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Spatial characterization of dissolved trace elements and heavy metals in the upper Han River (China) using multivariate statistical techniques

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ABSTRACT

A data matrix (4032 observations), obtained during a 2-year monitoring period (2005–2006) from 42 sites in the upper Han River is subjected to various multivariate statistical techniques including cluster analysis, principal component analysis (PCA), factor analysis (FA), correlation analysis and analysis of variance to determine the spatial characterization of dissolved trace elements and heavy metals. Our results indicate that waters in the upper Han River are primarily polluted by Al, As, Cd, Pb, Sb and Se, and the potential pollutants include Ba, Cr, Hg, Mn and Ni. Spatial distribution of trace metals indicates the polluted sections mainly concentrate in the Danjiang, Danjiangkou Reservoir catchment and Hanzhong Plain, and the most contaminated river is in the Hanzhong Plain. Q-model clustering depends on geographical location of sampling sites and groups the 42 sampling sites into four clusters, i.e., Danjiang, Danjiangkou Reservoir region (lower catchment), upper catchment and one river in headwaters pertaining to water quality. The headwaters, Danjiang and lower catchment, and upper catchment correspond to very high polluted, moderate polluted and relatively low polluted regions, respectively. Additionally, PCA/FA and correlation analysis demonstrates that Al, Cd, Mn, Ni, Fe, Si and Sr are controlled by natural sources, whereas the other metals appear to be primarily controlled by anthropogenic origins though geogenic source contributing to them.

1. Introduction

There is worldwide water quality deterioration primarily contributable to growing human populations and economical development, particularly elevating nutrients leading to eutrophication and heavy metals in the aquatic environment [1–6]. Metal's natural sources include volcanism, bedrock erosion, atmospheric transport and the release from plants [1,6], and anthropogenic activities, particularly mining and mineral processing have dominant influences on the biogeochemical cycles of trace metals [1,2,7,8]. As heavy metal pollution leads to a serious human health hazards through the food chain and the loss of biodiversity and harms the environmental quality, researches into trace elements and heavy metals preserve highly interesting records (e.g. [1,2,8,9]). Of which, their spatial variability reflects geological parent materials and anthropogenic sources in geographic heterogeneity [10].

There has been long-time history of study on water pollution caused by heavy metals [9]. These studies concerning with varying scale including global and regional [1,2,8,11] and different ecosystems such as forest [12], grassland [13], fluvial systems [14–17], agriculture [18] and urban [10], have reported the increasing water pollution due to anthropogenic activities. In China, serious water shortage and wide-spread water contamination with heavy metals pose genuine threats to ecological security and economical sustainable development, thus, many studies have been focusing on trace metals, especially in the Changjiang River (e.g., [9,19]). The Han River, a main tributary of the Changjiang River, is the water source area of the China's Middle Route of the South-to-North Water Transfer Project. Past studies have characterized its water quality including nutrients [20–22], hydro-geochemistry [23,24] and water quality and landscape setting interactions using stepwise multiple linear regression [25,26], whilst the concentrations and distributions of trace metals in the Han River are unavailable.

Multivariate statistical approaches such as cluster analysis (CA), principal component analysis (PCA), factor analysis (FA), correlation analysis and analysis of variance (ANOVA) have been increasingly in use for environmental studies on measurements and monitoring, particularly assessing huge and complex chemical datasets and these multidimensional data analysis methods are the powerful tools for drawing a meaningful data reduction and the interpretation of geochemical data [27–31].

The present study was carried out as a preliminary survey on water pollution by trace metals in the upper Han River.

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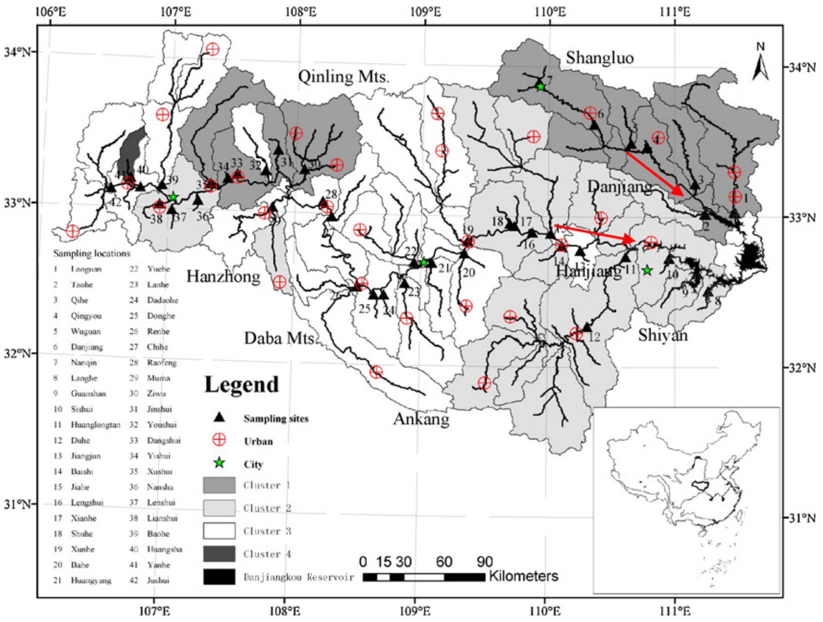

Fig. 1. The upper Han River basin showing sampling locations, urbans, clusters and drainage systems, China.

The objectives of the study are to (1) determine the spatial characterization of dissolved trace elements and heavy metals using multivariate statistical techniques, (2) identify the natural and/or anthropogenic sources of these trace elements and heavy metals and (3) define trace metals causing pollutions in river waters. Ultimately, the research would help develop water management and conservation strategies in the upper Han River basin for the China's interbasin water transfer project.

2. Materials and methods

2.1. The study area

The upper Han River, the water source area for the China's Middle Route of the South-to-North Water Division Project, transfers water to north China including Beijing and Tianjin city for various usages. The drainage basin (31°20′–34°10′N, 106–112°E; 210–3500 m *a.s.l.*; Fig. 1) is located in a mountainous region with a north subtropic monsoon climate and covers a total area of approximate $95.2 \times 10^3\,\text{km}^2$ with 925 km in length. Vegetation, the dominant land coverage, covers about 77% of the total area in the basin with higher composition in uplands. Agriculture and urban respectively representing approximate 15% and 0.5% of the total drainage area concentrates along river networks, i.e., Hanzhong Plain, Ankang Plain and Danjiangkou Reservoir catchment. There are several industrial cities such as Hanzhong, Ankang, and Shiyan and Shangluo in headwaters, middle section and down section, respectively ([21,22,26]; Fig. 1).

2.2. Water sampling and analytical methods

Six sampling campaigns from 42 sites representing varying landscape settings throughout the upper Han River basin during 2005–2006 (June, August and November 2005, and April, June and October 2006) in the upper Han River were conducted. Thus, a total of 252 grab water samples were collected at a depth of approximate 10 cm using previously acid-washed 51 high density polyethylene (HDPE) containers, and filtered through pre-washed 0.45 μm Millipore nitrocellulose filters on the sampling day. The initial portion of the filtration was discarded to clean the membrane, and the following ones were acidified to $\text{pH} < 2$ with ultra-purified 6 M HNO_3 and then stored in pre-cleaned HDPE bottles for trace metal analyses. Cleaning of plastic bottles was carried out by soaking in 15% (v/v) HNO_3 for 24 h and then rinsing with milli-Q deionised water (analytical grade). Acid-cleaned polyethylene gloves were used while handling all plastic and glass ware and analytical reagents were used throughout the determinant processes.

Concentrations of Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Si, Sr and V were determined using an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) (IRIS Intrepid II XSP DUO, USA) with a analytical precision better than 10% [5]. Reagent and procedural blanks were measured in parallel to the sample treatment using identical procedures. Each calibration curve was evaluated by determination of quality control standards before, during and after a set of sample measures.

2.3. Statistical analyses

Analysis of variance (ANOVA) was used to classify and test the significance ($p < 0.05$, least-significance difference, LSD) of spatial sites and groups founded by cluster analysis. Relationships among the considered variables were tested using Pearson's coefficient as a non-parametric measure with statistical significance set priori at $p < 0.05$ [25,30].

Principal component analysis (PCA) and factor analysis (FA) were employed to find and interpret the structure of the underlying data set through a reduced new set of orthogonal (non-correlated) variables (principal components, PCs), arranged in decreasing order of importance. Besides considerable data reduction, PCs can explain the entire multidimensional data set variability without losing much original information. FA and PCA with Varimax rotation of standardized component loadings were conducted for extracting and deriving factors, respectively, and those PCs with eigenvalue >1 were retained [27–29].

Table 1

Concentrations of dissolved trace elements and heavy metals in the upper Han River basin, China (unit in μg/l).

	Min	Max	Mean	S.E.	Drinking water guidelines				Background values[a]	Danjiangkou Reservoir [5]	Nakkavagu [1]	Dil Deresi [6]	Mekong delta drinking water [14]	
					WHO[b]	China[c]	US EPA[d]						Cambodia	Southern Vietnam
							MCLG	MCL						
Al	nd	2527	187.99	23.99	200	200				203.69		8460		
As	nd	165.7	14.2	1.18	10	10	0	10	0.86	11.08	29.2	50		
Ba	nd	1661	87.47	9.08	700	700				219.31	77.6	1480	337	280
Cd	nd	196.5	2.31	1	3	5	5	5	0.015	1.17		8	0.2	<0.1
Co	nd	16.3	2.24	0.17					0.24	1.08	2.8	21	2.8	0.8
Cr	nd	53.4	8.14	0.66	50	50	100	100	0.26	6.29	16.8	42	0.1	0.4
Cu	nd	69.8	13.35	1.11	2000	1000	1300	1300	0.63	13.32		37	6	8.4
Fe	nd	170.29	30.64	2.24	300	300			12.53	19.14	161.8	4030	2.7	3.5
Hg	nd	4.6			1	1	2	2	0.002					
Mn	nd	2181	30.72	9.37	400	100			2.53	5.69	72.9		3.3	0.4
Ni	nd	63.4	1.71	0.3	70	20			0.18	1.73	26.7		1.6	3.2
Pb	nd	59.5	9.26	0.88	10	10	0	15	0.76	10.59	2.1	120		
Sb	nd	399.1	41.58	5.79	20	5	6	6		92.5				
Se	nd	48	9.56	0.86	10	10	50	50	0.13	15.36			5.8	0.4
Si	74.2	11770	4395.69	121.73										
Sr	nd	577	234.62	5.96						231.76	762.5			
V	nd	179.2	69.95	3.04					0.23	71.33				

Maximum Contaminant Level Goal (MCLG); Maximum Contaminant Level (MCL) and nd—not detected.

[a] Background values of trace metals in the source area of the Yangtze River [35].

[b] WHO (2006) Drinking water guidelines [32].

[c] Chinese (2007) Drinking water guidelines [33].

[d] US EPA (2006) Drinking Water Standards [34].

Cluster analysis (CA) was applied to group objects (cases) into categories or clusters on the basis of similarities within a cluster and dissimilarities between different clusters with respect to distance between objects. In the present study, Q-model hierarchical agglomerative CA was performed on the normalized data set using squared Euclidean distances as a measure of similarity and Ward's method to obtain dendrograms, and stations in the same category have the similar source of pollutants [28,29,31]. The total 4032 observations during a 2-year monitoring period were treated statistically using SPSS 15.0 for Windows.

3. Results and discussion

3.1. Spatial characterization of trace metals

Dissolved trace elements and heavy metals including Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Si, Sr and V over a period of 2 year (2005–2006) at 42 different sites in the upper Han River were summarized in Table 1. In order to precisely present their spatial characterization, their mean values and standard errors are presented in Fig. 2 and Table 2, respectively. While Hg was only

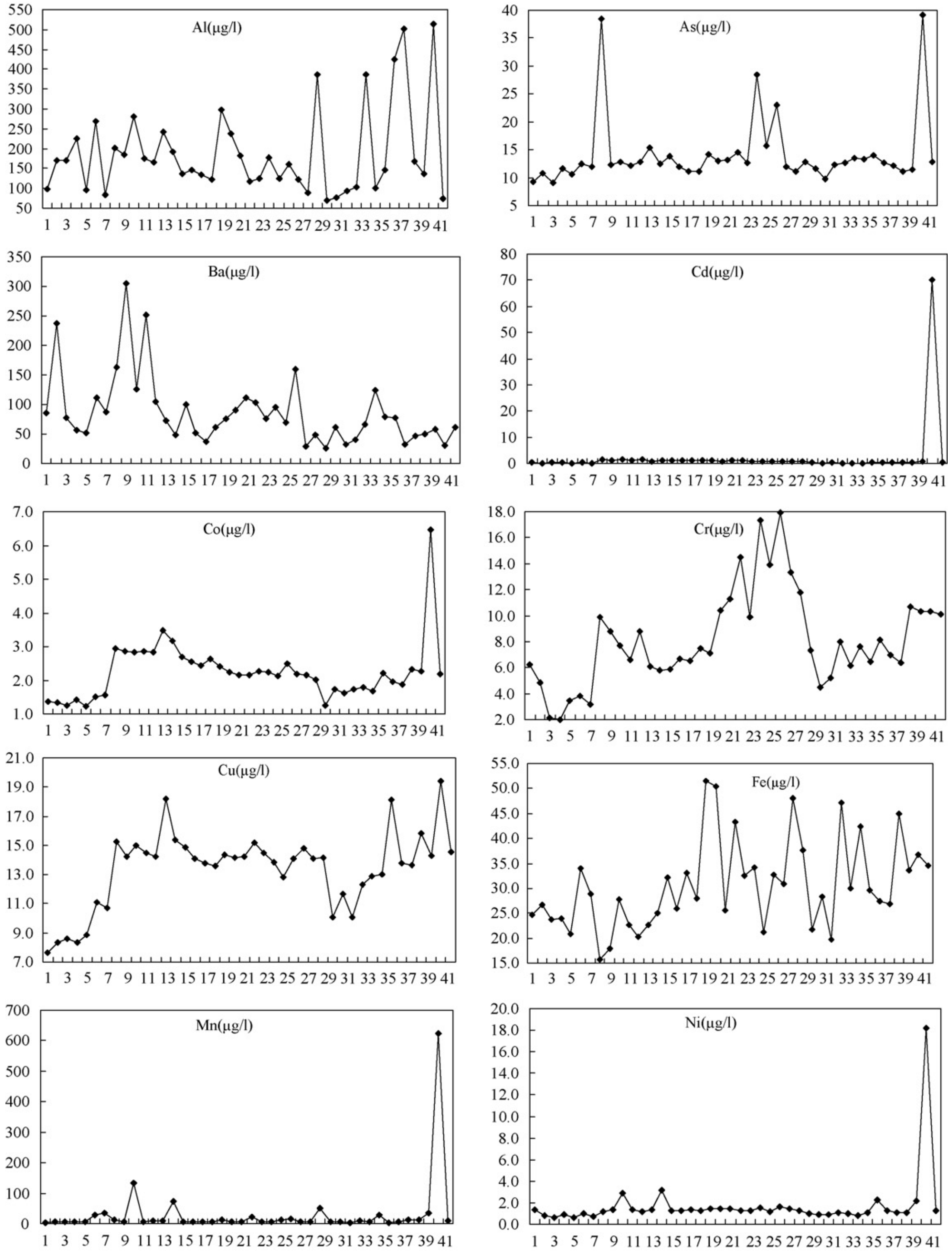

Fig. 2. Spatial distributions of the averaged trace metals in the upper Han River basin, China.

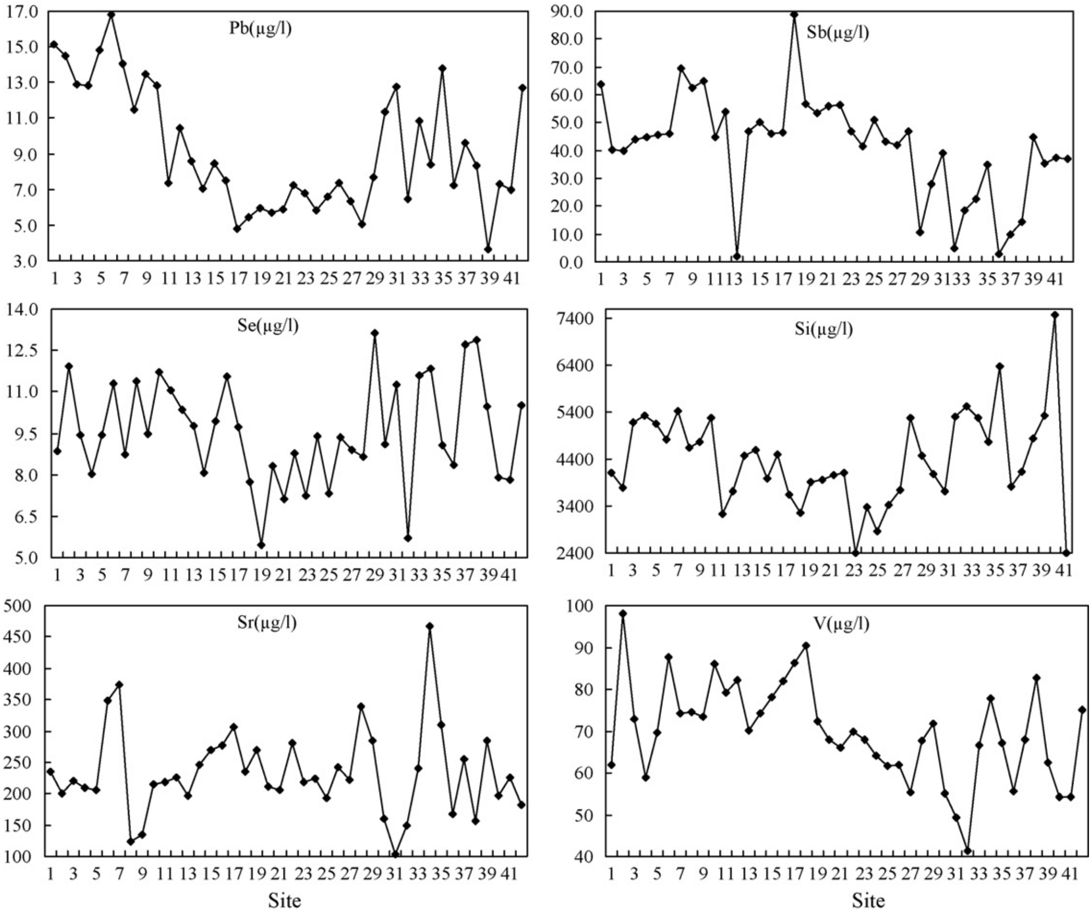

Fig. 2. (*Continued*).

detected in 10 water samples (sites 1, 2, 5, 21–23, 31, 33, 38 and 39), so its spatial distribution is not analyzed in the present study (Tables 1 and 2; Fig. 2). Each individual element exhibits a wide variation as reflected by the large standard deviation values indicative of seasonal changes and chemical–physical properties of the sampling sites [26,28,29]. Si, Sr and Al are the most abundant elements in the river water whereas Cd, Co and Ni are the less abundant (Table 1), and the concentrations of most elements including Al, As, Cd, Co, Cu, Mn, Ni and Si tend to have the notable rises in site 41 (Fig. 2).

When compared to other rivers in industrial areas and drinking water, our results are comparable with the low polluted river (Table 1). While by comparing with drinking water guidelines established by WHO, China and US EPA [32–34], the maximum concentrations of Cu and Fe are lower than the guideline values. The averages of Ba, Cr, Mn and Ni are much lower than the critical values while their peak contents are higher than the critical values for drinking water quality, the average concentrations of Al, Cd, Pb and Se are close to levels by WHO and China with the maximum concentrations much higher than the guidelines, and the averages of As and Sb are much higher than those recommended for drinking purposes (Table 1). Although most of the samples were not detectable, the peak concentrations of Hg in the samples are higher than standards established by WHO, China and US EPA. Thus, Al, As, Cd, Pb, Sb and Se, particularly As and Sb are the major pollutants, while the potential pollutants include Ba, Cr, Hg, Mn and Ni, similar to the results of Danjiangkou Reservoir on the Han River [5]. Considering the priority toxic pollutants, i.e., As, Cd, Cr, Cu, Pb, Ni and Se presented in US EPA, 2006 for aquatic life protection, much greater attention should be paid to As, Cd, Pb and Se.

Spatial distributions of trace metals show the increases in Al, As, Co, Cr, Cu, Fe, Se and Si from downstream to upper stream, while Ba, Pb, Sb and V show the opposite trend (Fig. 2). Cd, Mn and Ni have the similar trend showing very high abnormalities in site 41 (headwater of the basin), reflected by ANOVA results (Table 3), which is primarily contributable to an intensification of agricultural and urban industrial practices along the river [22,25,26]. Si and Sr, abundant in earth crust, also have significant spatial differences (Table 3), reflecting the integration of crustal contribution and anthropogenic additions [6,24]. However, the rest metals largely vary with no significant differences in sites ($p < 0.05$; Table 3). That may be explained by human activities changing their distributions or alleviating the spatial differences though such a large drainage area with varying landscape setting and geology in the upper Han River (Fig. 1; [25]). Regarding their spatial averages with guidelines, As and Sb of 39 sites have averages larger than permissible limits of pollutions, about 15 sites for Pb and Se, 11 sites for Al, and 1 site (site 41) for Cd and Mn, respectively (Table 1; Fig. 2), indicating that polluted rivers concentrate in Danjiang (i.e., site 6), Danjiangkou Reservoir catchment (sites 8 and 10) and Hanzhong Plain (i.e., site 41) respectively (Fig. 2).

Natural contents of trace metals in rivers derived from soils and mineral weathering [1,2,6] and understandably geology and pedogenesis seem to play important roles in mediating dissolved elements and heavy metals in natural river waters [35]. Our results illustrate trace metal concentrations in water sam-

Table 2
Standard error mean (S.E. mean) of trace metals in 42 sites of the upper Han River basin, China (unit in μg/l).

Sites	Al	As	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sb	Se	Si	Sr	V
1	57.61	3.96	33.75	0.13	0.62	3.73	4.90	16.35	2.68	0.55	8.49	35.39	3.92	556.30	22.27	17.54
2	64.69	4.70	44.25	0.11	0.49	2.44	5.49	16.43	3.07	0.65	9.83	34.03	5.50	612.27	23.38	22.37
3	103.62	3.96	19.41	0.13	0.43	1.20	5.72	15.09	3.73	0.52	9.66	33.17	4.33	1141.90	16.75	18.46
4	154.84	5.16	29.79	0.10	0.53	1.02	5.46	11.54	3.82	0.43	7.60	39.22	3.87	538.18	26.39	18.53
5	35.80	4.78	11.76	0.05	0.56	1.63	5.49	11.77	3.27	0.52	9.50	38.86	4.96	969.92	24.95	22.37
6	170.58	5.45	18.32	0.21	0.51	1.87	6.44	22.39	7.23	0.52	8.47	36.72	5.30	887.08	37.08	25.20
7	39.88	5.25	15.65	0.08	0.50	1.46	6.29	17.67	21.79	0.62	9.51	38.53	4.49	1296.20	27.31	22.45
8	200.26	26.02	138.38	0.89	1.73	3.34	8.71	8.44	4.28	1.07	7.09	65.98	7.21	616.37	13.92	21.72
9	182.83	7.18	271.28	0.77	1.71	3.23	7.83	9.14	4.64	1.18	7.93	60.52	6.03	470.40	12.69	22.09
10	189.16	6.68	70.00	0.81	1.70	3.04	7.85	11.46	46.20	1.08	7.51	62.24	6.87	988.81	31.02	25.23
11	174.07	6.35	148.66	0.76	1.70	2.35	7.55	12.99	4.16	1.19	4.33	42.73	6.89	135.94	16.15	22.57
12	163.18	6.51	19.24	0.73	1.68	3.24	7.36	10.74	4.98	0.94	4.66	51.36	7.31	382.40	24.08	24.43
13	166.96	7.02	22.19	0.73	1.77	2.72	7.05	11.59	3.60	0.96	4.25	1.16	7.96	669.69	20.70	21.92
14	150.49	6.15	11.81	0.73	1.58	2.88	7.12	11.06	29.80	1.12	5.59	43.40	6.23	609.73	28.35	20.72
15	135.84	6.26	13.93	0.71	1.43	3.00	7.30	18.20	3.24	1.03	4.63	46.79	7.17	503.48	31.45	22.09
16	143.56	5.88	13.89	0.64	1.53	3.09	7.05	14.98	3.68	1.04	4.59	44.24	7.36	321.62	34.42	22.77
17	132.92	5.32	7.12	0.62	1.41	3.48	6.73	19.00	4.08	1.08	3.82	39.80	6.95	757.43	26.45	24.56
18	120.70	5.51	14.73	0.63	1.40	3.20	6.55	15.45	3.97	1.17	3.89	56.51	4.94	673.60	20.59	24.97
19	189.37	6.28	9.78	0.60	1.32	4.35	6.60	22.39	4.58	1.19	4.17	51.72	5.25	485.21	28.73	20.65
20	142.94	6.51	17.02	0.55	1.35	4.65	6.66	22.61	2.99	1.14	4.54	50.43	6.90	514.45	29.04	18.43
21	132.52	6.13	24.01	0.78	1.38	5.32	6.94	10.62	3.02	1.26	4.39	53.45	6.41	455.72	30.49	20.77
22	111.10	6.29	17.30	0.51	1.14	6.49	7.47	17.83	16.26	1.05	4.56	53.59	7.52	676.05	32.05	20.61
23	101.51	5.74	9.40	0.53	1.28	6.58	7.16	11.60	2.74	1.11	4.98	44.69	7.11	281.97	28.42	19.64
24	95.94	13.90	25.67	0.48	1.26	8.97	7.43	11.29	2.42	1.21	4.23	38.12	6.64	189.99	25.82	17.31
25	88.52	5.83	23.28	0.48	1.06	7.78	7.07	8.78	5.72	1.12	5.15	48.49	6.75	753.53	39.72	16.88
26	99.60	9.75	47.97	0.37	1.20	8.79	7.57	14.06	5.95	1.14	4.92	37.47	6.70	266.95	12.74	17.28
27	81.82	5.18	5.95	0.36	1.14	6.52	8.79	13.14	2.35	1.20	3.72	38.68	5.63	381.95	33.19	17.50
28	71.44	4.86	7.78	0.40	1.13	5.21	8.43	18.83	2.83	1.08	4.13	44.72	4.63	717.14	47.68	18.67
29	287.28	5.78	6.59	0.34	1.03	4.61	9.03	13.86	27.25	0.94	4.83	8.24	7.22	774.33	25.96	20.70
30	39.81	5.28	29.95	0.13	0.40	2.21	5.88	10.87	2.21	0.55	7.67	25.31	5.85	478.35	16.22	18.45
31	51.44	4.55	4.88	0.12	0.61	3.20	7.40	11.22	4.27	0.69	8.12	35.17	5.13	573.77	14.18	14.72
32	53.15	5.59	23.57	0.15	0.61	4.07	6.65	13.33	1.12	0.74	3.86	2.15	3.54	924.72	34.83	17.77
33	53.43	5.64	17.24	0.13	0.71	3.94	8.64	25.80	2.78	0.78	5.25	15.80	5.69	911.21	16.03	19.95
34	270.45	6.30	54.54	0.15	0.66	4.92	8.81	17.09	2.04	0.72	5.01	18.55	5.38	638.78	36.86	21.89
35	64.36	6.12	39.36	0.21	0.62	3.64	8.90	22.65	12.48	0.83	7.14	29.37	4.67	1038.91	43.90	21.20
36	74.78	4.83	48.74	0.33	0.75	4.24	9.31	12.14	1.55	1.21	3.95	1.44	5.45	759.58	17.80	17.17
37	289.15	5.61	13.36	0.26	0.74	3.88	9.64	10.92	1.32	1.15	4.58	7.20	6.35	711.98	24.18	20.37
38	398.08	5.34	15.50	0.31	0.75	3.69	9.46	9.95	3.37	0.88	4.78	9.12	5.95	680.30	21.22	23.16
39	87.84	4.92	17.26	0.36	1.02	4.54	10.00	20.86	3.45	0.93	2.83	39.47	6.18	931.15	38.67	18.69
40	70.67	5.15	21.50	0.37	0.97	4.78	10.22	11.04	8.09	2.03	5.21	33.04	5.10	809.09	43.21	17.97
41	405.06	19.22	12.52	33.72	2.17	4.47	10.59	13.85	316.56	9.34	4.55	34.94	5.02	1575.76	47.07	22.99
42	46.58	5.73	19.01	0.18	0.94	4.57	9.29	16.13	4.33	0.84	6.25	34.51	6.01	353.77	24.53	22.18

ples much higher than background values in the Yangtze River and decreasing as following order; Si > Sr > Al > Ba > V>Sb > Mn > Fe > As > Cu > Se > Pb > Cr > Cd > Co > Ni, which is distinctly different to that in the headwater of the Yangtze River (Table 1; [35]), reflecting their changed constituents due to pronounced anthropogenic inputs and weathering process. Our results are also different from the orders in polluted riverine waters and drinking water, while compatible with the order in the Danjiangkou Reservoir on the Han River (Table 1). However, elements such as As, Cd, Co, Cr and Mn have much higher contents in the Han River due to the

Table 3
Analysis of variance for spatial trace metal concentrations in the upper Han River basin, China.

	Sum of squares	df	Mean square	*F*	*p*-Value
Al	3068033.853	41	74830.094	0.475	0.997
As	10250.517	41	250.013	0.682	0.928
Ba	885938.750	41	21608.262	1.059	0.386
Cd	28219.715	41	688.286	4.163	<0.001
Co	182.143	41	4.443	0.540	0.990
Cr	3275.198	41	79.883	0.688	0.923
Cu	1644.074	41	40.099	0.111	1.000
Fe	19890.840	41	485.142	0.345	1.000
Mn	2302550.973	41	56159.780	3.694	<0.001
Ni	1726.853	41	42.118	2.272	<0.001
Pb	2902.122	41	70.783	0.321	1.000
Sb	81469.107	41	1987.051	0.206	1.000
Se	837.584	41	20.429	0.093	1.000
Si	205951974.357	41	5023218.887	1.899	0.002
Sr	1165807.256	41	28434.323	5.653	<0.001
V	33857.433	41	825.791	0.317	1.000

df: degrees of freedom.

Table 4
Pearson correlation matrix of trace metals in the upper Han River basin, China.

	Al	As	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sb	Se	Si	Sr	V
Al	1.000															
As	**0.336**[b]	1.000														
Ba	−0.053	0.099	1.000													
Cd	**0.461**[a]	**0.620**[a]	−0.136	1.000												
Co	**0.413**[a]	**0.644**[a]	0.030	**0.789**[a]	1.000											
Cr	−0.048	**0.444**[a]	0.071	0.111	0.301	1.000										
Cu	**0.320**[b]	**0.444**[a]	−0.048	**0.383**[b]	**0.769**[a]	**0.486**[a]	1.000									
Fe	0.068	−0.030	−0.275	0.103	0.045	0.267	0.260	1.000								
Mn	**0.492**[a]	**0.587**[a]	−0.148	**0.973**[a]	**0.785**[a]	0.081	**0.391**[b]	0.116	1.000							
Ni	**0.462**[a]	**0.612**[a]	−0.144	**0.984**[a]	**0.827**[a]	0.147	**0.453**[a]	0.109	**0.982**[a]	1.000						
Pb	−0.117	−0.153	0.282	−0.120	−0.**375**[b]	−0.575[a]	−0.**589**[a]	−0.**347**[b]	−0.069	−0.161	1.000					
Sb	−0.280	0.090	**0.322**[b]	−0.011	0.121	0.155	−0.085	−0.018	0.003	−0.011	0.053	1.000				
Se	**0.344**[b]	−0.039	0.166	−0.154	−0.124	−0.217	−0.023	−0.103	−0.107	−0.182	**0.334**[b]	−0.241	1.000			
Si	0.281	0.214	−0.136	**0.475**[a]	0.247	−0.285	0.083	0.071	**0.521**[a]	**0.488**[a]	0.142	−0.280	−0.041	1.000		
Sr	0.146	−0.154	−0.114	−0.025	−0.090	−0.059	−0.016	**0.437**[a]	0.010	−0.047	−0.083	0.018	0.113	0.154	1.000	
V	0.180	−0.152	**0.390**[b]	−0.198	−0.013	−0.268	−0.031	−0.051	−0.154	−0.210	0.199	**0.358**[b]	**0.465**[a]	−0.255	**0.331**[b]	1.000

Bold values represent correlation with significance.

[a] Significance at the 0.01 probability level.

[b] Significance at the 0.05 probability level.

Table 5
Total variance explained and component matrixes for trace metal contents (principal component analysis with Varimax rotation).

Component	Initial Eigen values			Rotation sums of squared loadings		
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %
1	5.231	32.692	32.692	4.771	29.821	29.821
2	2.363	14.769	47.461	2.549	15.932	45.754
3	1.979	12.366	59.827	1.933	12.079	57.833
4	1.807	11.293	71.120	1.788	11.176	69.009
5	1.328	8.300	79.420	1.666	10.411	79.420
6	0.757	4.729	84.150			
7	0.632	3.953	88.103			
8	0.499	3.118	91.221			
9	0.433	2.706	93.927			
10	0.340	2.127	96.054			
11	0.251	1.567	97.621			
12	0.193	1.206	98.828			
13	0.132	0.825	99.653			
14	0.031	0.195	99.848			
15	0.018	0.111	99.959			
16	0.006	0.041	100.000			

Variables	Component					Communalities
	1	2	3	**4**	5	
Al	0.500	0.080	−0.136	**0.656**	0.121	0.719
As	**0.674**	0.356	0.125	0.049	−0.255	0.663
Ba	−0.051	−0.043	**0.696**	0.176	−0.312	0.618
Cd	**0.965**	0.048	−0.073	−0.045	0.027	0.941
Co	**0.826**	0.428	0.139	0.077	−0.049	0.893
Cr	0.061	**0.839**	0.092	−0.200	−0.051	0.758
Cu	0.422	**0.739**	−0.039	0.220	0.062	0.778
Fe	0.041	0.310	−0.158	−0.105	**0.752**	0.699
Mn	**0.973**	0.006	−0.062	−0.005	0.069	0.955
Ni	**0.971**	0.097	−0.084	−0.053	0.021	0.963
Pb	−0.051	−0.**816**	0.211	0.124	−0.237	0.785
Sb	0.047	0.023	**0.818**	−0.419	0.100	0.857
Se	−0.134	−0.157	0.086	**0.858**	−0.033	0.788
Si	0.581	−0.391	−0.372	0.021	0.148	0.651
Sr	−0.023	−0.091	0.082	0.159	**0.859**	0.778
V	−0.135	−0.144	**0.691**	0.511	0.287	0.860

Bolded values are >0.6.

biogeochemical processes, affinity by particles and aquatic mechanisms, and physical separation, i.e., suspended solids, gravels and logs settle out of waters as water slows down in the reservoir [5]. In addition, there are much higher compositions of trace elements associated with suspended particulates in the Yangtze River due to the dominant physical weathering [35], thus further study would determine trace metals in the unfiltered water in the Han River.

3.2. *Multivariate statistical analysis*

Correlation analysis demonstrates that there are significant relationships among trace elements, i.e., Al, As, Cd, Co, Cu, Mn and Ni. Major elements in earth crust such as Si and Fe have strong positive correlations with Cd, Mn, Ni, Sb and V, and Sr, respectively ($p < 0.05$; Table 4). FA/PCA on the entire data set (Fig. 2) evolve five PCs with eigenvalues >1 explaining about 79.4% of the total variances. Our results of overall component loadings (79.4%) are comparable to other studies, i.e., component loadings for 11 experimental variables and 14 variables were 75.3% and 82.4%, respectively [1,6]. Many authors have conducted PCA/FA for trace metals in fluvial system and obtained different results (e.g., [1,6]), we attribute these discrepancies to different river environments and different water variables.

Previous studies reported combined sources for trace metals, i.e., Cd and Hg primarily from agrochemicals, phosphate fertilizers and pesticides, Ba, Sr, Fe, Co, Mn, Ni and Cr from natural sources of weathering of parent material and subsequent pedogenesis, and As, Cu, Pb, Sb and V from urban and industrial activities such as energy production, mining, metal smelting and refining, manufacturing processes, automobile exhausts and waste incineration [7,18,31,36,37]. Our results demonstrate that the first PC accounting for 29.8% of the total variance has high loadings on As, Cd, Co, Mn and Ni, and moderate loadings on Al and Si. As and Co are mainly of anthropogenic signatures, i.e., paint, fertilizer and agrochemical industries [1,6,18,36], also reflected by their strong correlations and their surprising values in intense anthropogenic areas (Table 4; Fig. 2). Si and Al can be primarily from crust due to their most abundant crustal compositions [6,31], while Cd, Mn and Ni have low contents with small variability when the abnormal local site (site 41) were excluded, they also have good positive relationships with key component in earth crust (Al and Si). Therefore, these three elements are predominantly originating from pedogenic process and mineral weathering [18,31].

The second PC accounts for 15.9% of the total variance with positive loadings on Cr and Cu, and negative loadings on Pb. Cr and Cu are used as markers of paint and metal industries, while Pb as tracers of vehicles, agrochemicals and industrial wastes [1,5,6,18]. Hence the factor is predominantly ascribed to anthropogenic origins. However, the inverse relations of Pb with Cr and Cu are indicative of external inputs of Cr and Cu.

The third PC accounting for 12.1% of the total variance is mainly contributed by Ba, Sb and V. Sb and V is greatly impacted by anthropogenic activities such as mining and agricultural processes [5], while higher Ba concentration primarily derive from geology [1]. Therefore, this component can be attributable to mixed sources of anthropogenic especially agriculture and mining in the basin and geogenic origins.

The fourth and fifth PCs accounting for 11.2% and 10.4% of the total variance, respectively (Table 5) are characterized by Al and Se, and Fe and Sr, respectively. Al and Fe are found abundant in the earth, the two PCs are therefore assumed to originate from natural contribution, also confirmed by their strong geochemical correlations (Tables 4 and 5) [37]. However, key component Si in crust exhibit slight correlations with the last two PCs (Table 5), which indicates their combined sources, particularly for Se [6,27,31]

The dendrogram resulting from Q-model CA shows 4 major clusters (groups), i.e., cluster 1 (sites 1, 3–7, 30, 31, 33 and 35), cluster 2 (sites 2, 8–12, 14–18, 29, 34, 37 and 38), cluster 3 (sites 13, 19–28, 32, 36, 39, 40 and 42) and cluster 4 (site 41) (Fig. 3), and these clusters depend on geographical location of sampling sites locating at Danjiang, Danjiangkou Reservoir region (lower catchment), upper catchment and site 41 (headwaters) respectively (Fig. 1). Clusters show the significant differences in trace metals except Cu, Fe, Pb, Se, Sr and V with significant high levels of Al, As, Cd, Co, Mn, Ni and Si in cluster 4, Cr in cluster 3, Ba in Cluster 2 and Pb in cluster 1 (Table 6). Also, cluster 2 has the highest concentrations of main pollutants of Sb and Se (Table 6). Compared to their averages data and information in clusters with drinking water guidelines, we can conclude that cluster 4, clusters 1 and 2, and cluster 3 correspond to very high polluted, moderate polluted and relatively low polluted regions, respectively, confirmed by their spatial characterization and consistent with the result using water physio-chemicals (Fig. 2; [26]). Besides, rivers in the same category have the same source of pollution; we ascribe the above classified regions to predominantly anthropogenic activities, the mixed origin of anthropogenic and geogenic sources, and primarily natural contributions, respectively.

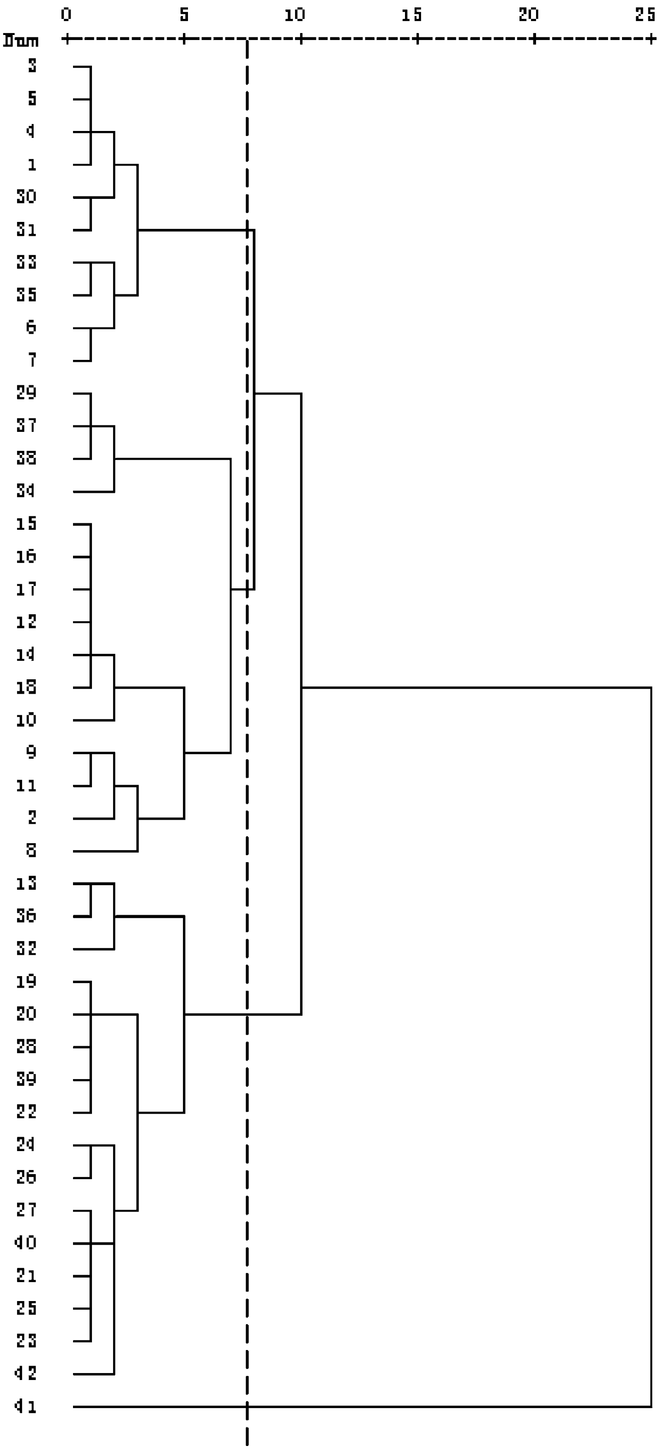

Fig. 3. Dendrogram showing clustering of sampling sites according to Ward's method using squared Euclidean distance.

Generally, CA technique is well known to classify waters in the whole region and categorize water variables in order to design a future spatial sampling strategy and reduced water variable examinations in an optimal monitoring network [28,31]. Consequently, decreased costs and labors with minimum loss of any significant data and information are obtained.

Table 6
Mean values with standard errors (S.E.) and ANOVA for trace metals in different clusters of the upper Han River basin, China (unit in μg/l).

	Cluster 1		Cluster 2		Cluster 3		Cluster 4	
	Mean	S.E.	Mean	S.E.	Mean	S.E.	Mean	S.E.
Al	128.86(b)	27.57	240.52(ab)	51.39	154.68(b)	25.89	513.16(a)	405.06
As	11.23(b)	1.48	14.06(b)	2.22	14.65(b)	1.66	39.08(a)	19.22
Ba	70.79(ab)	7.56	114.16(a)	23.56	76.16(ab)	6.47	30.95(b)	12.52
Cd	0.20(b)	0.04	0.88(b)	0.15	0.72(b)	0.12	70.02(a)	33.72
Co	1.47(cd)	0.16	2.45(b)	0.33	2.27(bd)	0.27	6.45(a)	2.17
Cr	4.32(b)	0.79	7.16(b)	0.82	11.38(a)	1.40	10.36(ab)	4.47
Cu	10.23	1.95	13.85	1.87	14.49	1.88	19.38	10.59
Fe	29.58	5.16	26.48	3.30	34.91	3.73	36.68	13.85
Mn	13.56(b)	2.93	22.98(b)	5.32	11.13(b)	1.57	625.17(a)	316.56
Ni	0.92(b)	0.18	1.43(b)	0.25	1.45(b)	0.28	18.16(a)	9.34
Pb	13.53(a)	2.41	9.16(ab)	1.40	6.77(b)	1.07	6.97(ab)	4.55
Sb	40.42	9.86	44.73	10.65	39.55	9.53	37.58	34.94
Se	9.68	1.42	10.90	1.56	8.31	1.46	7.82	5.02
Si	4814.70(b)	266.40	4207.74(c)	162.59	4118.01(c)	184.58	7467.89(a)	1575.76
Sr	240.96	12.78	241.14	10.38	224.89	8.88	225.60	47.07
V	66.29	6.00	80.32	5.44	63.36	4.53	54.25	22.99

Cluster 1 (sites 1, 3–7, 30, 31, 33, 35); cluster 2 (sites 2, 8–12, 14–18, 29, 34, 37, 38); cluster 3 (sites 13, 19–28, 32, 36, 39, 40, 42) and cluster 4 (site 41). The different letters indicate statistical difference among zones at $p < 0.05$; LSD test.

4. Conclusion

Si, Sr and Al are the most abundant elements in the river water whereas Cd, Co and Ni are the less abundant in the upper Han River. The river basin has been affected by anthropogenic activities including agricultural, mineral and urban industrial processes leading to a high pollution of Al, As, Cd, Pb, Sb and Se, and the potential pollutants of Ba, Cr, Hg, Mn and Ni. Special attention should be paid to As, Cd, Pb and Se listed in the priority toxic pollutants of US EPA. Spatial distribution of trace metals by multivariate statistical techniques indicates the polluted rivers mainly concentrating in Danjiang, Danjiangkou Reservoir catchment and Hanzhong Plain, and the most contaminated river section is in the Hanzhong Plain. Q-model clustering depends on geographical location of sampling sites and these four clusters are located at a river in headwaters, Danjiang and Danjiangkou Reservoir region (lower catchment), and upper catchment, corresponding to very high polluted, moderate polluted and relatively low polluted regions, respectively. In addition, PCA/FA and correlation analysis demonstrates Al, Cd, Mn, Ni, Fe, Si and Sr controlled by natural sources, Ba, Sb, Se and V by the mixed sources of anthropogenic origins and pedogenesis, whereas As, Co, Pb, Cr and Cu seem to be primarily from anthropogenic inputs.

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