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Response of dissolved trace metals to land use/land cover and their source apportionment using a receptor model in a subtropic river, China

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ABSTRACT

Water samples were collected for determination of dissolved trace metals in 56 sampling sites throughout the upper Han River, China. Multivariate statistical analyses including correlation analysis, stepwise multiple linear regression models, and principal component and factor analysis (PCA/FA) were employed to examine the land use influences on trace metals, and a receptor model of factor analysis-multiple linear regression (FA-MLR) was used for source identification/apportionment of anthropogenic heavy metals in the surface water of the River. Our results revealed that land use was an important factor in water metals in the snow melt flow period and land use in the riparian zone was not a better predictor of metals than land use away from the river. Urbanization in a watershed and vegetation along river networks could better explain metals, and agriculture, regardless of its relative location, however slightly explained metal variables in the upper Han River. FA-MLR analysis identified five source types of metals, and mining, fossil fuel combustion, and vehicle exhaust were the dominant pollutions in the surface waters. The results demonstrated great impacts of human activities on metal concentrations in the subtropical river of China.

1. Introduction

Escalating human populations and economic development have significantly contributed to the current worldwide deterioration in water quality, including accumulation of heavy metals in the aquatic environment [1–6]. Additionally, anthropogenic activities particularly electroplating, mining and mineral processing have been greatly influencing the local and global geochemical cycles of trace metals [7,8]. Past studies have demonstrated that spatial heterogeneity and seasonal variations in river characteristics such as geological parent materials, anthropogenic practices, storm water runoff, and atmospheric deposition have strong effects on trace metal concentrations [3,9,10]. Also, land use and seasonal hydrological routines are important factors regulating dissolved trace metals in river waters.

Numerous studies have related land use/land cover to water quality including nutrients and sediments using empirical statistical techniques [11–15], and indicated that water quality parameters could be predictable by one or more landscape variables [12,14], and water quality variability in different hydrological pathways could be explained by various landscape factors [15]. Meanwhile, the relative influences of riparian zone with respect to an entire catchment in mediating chemical loads (i.e., nutrients and sediment) into fluvial system are varying [11–13,15]. In terms of heavy metals in the riverine system, several studies have qualitatively determined land use effects on metals in waters and soils [9,10,16–18], and reported that anthropogenic practices significantly contribute to metal concentrations and pristine and forest areas could mitigate trace elements to waters. However, there have been very few reports on quantifying the associations between land use and trace metals and identifying the predictors of metals by landscape variables.

A variety of receptor models such as factor analysis-multiple linear regression (FA-MLR) have been developed to quantitatively identify and estimate the source contributions to water chemicals [19]. This technique was widely used and could offer valuable tools for developing water conservation strategies [i.e., 19–23]. The eigenvector model, FA-MLR uses multivariate linear regression of sample mass concentration on factor scores to the apportionment of water pollution sources, while the model requires no input data on source profiles [20–22]. The process of FA-MLR receptor modeling was described in detail by Thurston and Spengler [24] and Singh et al. [19].

The Han River is the largest tributary of the Changjiang River in the subtropical region of China. Past studies on the Han River have characterized water physico-chemicals, the relationships between water quality and land use, and spatio-temporal variability in dissolved trace metals [14,15,25–30], indicating that the Han River are polluted by nitrogen and several heavy metals such as As and

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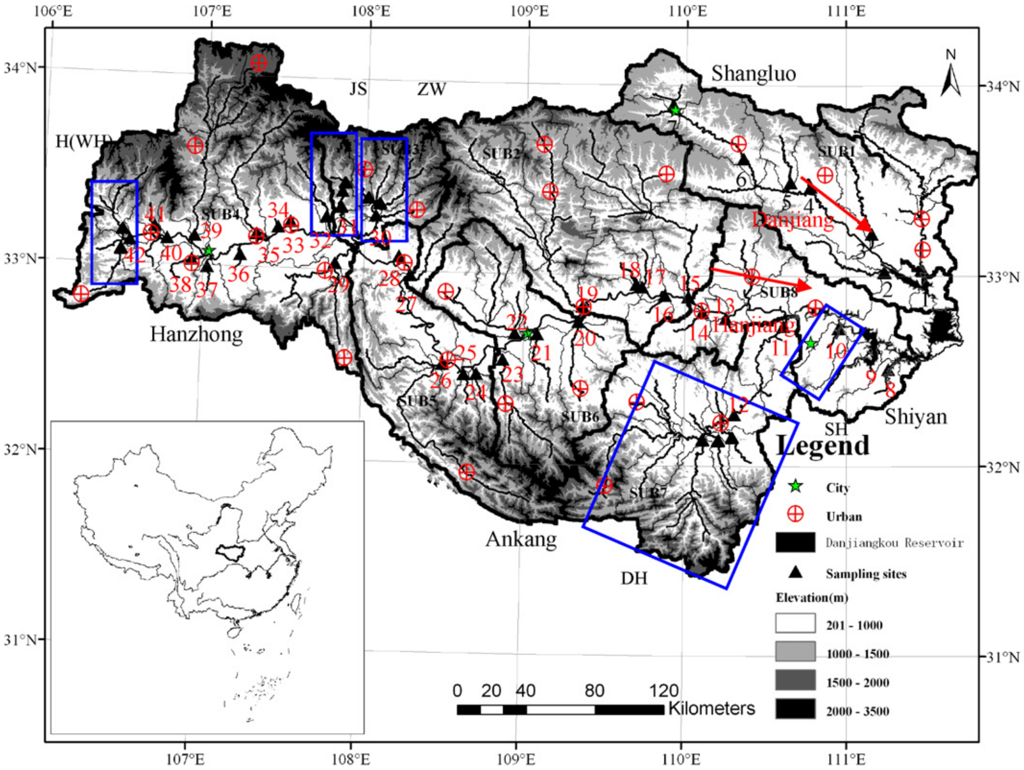

Fig. 1. The upper Han River basin showing sampling locations, urbans, DEM and drainage systems, China. SUB 1-Dan River, SUB 2-the South of the Qinling Mountain, SUB 3-Ziwu River, SUB 4-Hanzhong Plain, SUB 5-the North of the Daba Mountains, SUB 6-Ankang Plain, SUB 7-Du River, SUB 8-Danjiangkou Reservoir region with the drainage area of 15444.91, 15746.96, 4027.06, 18905.06, 9225.28, 8878.49, 12507.57 and 9943.74 km^2, respectively. H(WH)-Hanjiang (Wuhou Zhen, representing Jushui River), ZH-Ziwu, JS-Jinshui, DH-Duhe and SH-Sihe (Shiyan City).

Pb. However, no quantification of source contribution on metals in this area is conducted. This study is the first attempt to determine the interactive influence of land use and water flow seasonality on trace metals in the fluvial system and estimate the contribution of possible sources of metals using the FA-MLR receptor model as a sequel to previous studies [27,28].

2. Materials and methods

2.1. Study area

The upper Han River is the water source area for the China's Middle Route of the South to North Water Division Project. It transfers water to northern China including the major metropolises of Beijing and Tianjin city for a variety of domestic, agricultural and industrial uses. 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 and covers a total area of approximately 95.2 × 10^3 km^2 with 925 km in length. This basin belongs to northern sub-tropic monsoonal climate. Average annual precipitation is 700–1800 mm with large intra-annual and inter-annual variability, and 80% of which falls between May and October. Vegetated coverage accounts for about 77% of the total area in the basin with higher composition in upland areas. Agricultural and urban areas represent approximately 15% and 0.5% respectively of the total drainage area primarily along the river networks, i.e., Hanzhong Plain, Ankang Plain and Danjiangkou Reservoir catchment, thus, there are more intense human activities in the riparian strip. Several industrial cities such as Hanzhong, Ankang, and Shiyan and Shangluo are located at the headwa-

Table 1
Characteristics of several selective streams in the Han River, China.

River	Area (km^2)	Length (km)	Human activities	Discharge (10^8 m^3)	T (°C)	Precipitation (mm)	Num.
Hanjang (Wuhou)	3092	976	Vegetated land 77%, agriculture 21%, urban 1.3%	12	14.2	822	3
Ziwu	3028	153.8	Vegetated land 95.7%, agriculture 3.4%; urban 0.08%		12	920–1200	3
Jinshui	730	87	Vegetated land 96.4%, agriculture 2.21%, non-agricultural land 1.33%	2.7	11.66	924–1244	3
Duhe	12,000	343	Vegetated land 85%, agriculture 13.5%, urban 0.28%	60	12–15	800–1000	5
Sihe (Shiyan city)	475	17	Seriously polluted by industrial and domestic wastes in Shiyan city, which has 700,000 in population and is the home of automobile manufacturer		15	830	5

Num.: number of sampling sites.

ters, middle section, and downstream, respectively ([14,15,29]; Fig. 1).

2.2. Data sources

Three field campaigns were conducted from 56 sampling sites in April, June and October 2006, which represented snow melt, base flow and high flow periods, respectively (Table S1). Detailed samplings were also carried out in the Ziwu and Jinshui (SUB3), Han River (Wuhou) (SUB4), Duhe (SUB7), and Sihe Rivers (in SUB 8) in October 2006, and their physical characteristics such as hydrology and human activities were presented in Table 1. Thus, a total of 160 grab water samples were collected at a depth of approximate 10 cm using previously acid-washed 5 l high-density polyethylene (HDPE) containers, and filtered through pre-washed 0.45 μm millipore nitrocellulose filters on the sampling day. The pretreatments and analytical processes were following the previous reports [8,27] and the selected trace metals included Al, As, Ba, Cd, Co, Cr, Cu, Li, Fe, Mn, Mo, Ni, Pb, Sb, Se, Si, Sr, V and Zn. Elements were determined using ICP-MS (Inductively Coupled Plasma Mass Spectrometry), and ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometer) (IRIS Intrepid II XSP DUO, USA). Method validation and analytical quality assurance were conducted by using a standard reference material (SRM, SPEX CertiPrep, Inc, USA). All specimens and SRM were analyzed in batches, which included a procedural blank. The analytical precision was better than ±10% (see the percentage recoveries of metals in [8]) and the method detection limit was listed in Table S2.

Previous studies reported the associations between water physico-chemicals and land use/land cover both within the entire catchment and along the 100 m riparian zone [14,15]. In the present work, 8 subcatchments were derived using DEM and more than 4 sampling sites were located in the individual subcatchments (Fig. 1). Land use/land cover was derived from Landsat TM and +ETM with a hybrid of supervised and unsupervised classification algorithms. Considering their diverse impacts on stream water, six major land cover types, *i.e.*, forest, shrub, agriculture, urban, bareland, and waterbody, were categorized at the catchment level and in 100 m buffer along the stream network, respectively [14,15]. Each physical factor was expressed as a proportion of the respective watershed area [14,15]. Monthly and spatial patterns of partial trace metals in the Han River were reported by Li and Zhang [27,28], and a basic statistics for concentration spectrum of the analytes were presented in Table S3. The selective rivers with detailed sampling were investigated to confirm the source apportionment (Fig. 2).

2.3. Statistical analyses

The Pearson's correlation coefficients were employed to examine the strength and significance of the relationships between land use/land cover and trace metals in the three hydrological seasons. Two-sample *t*-tests at 0.05-level were considered to be significant. Stepwise multiple linear regression models were built with trace elements as dependent variables, and significance at the 0.05 probability level was considered for the models [14]. Principle component analysis (PCA) and factor analysis (FA) were employed to identify possible source types and those PCs with eigenvalue > 1 was retained. Mathematically, the PCs, computed from covariance or other cross-product matrix, describes the dispersion of the multiple measured parameters to obtain eigenvalues and eigenvectors. PCs are the linear combinations of the measured variables and the eigenvectors. Factor analysis attempts to decipher the correlations between the observations in terms of the underlying factors, which are unobservable [19]. The *z*-scale transformation for data was pre-processed before PCA/FA, which rendered the data normalized with mean and variance of zero and one, respectively. To improve the interpretation of pollution patterns, Kaiser's Varimax orthogonal rotation of PCs was performed [19–21]. Consequently, FA-MLR model was applied to estimate source contributions of environmental contaminants following Thurston and Spengler [24] and Simeonov et al. [23]. All the statistical analyses were performed using SPSS 15.0 statistical software packages for windows.

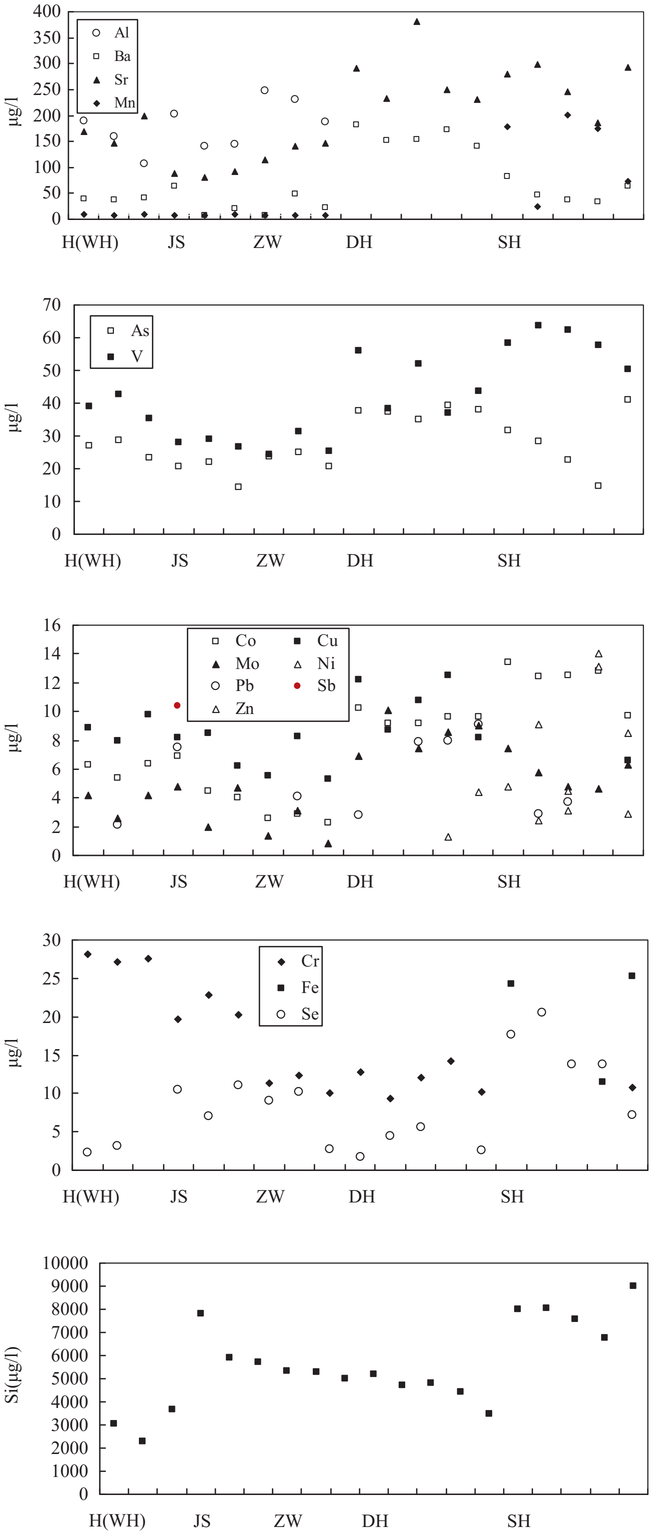

Fig. 2. Trace metal variables in several streams with detailed sampling (samplings were ranged from upper to down streams in each river).

Researchers reported that values less than the detection limit were simply substituted by one half of the detection limit in statistical process [31]. This was an arbitrary decision due to the large variations in detection limit among methods. In the present study, those metals with more than 50% observations below detection limit were excluded and others non-detectable were simply absent or substituted by zero.

3. Results

At the subcatchment level, forest, shrub and vegetation tended to mitigate metals in river waters, i.e., vegetation was significantly and negatively correlated to Cu, Mn and Ni, respectively. Whereas, agriculture, urban, bareland and waters tended to contribute to river metals, i.e., urban was significantly and positively correlated to As and Cd ($r = 0.87$, $p < 0.01$), bareland to Mn ($r = 0.8$, $p < 0.01$), and waters to Al, Ba, Mn and Ni ($p < 0.05$), respectively in the snow melt flow period. In the base flow period, urban was significantly and positively related to Cd and Ni ($r > 0.86$, $p < 0.01$), waters was significantly related to Mn, and area was significantly related to Sr and V, while an opposite observation of vegetation strongly contributing to Ba was found in this period. In the high flow period, only one landscape variable (urban) showed strong associations with Mn ($r = 0.90$, $p < 0.01$) (Table 2).

Within the 100 m riparian strip, similar to the observations at the subcatchment level, landscape variables were more associated with dissolved trace metals in the snow melt flow period. In the base flow period, shrub was significantly and negatively correlated to Cd and Pb, urban was positively correlated to Cd and bareland to Al, respectively. While only bareland was significantly related to Cr and Si in the high flow period (Table 2).

Stepwise multiple linear regression models indicated that more variables in the snow melt flow period could be explained by land use factors both within the subcatchment and along the 100 m riparian zone, followed by base flow period and only two elements were predictable by landscape variables in the high flow period (Table 3).

Generally, metal concentrations showed lowest values in the Jinshui and Ziwu Rivers (Fig. 2), where human activities were rare with highest vegetated coverage of 96% (Table 1). Highest concentrations of trace metals occurred in the downstream particularly the industrial polluted river (Sihe) (Fig. 2).

The varimax rotated PCA/FA results were presented in Table 4 with probable source types. Five factors were obtained which explained about 81% of the total variance, with the first factor accounting for 24.7%, the second factor for 24.4%, the third factor for 13%, the fourth factor for 11% and the fifth factor for 8.3%, respectively.

4. Discussion

4.1. Land use influences on trace metals

Past studies demonstrated that the concentrations of dissolved trace metals showed great spatio-temporal variations in the upper Han River [27,28]. It seemed that hydrological seasonality and spatial heterogeneity in land use and anthropogenic activities had strong effects on trace metals. Similar to the results on water physical-chemicals, our results demonstrated that landscape characteristics showed significant correlations with trace metals, particularly in the snow melt flows (Table 2). However, this result was opposite to the observation of water quality parameters (i.e., nitrogen), better explained by the landscape characteristics in high flows rather than in low flows (Table 3) [32], which might result from that non-point pollutants due to rain runoff greatly increased nutrients [29,33] while diluted effects by precipitation and spatial heterogeneity in landscape setting such as mineral and geology [9,17,34–36]. In addition, there were more metals showing strong correlations with land use characteristics at sucatchment level than within the 100 m riparian zone (Tables 2 and 3), which was similar to the results of land use and water quality interactions in the Han River [14,15] and other streams [12,13,37].

Basin physical characteristics in a watershed such as area, slope and soil properties also influenced trace metal compositions [13,38]. Area showed significant positive correlations with Fe, Sr, and Zn in the snow melt flows both at the catchment scale and in the riparian zone, while there were no significant relationships between area and metals in the high flows (Table 2). Table 3 showed that area at catchment scale better predicted Fe, Sr and Zn in the snow melt flows, and Sr and V in the base flows, similar results were found in the riparian strip except Sr in the base flows (Table 3). Thus, water flow seasonality played important roles in regulating river metals, as the increasing water flows and anthropogenic activities resulting in the weak associations between area and trace metals. We could hypothesize that area and other basin physical properties such as slope and soils greatly contribute to water variables in areas with little human disturbances in the low flow season.

Table 3 demonstrated metals predictable by varied landscape variables and some similar metals predictable by land use in the subcatchment level in both base flow and snow melt flow periods, while remarkably varying metals were predictable by landscape variables in all periods at buffer scale (Table 3). This could be explained by hydrological seasonality within the buffer strip having much higher explanative values to metals [13]. Compared to metals predictable by landscape variables in the snow melt flow period with little human disturbance, metals except Cr explained by land use within the 100 m buffer could be explained by land use in the subcatchment, while only Fe, Sr and Zn were predictable by the same variables in the both scales (Table 3). Few metals could be predictable by the same land variables in other water flow periods. Thus, there was great seasonality in terms of the influence of land use on metal concentrations [12], and intense anthropogenic activities and precipitation would weaken the land use and metal interactions in the upper Han River. Furthermore, those metals (i.e., As, Cd, Cr, Cu, Fe, Mn and Sr) which were significantly controlled by land use in different water flow periods were considered sensitively to landscape structure and could be used as reliable markers for anthropogenic processes in relation to land use [9].

Researchers reported that elevated metal compositions occurred in the industrial, residential, agricultural and traffic areas and low concentrations in the less developed areas [9,36]. Urban and agriculture mainly concentrated along river networks, i.e., agriculture accounted for 22–42% of the respective land area in the 100 m riparian zone, while in the subcatchment level, vegetated coverage and agriculture accounted for 71–96% and 3–21% of the respective land area in the upper Han River, respectively (Table 3). Consequently, anthropogenic contributions such as urban and agriculture within the 100 m riparian strip were more associated with metals rather than that in the subcatchment level. Our results demonstrated that urban areas showed strong positive correlations with more metal variables and could better explain metals at the subcatchment scale, while metals could be explained by forest, shrub and vegetation within the 100 m buffer (Table 3). This indicated that vegetated coverage in the riparian zone played a much more important role in mediating river metals.

Spatial characterization of trace metals in the Han River indicated higher concentrations of metals in rivers with intense human activities [27], and long-term use of chemical fertilizers and organic manures led to higher concentrations of As, Cd, Cr, Cu, Pb and Zn ([17]; Fig. 2). Most metals reached higher concentrations in the downstream particularly in the Sihe River, locating in an indus-

Table 2
Pearson correlation coefficients between trace metal concentration and landscape composition at the catchment level and in the 100 m riparian zone in the upper Han River basin, China.

	Forest	Shrub	Vegetation	Agriculture	Urban	Bareland	Waters	Area
Subcatchment Level								
Snow melt flow (April 2006)								
Al	−0.643	0.326	−0.699	0.275	0.191	0.605	0.931[a]	−0.179
As	0.307	−0.700	−0.124	0.324	0.872[a]	−0.246	−0.150	0.670
Ba	−0.350	0.142	−0.410	0.096	0.106	0.385	0.709[b]	−0.092
Cd	0.313	−0.715[b]	−0.127	0.275	0.873[a]	−0.170	−0.151	0.703
Cr	−0.219	-0.242	−0.534	0.436	0.308	0.349	0.131	0.318
Cu	−0.428	−0.162	−0.784[b]	0.582	0.621	0.479	0.446	0.345
Fe	−0.063	−0.081	−0.163	0.265	0.106	0.101	−0.436	0.848[a]
Mn	−0.436	−0.058	−0.709[b]	0.174	0.616	0.804[b]	0.720[b]	0.369
Mo	−0.159	0.321	0.028	0.386	−0.475	−0.401	−0.393	−0.427
Ni	−0.751[b]	0.325	−0.863[a]	0.463	0.357	0.648	0.920[a]	0.046
Sb	−0.053	0.218	0.103	−0.273	−0.362	0.318	−0.255	0.454
Si	0.468	−0.640	0.171	−0.490	0.320	0.216	0.283	−0.087
Sr	−0.166	0.020	−0.235	0.432	0.154	−0.014	−0.399	0.847[a]
Zn	0.183	−0.515	−0.155	0.086	0.594	0.198	−0.204	0.844[a]
Base flow (June 2006)								
Al	−0.086	−0.074	−0.192	−0.063	0.095	0.524	−0.184	0.385
As	0.291	−0.206	0.267	0.131	0.184	−0.512	−0.563	0.072
Ba	0.680	−0.344	0.739[b]	−0.616	−0.257	−0.377	−0.459	−0.534
Cd	0.335	−0.731	−0.107	0.334	0.892[a]	−0.306	−0.123	0.590
Co	0.481	−0.527	0.286	−0.304	0.316	−0.012	−0.399	0.219
Cu	−0.329	0.363	−0.193	0.209	−0.179	−0.075	0.465	−0.237
Li	−0.065	0.115	−0.003	0.161	−0.017	−0.350	0.344	−0.256
Mn	−0.403	−0.030	−0.635	0.270	0.687	0.462	0.866[a]	0.151
Mo	−0.303	0.471	−0.063	0.258	−0.370	−0.090	−0.297	−0.362
Ni	−0.205	−0.269	−0.536	0.277	0.865[a]	0.347	0.585	0.481
Pb	0.444	−0.660	0.117	−0.171	0.613	0.029	−0.209	0.404
Sb	−0.041	−0.002	−0.064	−0.268	−0.045	0.577	−0.188	0.443
Se	−0.192	0.235	−0.093	0.353	−0.118	−0.393	0.240	−0.279
Si	0.068	−0.367	−0.206	−0.057	0.606	0.401	0.054	0.535
Sr	−0.373	0.110	−0.473	0.643	0.368	0.035	−0.146	0.799[b]
V	−0.208	−0.015	−0.327	0.432	0.372	0.100	−0.285	0.883[a]
High flow (October 2006)								
Al	0.463	−0.510	0.273	−0.385	0.224	0.123	−0.359	0.171
As	−0.538	0.378	−0.496	0.471	−0.036	0.122	0.496	0.007
Ba	−0.280	0.298	−0.172	0.433	−0.321	−0.145	−0.250	0.002
Co	−0.413	0.368	−0.315	0.355	−0.072	−0.051	0.456	−0.064
Cr	−0.095	0.194	0.019	0.496	0.008	−0.645	−0.241	−0.137
Cu	−0.352	0.486	−0.124	0.446	−0.414	−0.264	−0.208	−0.027
Mn	−0.118	−0.393	−0.509	0.355	0.898[a]	0.239	0.429	0.384
Mo	−0.431	0.443	−0.281	0.573	−0.348	−0.211	−0.033	−0.214
Pb	0.211	0.064	0.373	−0.018	−0.480	−0.518	−0.356	−0.150
Sb	0.056	0.044	0.122	−0.431	−0.297	0.512	−0.299	0.243
Se	0.317	−0.329	0.203	−0.329	0.041	0.196	−0.353	0.033
Si	−0.004	−0.338	−0.290	−0.220	0.421	0.703	0.341	0.236
Sr	−0.579	0.424	−0.519	0.601	−0.016	0.166	0.008	0.528
V	−0.721[b]	0.650	−0.545	0.415	−0.191	0.451	0.128	0.332

	Forest	Shrub	Vegetation	Agriculture	Urban	Bareland	Area
100 m Riparian Zone							
Snow melt flow (April 2006)							
Al	−0.410	0.240	−0.245	0.070	−0.194	0.382	−0.520
As	0.556	−0.934[a]	−0.414	0.424	0.681	−0.143	0.658
Ba	−0.148	0.245	0.105	−0.269	−0.094	0.261	−0.401
Cd	0.527	−0.930[a]	−0.447	0.409	0.633	−0.047	0.692
Cr	−0.441	−0.142	−0.753[b]	0.611	0.016	0.371	0.264
Cu	−0.350	−0.305	−0.832[a]	0.614	0.182	0.452	0.177
Fe	−0.301	−0.206	−0.648	0.648	0.020	0.126	0.897[a]
Mn	−0.226	−0.198	−0.539	0.101	−0.022	0.797[b]	0.068
Mo	−0.352	0.422	0.054	0.171	0.076	−0.383	−0.204
Ni	−0.424	0.172	−0.347	0.087	−0.011	0.477	−0.327
Sb	−0.445	0.153	−0.398	0.439	−0.590	0.202	0.485
Si	0.291	−0.493	−0.222	0.199	−0.283	0.169	−0.132
Sr	−0.204	−0.134	−0.433	0.407	0.262	0.047	0.853[a]
Zn	0.095	−0.695	−0.726[b]	0.610	0.159	0.280	0.846[a]
Base flow (June 2006)							
Al	−0.355	0.018	−0.445	0.039	−0.152	0.768[b]	0.454
As	0.394	−0.378	0.054	0.055	0.490	−0.333	0.315
Ba	0.449	−0.084	0.487	−0.421	−0.088	−0.175	−0.237
Cd	0.625	−0.945[a]	−0.337	0.359	0.739[b]	−0.197	0.577
Co	0.356	−0.490	−0.132	−0.054	0.149	0.267	0.408
Cu	−0.102	0.327	0.266	−0.065	−0.051	−0.351	−0.456

Table 2 (*Continued*)

	Forest	Shrub	Vegetation	Agriculture	Urban	Bareland	Area
Li	0.234	0.018	0.330	−0.001	0.134	−0.619	−0.415
Mn	0.106	−0.265	−0.185	−0.071	0.238	0.361	−0.210
Mo	−0.355	0.479	0.121	−0.192	0.081	0.061	−0.169
Ni	0.270	−0.561	−0.333	0.085	0.400	0.327	0.192
Pb	0.473	−0.716[b]	−0.256	0.058	0.305	0.265	0.487
Sb	−0.360	0.082	−0.373	0.001	−0.349	0.762[b]	0.488
Se	0.070	0.186	0.320	−0.007	0.209	−0.615	−0.398
Si	0.155	−0.502	−0.410	0.051	0.169	0.588	0.488
Sr	−0.127	−0.125	−0.321	0.178	0.521	0.125	0.705
V	−0.090	−0.249	−0.423	0.249	0.394	0.233	0.855[a]
High flow (October 2006)							
Al	0.219	−0.393	−0.194	−0.032	−0.022	0.397	0.359
As	−0.345	0.311	−0.072	0.159	0.008	−0.123	−0.246
Ba	−0.389	0.459	0.051	−0.038	0.137	−0.075	0.063
Co	−0.137	0.266	0.146	0.032	0.050	−0.320	−0.306
Cr	0.197	−0.072	0.170	0.166	0.513	−0.717[b]	−0.042
Cu	−0.442	0.354	−0.147	0.474	−0.049	−0.460	0.029
Mn	0.259	−0.662	−0.470	0.263	0.469	0.271	0.205
Mo	−0.459	0.480	−0.016	0.207	0.088	−0.321	−0.203
Pb	0.033	0.242	0.339	0.025	−0.055	−0.616	−0.050
Sb	−0.445	0.185	−0.358	0.108	−0.581	0.643	0.372
Se	0.003	−0.135	−0.161	−0.111	−0.110	0.489	0.237
Si	−0.140	−0.270	−0.514	0.106	−0.238	0.813[b]	0.137
Sr	−0.466	0.312	−0.231	0.128	0.191	0.147	0.392
V	−0.654	0.588	−0.139	−0.144	−0.046	0.481	0.192

Vegetation includes Forest and Shrub The neglected variables have values lower than MDL.

[a] Significance at the 0.01 probability level.

[b] Significance at the 0.05 probability level.

trial region. However, weak associations between agriculture and metals were found and urban areas existed positive correlations with less than 2 metals (Table 2). Past reports also demonstrated the weak associations between human activities and major elements [15], though they were remarkably higher in the polluted river (Fig S1). Therefore, we could argue that, similar to the water quality and major chemical variables which were largely impacted by human activities in some rivers, trace metals in the Han River were slightly explained by anthropogenic activities at the catchment scale.

4.2. Source identification and apportionment

Kaiser-Meyer-Olkin (KMO) and Bartlett's sphericity tests were performed to examine the validity of PCA. KMO and Bartlett's results were 0.69 and 1621 (df = 105, $p < 0.001$), respectively, indicating that PCA would be effective in reducing dimensionality of the data set.

Five PCs with eigenvalue > 1, explaining about 81.2% of the total variance were extracted by varimax rotated PCA/FA (Table 4). The first component had high loadings on Cd, Mn, Ni and Zn, and appeared to represent industry including mining activities and associating oil combustion (V, Ni). That had been evident of higher concentration in the polluted river (Sihe, Fig. 2). The second component was largely dependent upon the combination of natural (Fe), mineral (As and Cu) and fuel combustion (Se and V) [21,24]. The third component was associated with As, Cr, Mo and Pb. Both As and Pb were known as markers of paint industries, and Pb was also highly enriched in vehicle exhaust [20,24]. The fourth component was characterized by high loading of Al and Si, and weak loadings of Fe. These elements were often found in crustal components [20,21], and therefore could be identified as crustal origin. The fifth component included Sb with weak loading of Cr and Mo, which was assumed to be from Sb-contained mineral and mining activities. Also, another major source for Sb was the wear of the brake lining and other metallic parts of vehicles.

After qualitative determination of possible sources using rotated PCA/FA, source apportionment of each source type was estimated using FA-MLR (Table 4), a proven effective receptor modeling quantifying source contributions [20–24]. The accuracy of the FA-MLR model was tested by the ratio of mean observed to predicted values of the elements (Table 5). The results showed that the predicted values were very close to observed values and all the trace metals had higher correlation coefficients (R^2) except Pb.

The source contribution demonstrated that there were combined contributions particularly on factor 2, indicating by the second component with moderate/low loadings on As and Pb (Table 4). This observation was not the same clearer source identification of major concern variables showing high loadings with factor representing anthropogenic source as in the industrial polluted area [i.e., 20]. However, natural source (crustal) (Factor 4) and Sb-mineral (Factor 5) had critic markers, supporting our observation of anthropogenic activities such as urban and agriculture could not better predict trace metals. Nevertheless, source apportionment indicated that major metals of As ($\sim$63%), Pb ($\sim$63%) and Se ($\sim$86%) and V ($\sim$74%) largely contributed by mining, vehicle and paint industry (Table 5). 76% of Sb could be contributed by both high background value and Sb-rich mineral processes and brake lining wear (Table 5). In terms of natural tracers of Al and Si, geological sources contributed about 70% to the both variables, as reflected by factors 2 and 4 (Table 5).

The correlation analysis was used for land use influences on metals (Table 2). Yet, multivariate analysis was applied for source apportionments (Table 5). The correlation coefficient matrix measures how well the variance of each constituent can be explained by relationship with each others, it discovers the common sources of some variables with strong associations, and however, it could not identify the sources and quantify the contributions of each source.

Because of geographical heterogeneity in anthropogenic activities, each source to measured variables in each subcatchment was understandably varying, i.e., Hanzhong Plain (SUB 4) and Reservoir region (SUB 8) with higher contents of metals due to intense agricultures and urbanization (Hanzhong city, and Danjiangkou and Shiyan cities) (Table S3) [14,15]. Industrial effluents in this region would contribute more to metal species; however, this work presented general information on the source apportionment of metals

Table 3
Stepwise multiple regression models for trace metals and land use composition at the catchment level and in the 100 m riparian zone in the upper Han River basin, China.

	Variable	Independent variables	Regression equations	R^2	Adjusted R^2
Subcatchment level					
Snow melt flow (April 2006)	Al	Waters	1.725 + 6.613WAT	0.868	0.845
	As	Urbans, Waters	−0.157 + 8.289URB −0.952WAT	0.924	0.894
	Ba	Waters	55.697 + 122.117WAT	0.503	0.420
	Cd	Urbans, Waters	−0.007 + 0.547 + URB −0.063WAT	0.929	0.900
	Cu	Vegetation	4.176 − 0.041VEG	0.614	0.550
	Fe	Area, Urbans	44.465 + 3.576AREA −22.326URB	0.916	0.883
	Mn	Bareland, Urbans, Area	−0.900 + 3.523BAR +28.602URB − 0.491AREA	0.996	0.994
	Ni	Waters, Vegetation	3.869 + 0.255WAT −0.037VEG	0.969	0.956
	Sr	Area	70.503 + 5.895AREA	0.717	0.670
	Zn	Area	−2.434 + 0.406AREA	0.713	0.665
Base flow (June 2006)	Ba	Vegetation	517.504 + 8.553VEG	0.547	0.471
	Cd	Urbans, Waters	−1.082 + 10.837URB −1.160WAT	0.943	0.920
	Mn	Waters, Urbans	−11.022 + 14.160WAT + 34.881URB	0.968	0.955
	Ni	Urbans	0.020 + 1.222URB	0.749	0.707
	Sr	Area	116.368 + 7.792AREA	0.639	0.579
	V	Area	61.861 + 1.388AREA	0.781	0.744
High flow (October 2006)	Mn	Urbans	3.752 + 19.230URB	0.806	0.773
	V	Forest	65.728 − 0.480FOR	0.520	0.440
100 m Riparian zone					
Snow melt flow (April 2006)	As	Shrub	12.796 − 0.288SHR	0.873	0.852
	Cd	Shrub	0.842 − 0.019SHR	0.865	0.843
	Cr	Vegetation	12.655 − 0.104VEG	0.568	0.496
	Cu	Vegetation	2.997 − 0.038VEG	0.693	0.641
	Fe	Area, Forest	59.905 + 2.546AREA −0.526FOR	0.939	0.915
	Mn	Bareland	0.448 + 2.718BAR	0.636	0.575
	Sr	Area	78.496 + 5.257AREA	0.728	0.683
	Zn	Area	−1.862 + 0.360AREA	0.716	0.669
Base flow (June 2006)	Al	Bareland	−19.796 + 8.327BAR	0.590	0.522
	Cd	Shrub, Urban	11.253 − 0.307SHR +0.866URB	0.963	0.949
	Pb	Shrub	6.329 − 0.123SHR	0.513	0.432
	Sb	Bareland	1.828 + 0.744BAR	0.580	0.510
	V	Area	64.358 + 1.189AREA	0.731	0.686
High flow (October 2006)	Cr	Bareland	28.983 − 1.745BAR	0.514	0.433
	Si	Bareland, Shrub	6413.677 + 234.858BAR −57.061SHR	0.880	0.833

Water quality variables without regression models are not listed. Vegetation includes Forest and Shrub. Significance at the 0.05 probability level.

Table 4
Varimax rotated factor loading and corresponding possible source type (the significance of KMO and Bartlett's sphericity test is <0.001).

	F1	F2	F3	F4	F5
Al	−0.096	−0.018	0.110	0.871	0.166
As	0.167	0.511	0.520	0.252	−0.194
Cd	0.945	0.108	0.016	0.035	−0.011
Cr	−0.096	−0.205	0.789	0.123	−0.323
Cu	0.037	0.916	−0.082	−0.184	−0.034
Fe	0.084	−0.815	−0.279	−0.317	0.085
Mn	0.888	0.044	−0.019	0.052	−0.085
Mo	−0.054	−0.205	0.758	−0.182	0.387
Ni	0.930	−0.125	−0.002	0.047	0.054
Pb	0.252	0.379	0.435	0.172	0.055
Sb	−0.051	0.075	−0.043	0.125	0.928
Se	0.026	0.856	−0.413	−0.066	0.108
Si	0.318	0.157	−0.022	0.746	−0.057
V	0.046	0.931	−0.096	0.164	0.142
Zn	0.962	0.084	0.039	0.067	−0.039
Eigenvalue	4.23	3.32	2.14	1.36	1.13
Cumulative %	24.67	49.07	61.98	72.97	81.23
Possible source type	Mining activity	Natural, mineral, fuel combustion	Mixing of vehicle exhaust, paint	Crustal	Sb-mineral and brake lining wear

Extraction method: Principal Component Analysis; Rotation method: Varimax with Kaiser Normalization.

Table 5
Source contribution (in %) and the observed to predicted ratios (O/P) of elements calculated using FA-MLR technique.

	F1	F2	F3	F4	F5	O/P[a]	R^2	Communality[b]
Al	7.60	1.40	8.73	69.08	13.20	1.00	0.80	0.808
As	10.18	31.09	31.61	15.35	11.77	1.00	0.65	0.661
Cd	84.73	9.70	1.45	3.12	1.00	1.00	0.90	0.906
Cr	6.23	13.35	51.37	8.02	21.03	1.00	0.78	0.793
Cu	2.94	73.14	6.52	14.72	2.69	1.00	0.88	0.882
Fe	5.34	51.62	17.64	20.04	5.36	1.00	0.85	0.857
Mn	81.65	4.04	1.72	4.79	7.80	1.00	0.79	0.802
Mo	3.38	12.92	47.82	11.47	24.41	1.00	0.80	0.803
Ni	80.29	10.82	0.18	4.02	4.70	1.00	0.88	0.886
Pb	19.50	29.36	33.63	13.28	4.23	1.00	0.41	0.429
Sb	4.20	6.13	3.53	10.19	75.96	1.00	0.88	0.888
Se	1.80	58.23	28.11	4.51	7.36	1.00	0.92	0.921
Si	24.44	12.08	1.69	57.42	4.36	1.00	0.67	0.686
V	3.31	67.54	6.93	11.87	10.34	1.00	0.92	0.924
Zn	80.74	7.04	3.28	5.64	3.30	1.00	0.94	0.941

F1 – mining activity and other industry. F2 – natural, mineral and fuel (coal) combustion. F3 – mixing of vehicle exhaust and paint. F4 – crustal. F5 – Sb-rich mineral and brake lining wear. *R* is the adjusted multiple correlation coefficient.

[a] Mean ratio of average observed to predicted values of element.

[b] Derived from rotated PCA.

for the whole catchment, which is more important for water conservation for the interbasin South–North Water Transfer project.

5. Conclusions

Our results demonstrated the influence of the interaction of hydrological seasonality and landscape structure on metal concentrations in rivirine network. Metal variables were better predicted by land use away from rivers than land use close to rivers. At the catchment scale, urban was a better predictor of metals, while at the buffer scale, vegetation and shrub were the better predictors in the snow melt and base flow periods, and bareland was the predictor in the high flow period. Furthermore, remarkably varied metals were predictable by landscape variables along river networks among water flow sesonality, which suggested that hydrological seasonality within the buffer zone had much higher explanative values to metals. However, almost similar metals were explained by land use in the both subcatchment and buffer zone in the snow melt flow period. FA-MLR model provided apportionment of five sources to trace metals. It revealed that mining, fuel combustion and vehicle exhaust were among the major polluting sources responsible for metal concentrations in river water. This study also demonstrated the value of multivariate statistic techniques in identification and apportionment of pollution sources, which would help to develop strategies for water resource management.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.03.026.

References

[1] J.O. Nriagu, A history of global metal pollution, Science 272 (1996) 223–224.

[2] K. Bengraine, T.F. Marhaba, Using principal component analysis to monitor spatial 359 and temporal changes in water quality, J. Hazard. Mater. B100 (2003) 179–195.

[3] R. Cidu, R. Biddau, Transport of trace elements under different seasonal conditions: effects on the quality of river water in a Mediterranean area, Appl. Geochem. 22 (2007) 2777–2794.

[4] E. Pertsemli, D. Voutsa, Distribution of heavy metals in Lakes Doirani and Kerkini, Northern Greece, J. Hazard. Mater. 148 (2007) 529–537.

[5] A.K. Krishna, M. Satyanarayanan, P.K. Govil, Assessment of heavy metal pollution in water using multivariate statistical techniques in an industrial area: a case study from Patancheru, Medak District, Andhra Pradesh, India, J. Hazard. Mater. 167 (2009) 366–373.

[6] S. Li, X. Cheng, Z. Xu, H. Han, Q. Zhang, Spatial and temporal patterns of the water quality in the Danjiangkou Reservoir, China, Hydrol. Sci. J. 54 (2009) 124–134.

[7] B.L. Peierls, N.F. Caraco, M.L. Pace, J.J. Cole, Human influence on river nitrogen, Nature 350 (1991) 386–387.

[8] S. Li, Z. Xu, X. Cheng, Q. Zhang, Dissolved trace elements and heavy metals in the Danjiangkou Reservoir China, Environ. Geol. 55 (2008) 977–983.

[9] S.S. Park, S.O. Kim, S.T. Yun, G.T. Chae, S.Y. Yu, S. Kim, Y. Kim, Effects of land use on the spatial distribution of trace metals and volatile organic compounds in urban groundwater, Seoul, Korea, Environ. Geol. 48 (2005) 1116–1131.

[10] P. Panichayapichet, S. Nitisoravut, W. Simachaya, Spatial distribution and transport of heavy metals in soil, ponded-surface water and grass in a Pb-contaminated watershed as related to land-use practices, Environ. Monit. Assess. 135 (2007) 181–193 (x).

[11] L.B. Johnson, C. Richards, G.E. Host, J.W. Arthur, Landscape influences on water chemistry in Midwestern stream ecosystems, Freshwater Biol. 37 (1997) 193–208.

[12] L. Sliva, D.D. Williams, Buffer zone versus whole catchment approaches to studying land use impact on river water quality, Water Res. 35 (2001) 3462–3472.

[13] J. Meynendonckx, G. Heuvelmans, B. Muys, J. Feyen, Effects of watershed and riparian zone characteristics on nutrient concentrations in the River Scheldt Basin, Hydrol. Earth Syst. Sci. 10 (2006) 913–922.

[14] S. Li, S. Gu, W. Liu, H. Han, Q. Zhang, Water quality in relation to the land use and land cover in the Upper Han River basin, China, Catena 75 (2008) 216–222.

[15] S. Li, S. Gu, X. Tan, Q. Zhang, Water quality in the upper Han River basin, China: the impacts of land use/land cover in riparian buffer zone, J. Hazard. Mater. 165 (2009) 317–324.

[16] W. Luo, Y. Lu, J.P. Giesy, T. Wang, Y. Shi, G. Wang, Y. Xing, Effects of land use on concentrations of metals in surface soils and ecological risk around Guanting Reservoir, China, Environ. Geochem. Health 29 (2007) 459–471.

[17] S. Huang, J. Jin, Status of heavy metals in agricultural soils as affected by different patterns of land use, Environ. Monit. Assess. 139 (2008) 317–327.

[18] H. Hertler, A.R. Boettner, G.I. Ramirez-Toro, H. Minnigh, J. Spotila, D. Kreeger, Spatial variability associated with shifting land use: Water quality and sediment metals in La Parguera, Southwest Puerto Rico, Mar. Pollut. Bull. 58 (2009) 672–678.

[19] K.P. Singh, A. Malik, S. Sinha, Water quality assessment and apportionment of pollution sources of Gomti river (India) using multivariate statistical techniques-a case study, Anal. Chim. Acta 538 (2005) 355–374.

[20] H. Pekey, D. Karakas, M. Bakoglu, Source apportionment of trace metals in surface waters of a polluted stream using multivariate statistical analyses, Mar. Pollut. Bull. 49 (2004) 809–818.

[21] H. Guo, A.J. Ding, K.L. So, G. Ayoko, Y.S. Li, W.T. Hung, Receptor modeling of source apportionment of Hong Kong aerosols and the implication of urban and regional contribution, Atmos. Environ. 43 (2009) 1159–1169.

[22] V. Simeonov, J. Stratis, C. Samara, G. Zachariadis, D. Voutsa, A. Anthemidis, M. Sofoniou, Th. Kouimtzis, Assessment of the surface water quality in Northern Greece, Water Res. 37 (2003) 4119–4124.
[23] V. Simeonov, J.W. Einax, S. Tsakovski, J. Kraft, Multivariate statistical assessment of polluted soils, Cent. Eur. J. Chem. 3 (2005) 1–9.
[24] G.D. Thurston, N.D. Spengler, A quantitative assessment of source contributions to inhalable particulate matter pollution in metropolitan Boston, Atmos. Environ. 19 (1985) 9–25.
[25] S. Li, Q. Zhang, Geochemistry of the upper Han River basin, China. 1: spatial distribution of major ion compositions and their controlling factors, Appl. Geochem. 23 (2008) 3535–3544.
[26] S. Li, Q. Zhang, Geochemistry of the upper Han River basin, China. 2: seasonal variations in major ion compositions and contribution of precipitation chemistry to the dissolved load, J. Hazard. Mater. 170 (2009) 605–611.
[27] S. Li, Q. Zhang, Spatial characterization of dissolved trace elements and heavy metals in the upper Han River (China) using multivariate statistical techniques, J. Hazard. Mater. 176 (2010) 579–588.
[28] S. Li, Q. Zhang, Risk assessment and seasonal variations of dissolved trace elements and heavy metals in the Upper Han River, China, J. Hazard. Mater. 181 (2010) 1051–1058.
[29] S. Li, W. Liu, S. Gu, X. Cheng, Z. Xu, Q. Zhang, Spatio-temporal dynamics of nutrients in the upper Han River basin, China, J. Hazard. Mater. 162 (2009) 1340–1346.
[30] S. Li, Z. Xu, H. Wang, J. Wang, Q. Zhang, Geochemistry of the upper Han River basin, China. 3: anthropogenic inputs and chemical weathering to the dissolved load, Chem. Geol. 264 (2009) 89–95.
[31] R.M. Harrison, D.J.T. Smith, L. Luhana, Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, U.K, Environ. Sci. Technol. 30 (1996) 825–832.
[32] S. Li, Q. Zhang, Interaction of landscape setting and stream flow seasonality on nitrogen concentrations in a subtropical river, China. Acta Oecologica. Under review.
[33] S.R. Carpenter, N.F. Caraco, D.R. Correll, R.W. Howarth, A.N. Sharpley, V.H. Smith, Non-point pollution of surface waters with phosphorus and nitrogen, Ecol. Appl. 8 (1998) 559–568.
[34] A. Sainz, J.A. Grande, M.L. de la Torre, Characterisation of sequential leachate discharges of mining waste rock dumps in the Tinto and Odiel rivers, Environ. Manage. 64 (2002) 345–353.
[35] M.B. Lohani, A. Singh, D.C. Rupainwar, D.N. Dhar, Seasonal variations of heavy metal contamination in river Gomti of Lucknow city region, Environ. Monit. Assess. 147 (2008) 253–263.
[36] L.L. Tiefenthaler, D.D. Stein, K.C. Schiff, Watershed and land use-based sources of trace metals in urban storm water, Environ. Toxicol. Chem. 27 (2008) 277–287.
[37] C.T. Hunsaker, D.A. Levine, Hierarchical approaches to the study of water quality in rivers, BioScience 45 (1995) 193–203.
[38] R.B. Alexander, R.A. Smith, G.E. Schwarz, Effects of stream channel size on the delivery of nitrogen to the Gulf of Mexico, Nature 403 (2000) 758–761.