# Groundwater trace metal pollution and health risk assessment in agricultural areas

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Abstract Irrigation projects have diverted water from the lower reaches of the Yellow River for more than 50 years in China. This study was conducted to quantify the hydrochemical and trace metal characteristics, map the spatial distribution of the health risk caused by trace metals, and identify the origin of trace metals in groundwater in the north part of Henan-Liaocheng Irrigation Area (HLIA). Results show that the mean value of the sum of hazard quotients ( $\Sigma$ HQs) exceeded the generally acceptable risk level recommended by the US EPA. The maximum  $\Sigma$ HQs was 3.79 for the local residents, and the spatial distribution of  $\Sigma$ HQs did not show a significant trend in relation to distance perpendicular to the Yellow River. Primary sources of Fe, Se, Zn, Ba and Mn were associated with geogenic origin; B, Mo Sr, and V were from industrial and agrochemical processes.

Key words trace metal; hazard quotients (HQs); groundwater; spatial distribution; origin; Yellow River

# **INTRODUCTION**

The world is currently facing an unprecedented water resources crisis. Groundwater contamination is increasing as a result of population growth and rapid development of industrial and agricultural production (Zhang *et al.*, 2013). Increasing water requirements are further accelerating water shortages. Approximately half of the urban groundwater in China is polluted (Jiang, 2007), especially in the large and medium size cities, and this pollution is gradually reaching deep aquifers. In Shandong, Henan, Shanxi, Liaoning and Shaanxi provinces, the exploitation ratio of total groundwater exceeds 50%.

Metals are ubiquitous in the environment. In China, the geological background level of heavy metals is low (Cheng, 2007), but concentrations of trace metals in water have been increasing (Pan *et al.*, 2012; Zhang *et al.*, 2013). Water has been polluted by heavy metals in some cases, and even affects human health through the food chain. Trace metals in water may originate from industrial wastes, agricultural sources, urban runoff, atmospheric deposition and automobile emissions (Taebi *et al.*, 2004). Therefore, evaluation of the health risk and identification of the sources of trace metal contamination is critical to manage these resources and limit the potential for harmful consequences.

Henan-Liaocheng Irrigation Area (HLIA, 113.938°–117.076°E and 34.982°–37.391°N) is part of the North China Plain (NCP). The total area is approximately 28 500 km<sup>2</sup>, and includes the four administrative districts of Anyang, Hebi, Puyang and Liaocheng. Extensive water diversion irrigation from the Yellow River started with the opening of the People's Victory Canal in 1952. Recently, researchers have assessed and forecast the regional water resources in the Yellow River irrigated areas (Berkoff, 2003). However, data related to the impact of trace metal transfer resulting from irrigation projects and the health risks posed by the trace metals in the groundwater remain limited.

The purposes of this study are to: (a) quantify the hydrochemical and trace metal characteristics of the groundwater; (b) determine and map the spatial distribution of the health risk caused by trace metals; and (c) identify the origin of trace metals in groundwater in the HLIA.

#### **MATERIALS AND METHODS**

#### Study area and water sampling

The area is in a warm-temperate continental monsoon climate. Rivers include the Yellow, Wei, Majia and Tuhai rivers and their main tributaries. The annual average air temperature  $(14-15^{\circ}C)$  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 most of that available between June and September. The groundwater source is mainly from lateral runoff, recharge of atmospheric precipitation, and surface water supplies. Drainage losses are mainly from discharge to the Majia, Tuhai and other rivers, and manual drainage. Groundwater flows slowly from the southwest to the 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).

Groundwater samples were collected from 23 to 30 July 2010, at 26 sites. Selected sites were distributed around the old channels, irrigation ditches, reservoirs, and around cities, towns and branch afflux sites. All samples were immediately filtered through acid treated millipore filters (0.45  $\mu$ m mesh) into polyethylene-terephthalate (PET) bottles in the field. A general overview of the study area showing the hydrogeology and the sampling locations is presented in Fig. 1.



**Fig. 1** Location of sampling sites, hydrogeology and topography within the HLIA. Note: L. loose salts porous aquifer group (water-rich intensity gradually increasing from L1 to L5); M. metamorphic rocks fractured aquifer rock group; C. carbonate fissure salt dissolved water content of salt groups (water-rich intensity gradually increasing from C1 to C3); S. broken nitrate aquifer group (water-rich intensity gradually increasing from S1 to S2).

# **Experimental analysis**

Electrical conductivity (EC) and pH were measured with a portable pH and EC meter (Compact meter, Horiba, Japan) *in situ*. Trace metals were analysed using an ICP-OES (PerkinElmer Co. Ltd, USA). Reagent, procedural blanks and samples were measured six times in parallel and the average of the last three values is reported. The chemical results were only accepted when the charge balance error was within  $\pm 5\%$ . The detection limits for each element were 0.0001 mg/L for Zn, Ba, Fe, Mn, Mo, V, Al, Li, Sr, Be, Cd, Cr, and Cu, and 0.001 mg/L for Se, B and Pb.

#### **RESULTS AND DISCUSSION**

#### Trace metals concentration and comparison with background values

EC values in groundwater ranged from 405 to 3060  $\mu$ S/cm, with a mean value of 1136  $\mu$ S/cm. No significant spatial variations in the pH values were observed, and most of the groundwater was weakly alkaline (pH 7.05–7.59). The values of Al, Cd, Cr, Cu, Li, Be and Pb were small or below detection limits in most samples. The distributions of B, Ba, Fe, Mn, Mo, Se, Sr, V and Zn were further analysed to identify metal pollution and assess its health risk. B and Ba were quantifiable in all samples; Mn and Fe were quantifiable in 73.1% and 46.2% of samples, respectively; while the others were quantifiable in 96.2% of samples. Metal concentrations were of the following order: Sr > Zn > B > Ba > V > Mn > Fe = Se = Mo.

Detected levels of dissolved trace metals in groundwater of HLIA were generally higher than estimated world averages (Klavins *et al.*, 2000), and higher than other rivers impacted by agriculture and urban pollution in China and abroad, such as the levels in the Congo, Niger, Rhine, Changjiang and Han rivers, and Danjiangkou Reservoir (Gaillardet *et al.*, 2003; Buschmann *et al.*, 2008; Li *et al.*, 2010; Pan *et al.*, 2012). On average, the ratios of concentrations of B, Ba, Fe, Mn, Se and Zn in the HLIA, relative to drinking water standards established by WHO (WHO, 2006) and US EPA (US EPA, 2006), were 11.5%, 3.8%, 3.8%, 11.5%, 23.1% and 7.7%, respectively.

	N	Min.	Max.	Mean	Std.	Coefficient of variation (CV)	Detected ratio	Overstandard ratio
В	26	0.03	0.63	0.36	0.13	0.37	100.0%	11.5%
Ba	26	.00	0.74	0.18	0.15	0.82	100.0%	3.8%
Fe	26	.00	0.31	0.01	0.06	4.77	46.2%	3.8%
Mn	26	.00	0.33	0.03	0.07	2.36	73.1%	11.5%
Mo	26	.00	0.03	0.01	0.01	0.79	96.2%	0.0%
Se	26	.00	0.02	0.01	0.00	0.68	96.2%	23.1%
Sr	26	.00	3.08	1.36	0.60	0.44	96.2%	0.0%
V	26	.00	0.05	0.04	0.01	0.37	96.2%	0.0%
Zn	26	.00	22.21	0.94	4.35	4.65	96.2%	7.7%

Table 1 Descriptive statistics of trace metals in groundwater (mg/L).

#### Spatial pattern of health risk caused by trace metals

A risk assessment model adapted from the US EPA (Karim, 2011) was used to evaluate the potential health risk of exposure to trace metals through groundwater. Hazard quotients (HQs) associated with corresponding metals were simulated under a residential land-use scenario (US EPA, 2002), through the two main routes of exposure in groundwater environment: ingestion and dermal absorption (Song *et al.*, 2012).

$$D_{ingestion} = \frac{C_w \times IRW \times EF \times ED}{BW \times AT}$$
(1)

$$D_{dermal} = \frac{C_w \times SA \times K_p \times ABS \times ET \times EF \times ED \times CF}{BW \times AT}$$
(2)

$$HQs = D / RfD \tag{3}$$

where *D*: exposure dose, mg/kg/day;  $C_w$ : average concentration of trace metal in water, mg/L; *IRW*: drinking water ingestion rate, 2 L/day; *EF*: exposure frequency, 350 day/year (US EPA 1991); *ED*: exposure duration, triangular type (50%: 9; 90%: 30), year; *BW*: average body weight, as lognormal type (mean: 60.2, sd: 2.9), kg (Li *et al.*, 2010); *AT*: averaging time, for non-carcinogens, 30 year (Zabin *et al.*, 2008); *SA*: exposed skin area, 2800 cm<sup>2</sup>;  $K_p$ : dermal permeability constant, cm/h, Co: 0.0004, Ni: 0.0002, Zn: 0.0006, other metals: 0.001; *ABS*: dermal absorption factor, 0.001; *ET*: exposure time, 0.6 h/day; *CF*: unit conversion factor, for water: 1 L/1000 cm<sup>3</sup>; *RfD* is the reference dose for different analytes (Table 2), expressed in µg/kg/day (US EPA, 2006).



Fig. 2 Probability of exceedence of risk level of HQs and its spatial distribution.

A Monte Carlo analysis was conducted based on probability distributions for each parameter. The HQ output was presented as a normal distribution (Fig. 2), and the probability of exceedence of the specified probability of effect was calculated. The predominant pathway of residues in groundwater for local residents was ingestion exposure (Table 2). In fact, dermal exposure of trace metals can be disregarded, especially if there was no sufficient data or not readily available for dermal exposure.

The mean  $\Sigma$ HQs was estimated to be 1.32 for local residents. That value exceeded the generally acceptable risk level recommended by the US EPA for HQs > 1 (Karim, 2011). In addition, the maximum HQ was 3.79, which was greater than the acceptable range. In fact, only 23% of all groundwater in the area had HQs from trace metals that were below unity, which indicates that the adsorption of trace metals may have little or no health threat. Approximately 77% of the area's groundwater could possibly have deleterious effects on the residents' health.

Element	<i>RfD</i> <sub>ingestion</sub>	<i>RfD<sub>dermal</sub></i>	HQ <sub>ingestion</sub>	$HQ_{dermal}$	$\Sigma H Q_s = (a) + (b)$
	(µg/kg/day)	(µg/kg/day)	0		
В	2.0E+02	1.8E+02	1.29E+00	1.26E-06	1.29E+00
Ba	7.0E+01	1.4E+01	1.80E+00	7.89E-06	1.80E+00
Fe	3.0E+02	4.5E+01	3.06E-02	1.79E-07	3.06E-02
Mn	2.0E+01	8.0E-01	1.05E-01	2.29E-05	1.05E-01
Мо	5.0E+00	1.9E+00	1.06E+00	2.44E-06	1.06E+00
Se	5.0E+00	2.2 E+00	9.75E-01	1.94E-06	9.75E-01
Sr	6.0E+02	1.2E+02	1.61E+00	7.07E-06	1.61E+00
V	1.0E+00	1.0E-02	2.51E+01	2.20E-03	2.51E+01
Zn	3.0E+02	6.0E+01	2.22E+00	5.84E-06	2.22E+00
Total	-	-	3.42E+01	2.25E-03	3.42E+01

 Table 2 Reference dose and HQ for each element.

Among the nine trace metals, due to its greater concentrations, the proportion contributed by vanadium, V, to the  $\Sigma$ HQ was the greatest (73%). The oxide and some other salts of vanadium have moderate toxicity (Hosokawa *et al.*, 1989). Though vanadium compounds are poorly absorbed through the gastrointestinal system, high doses of vanadium by oral ingestion may alter blood conditions, or cause liver or kidney damage (Hosokawa *et al.*, 1989). Due to the smaller *RfD* factors and greater concentrations, the contribution of Zn (7%), Sr (5%), Ba (5%) to the  $\Sigma$ HQ were larger than others, suggesting these elements could also pose a mild hazard to local residents. The relative contribution of each residue to the  $\Sigma$ HQ in groundwater of the HLIA is shown in Fig. 3.

The concentrations of dissolved trace metals in groundwater fluctuated irregularly; some sites exhibited elevated levels for some elements but showed no trend in relation to distance



Fig. 3 HQ proportions of trace metals in the study area.

perpendicular to the Yellow River. Fe, Zn, and Mn varied greatly in their spatial distribution, and the CVs were 477%, 465% and 236%, respectively. HQ exhibited very high anomalies at sites DA03 in the southeast, PY03 in the north, GT03 in the upper middle, and PY09 in the south. These abnormal concentrations are primarily attributable to intensive agricultural and urban industrial practices (Smail *et al.*, 2012). The local government should pay more attention to trace metal contamination. However, HQ exhibited its lowest value at site SX05 in the middle, and was low at site JX02 in the west and at site CP06 in the east.

It was 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. Actually, the metal concentrations will not be constant over time due to hydrological 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

As individual metal concentrations were several times higher than background levels in uncontaminated groundwater sampled from far-off locations, it was inferred that anthropogenic activities were affecting the water in the area (Li *et al.*, 2012). Further confirmation of this hypothesis was secured through multivariate methods of statistical analysis. Accordingly, using Varimax normalized rotation, three principal components with eigenvalues of >1 identified by PCA, accounted for 68.9% of variance in the data set (Table 3).

Element	F1	F2	F3
В	0.263	0.770	-0.398
Ba	-0.155	0.073	0.790
Fe	0.968	-0.063	0.067
Mn	0.317	-0.029	0.546
Mo	-0.116	0.715	0.205
Se	0.627	0.400	-0.227
Sr	-0.233	0.727	0.120
V	0.353	0.727	-0.113
Zn	0.970	-0.066	0.092
Total variance explained	32.0%	23.9%	13.0%

Table 3 Total variance explained and component matrices of PCA.

Previous studies have reported comprehensively on sources of trace metals, i.e. Fe is abundant in the Earth; and Zn can have a lithogenic source as it forms a number of soluble salts or insoluble salts according to the prevailing pedogenic processes (Pan *et al.*, 2012). Our results demonstrate that the first PC accounts for 32.0% of total variance and has high loadings of Fe, Se

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and Zn, which is indicative of a natural source. This interpretation is further confirmed by their strong pairwise geochemical correlations (Fe and Zn, R = 0.99, P < 0.01).

The second PC, with 23.9% variance, showed higher loadings for B, Mo, Sr and V. B is not abundant in the Earth's crust, but previous studies reported that concentrations of boride could be unusually high in oilfield brines (Tan *et al.*, 2011). V derives from urban and industrial activities such as energy production, mining, metal smelting and refining, manufacturing processes, automobile exhausts and waste incineration. V concentrations have been shown to be greatly influenced by anthropogenic activities such as mining and agricultural processes (Song *et al.*, 2012). Significant spatial differences of Mo (sites PY05 and GT03) and Sr (site GX02) indicate anthropogenic sources. Therefore, the second PC can be identified as industrial and agrochemical processes (Yalcin *et al.*, 2008).

The third PC, accounting for 13.0% of total variance, was mainly influenced by Ba and Mn. Ba and Mn originate from natural sources of weathering of parent materials and subsequent pedogenesis (Nriagu, 1989). High Ba concentrations primarily derive from geological processes (Krishna *et al.*, 2009). Therefore, this component may be attributable to a geogenic origin.

# **CONCLUSIONS AND PERSPECTIVE**

This study assessed water quality, determined the spatial distribution of health risk, and identified the origin of trace metals in groundwater in HLIA. The main conclusions are: (a) trace metals detected in all samples exceeded levels reported for other rivers in China and abroad; detected residue levels of dissolved metals in groundwater are similar to highly polluted rivers; (b) the mean  $\Sigma$ HQs was 1.32 for local residents, which is higher than the generally acceptable risk level recommended by the US EPA, and approximately 77% of water in the area could possibly have deleterious effects on residents' health; (c) Fe, Se, Zn, Ba and Mn were associated with geogenic origin, the remaining elements were from industrial and agrochemical processes in the study area.

The Yellow River Irrigated Area in China consists mostly of arid and semi-arid areas. Groundwater is the major source of water for drinking and for domestic use, industries, and agriculture in HLIA. The most severe kind of pollution is covert, long-term and non-reversible. Therefore, protecting groundwater in this region has important implications for human health.

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