



Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat



Risk assessment and seasonal variations of dissolved trace elements and heavy metals in the Upper Han River, China

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ARTICLE INFO

Article history:

Received 18 December 2009
Received in revised form 2 April 2010
Accepted 26 May 2010
Available online xxx

Keywords:

Han River
Trace metals
Risk assessment
Seasonal variations

ABSTRACT

Surface water samples were collected from 42 sampling sites throughout the upper Han River during the time period of 2005–2006. The concentrations of trace metals were determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES) for the seasonal variability and preliminary risk assessment. The results demonstrated that concentrations of 11 heavy metals showed significant seasonality and most variables exhibited higher levels in the rainy season. Principal component analysis (PCA) and factor analysis (FA) revealed that variables governing water quality in one season may not be important in another season. Risk of metals on human health was then evaluated using Hazard Quotient (HQ) and carcinogenic risk, and indicated that As with HQ >1 and carcinogenic risk >10⁻⁴, was the most important pollutant leading to non-carcinogenic and carcinogenic concerns, in particular for children. The first five largest elements to chronic risks were As, Pb, V, Se and Sb, in the dry season, while they were As, V, Co, Pb and Sb in the rainy season. This assessment would help establish pollutant loading reduction goal and the total maximum daily loads, and consequently contribute to preserve public health in the Han River basin and develop water conservation strategy for the interbasin water transfer project.

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1. Introduction

Pollutions of surface water with toxic heavy metals and elevated nutrients due to natural processes such as atmospheric deposition, erosion and mineral weathering as well as anthropogenic activities such as urban, industry and agriculture are of great concern worldwide [1–7]. The accumulation of heavy metals in aquatic ecosystems can lead to hazards on human and wildlife, researchers therefore have been focusing on quantifying the trace metals and their assessments on the aqueous environment (i.e., [2,4,5,8,9]). Past studies have reported intake of water with significant amounts of metals particularly arsenic might result in varying cancers, thus numerous researchers were conducted on human health risk assessment relating to metals (e.g., [2,10–12]). Simultaneously, seasonal variations in agricultural activity, storm water runoff, interflow and atmospheric deposition have strong effects on river water quality [13–15]. Thus, characterization of seasonal variability in surface water quality is imperative for evaluating tem-

poral variations of river pollution from natural or anthropogenic contributions.

In China, publications covering the subject of heavy metal contamination are numerous and primarily deal with trace metals of sediments in the Changjiang River (i.e., [8,12,16]). The Han River, the main tributary of the Changjiang River, will supply water to northern China through the China's Middle Route of the South-to-North Water Transfer Project. Previous studies have characterized its water quality [6,7,17], aquatic geochemistry [18–20] and the associations between water quality and landscape settings using empirical statistical techniques such as correlation and regression analyses [21,22]. To our best knowledge, there is no report on risk assessment on trace metals and their temporal characterizations in the Han River. The objectives of this work are to characterize the seasonal variations of trace metals, identify the most important parameters in evaluating surface water quality pertaining to metals, and assess the human health risk with hazard quotients (HQs) and carcinogenic risk via risk assessment model in the Han River, China. The present work is intended as a sequel to a previous article on the spatial patterns and possible sources of metals in the river [23]. This approach would help establish pollutant loading reduction goal and the total maximum daily loads, and consequently contribute to preserve public health in the Han River basin and develop water conservation strategy for the interbasin water transfer project.

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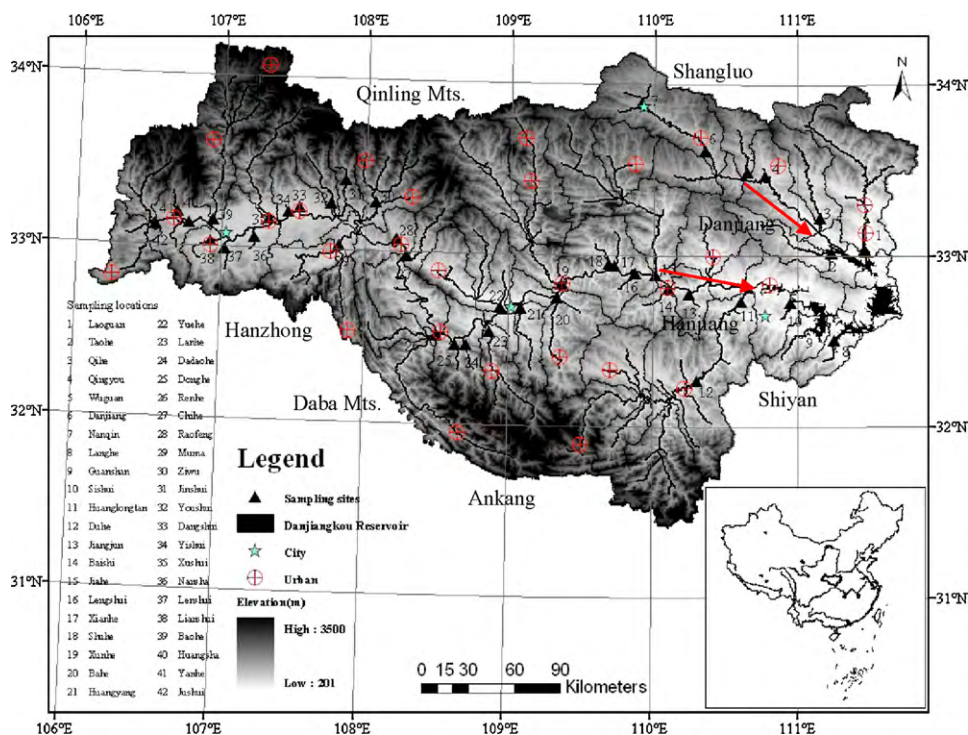


Fig. 1. The upper Han River basin showing sampling locations, urban areas, DEM and drainage systems, China.

2. Materials and methods

2.1. Study area

The upper Han River serves as the water source area for the Middle Route of China's South-to-North Water Transfer Project diverting water to northern China including Beijing and Tianjin city for various usages. The drainage basin is located in a mountainous region between $31^{\circ}20'$ and $34^{\circ}10'$ north and between 106° and 112° west ($210\text{--}3500$ m a.s.l.; Fig. 1). The river drains a total area of approximately 95.2×10^3 km² and traverses a total distance of about 925 km with a north subtropic monsoon climate. Its annual average temperature is 15°C with the highest and the lowest temperatures of 43°C and -13°C , respectively. Annual mean precipitation is about 700–1800 mm, mainly from June to November, and river flow thus displays a very strong inter- and intra-annual variations response to rainfall routine. Vegetation including forest and shrub is the dominant land coverage and accounts for approximate 77% of the total area in the basin with higher composition in uplands. Agriculture and urban respectively representing about 15% and 0.5% of the total drainage area concentrates along river networks, i.e., Hanzhong Plain, Ankang Plain and Danjiangkou Reservoir catchment. Cities such as Hanzhong, Ankang, and Shiyuan and Shangluo in headwaters, middle section and down section respectively are the four major settlements on the banks of river and directly discharge domestic wastewater and industrial influents, thus water quality consequences have been identified and addressed in the Han River [5–7,21,22].

2.2. Water sampling and analytical methods

Six sampling campaigns were conducted in 42 sites reasonably representing the riverine system's water quality throughout the upper Han River basin during 2005–2006 (June, August and November 2005, and April, June and October 2006). In each site, three replicates including the waters near river banks and cen-

ter were collected and subsequently well mixed *in situ*, thus, 126 samples were collected in each sampling month at a depth of approximate 10 cm using previously acid-washed 5-l high density polyethylene (HDPE) containers. Ultimately, a total of 252 grab water samples with 42 samples in each month were therefore pre-treated for laboratory analysis. The samples were filtered through pre-washed $0.45\ \mu\text{m}$ Millipore nitrocellulose filters on the sampling day. The initial portion of the filtration was discarded to clean the membrane, and the following ones destined for metal determination were acidified to $\text{pH} < 2$ using suprapure nitric acid and then stored refrigerated in pre-cleaned HDPE bottles until analysis.

Water samples were determined using an Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) (IRIS Intrepid II XSP DUO, USA) with an analytical precision better than 10% [5]. Method validation and quality control samples were done by using a standard reference material (SRM, SPEX CertiPrep, Inc, USA). All specimens and SRM were analyzed in batches, which included a procedural blank. Each calibration curve was evaluated by analyses of quality control standards before, during and after the analyses of a set of samples. The elements analyzed included Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, Si, Sr and V. Of which, Si in June 2005 was unavailable, and Cu in June 2005, As and Cr in August 2005, Co and Se in November 2005, Co, Pb and Se in April 2006, and Cr and Fe in June 2006 were non-detectable, and these variables were excluded in the multivariate statistical procedures of principal component analysis (PCA) and factor analysis (FA).

2.3. Statistical analyses

Factor analysis attempts to identify underlying variables, or factors, that explain the pattern of correlations within a set of observed variables. PCA is often used in data reduction to identify a small number of factors (principal components, PCs) that explain most of the variance observed in a large number of manifest variables. The reduced new set of orthogonal (non-corrected) PCs by PCA is

Table 1Dissolved trace elements and heavy metals in the upper Han River, China (unit in $\mu\text{g/l}$).

	June 2005		August 2005		November 2005		April 2006		June 2006		October 2006	
	Mean	S.E.	Mean	S.E.	Mean	S.E.	Mean	S.E.	Mean	S.E.	Mean	S.E.
Al	304.65	109.75	520.44	51.93	157.31	47.35	8.59	3.27	32.98	9.51	109.52	17.22
As	8.33	4.91	ND		23.94	0.71	3.81	3.03	20.05	0.92	28.81	1.06
Ba	53.69	5.13	43.65	4.58	51.90	4.21	143.86	48.18	161.14	13.80	68.94	9.11
Cd	5.89	4.89	3.18	0.78	0.57	0.34	0.26	0.20	3.78	3.63	0.38	0.35
Co	0.42	0.41	3.81	0.27	ND		ND		1.59	0.22	6.18	0.40
Cr	11.39	2.33	ND		10.51	0.50	6.67	0.56	ND		20.44	1.76
Cu	ND		46.35	1.44	0.66	0.18	0.94	0.17	21.65	1.22	9.89	0.68
Fe	36.64	3.16	34.02	2.35	27.27	4.85	85.59	4.81	ND		0.60	0.60
Mn	85.03	53.99	19.92	10.18	21.20	7.16	20.12	6.28	25.37	15.02	15.25	5.43
Ni	1.64	1.58	6.13	0.36	0.14	0.11	1.18	0.17	0.69	0.40	0.50	0.16
Pb	20.70	3.67	4.27	0.53	26.12	0.63	ND		2.31	0.48	2.67	0.48
Sb	233.05	14.52	3.91	1.00	10.37	1.03	3.14	1.09	6.14	1.22	1.97	0.81
Se	15.97	1.61	1.33	0.33	ND		ND		34.33	1.30	5.50	0.76
Si	NA		4007.67	111.32	2825.89	135.72	4041.48	212.24	5281.57	260.93	5821.86	313.29
Sr	320.18	17.16	203.35	9.32	276.73	13.66	155.68	10.90	230.93	11.01	224.90	10.59
V	98.34	5.99	59.58	2.24	140.01	2.84	0.93	0.08	81.63	1.97	40.57	1.75

ND, below the detection limit; NA, not measured.

arranged in decreasing order of merit. FA and PCA with Varimax rotation of standardized component loadings were conducted for maximizing the variation among the variables under each factor, and those PCs with eigenvalue >1 were retained [3,13].

The samplings were categorized into rainy (June–November) and dry (December–May) seasons according to the hydrological regime in the basin. Subsequently, one-way analysis of variance (ANOVA) was employed to compare the different seasonal trends ($p < 0.05$, least-significance difference, LSD) of the variables monitored in the present study. All the statistical procedures were conducted using SPSS 15.0 for Windows.

3. Results and discussion

3.1. Seasonal variations of trace metals

Characteristics of the monthly dissolved trace elements and heavy metals (mean and standard errors) were presented in Table 1. The concentrations of variables displayed great seasonality. For instance, the peak values of Cd, Mn, Sb and Sr appeared in June 2005, Al, Cu and Ni in August 2005, Pb and V in November 2005, Fe in April 2006, Ba and Se in June 2006, and As, Co, Cr and Si in October 2006, respectively. Si, a key component of earth crust, exclusively tended to have much higher concentration in each sampling time (Table 1). The total concentrations of fifteen metals (Si excluded) in surface water had an average of $747 \mu\text{g/l}$, followed in order of abundance by June 2005 ($1195.92 \mu\text{g/l}$), August 2005 ($949.97 \mu\text{g/l}$), November 2005 ($746.72 \mu\text{g/l}$), June 2006 ($622.59 \mu\text{g/l}$), October 2006 ($536.11 \mu\text{g/l}$) and April 2006 ($430.77 \mu\text{g/l}$) (Fig. 2).

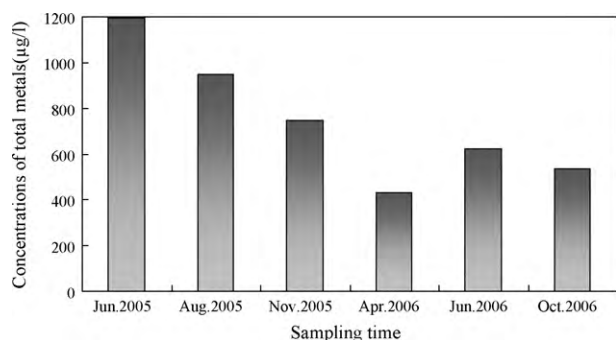


Fig. 2. Total concentrations of 15 metals (Si excluded) in the different sampling time of the upper Han River, China ($\mu\text{g/l}$).

The highest total concentrations in June 2005 was owing to the high evaporation and intense anthropogenic activities (agriculture and high degree of mining activities) in summer (Table 1; [24]). The diluting effect in flood season (July–November 2005) due to monsoon climate resulted in the consequent reduction of the total concentration of 15 metals (from June to August 2005). As regard the two sampling months in the rainy season, large storms in the Han River could initially increase the contaminant mining waste loads [25], as the mixing of large volumes of non-contaminated runoff water, most individual metal content and their total concentration tended to decrease (from August to November 2005; Fig. 2) [26]. During April, great spring precipitation and snow melt were the most plausible explication for the lowest total concentrations and more variables owning their lowest concentrations (Table 1; [24]). Then, increasing anthropogenic activities such as agriculture and mineral processes in the summer elevated the total concentrations of metals (from April to June, 2006; Fig. 2). However, there was little difference relating to their total concentrations between the rainy ($744.71 \mu\text{g/l}$) and dry ($737.92 \mu\text{g/l}$) seasons (Table 2).

All variables except Cd, Mn, Ni, Si and Sr showed significant differences between rainy (June–November) and dry (December–May) seasons. Al, As, Co, Cr, Cu, Ni, Pb and V exhibited significantly higher concentrations in the rainy season compared to the dry season with significant higher concentrations of Ba, Fe, Sb and Se (Table 2). 80% of Annual precipitation fell in the rainy season and subsequently diluted the river pollutants especially in the industrial area, while various metals showed higher compositions in varying hydrological seasonality, which were resulted from their mixed sources due to natural contributions and seasonal anthropogenic activities [27]. Further, more variables with higher contents in the rainy season demonstrated their predominant increasing mining wastes caused by storms and non-point sources [24], as confirmed by the low urbanization in the pristine basin (less than 0.5% of the total drainage area) [7,21,22]. Thus, precipitation and seasonal anthropogenic activities played important roles in governing trace metals in stream water [16].

When compared with drinking water guidelines by WHO 2006 [28], China 2007 [29] and US EPA 2006 [30], there were a number of metals with concentrations higher than the levels for drinking water in different sampling times, i.e., more variables (Al, Cd, Pb, Sb and Se for June 2005, while As, Cd, Sb and Se for June 2006) in June, Al and Cd for August 2005, As, Pb and Sb for November 2005, As for October 2006, whereas no variables for April (Table 1). This also pointed to the varying seasonal inputs to river water due to hydrological regime and seasonal anthropogenic activities. In terms of

Table 3

Total variance explained and component matrixes for monthly trace metal contents (principal component analysis with Varimax rotation; the significance of KMO and Bartlett's sphericity test is <0.001).

(a) June 2005					
	1	2	3	4	5
Al	0.559	0.128	-0.536	0.009	-0.108
As	-0.010	0.177	0.128	-0.229	0.833
Ba	-0.204	0.074	0.504	0.552	-0.115
Cd	0.986	-0.130	-0.040	0.008	0.024
Co	0.986	-0.121	-0.059	0.018	0.017
Cr	0.048	-0.397	0.139	0.175	0.773
Fe	-0.053	-0.112	-0.276	0.844	0.209
Mn	0.984	-0.131	-0.037	0.021	0.016
Ni	0.985	-0.126	-0.061	0.018	0.015
Pb	-0.086	0.801	-0.051	0.086	0.022
Sb	0.010	-0.081	0.892	-0.034	0.261
Se	-0.094	0.921	-0.191	-0.061	0.001
Sr	0.214	0.026	0.151	0.736	-0.257
V	-0.283	0.738	0.401	-0.148	-0.241
Eigenvalues	4.383	2.330	1.682	1.679	1.555
Cumulative %	31.310	47.954	59.967	71.958	83.062
(b) August 2005					
	1	2	3	4	5
Al	0.923	-0.027	0.001	-0.227	-0.132
Ba	0.066	-0.057	-0.282	0.792	-0.095
Cd	0.176	0.945	0.123	-0.071	-0.050
Co	0.909	0.249	0.108	-0.106	-0.172
Cu	-0.086	0.301	0.872	-0.036	-0.077
Fe	0.179	-0.108	0.777	-0.310	-0.061
Mn	-0.037	0.963	0.149	-0.046	-0.024
Ni	0.459	0.626	0.523	-0.058	-0.067
Pb	0.652	-0.108	-0.218	0.012	0.551
Sb	-0.241	0.074	-0.137	-0.048	0.864
Se	-0.375	0.280	0.731	-0.002	0.028
Si	0.038	0.323	-0.216	-0.408	-0.585
Sr	-0.129	-0.059	-0.006	0.754	0.151
V	0.737	0.186	-0.212	0.399	-0.103
Eigenvalues	3.150	2.618	2.459	1.694	1.499
Cumulative %	22.504	41.205	58.768	70.869	81.578
(c) November 2005					
	1	2	3	4	5
Al	-0.063	0.221	0.025	-0.269	0.829
As	0.435	0.268	0.567	-0.030	-0.350
Ba	-0.198	0.570	-0.016	0.198	0.242
Cd	0.945	-0.107	0.066	0.013	0.045
Cr	-0.049	0.253	-0.132	0.826	-0.090
Cu	0.461	-0.069	-0.012	0.665	0.272
Fe	0.306	-0.087	0.042	0.230	0.656
Mn	0.882	-0.036	0.116	0.083	0.062
Ni	0.953	-0.063	0.097	0.056	0.053
Pb	0.038	-0.032	0.523	0.557	-0.181
Sb	0.004	-0.092	-0.848	0.082	-0.114
Si	0.193	-0.368	0.688	0.004	0.089
Sr	0.012	0.781	-0.010	-0.212	-0.035
V	-0.016	0.827	-0.016	0.281	-0.018
Eigenvalues	3.158	1.978	1.835	1.741	1.445
Cumulative %	22.557	36.682	49.789	62.224	72.545
(d) April 2006					
	1	2	3	4	5
Al	0.058	-0.047	0.949	-0.071	-0.022
As	0.973	-0.109	-0.007	0.016	-0.011
Ba	-0.054	-0.074	-0.003	0.085	-0.746
Cd	0.971	-0.106	-0.001	0.006	-0.016
Cr	-0.053	-0.007	0.116	0.847	0.035
Cu	0.848	0.110	0.305	-0.031	0.086
Fe	-0.081	0.905	-0.067	0.089	0.147
Mn	0.650	0.281	0.177	-0.179	-0.070
Ni	0.553	0.058	0.738	0.154	-0.028
Sb	-0.017	0.097	-0.101	0.740	0.006
Si	0.198	0.754	0.140	0.062	-0.204

Table 3 (Continued)

(d) April 2006					
	1	2	3	4	5
Sr	-0.036	0.886	-0.077	-0.016	0.243
V	-0.055	0.052	-0.032	0.133	0.764
Eigenvalues	3.397	2.310	1.623	1.364	1.278
Cumulative %	26.130	43.901	56.387	66.882	76.713
(e) June 2006					
	1	2	3	4	
Al	0.379	-0.105	0.776		0.178
As	0.602	0.408		-0.325	0.354
Ba	0.003	-0.149		0.443	0.625
Cd	0.248	0.922		-0.132	0.077
Co	0.822	0.286		0.330	0.204
Cu	-0.782	0.199		-0.402	-0.267
Mn	0.074	0.928		-0.082	-0.010
Ni	0.164	0.966		-0.031	0.038
Pb	0.685	0.362		0.195	-0.098
Sb	0.099	-0.044	0.873		0.104
Se	-0.713	0.091		-0.574	0.082
Si	0.678	0.323		-0.059	0.177
Sr	0.200	-0.049		-0.030	0.787
V	0.071	0.347		0.138	0.693
Eigenvalues	3.377	3.333		2.353	1.827
Cumulative %	24.122	47.932		64.736	77.786
(f) October 2006					
	1	2	3	4	5
Al	-0.918	0.211	0.033	-0.077	-0.148
As	0.785	-0.032	0.325	0.277	0.141
Ba	-0.048	-0.184	0.796	-0.072	0.357
Cd	0.047	0.935	-0.068	-0.204	0.047
Co	0.908	-0.011	0.047	0.135	0.200
Cr	0.483	0.015	-0.233	-0.417	0.217
Cu	0.696	0.108	0.366	-0.407	0.064
Fe	0.163	0.183	0.098	0.857	-0.026
Mn	0.072	0.967	-0.044	0.045	0.012
Ni	-0.152	0.735	-0.235	0.330	0.020
Pb	0.148	-0.002	0.259	-0.193	0.731
Sb	-0.265	-0.024	0.384	-0.144	-0.684
Se	-0.865	0.031	0.231	0.139	0.053
Si	-0.348	0.665	0.007	0.339	-0.148
Sr	0.180	0.052	0.641	0.074	-0.172
V	-0.103	-0.200	0.852	0.131	-0.016
Eigenvalues	4.065	2.962	2.406	1.547	1.320
Cumulative %	25.404	43.914	58.952	68.620	76.869

Bold values represent strong loadings >0.75.

spring (April 2006), Al, As, Cd, Cr, Cu, Fe and Sr were positively correlated to water quality variations. It should be noted that there was the distinct differences between spring and summer, which might be explained by little anthropogenic activities and more rainfall in spring indicating by the important components of Al, Fe and Sr in the earth (Table 4), whereas in summer, there were intense mineral and agricultural activities. During the wet autumn season (November 2005 and October 2006), there existed some variables negatively correlated to water quality variability (Sb in November 2005 and Al, Se in October 2006) and varying metals positively

Table 4

The most important water quality variables for each sampling time in the upper Han River, China.

Season	Positively correlated variables	Negatively correlated variables
Jun. 2005	As, Cd, Co, Fe, Mn, Ni, Pb, Sb, Se	
Aug. 2005	Al, Cd, Co, Cu, Mn, Sb	
Nov. 2005	Al, Cd, Cr, Mn, Ni, V	Sb
Apr. 2006	Al, As, Cd, Cr, Cu, Fe, Sr	
Jun. 2006	Cd, Co, Mn, Ni, Sb	
Oct. 2006	Cd, Co, Fe, Mn, V	Al, Se

Table 5
Reference dose, Hazard quotient and cancer risk for each element of the upper Han River, China.

Element	RfD _{ingestion} ($\mu\text{g}/\text{kg}/\text{day}$)	RfD _{dermal} ($\mu\text{g}/\text{kg}/\text{day}$)	HQ _{ingestion}		HQ _{dermal}		HI = \sum HQs		Cancer risk	
			Adult	Child	Adult	Child	Adult	Child	Adult	Child
(a) Dry season										
Al	1000	200	6.075E-04	2.835E-03	7.927E-05	2.339E-04	6.868E-04	3.069E-03		
As-non cancer	0.3	0.285	9.320E-01	4.349E+00	5.390E-03	1.590E-02	9.374E-01	4.365E+00		
As-cancer	1500	3660	7.988E-05	7.456E-05	1.79892E-07	1.06143E-07			8.006E-05	7.467E-05
Ba	200	14	1.158E-03	5.403E-03	1.233E-03	3.639E-03	2.391E-03	9.042E-03		
Cd-non cancer	0.5	0.025	8.808E-03	4.110E-02	1.839E-02	5.426E-02	2.720E-02	9.536E-02		
Co	0.3	0.06	1.287E-02	6.007E-02	6.718E-04	1.982E-03	1.354E-02	6.205E-02		
Cr-non cancer	3	0.075	1.344E-04	6.273E-03	2.245E-02	6.624E-02	2.258E-02	7.251E-02		
Cu	40	8	1.062E-04	4.958E-03	1.386E-04	4.090E-04	2.448E-04	5.367E-03		
Fe	700	140	3.182E-04	1.485E-03	4.153E-05	1.225E-04	3.597E-04	1.608E-03		
Mn	24	0.96	1.927E-03	8.992E-03	6.286E-03	1.855E-02	8.213E-03	2.754E-02		
Ni-non cancer	20	0.8	6.310E-05	2.94E-04	4.116E-05	1.215E-04	4.116E-05	2.940E-04		
Pb	1.4	0.42	4.330E-02	2.021E-01	2.511E-04	7.409E-04	4.355E-02	2.028E-01		
Sb	0.4	0.06	7.923E-01	3.697	1.838E-01	5.423E-01	9.761E-01	4.239E+00		
Se	5	0.15	2.795E-02	1.304E-01	1.621E-02	4.782E-02	4.416E-02	1.304E-01		
Sr	600	120	2.129E-03	9.936E-03	2.778E-04	8.198E-04	2.407E-03	1.076E-02		
V	5	0.13	8.456E-03	3.946E-02	6.529E-02	1.926E-01	7.375E-02	2.321E-01		
(b) Rainy season										
Al	1000	200	1.438E-03	6.710E-03	1.876E-04	5.536E-04	1.626E-03	7.264E-03		
As-non cancer	0.3	0.285	1.526	7.120	8.823E-03	2.603E-02	1.535E+00	7.146E+00		
As-cancer	1500	3660	1.308E-04	1.221E-04	2.945E-07	1.738E-07			1.311E-04	1.223E-04
Ba	200	14	5.258E-04	2.454E-03	5.600E-04	1.652E-03	1.086E-03	4.106E-03		
Cd-non cancer	0.5	0.025	3.768E-03	1.759E-02	7.867E-03	2.321E-02	1.164E-02	4.080E-02		
Co	0.3	0.06	6.855E-02	3.199E-01	3.578E-03	1.056E-02	7.213E-02	3.305E-01		
Cr-non cancer	3	0.075	2.355E-03	1.099E-02	3.934E-02	1.161E-01	4.170E-02	1.271E-01		
Cu	40	8	2.598E-03	1.213E-02	3.391E-04	1.000E-03	2.937E-03	1.313E-02		
Fe	700	140	1.615E-04	7.540E-04	2.107E-05	6.217E-05	1.826E-04	8.162E-04		
Mn	24	0.96	8.580E-04	4.004E-03	2.799E-03	8.258E-03	3.657E-03	1.226E-02		
Ni-non cancer	20	0.8	1.237E-04	5.770E-04	8.069E-05	2.381E-04	2.044E-04	8.151E-04		
Pb	1.4	0.42	6.471E-02	3.020E-01	3.753E-04	1.107E-03	6.509E-02	3.031E-01		
Sb	0.4	0.06	5.567E-02	2.598E-01	1.291E-02	3.810E-02	6.858E-02	2.979E-01		
Se	5	0.15	3.782E-03	1.765E-02	2.193E-03	6.472E-03	5.975E-03	2.412E-02		
Sr	600	120	2.146E-03	1.002E-02	2.800E-04	8.262E-04	2.426E-03	1.085E-02		
V	5	0.13	1.140E-02	5.322E-02	8.806E-02	2.598E-01	9.946E-02	3.130E-01		

Oral reference dose of elements from Regional Screening Level (RSL) Table Tap Water APRIL 2009 except Pb from Wu et al. [12].

correlated to seasonal water quality (Table 3). Thus, the important water quality variables in one season might not be important in another season, and we argued that the integration of seasonal water quality variables and main pollutants must be considered for establishing the pollutant load reduction goals and developing the total maximum daily loads.

3.3. Risk assessment on human health

Exposure of human being to trace metals could occur via three main pathways including direct ingestion, inhalation through mouth and nose, and dermal absorption through exposures skin, while ingestion and dermal absorption are common for drinking water [11,12,38]. The dose received through the individual pathway considered was determined using Eqs. (1) and (2) modified from the US Environmental Protection Agency [38].

$$\text{ADD}_{\text{ingestion}} = \frac{C_w \times \text{IR} \times \text{ABS}_g \times \text{EF} \times \text{ED}}{(\text{BW} \times \text{AT})} \quad (1)$$

$$\text{ADD}_{\text{dermal}} = \frac{C_w \times \text{SA} \times K_p \times \text{ET} \times \text{EF} \times \text{ED} \times 10^{-3}}{\text{BW} \times \text{AT}} \quad (2)$$

where ADD, average daily dose by ingestion ($\text{ADD}_{\text{ingestion}}$) and dermal absorption ($\text{ADD}_{\text{dermal}}$), unit in $\mu\text{g}/\text{kg}/\text{day}$; BW, body weight, unit in kg; EF, exposure frequency, unit in days/year; ED, exposure duration, unit in years; IR, ingestion rate, unit in l/day; ABS_{GI} , gastrointestinal absorption factor (dimensionless); C_w , average concentration of trace metals in water, unit in $\mu\text{g}/\text{l}$; SA, exposed skin area, unit in cm^2 ; K_p , dermal permeability coefficient in water, unit in cm/h ; ET, exposure time, unit in h/day; AT, averaging time (days). Their values originated from the US EPA [38] except Pb of

ABS_{GI} from Wu et al. [12], and ABS_{GI} for Al, Co, Cu, Fe, Si and Sr from Rodriguez-Proteau1 and Grant [39].

Risk characterization was quantified by carcinogenic risk and non-carcinogenic risk. Potential non-carcinogenic risks, reflected by the hazard quotient (HQ), were estimated by comparing exposure or average intake of contaminants from each exposure route (ingestion, dermal) with the corresponding reference dose (RfD) using Eqs. (3) and (4). If the HQ exceeds 1, there might be concern for non-carcinogenic effects. To evaluate the total potential non-carcinogenic risks posed by more than one pathway, the hazard index (HI) was introduced, which was the sum of the HQs from all applicable pathways. $\text{HI} > 1$ indicated a potential for an adverse effect on human health or the necessity for further study [38].

$$\text{Hazard Quotient}(\text{HQ}) = \frac{\text{ADD}}{\text{RfD}} \quad (3)$$

$$\text{RfD}_{\text{dermal}} = \text{RfD} \times \text{ABS}_{\text{GI}} \quad (4)$$

where $\text{RfD}_{\text{ingestion}}$ originate from risk-based concentration table, the US EPA, April, 2009 (Table 5).

Carcinogenic risks were evaluated by Eq. (5) and the detailed calculating process was followed by De Miguel et al. [11] and Wu et al. [12]. The estimated value was the incremental probability of an individual developing any type of cancer over a lifetime due to carcinogenic exposure. The range of carcinogenic risks acceptable or tolerable by the US EPA was 10^{-6} to 10^{-4} [39].

$$\text{Cancer Risk} = \text{DAD} \times \text{CSF}(\text{cancer slope factor}) \quad (5)$$

Table 5 presented HQ, HI and risk values for the oral and dermal pathways for dry and rainy seasons relating to adult and child, respectively. In the dry season, $\text{HQ}_{\text{ingestion}}$ (hazard quotient by

ingestion) of all elements except As for adult were smaller than 1, suggesting that these elements posed little hazard. However, $HQ_{\text{ingestion}}$ of Sb and particularly As were nearly 1, implying that As and Sb may cause adverse health effects and potential non-carcinogenic concern. In addition, HQ_{dermal} (hazard quotient by dermal absorption) of 9 elements (Al, As, Co, Fe, Ni, Pb, Sb, Se and Sr) for adult was all below unity, indicated that these metals posed little hazards via dermal absorption. For child in the dry season, $HQ_{\text{ingestion}}$ of As and Sb were much higher than unity, indicating their serious health concerns. Similar to adult, HQ_{dermal} of elements for child was below unity, and the largest value was 0.54 for Sb. Overall, HI of As for adult and child, and Sb for child exceeded 1, and HI of Sb for adult was near unity. We therefore concluded that the first five largest contributors to chronic risks were As, Pb, V, Se and Sb, while the least were Ni, Al, Fe, Cu and Ba for both the adult and child, respectively.

In the rainy season, $HQ_{\text{ingestion}}$ of As for adult and child were above 1, followed by Co, Pb and Sb, while HQ_{dermal} of elements for both adult and child were below unity. This indicated that As posed serious health concerns to the local residents via oral intake, while other elements via oral intake and all the metals via dermal absorption had no or little health threat. Additionally, As exclusively with the HI for adult and child above unity was the largest contributor to non-carcinogenic concern, followed by V, Co, Pb and Sb, while the least contributors were Sr, Al, Ba, Fe and Ni. Thus, there were some differences for the order of HI and HQ of chemicals between the dry and rainy seasons, while As, Pb and Sb were the most contributors in both seasons and the oral intake was the primary exposure pathway, which were consistent with the results in the Nanjing section of the Yangtze River [12] and other studies (e.g., [11]). Carcinogenic risk of As through oral intake in the rainy season exceeded the target risk of 1×10^{-4} (Table 5) and indicated that the ingestion of water over a long life time could increase the probability of cancer.

The risk assessment indicated that As was the most important pollutant in the upper Han River, similar to the result compared to water drinking guidelines (Table 2). Previous studies reported the potentially carcinogenic effects such as the cancers of liver, lung, bladder, kidney and skin, and other adverse health effects including hypertension, neuropathy, diabetes, shin lesions, and cardiovascular and cerebrovascular diseases through high arsenic intake [12]. Therefore, special attention should be paid to arsenic for local residents particularly for the sensitive children, and measures needed to be taken for sustaining the healthy aquatic ecosystem.

However, there existed uncertainties for risk characterization, which was emphasized by the US EPA and other documents [12,38]. Uncertainties in some methodological aspects such as water and dermal contact factor (K_p), varied exposure condition due to different age and receptor, temporal variations in contaminant concentrations and daily water intake rate could not be quantified. In addition, exposure parameters employed in the study were from the US EPA and WHO, which might not be specific to Chinese. Therefore, further precise risk characterization should be defined and risk assessment approaches may be modified through the investigation on the risk levels in the upper Han River.

4. Conclusions

Concentrations of dissolved trace elements and heavy metals (Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, Si, Sr and V) in the surface water of the upper Han River demonstrated great seasonality. The minimum total concentration of trace metals was found in spring, and most variables tended to have higher levels in the rainy season. PCA and FA demonstrated different elements were predominantly contributable to water flow seasonality and anthropogenic activities, implying that variables regulating water quality

in one environment may not be important in another environment. When compared to drinking water guidelines established by WHO, China and the US EPA, much greater attention should be paid to Al, As, Cd, Pb, Sb and Se though varied chemicals above the critical values in the different sampling time. Human risk was assessed in people exposed to trace metals using exposure risk assessment model indicated As was the most important pollutant causing non-carcinogenic and carcinogenic concerns, particularly for sensitive children. As, Sb and Se were the largest contributors to chronic risks while the least for Ni, Al, Fe and Ba in both the dry and rainy seasons.

Acknowledgements

The research was funded by the “Hundred-talent Project” of the Chinese Academy of Sciences (O629221C01) and the National Key Sciences Research Program of China (2008CB418000). We would like to thank Sheng Gu and Jia Li for their field sampling, and Hongyin Han of the Chinese University of Geosciences for trace metal analysis. We also thank Dr. Gerasimos Lyberatos and other two anonymous reviewers for their comments and suggestions.

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