zn exhibited high anomalies at SW 19 in the Wei River. Those three abnormal sites are primarily

attributable to intensified agricultural and urban industrial practices (Zeng et al., 2009; Smail et al., 2012). The highest concentration of Fe, B, Mn, and Zn in the groundwater was observed at GW 24 along the Yellow River and GW 15 along the Majia River.

4.4. Recommendations for trace metal management in surface water and groundwater in agricultural areas

Water quantity and quality are two key factors influencing its utilization and management. Groundwater along the river is not an isolated component of the hydrologic system, but is instead connected with the surface water. 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 HLIA since water diversion projects were first implemented in 1952. Surface water and groundwater are the critical source of water for agricultural irrigation in the HLIA, and groundwater is also a drinking water source in the part of rural area. Considering that the trace metal pollution is covert, long-term, and non-reversible, more attention should be given to protecting the health of crops and humans and effective management of the surface water and groundwater in this region is needed. Measures required after identification of pollution risk levels and division of the

Table 3

Comparison of trace metals in surface water and groundwater in the area with a strong hydraulic connection.

	Range in surface water (mg/L)	Range in groundwater (mg/L)	P value
B	0.06–0.73	0.19–0.48	0.47
Fe	0–0.83	0–0.31	0.31
Mn	0–0.16	0–0.33	0.49
Se	0–0.04	0–0.02	0.48
V	0–0.05	0–0.05	0.38
Zn	0.03–10.02	0–22.21	0.80

$P > 0.05$: achieving significant differences between group means as determined by one-way ANOVA.

pollution zone into major risks categories are as follows: (1) adopt management measures to control the origin of heavy metals, such as changing the land use type, controlling non-point pollution sources, and constructing sewage treatment plants; (2) explore techniques to reduce the residue level of trace metals and control their migration and bio-availability in water; and (3) develop a monitoring net to warn of pollution risk.

5. Conclusions

This study assessed the trace metal content, revealed the source of trace metals in surface water, identified the influence of surface-groundwater interactions on trace metal distribution in the groundwater, and suggested necessary management measures. The main conclusions of this study are: (1) Groundwater in the study region exhibited higher EC and more complex saline conditions than that in surface water, resulting from alkaline conditions and lixiviation. (2) Compared with the drinking water quality standard proposed, pollution of trace metals in surface water was higher than in groundwater, and was also higher than that in the common groundwater irrigation areas in NCP. (3) The distribution and sources of trace metals in the surface water are impacted not only by geogenic factors, but also by agriculture and industrial activities. (4) The environmental isotope evidence shows that the groundwater sources was affected by seepage along the Yellow River, and the apparent surface water-

groundwater interactions which have been influencing the spatial distribution of trace metals. (5) To confront the ongoing serious metal pollution in China, effective measures on trace metal origin and discharge control, scientific research on its transfer and dynamic monitoring in the multi-media environment, and remediation require more attention.

Conflict of interest statement

No conflict of interest exists in the submission of this manuscript, and the manuscript is approved by all authors for publication. On behalf of my co-authors, I would like to declare that the work described was original research that has not been published previously, and not under consideration for publication elsewhere, in whole or in part.

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Appendix A

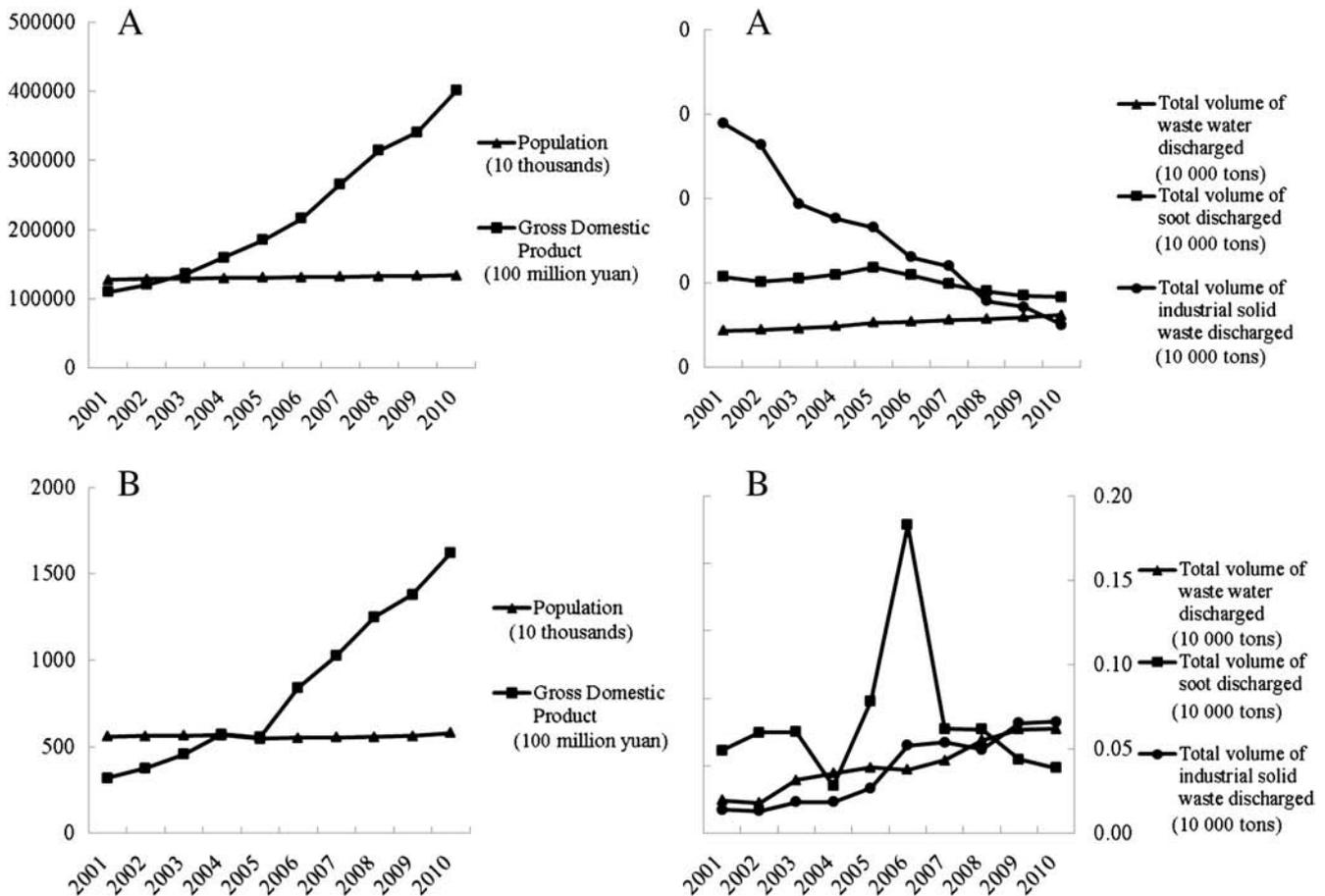


Fig. A. Discharge of key pollutants in China (A) and typical agriculture area—Liaocheng City (B) from 2001 to 2010.

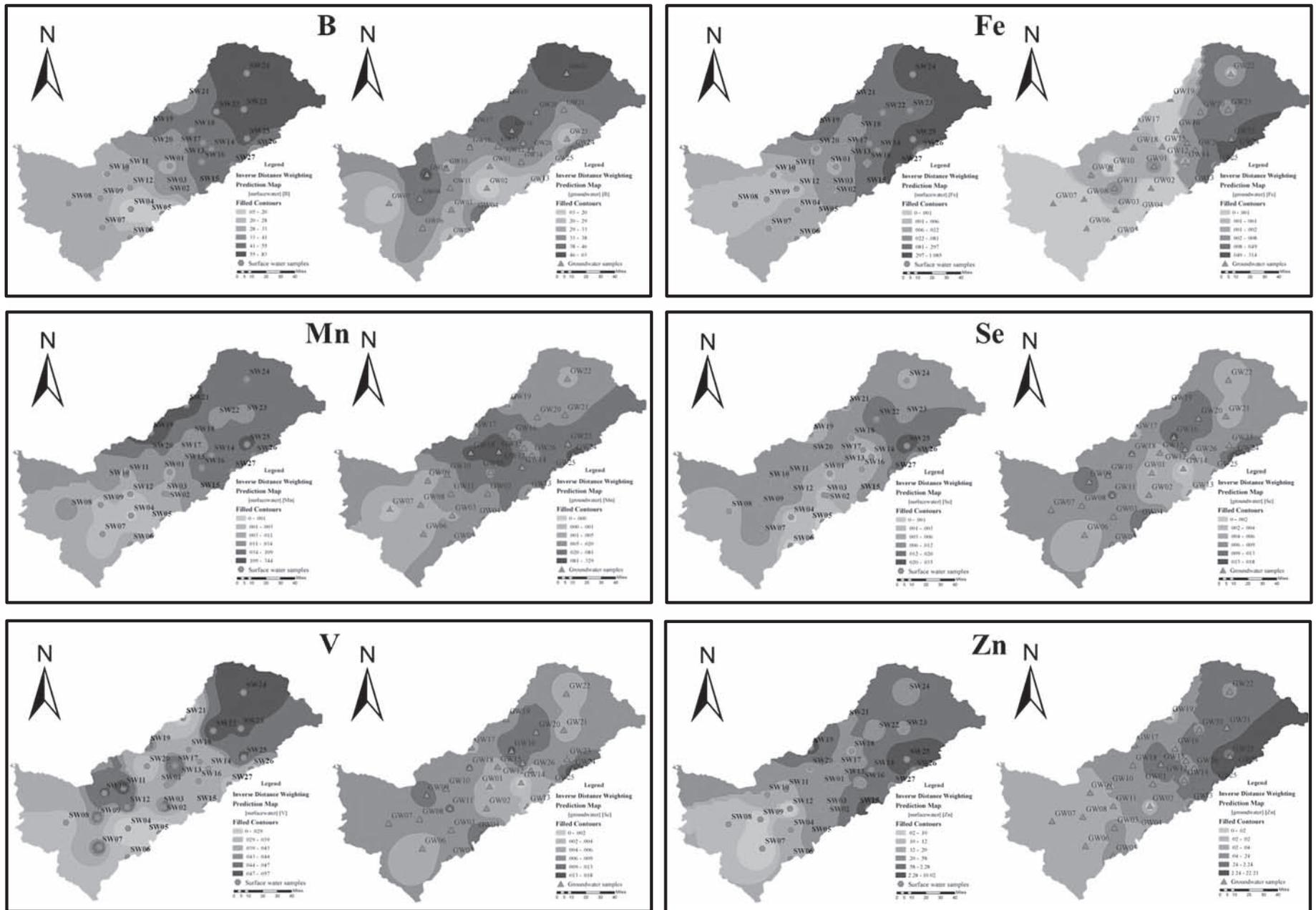


Fig. B. Spatial pattern of trace metals in surface water and groundwater.

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