Effects of Catchment and Riparian Landscape Setting on Water Chemistry and Seasonal Evolution of Water Quality in the Upper Han River Basin, China

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Abstract

Six-year (2005–2010) evolution of water chemistry (Cl\(^{-}\), NO\(_3\)\(^{-}\), SO\(_4\)\(^{2-}\), HCO\(_3\)\(^{-}\), Na\(^{+}\), K\(^{+}\), Ca\(^{2+}\) and Mg\(^{2+}\)) and their interactions with morphological properties (i.e., slope and area), land cover, and hydrological seasonality were examined to identify controlling factors and processes governing patterns of stream water quality in the upper Han River, China. Correlation analysis and stepwise multiple regression models revealed significant correlations between ions (i.e., Cl\(^{-}\), SO\(_4\)\(^{2-}\), Na\(^{+}\) and K\(^{+}\)) and land cover (i.e., vegetation and bare land) over the entire catchment in both high- and low-flow periods, and in the buffer zone the correlation was much more stronger in the low-flow period. Catchment with steeper slope (>15°) was negatively correlated with major ions, largely due to multicollinearity of basin characteristics. Land cover within the buffer zone explained slightly less of major elements than at catchment scale in the rainy season, whereas in the dry season, land cover along the river networks in particular this within 100 m riparian zone much better explained major elements rather than this over the entire catchment. Anthropogenic land uses (i.e., urban and agriculture) however could not explain water chemical variables, albeit EC, TDS, anthropogenic markers (Cl\(^{-}\), NO\(_3\)\(^{-}\), SO\(_4\)\(^{2-}\)), Na\(^{+}\), K\(^{+}\) and Ca\(^{2+}\) significantly increased during 2005–2010, which was corroborated by principal component analyses (PCA) that indicated anthropogenic inputs. Observations demonstrated much higher solute concentrations in the industrial-polluted river. Our results suggested that seasonal evolution of water quality in combined with spatial analysis at multiple scales should be a vital part of identifying the controls on spatio-temporal patterns of water quality.

Introduction

The geochemical study of water major ions reveals the character of water–rock interactions and other various natural (i.e., evaporation and precipitation) and anthropogenic processes in the drainage basin and plays an important role in understanding stream mineralogy/petrology, as well as chemical weathering rates and associating CO\(_2\) consumption, which are greatly affected by meteoric water and land coverage [1–6]. Studies indicated that human activities strongly modified the compositions of major chemical species (e.g., [5], [7]), for instance, nitrate was predominantly controlled by anthropogenic origins especially with the applications of fertilizers [8], [9] and urbanisation [10]. Chen et al [5], [11] also reported persistent increases in Cl\(^{-}\) and SO\(_4\)\(^{2-}\) concentrations in the large China’s Rivers of Yangtze and Yellow. Numerous studies have related landscape to water quality especially nutrients using empirical techniques such as correlation analysis and stepwise multiple linear regression models [7], [12–15], and indicated that basin physical characteristics such as land use types, morphological characteristics and local geology substantially influence the hydrology and water variables, and consequently mediate fluvial chemical compositions [10], [16], [17]. Their relative impacts on water chemistry depend on geographical scale (e.g., local, regional, national, continental and global) and sampling factors (e.g., random versus geostatistical; high versus low density). In general, large geographical scale with low density or random sampling tends to identify geologic factors whereas limited geographical scale with high density or geostatistical sampling tends to identify land use/land cover factors. However, the relative influences of land cover in catchment vs riparian zone and diverse riparian land cover on water quality are mixed (cf. [10], [13], [14]).

Previous studies on the upper Han River have characterized water quality [18], water geochemistry and chemical weathering process [19–21], and relationships between water quality and land use/land cover using multivariate statistics from samples over 2005–2006 [22], [23]. They revealed that water quality parameters (e.g., nitrogen, phosphorus, total suspended solid and chemical oxygen demand) were better explained by land cover (bare land, agriculture and urbanisation) within the catchment rather than land cover close to rivers, as well as major elements were predictable by bare land and vegetation within 100 m riparian zone [23]. Whereas, the influences of interactions of land use/land cover relating to multiple spatial scales, topography, and hydrological seasonality on water chemistry, as well as their long-term trends are unavailable. Recent reports have emphasized the

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effects of basin physical characteristics (topography, soil, geology and hydrology) on water quality [10], [17]. The relative importance of varying riparian land cover on major chemical species is, however, poorly understand, which is critical for determining the desirable width of a riparian zone in water conservation [14].

The objectives of the present study were therefore to (1) examine the relationships between major chemical species, catchment landscape variables (i.e., composition of land cover) and physical characteristics (i.e., slope and hydrology), (2) determine the effective riparian width (100 m, 200 m or 500 m) on water chemistry, and (3) reveal 6-year evolution of water quality in the river. Thus, the original contribution of the manuscript, with respect to earlier works, is that varied riparian land cover and landscape variables such as slope and area within the subcatchment are taken into consideration. The other important contribution is long-term variations in water quality particularly anthropogenic markers of variables such as Cl⁻, NO₃⁻, SO₄²⁻, etc.

Materials and Methods

2.1. Ethics statement

No specific permits were required for the described field studies and our field studies did not involve endangered or protected species.

2.2. Study area

The upper Han River (31°20’–34°10’N, 106°–112°E; 210–3500 m a.s.l.), a north sub-tropic basin supplying water to north China through the South-to-North Water Transfer Project (SNWTP), is situated between the northern Daba Mountains and the southern Qinling Mountains with a drainage area of approximately 95, 200 km² and 925 km long (Fig. 1). The average annual precipitation is 700–1,800 mm, and 80% of which falls in the rainy season, generally from May to October. The dominant land cover categories are vegetated lands, followed by cultivated land and bare land, respectively 77%, 15% and 6% of the total area. Areas with intensive anthropogenic activities including cultivation and urban lands are distributed along the river.

Figure 1. Sampling locations and the delineation of 9 subcatchments in the upper Han River basin, China. (SUB 1-Laoguan River, SUB 2-Dan River, SUB 3-South of the Qinling Mountains, SUB 4-Ziwu River, SUB 5-Hanzhong Plain, SUB 6-North of the Daba Mountains, SUB 7-Ankang Plain, SUB 8-Du River, and SUB 9-Danjiangkou Reservoir region). (42 sampling sites during 2005–2006, while 24 sampling sites from 2007 onwards including sites no. 1, 6, 7, 10-13, 15, 18-23, 26, 27, 29, 31, 32, 35, 38, 39, 41 and 42). doi:10.1371/journal.pone.0053163.g001
Figure 2. Land use compositions within the subcatchment (a), 100 m (b), 200 m (c) and 500 m (d) riparian zones in the upper Han River basin, China. Symbols are the same for these 4 panels except no waters for b, c and d.
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analyses of a set of samples. The analytical precision was within these quality control standards before, during and after the procedures. Each calibration curve was evaluated by analyses of determined in parallel to the sample treatment using identical determined using Dionex Ion Chromatograph (Dionex Corporation, Sunnyvale, CA, USA). Reagent and procedural blanks were determined in parallel to the sample treatment using identical procedures. Each calibration curve was evaluated by analyses of these quality control standards before, during and after the analyses of a set of samples. The analytical precision was within ±10%.

Previous studies reported the relationships between water quality and land use/land cover (LULC) near the Danjiangkou Reservoir [18], [22], [23]. Rapid urbanisation is challenging local water and soil conservation.

### 2.3. Data sources

17 field campaigns (Jun., Aug., and Nov. 2005, Apr., Jun. and Oct. 2006, May and Nov. 2007, Jul. and Nov. 2008, Apr., Aug. and Nov. 2009, Jan., Apr., Aug. and Nov. 2010) during 2005–2010 were conducted. Of which, the first six surveys in 2005–2006 included 42 sites representing varied landscape settings of the upper basin, while surveys from 2007 onward included 24 sites (Fig. 1). Samples during 2005–2006 were selected for modeling the relations between water quality and landscape settings. August and November 2005 and October 2006 were the rainier season; thus there were 126 water samples in the high and low flow periods, respectively. Waters were collected at a depth of 10 cm using a small portion of filtered solution for anion measurements and another portion acidified using ultra-pure concentrated nitric acid on the sampling day. Major cations (Na\(^+\), K\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\)) were determined using Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) (IRIS Intrepid II XSP DUO, USA). Anions (Cl\(^-\), NO\(_3\)\(^-\), SO\(_4\)\(^{2-}\) and HCO\(_3\)\(^-\)) were determined using Dionex Ion Chromatograph (Dionex Corporation, Sunnyvale, CA, USA). Reagent and procedural blanks were determined in parallel to the sample treatment using identical procedures. Each calibration curve was evaluated by analyses of these quality control standards before, during and after the analyses of a set of samples. The analytical precision was within ±10%.

Previous studies reported the relationships between water quality and land use/land cover (LULC) in 100 m buffer along networks, i.e., Hanzhong Plain, Ankang Plain and catchments near the Danjiangkou Reservoir [18], [22], [23]. Rapid urbanisation is challenging local water and soil conservation.

### Table 1. Morphological element compositions including slope, catchment area and land use in different slope in the upper Han River basin, China.

| Subcatchment | VEG | AGR | Area | VEG | AGR | Area | VEG | AGR | Area | Catchment Area |
|--------------|-----|-----|------|-----|-----|------|-----|-----|------|----------------|
| SUB 1 | 1.254 | 0.62 | 26.68 | 21.59 | 1.91 | 25.10 | 33.19 | 1.25 | 35.76 | 11.68 | 0.28 | 12.26 | 4180 |
| SUB 2 | 2.087 | 0.84 | 23.37 | 23.00 | 2.76 | 29.34 | 32.55 | 1.96 | 37.98 | 8.31 | 0.34 | 9.31 | 11300 |
| SUB 3 | 3.615 | 1.24 | 8.10 | 14.16 | 1.88 | 17.07 | 35.53 | 3.91 | 46.18 | 28.41 | 2.87 | 33.15 | 15700 |
| SUB 4 | 5.664 | 0.87 | 7.00 | 16.20 | 0.81 | 17.52 | 43.66 | 1.07 | 45.47 | 29.39 | 0.39 | 30.01 | 4030 |
| SUB 5 | 11.411 | 9.11 | 22.49 | 15.82 | 2.90 | 19.19 | 30.48 | 3.05 | 33.98 | 23.17 | 0.94 | 24.34 | 18900 |
| SUB 6 | 6.323 | 1.76 | 7.58 | 10.80 | 3.16 | 15.82 | 29.86 | 6.31 | 39.87 | 30.73 | 3.62 | 36.74 | 9230 |
| SUB 7 | 3.889 | 4.40 | 10.30 | 11.03 | 4.77 | 18.15 | 31.44 | 7.34 | 42.20 | 25.18 | 2.73 | 29.35 | 8880 |
| SUB 8 | 10.616 | 0.69 | 11.35 | 15.31 | 3.72 | 19.44 | 35.53 | 4.63 | 40.56 | 26.78 | 1.74 | 28.65 | 12500 |
| SUB 9 | 13.408 | 5.24 | 33.62 | 18.55 | 2.65 | 24.11 | 25.73 | 1.58 | 28.70 | 12.91 | 0.28 | 13.57 | 9940 |

### Table 2. Pearson correlation coefficients between land use/land cover (LULC) in the subcatchment and river major elements of the upper Han River basin, China.

| Subcatchment | URB | AGR | BAR | VEG | WAT | AREA |
|--------------|-----|-----|-----|-----|-----|------|
| Rainy season | T    | 0.247 | 0.347 | 0.315 | 0.394 | 0.080 |
| pH          | -0.682 | -0.284 | -0.279 | 0.476 | 0.074 | 0.283 |
| EC          | -0.079 | 0.210 | 0.650 | -0.498 | 0.022 | 0.257 |
| TDS         | -0.079 | 0.209 | 0.650 | -0.498 | 0.022 | 0.257 |
| NO\(_3\)\(^-\) | 0.231 | 0.178 | 0.857 | -0.776 | 0.854 | 0.035 |
| SO\(_4\)\(^{2-}\) | 0.138 | 0.219 | 0.848 | -0.765 | 0.704 | 0.027 |
| HCO\(_3\)\(^-\) | -0.245 | 0.155 | 0.175 | -0.095 | 0.508 | 0.386 |
| Na\(^+\) | 0.277 | 0.175 | 0.909 | -0.712 | 0.374 | 0.094 |
| K\(^+\) | 0.132 | 0.226 | 0.843 | -0.421 | 0.586 | 0.465 |
| Ca\(^{2+}\) | -0.126 | 0.139 | 0.401 | -0.258 | -0.282 | 0.289 |
| Mg\(^{2+}\) | -0.111 | 0.146 | 0.633 | -0.418 | -0.144 | 0.270 |

| Dry season | T    | 0.043 | 0.128 | 0.619 | 0.557 | 0.666 | 0.097 |
| pH          | -0.628 | -0.415 | 0.169 | 0.344 | -0.541 | -0.592 |
| EC          | 0.382 | 0.281 | 0.552 | -0.508 | -0.085 | 0.315 |
| TDS         | 0.382 | 0.280 | 0.552 | -0.508 | -0.085 | 0.315 |
| NO\(_3\)\(^-\) | 0.543 | 0.382 | 0.589 | -0.628 | 0.009 | 0.176 |
| SO\(_4\)\(^{2-}\) | 0.346 | 0.155 | 0.732 | -0.613 | 0.423 | -0.074 |
| HCO\(_3\)\(^-\) | 0.231 | 0.229 | 0.330 | -0.281 | -0.400 | 0.401 |
| Na\(^+\) | 0.464 | 0.146 | 0.742 | -0.570 | 0.172 | -0.093 |
| K\(^+\) | 0.254 | -0.291 | 0.666 | -0.211 | 0.209 | -0.487 |
| Ca\(^{2+}\) | 0.434 | 0.315 | 0.283 | -0.349 | -0.288 | 0.491 |
| Mg\(^{2+}\) | 0.200 | 0.122 | 0.550 | -0.346 | -0.280 | 0.212 |

Veg, vegetated lands (forest and shrub); AGR, agriculture; URB, urban; BAR, bareland; WAT, waters. Bold values represent correlation with significance (*Significance at the 0.05; probability level; **Significance at the 0.01 probability level). doi:10.1371/journal.pone.0053163.t002
The Pearson’s correlation coefficients were applied to examine the strength and significance of the relationships among watershed characteristics and major elements, and two-sample t-tests at 0.05-level were considered to be significant. Stepwise multiple linear regression models were built with major elements as dependent variables. Significance at the 0.05 probability level was considered for the models [22]. Kendall Tau tests were used to analyse the trends of major elements. Principle component analysis (PCA) is

| Table 3. Pearson correlation coefficients between LULC within 200 m and 500 m buffer zone and river major elements of the upper Han River basin, China. |
|---|
| **200 m riparian zone** |
| **Rainy season** | **Dry season** |
| URB | AGR | BAR | VEG | URB | AGR | BAR | VEG |
| T | 0.375 | –0.057 | **0.669** | –0.424 | –0.564 | 0.360 | 0.176 | –0.294 |
| pH | –0.205 | –0.492 | –0.426 | 0.657 | –0.439 | –0.224 | 0.311 | 0.027 |
| EC | –0.263 | 0.247 | 0.616 | –0.532 | 0.033 | 0.439 | **0.705** | –0.773 |
| TDS | –0.263 | 0.247 | 0.615 | –0.532 | 0.033 | 0.439 | **0.705** | –0.773 |
| Cl– | –0.409 | 0.258 | 0.574 | –0.480 | –0.189 | 0.613 | **0.697** | –0.864 |
| NO3– | –0.353 | 0.162 | **0.800** | –0.563 | 0.134 | 0.424 | **0.719** | –0.782 |
| SO42– | –0.411 | 0.358 | **0.682** | –0.626 | –0.203 | 0.430 | **0.849** | –0.816 |
| HCO3 | –0.067 | 0.137 | 0.211 | –0.233 | 0.099 | 0.351 | 0.501 | –0.593 |
| Na+ | –0.268 | 0.230 | **0.862** | –0.663 | –0.081 | 0.312 | **0.870** | –0.758 |
| K+ | –0.473 | –0.105 | **0.720** | –0.290 | –0.344 | 0.077 | **0.773** | –0.483 |
| Ca2+ | –0.141 | 0.204 | 0.485 | –0.440 | 0.213 | 0.477 | 0.491 | –0.697 |
| Mg2+ | –0.276 | 0.156 | 0.560 | –0.429 | –0.058 | 0.250 | **0.694** | –0.613 |
| **500 m riparian zone** |
| **Rainy season** | **Dry season** |
| URB | AGR | BAR | VEG | URB | AGR | BAR | VEG |
| T | 0.377 | 0.062 | 0.621 | –0.440 | –0.461 | 0.360 | 0.258 | –0.364 |
| pH | –0.339 | –0.479 | –0.420 | 0.641 | –0.469 | –0.225 | 0.298 | 0.067 |
| EC | –0.194 | 0.352 | 0.635 | –0.598 | 0.195 | 0.464 | **0.696** | –0.765 |
| TDS | –0.194 | 0.351 | 0.635 | –0.597 | 0.194 | 0.463 | **0.696** | –0.765 |
| Cl– | –0.298 | 0.311 | 0.638 | –0.561 | 0.038 | 0.628 | **0.720** | –0.884 |
| NO3– | –0.218 | 0.238 | **0.836** | –0.623 | 0.338 | 0.449 | **0.706** | –0.777 |
| SO42– | –0.317 | 0.430 | **0.735** | –0.701 | –0.073 | 0.446 | **0.864** | –0.814 |
| HCO3 | –0.054 | 0.220 | 0.205 | –0.272 | 0.225 | 0.372 | 0.479 | –0.577 |
| Na+ | –0.108 | 0.276 | **0.888** | –0.695 | 0.113 | 0.300 | **0.889** | –0.729 |
| K+ | –0.365 | –0.129 | **0.760** | –0.286 | –0.176 | –0.020 | **0.778** | –0.400 |
| Ca2+ | –0.107 | 0.284 | 0.484 | –0.472 | 0.367 | 0.479 | 0.466 | –0.669 |
| Mg2+ | –0.188 | 0.251 | 0.578 | –0.490 | 0.091 | 0.276 | **0.681** | –0.601 |

VLEG, vegetated lands (forest and shrub); AGR, agriculture; URB, urban; BAR, bareland.

Bold values represent correlation with significance (aSignificance at the 0.05; probability level; bSignificance at the 0.01 probability level).
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Table 4. Pearson correlation coefficients between morphological characteristics and river major elements of the upper Han River basin, China.

| Rainy season | 0°–8° | 8°–15° | 15°–25° | >25° |
|--------------|-------|--------|---------|------|
| T            | 0.688a| -0.170 | 0.381  | 0.399 |
| pH           | -0.470| -0.408 | -0.677a| -0.347|
| EC           | 0.534 | 0.247  | 0.331  | 0.420 |
| TDS          | 0.533 | -0.247 | 0.330  | 0.420 |
| Cl⁻          | 0.458 | 0.188  | 0.816b | 0.495 |
| NO₃⁻         | 0.758b| -0.078 | 0.736b | 0.012 |
| SO₄²⁻        | 0.491 | 0.051  | 0.730a | 0.446 |
| HCO₃⁻        | 0.207 | -0.314 | -0.169 | 0.096 |
| Na⁺          | 0.813b| 0.024  | 0.826b | 0.762b|
| K⁺           | 0.623 | -0.060 | 0.748b | 0.721b|
| Ca²⁺         | 0.403 | -0.307 | 0.086  | 0.252 |
| Mg²⁺         | 0.575 | -0.283 | 0.300  | 0.527 |

| Dry season   | 0°–8° | 8°–15° | 15°–25° | >25° |
|--------------|-------|--------|---------|------|
| T            | -0.041| 0.268  | 0.394  | 0.081|
| pH           | 0.217 | -0.743 | -0.296 | 0.266|
| EC           | 0.699a| 0.085  | 0.538  | 0.526|
| TDS          | 0.699a| 0.084  | 0.538  | 0.526|
| Cl⁻          | 0.674b| 0.255  | 0.740b | 0.614|
| NO₃⁻         | 0.815b| 0.235  | 0.727b | 0.679b|
| SO₄²⁻        | 0.684b| 0.052  | 0.747b | 0.544|
| HCO₃⁻        | 0.553 | -0.018 | 0.248  | 0.398|
| Na⁺          | 0.857b| 0.124  | 0.801b | 0.762b|
| K⁺           | 0.717b| -0.045 | 0.662  | 0.774b|
| Ca²⁺         | 0.539 | 0.175  | 0.346  | 0.346|
| Mg²⁺         | 0.756b| -0.133 | 0.425  | 0.648|

AGR, agriculture; VEG, vegetated lands (forest and shrub).
Bold values represent correlation with significance.
aSignificance at the 0.05 probability level.
bSignificance at the 0.01 probability level.
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Results

Catchment land use/land cover compositions including vegetation, agriculture, urban, waters and bare land (Fig. 2a) [22] and spatio-temporal variations of major ions from 2005–2006 (i.e., Cl⁻, SO₄²⁻, HCO₃⁻, Na⁺, K⁺, Ca²⁺ and Mg²⁺) at subcatchment level have been reported elsewhere [20], [23]. In the present study, detailed variations of major elements were shown in the Figure S1, which indicated large inter- and intra-variability among subcatchments. In addition, varied riparian land cover and landscape factors such as slope and area within the subcatchment were complemented (Fig. 2b–2d; Table 1). As the buffer width increased from 100 to 500 m, proportion of urban decreased from 0.3–5% in 100-m buffer to 0.3–3.9% in 500-m buffer, proportion of agriculture decreased from 22–43% in 100-m buffer to 17–40% in 500-m buffer, while the proportion of vegetation increased with a range of 53.5–80.7% in the 500-m buffer. Vegetated coverage accounted for 71.2–95.7% in the subcatchment level, while 3.4–21% and 0.04–1.2% for agriculture and urban, respectively.

Analysis for morphological characteristics was shown in Table 1. Lands with slope of 0°–8° varied between 7% (SUB 4) and 33.62% (SUB 9) of the total area in the respective zone, and 17.07% (SUB 3)–29.34% (SUB 2), 28.70% (SUB 9)–43.47% (SUB 4) and 9.31% (SUB 2)–33.15 (SUB 3) for lands with slope of 8°–15°, 15°–25° and greater than 25°, respectively. Generally, there were small proportion of lands with slope greater than 25° in regions with relatively lower elevation, i.e., SUBs 1, 2 and 9 (Fig. 1; Table 1). In areas (SUBs 3, 4 and 6) with high elevation of Qinling and Daba Mountainous regions, lands with slope greater than 15° accounted for more than 74% of the total area in the respective
subcatchment, while more than 30% for lands with slope greater than 25°. Agriculture thus mainly concentrated in lands with slope less than 25°, and consequently vegetation coverage showed the highest compositions in area with slope >25° (Table 1).

Correlation and regression analyses between landscape physical characteristics and major elements (mean values) were shown in Tables 2, 3, 4, 5 and 6. At the subcatchment scale, vegetation was negatively and significantly correlated to Cl⁻, NO₃⁻, SO₄²⁻ and Na⁺ (r<−0.7, p<0.05), bare land was positively and significantly correlated to Cl⁻, NO₃⁻, SO₄²⁻, Na⁺ and K⁺ (r>0.84, p<0.01), and also contributed to Ca²⁺ and Mg²⁺ in the rainy season. In the dry season, vegetation was only significantly related to Cl⁻, though mitigated other anions including NO₃⁻ and SO₄²⁻, while bare land was significantly related to Cl⁻, SO₄²⁻, Na⁺ and K⁺ (r>0.67, p<0.05), also contributed to NO₃⁻ (Table 2). Contrary to the observations in the subcatchment level, variable were more associated with land cover in the dry season in both the 200 m and 500 m buffer level. In the rainy season, bare land was positively and significantly related to NO₃⁻, SO₄²⁻, Na⁺ and K⁺, while in the dry season, bare land was significantly correlated with all the elements except HCO₃⁻ and Ca²⁺, and vegetation was significantly correlated to EC, TDS, Cl⁻, NO₃⁻, SO₄²⁻, Na⁺ and Ca²⁺ (Table 3).

Lands with slope of 0°–8° and 8°–15° were positively correlated with major ions (i.e., Cl⁻, NO₃⁻, SO₄²⁻, Na⁺ and K⁺), while lands with slope greater than 15° were negatively correlated to major ions, though slope and major element interactions were variable as hydrological seasonality. Overall, the dominant cation Ca²⁺ and the dominant anion HCO₃⁻ showed weak relationships with slope parameters (Table 4).

Stepwise multiple linear regression indicated that Cl⁻, SO₄²⁻, Na⁺ and K⁺ could be predictable by bare land in the subcatchment in the both water flow seasonality (Table 5). At the riparian level, NO₃⁻, SO₄²⁻, Na⁺ and K⁺ were predictable by bare land in the rainy season, while EC, dissolved materials and elements except HCO₃⁻ were predictable by land cover such as bare land and vegetation in the dry season (Table 6).

Seasonal variations of water variables were illustrated in Fig. 3. pH decreased significantly (r = −0.88, p<0.01) till July 2008, then significantly increased (r = 0.83, p<0.05). The pH values showed maximal and minimal levels of 9.3 (June 2006) and 6.5 (April 2009), respectively. EC and TDS showed similar seasonality with crest (Aug. 2009) and trough (Aug. 2005) in the flood season, moreover, they demonstrated increasing trends as time (R² = 0.3, p<0.05, detectable by Kendal Tau test). Cl⁻ concentration varied 0.7 (Oct. 2006)-71 (Jun. 2005) mg/l with highest average of 12 mg/l in summer (Jun. 2005). There was a significant increase in Cl⁻ (R² = 0.56, p<0.01) with sampling time if June 2005 excluded. Similar to Cl⁻, anions NO₃⁻ and SO₄²⁻ concentrations also showed highest dispersion. Seasonal NO₃⁻ concentration increased significantly as time with the variation factor (max./min.) of 84 in October 2006. The averaged NO₃⁻ ranged from 4.4 (Apr. 2009)-37.5 mg/l (Jan. 2010) with instantaneous highest and lowest levels in October 2006 (0.7 vs 61.5 mg/l). SO₄²⁻, with highest variations factors in June and October 2005, had the similar seasonality with Cl⁻, reflected by their strong relations (r = 0.82, p<0.01; Table 7). Compared to anions Cl⁻, NO₃⁻ and SO₄²⁻, HCO₃⁻ had less variability. HCO₃⁻ averaged 116 (Aug. 2009)-178 (Nov. 2008) mg/l with highest level (300 mg/l) in Nov. 2010 and lowest level (37 mg/l) in Aug. 2005, respectively. There were significant correlations among cations except K⁺-Mg²⁺ (p<0.05) (Table 7), and clearly increases in Na⁺, K⁺ and Ca²⁺ during sampling time (Fig. 5). Generally, cations were observed in the order of Ca²⁺>Mg²⁺>Na⁺>K⁺, and Ca²⁺ contributed 73.9% to the total cations, while 14.7%, 7.8% and 3.6% for Mg²⁺, Na⁺ and K⁺, respectively. The dominant ion of Ca²⁺ exhibited smaller variation factors (max./min.) in individual sampling time ranging from 2.1 (Jul. 2007) to 4.7 (June 2006), whereas, Na⁺, K⁺ and Mg²⁺ displayed larger dispersion.

### Discussion

#### 4.1. Landscape setting influences on water quality

Previous studies reported the water chemistry controlled by carbonate weathering in the Han River [19] and most water physico-chemical variables with stream flow seasonality driven by climatic and biotic factors and therefore mainly by the terrene processes in a basin [13,14,27]. Thus, land use types and

| Table 5. Stepwise multiple regression models for major elements and LULC in the subcatchment level of the upper Han River basin, China. |
|-----------------|-----------------|---------|---------|---------|
| **Rainy season** | **Independent variables** | **Regression equations** | **R²** | **Adjusted R²** | **P** |
| pH | URB | 8.253−0.270URB | 0.465 | 0.389 | 0.043 |
| Cl⁻ | BAR/WAT | 2.000+0.405BAR+1.133WAT | 0.974 | 0.949 | 0.002 |
| NO₃⁻ | BAR | 3.335+0.766BAR | 0.869 | 0.851 | 0.000 |
| SO₄²⁻ | BAR | 21.461+2.391BAR | 0.719 | 0.678 | 0.004 |
| Na⁺ | BAR | 2.058+0.270BAR | 0.826 | 0.802 | 0.001 |
| K⁺ | BAR | 0.797+0.059BAR | 0.711 | 0.670 | 0.004 |
| **Dry season** | **Independent variables** | **Regression equations** | **R²** | **Adjusted R²** | **P** |
| Cl⁻ | BAR | 4.812+0.679BAR | 0.566 | 0.504 | 0.019 |
| SO₄²⁻ | BAR | 25.784+2.648BAR | 0.537 | 0.470 | 0.025 |
| Na⁺ | BAR | 2.273+0.312BAR | 0.558 | 0.486 | 0.022 |
| K⁺ | BAR | 1.373+0.093BAR | 0.444 | 0.365 | 0.050 |

VEG, vegetated lands (forest and shrub); AGR, agriculture; URB, urban; BAR, bareland; WAT, waters. The elements without regression models are not listed. Significance at 0.05 probability level.

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hydrological regime could have important roles in mediating fluvial major element distributions, as reflected by their considerable variability (Fig. 3). This was also respectively corroborated by the strong positive correlations between Cl-, NO3-, SO42-, Na+ and K+ and bare land (Table 2) [16], and strong negative correlations between anions (Cl-, NO3- and SO42-) and the proportion of vegetation, in agreement with the conclusion of vegetation mitigating water chemicals [14, 16, 28, 29]. Our study showed remarkable variability in the interactions among hydrological regime, land use/land cover and major chemical species (Tables 2 and 3). Compared to the rainy season, fewer variables had significant associations with land use within the entire catchment in the dry season, which was primarily contributable to anthropogenic inputs especially the point sources. Whereas, variables were strongly more associated with land use along rivers such as 100 m [23], 200 m and 500 m in the dry season (Table 3), suggesting that precipitation within the buffer zone had much higher explanatory values to elements and hydrological pathways greatly mediated major element compositions [15].

Slope could greatly regulate water physico-chemicals. For instance, steeper slope could promote surface water flow rates and understandably increase soil erosion [14–16]. Our results indicated that low catchment slope (<15°) and major element interactions were consistent with commonly observed pattern of their positive associations while those in the catchment with high

### Table 6. Stepwise multiple regression models for major elements and LULC within varied riparian land use of the upper Han River basin, China.

| Riparian Zone | Independent variables | Regression equations | R² | Adjusted R² | P     |
|---------------|-----------------------|----------------------|----|-------------|-------|
| 200 m riparian zone | **Rainy season** | | | | |
| | T | 17.481+0.145BAR+0.441URB | 0.739 | 0.652 | 0.041 |
| | NO3- | 3.394+0.428BAR | 0.64 | 0.589 | 0.01 |
| | SO42- | 22.148+1.251BAR | 0.465 | 0.389 | 0.043 |
| | Na+ | 1.983+0.167BAR | 0.747 | 0.707 | 0.003 |
| | K+ | 0.802+0.033BAR | 0.518 | 0.450 | 0.029 |
| | **Dry season** | | | | |
| | EC | 602.865–5.170VEG | 0.597 | 0.540 | 0.015 |
| | TDS | 391.988–3.362VEG | 0.597 | 0.540 | 0.015 |
| | Cl- | 26.153–0.314VEG | 0.747 | 0.710 | 0.003 |
| | NO3- | 12.664–0.124VEG | 0.611 | 0.556 | 0.013 |
| | SO42- | 0.352+1.939BAR+0.727AGR | 0.862 | 0.816 | 0.048 |
| | Na+ | 1.910+0.238BAR | 0.757 | 0.722 | 0.002 |
| | K+ | 1.269+0.070BAR | 0.597 | 0.539 | 0.015 |
| | Ca2+ | 71.786–0.553VEG | 0.485 | 0.412 | 0.037 |
| | Mg2+ | 5.478+0.361BAR | 0.482 | 0.408 | 0.038 |
| 500 m riparian zone | **Rainy season** | | | | |
| | NO3- | 3.207+0.499BAR | 0.699 | 0.656 | 0.005 |
| | SO42- | 21.347+1.505BAR | 0.540 | 0.474 | 0.024 |
| | Na+ | 1.925+0.192BAR | 0.788 | 0.758 | 0.001 |
| | K+ | 0.786+0.039BAR | 0.578 | 0.517 | 0.017 |
| | **Dry season** | | | | |
| | EC | 623.755–5.185VEG | 0.585 | 0.526 | 0.016 |
| | TDS | 405.552–3.371VEG | 0.585 | 0.526 | 0.016 |
| | Cl- | 28.107–0.325VEG | 0.782 | 0.751 | 0.002 |
| | NO3- | 13.207–0.125VEG | 0.604 | 0.548 | 0.014 |
| | SO42- | 2.542+2.176BAR+0.715AGR | 0.880 | 0.840 | 0.041 |
| | Na+ | 1.875+2.265BAR | 0.754 | 0.719 | 0.002 |
| | K+ | 1.255+0.079BAR | 0.606 | 0.550 | 0.013 |
| | Ca2+ | 72.955–0.538VEG | 0.448 | 0.369 | 0.049 |
| | Mg2+ | 5.464+0.359BAR | 0.464 | 0.387 | 0.043 |

VEG, vegetated lands (forest and shrub); AGR, agriculture; URB, urban; BAR, bareland; WAT, waters.

The elements without regression models are not listed.

Significance at 0.05 probability level.

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slope (>15°) were somehow contradictory (Table 4). Though the negative correlations between base cations and alkalinity and steep slopes in unvegetated terrain were reported [16], [29], while Meyendonckx et al [15] concluded that there was no direct explanation for the negative associations. Thus, the slope influences on water chemistry were varying. It was established that watershed physical characteristics such as soil properties (soil texture and soil drainage), morphological variables (drainage
density and elongation) [10,13,14,15,17,30], particularly the surficial debris remarkably influenced water chemistry in river waters [16,29], we therefore ascribed the abnormal interactions to their multicollinearity. Also, hydrological regime and the proportion of vegetation might be another important factor impacting their correlations [14,15,31]. This was confirmed by increasing proportion of vegetation coverage in its respective gradient as slope increases (Table 1), which primarily resulted in their negative relationships (Table 4).

Numerous researches have characterized the relative importance of land use along rivers in comparison with this in the entire catchment on water quality variables [13–15,23,28], but they obtained varied results. Our results demonstrated that similar variables in the rainy season and more variables in the dry season could be predictable by landscape setting within varied buffer zone (Tables 5 and 6), indicating the interactive influence of hydrological routing/landscape overriding land cover [13,15]. Generally, land use close to rivers (100 m, 200 m and 500 m buffer) better explained major elements than land use away from rivers (Tables 5 and 6) [23], similar to the results of Johnson et al [13] and Chang [10], while contrary to other studies (e.g., [14,15,28]). This might be the result of their predominant natural origins in such a pristine area [19,21], confirmed by the weak associations between anthropogenic processes (urban and agriculture) and major elements (Tables 2 and 3). Also, multiple regression analysis demonstrated that HCO3 could not be explained by landscape variables, which was largely due to carbonate-rock weathering and associated CO2 dissolution in origin [19,21], which could be responsible for its insignificant trends at catchment and individual scale analyses, significant increases in water chemical concentrations such as EC, TDS, Cl−, NO2−, SO42−, Na+, K+ and Ca2+ (Fig. 3) demonstrated anthropogenic sources. We further compared major ion concentrations in the two rivers of the upper Han River, and much higher concentrations with large variations were observed in the Sishui River (Fig. 4), an industrial polluted river through the Shiyian city. The city was a home for motor manufacturer with a population of around 5 million. Industrial effluents and domestic discharges resulted in the highest chemical concentrations particularly Cl−, NO3−, SO42−, Na+ and K+. Industrial sources included electroplating industries, metallurgy, chemical fertilizers, pharmaceuticals, textiles manufacturing units, dyes, etc. The concentrations of EC, TDS and major ions except HCO3− in the Jinshui River (a pristine river) significantly increased as sampling time (p<0.05; Fig. 4), indicating the important roles of anthropogenic inputs such as domestics, excretion and agrochemical fertilizers, which directly contributed to Cl−, NO3−, SO42−, Na+ and K+, whereas the growth rate was smaller compared to the Sishui River. Researches have reported agricultural activities and road construction can accelerate mechanical erosion and chemical weathering process [11,32], resulting in increases of Ca2+ and Mg2+ concentrations (Fig. 4).

Results obtained from KMO and Bartlett’s sphericity test were 0.7 and 76.4 (df = 28, p<0.001), respectively, implying PCA would be effective in reducing dimensionality of datasets. PCA with Varimax normalized rotation yielded two PCs with eigenvalues >1, explaining 73.4% of the total cumulative variance (Table 8). PC1, explaining 50% of the total variance, had strong positive loadings on Cl−, SO42−, HCO3−, Na+, Ca2+ and Mg2+, and moderate positive loading on K+. Variables in this component were an indication of common sources (cf. carbonate dissolution) and similar geochemical characteristics. Natural sources such as parent rock weathering was primarily attributable to this component, confirmed by close associations among HCO3−, Ca2+ and Mg2+ (Table 7), which was consistent with the fact of typical carbonate-dominant drainage basin. There were persistent increases in anthropogenic markers of Cl− and SO42− in the China’s rivers including Yangtze and Yellow [5], [11], similar trends were also observed in our study, indicating their anthropogenic origins. PC2, explaining 24% of the total variance, had strong positive loading on NO3−, and moderate positive loadings on Na+, K+ and Ca2+. This component represented nutrient element and might be controlled by anthropogenic factors.

| Table 7. Pearson correlation matrix for major ions of the upper Han River basin, China. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | Cl−             | NO3−            | SO42−           | HCO3−           | Na+             | K+              | Ca2+            | Mg2+            |
| Cl−             | 1.00            |                |                |                |                |                |                |                |
| NO3−            | 0.13            | 1.00            |                |                |                |                |                |
| SO42−           | 0.82b           | −0.08           | 1.00            |                |                |                |                |
| HCO3−           | 0.44            | 0.14            | 0.37            | 1.00            |                |                |                |
| Na+             | 0.62b           | 0.30            | 0.48            | 0.47            | 1.00            |                |                |
| K+              | 0.47            | 0.49            | 0.43            | 0.35            | 0.59b           | 1.00            |                |
| Ca2+            | 0.78b           | 0.34            | 0.60b           | 0.65b           | 0.82b           | 0.61b           | 1.00            |
| Mg2+            | 0.56b           | 0.20            | 0.38            | 0.82b           | 0.52a           | 0.32            | 0.74b           | 1.00 |

*Correlation is significant at the 0.05 level (2-tailed).
*Correlation is significant at the 0.01 level (2-tailed).

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Figure 4. Comparison of water variables in the two selected rivers (Jinshui and Sishui rivers) of the upper Han River, China. (Jinshui-a pristine river with a portion of 95.7% by vegetation and Sishui-an industrial polluted river through a motor city.)
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Table 8. PCA for seasonal averages of major ions in the upper Han River, China.

| Component | 1 | 2 |
|-----------|---|---|
| Cl\(^-\)  | 0.88 | 0.09 |
| NO\(_3\)\(^-\) | -0.05 | 0.92 |
| SO\(_4\)\(^2-\) | 0.84 | -0.13 |
| HCO\(_3\) | 0.70 | 0.21 |
| Na\(^+\)  | 0.70 | 0.47 |
| K\(^+\) | 0.45 | 0.70 |
| Ca\(^{2+}\) | 0.85 | 0.46 |
| Mg\(^{2+}\) | 0.77 | 0.24 |

Eigenvalues: 4.67, 1.90

% of Variance: 67.49, 23.74

Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization.

The factor loadings were classified as strong, moderate and weak corresponding to absolute loading values of >0.7, 0.7–0.45 and 0.45–0.30, respectively.

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Excessive loading of nutrients such as nitrogen contributes to eutrophication, resulting in alga blooming and hypoxic ecosystems. Dodds et al [35] suggested total nitrogen greater than 1.5 mg/l in eutrophic rivers and streams. In the present study, around 30% of samples with nitrate-N concentration were found to be above 1.5 mg/l. Observed significant increases of nitrogen concentrations due to anthropogenic activities were the possible indications of eutrophication in the basin.

Compared to global averages (Table 9), major ion concentrations were much higher, for example, SO\(_4\)\(^2-\) concentrations was three-fold and other chemicals were two-fold the world spatial means. TDS and the dominant elements (HCO\(_3\) and Ca\(^{2+}\)) were intermediate relative to other Yangtze tributaries, while Cl\(^-\) and SO\(_4\)\(^2-\) were relatively higher, albeit water chemicals except NO\(_3\) were much lower compared to the Minjiang River. Our examination indicated major ion concentrations in the upper Han River were much lower than Huai and Yellow Rivers, the two water deteriorating rivers. For instance, the Huai River had highest concentrations of Cl\(^-\), NO\(_3\), SO\(_4\)\(^2-\), Na\(^+\) and K\(^+\). However, major element concentrations in the Han River were much higher than the international rivers of Ganges, Brahmaputra and Amazon.

Conclusion

The analysis suggested that major chemicals were largely regulated by hydrological regime, slope and land use/land cover (vegetation and bare land). Vegetation and bare land showed strong relations with water chemistry, while anthropogenic activities including urbanisation and agriculture showed weak associations with dissolved elements. The correlations between catchment slope greater than 15° and major elements contrasted to the more commonly observed pattern of steeper slope increasing water physico-chemicals, which was largely the result of multicollinearity of soil characteristics, other morphological properties including drainage density and elongation, land cover composition (the ratio of vegetation/agriculture) in the respective slope gradient.

Stepwise multiple regression models indicated great hydrological seasonality in landscape variables explaining major elements. Land cover within the buffer zone was not a better predictor for major elements than this over the entire catchment during the high flow period, while water variables were better explained by buffer scale analysis during the low flow period, reflecting the important mediating impact of hydrological routing on river water chemistry. Further, similar results were observed among varied buffer strip relating land cover to major variables, as a result, 100 m riparian land cover was enough to explain major elements in the Han River.

Seasonal evolution demonstrated diverging trends for in-stream water quality in the upper Han River. There were significant increases in EC, TDS, Cl\(^-\), NO\(_3\), SO\(_4\)\(^2-\), Na\(^+\), K\(^+\) and Ca\(^{2+}\) during 2005–2010. However, minimal proportion of urban and disperse patches of cropland could mask the associations between anthropogenic land covers (i.e., urban and agriculture) and water chemistry using chemometrics. Therefore, incorporating long-term trends and selected rivers into landscape setting effects on water quality could enhance our understanding of patterns and processes in water quality particularly the anthropogenic contributions. Landscape spatial analysis relating to water quality at multiple scales will be an essential component of examining the fundamental spatio-temporal patterns of water quality, however, highly spatial resolution with hydrology, land cover, topography and soil factors should be holistically included.

4.3. Quality assessment

Waters in the upper Han River have low mineralization with mildly alkaline pH, and the industrial polluted river (Sihe River) showed very high concentrations, for instance, Cl\(^-\) was ten-fold that in the Jinshui River, and four-fold for NO\(_3\) and SO\(_4\)\(^2-\). By comparison with World Health Organization [33] and China’s State Standard [34] for drinking water (Table 9), all the averaged variables were within the maximum desirable limits, whereas, Ca\(^{2+}\) and NO\(_3\)\(^-\) showed highly spatial variations, which was largely the result of increasing water physico-chemicals, which was largely the result of multicollinearity of soil characteristics, other morphological properties including drainage density and elongation, land cover composition (the ratio of vegetation/agriculture) in the respective slope gradient.

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Table 9. Major ion concentrations and with other rivers particularly in the Yangtze systems and guidelines (unit in mg/l except T in °C, pH, EC in μs/cm).

| Sources | T | pH | EC | TDS | Cl⁻ | NO₃⁻ | SO₄²⁻ | HCO₃⁻ | Na⁺ | K⁺ | Ca²⁺ | Mg²⁺ |
|---------|---|----|----|-----|-----|------|-------|-------|-----|-----|------|------|
| Total basin | Number | 458 | 458 | 459 | 462 | 485 | 481 | 484 | 486 | 507 | 507 | 507 | 509 |
| Mean | 19.3 | 8.0 | 309.6 | 202.0 | 6.4 | 8.5 | 31.9 | 143.2 | 4.1 | 1.9 | 40.5 | 8.1 |
| Std. Error of Mean | 0.3 | 0.0 | 5.0 | 3.2 | 0.3 | 0.5 | 0.8 | 2.1 | 0.2 | 0.1 | 0.5 | 0.2 |
| Std. Deviation | 6.3 | 0.6 | 160.1 | 69.5 | 6.7 | 10.2 | 17.8 | 45.5 | 3.4 | 1.4 | 12.0 | 3.7 |
| Minimum | 5.0 | 5.6 | 111.4 | 72.4 | 0.7 | 0.7 | 8.2 | 36.6 | 0.3 | 0.1 | 13.4 | 1.9 |
| Maximum | 35.7 | 9.3 | 878.3 | 570.9 | 70.7 | 63.7 | 161.9 | 300.1 | 35.0 | 10.4 | 83.9 | 25.9 |
| Percentiles (%) | 25 | 15.3 | 7.8 | 238.6 | 155.1 | 3.2 | 3.4 | 19.1 | 115.1 | 2.1 | 0.9 | 32.9 | 5.7 |
| 50 | 18.9 | 8.1 | 293.0 | 190.6 | 4.6 | 4.8 | 28.7 | 138.3 | 3.2 | 1.5 | 38.7 | 7.6 |
| 75 | 23.9 | 8.4 | 361.0 | 235.3 | 7.2 | 8.4 | 39.5 | 172.1 | 4.9 | 2.6 | 48.2 | 10.0 |
| Two selected rivers | Jinshui | Mean | 18.5 | 8.2 | 182.8 | 118.8 | 2.4 | 5.8 | 15.0 | 96.2 | 2.3 | 1.6 | 25.4 | 3.1 |
| | Median | 18.2 | 8.3 | 188.4 | 122.1 | 2.5 | 2.5 | 14.9 | 97.6 | 2.2 | 1.4 | 25.5 | 3.1 |
| | Sishui | Mean | 20.4 | 7.5 | 436.9 | 300.4 | 23.9 | 22.0 | 56.8 | 161.0 | 13.8 | 5.0 | 46.3 | 8.4 |
| | Median | 19.4 | 7.6 | 428.1 | 289.5 | 20.8 | 14.5 | 55.4 | 166.4 | 16.0 | 4.8 | 47.4 | 8.3 |
| WHO (2006) | Max desirable | 7.0–8.5 | 750 | 600 | 250 | 50 | 600 | 600 | 50 | 250 | 250 | 150 |
| | Max permissible | 6.5–9.2 | 1500 | 1000 | 600 | 50 | 600 | 600 | 50 | 250 | 250 | 150 |
| CSS (2006) | Average | 6.5–8.5 | 1000 | 250 | 50 | 250 | 200 |
| Yangtze systems* | Jinshaijiang | Mean | 436 | 45.0 | 0.6 | 37.2 | 235.3 | 55.0 | 2.3 | 44.0 | 12.8 | Wu et al., [37] |
| | Median | 327 | 6.5 | 1.2 | 26.8 | 211.4 | 7.0 | 0.1 | 57.8 | 11.0 | Wu et al., [37] |
| | Nujiang | Mean | 249 | 0.7 | 0.9 | 21.1 | 166.4 | 3.2 | 1.0 | 43.5 | 9.8 | Wu et al., [37] |
| | Median | 211 | 0.8 | 1.4 | 2.8 | 141.4 | 5.3 | 1.2 | 32.6 | 10.2 | Wu et al., [37] |
| | Yalongjiang | Mean | 190 | 0.4 | 1.0 | 8.8 | 134.1 | 2.3 | 1.4 | 33.1 | 7.3 | Wu et al., [37] |
| | Median | 190 | 0.3 | 0.6 | 29.0 | 177.0 | 9.6 | 2.1 | 49.1 | 9.4 | Wu et al., [37] |
| | Minjiang | Mean | 202.2 | 5.7 | 17 | 128.7 | Na⁺K⁺ | 9.7 | 32.3 | 8.3 | Chen et al., [5] |
| | Yellow River | Mean | 486.4 | 46.9 | 7.4 | 83.2 | 200.1 | 60 | 3.5 | 44.9 | 22.4 | Zhang et al., [38] |
| | Yellow River | Mean | 491 | 63.8 | 95.9 | 195.7 | 50.8 | 15.6 | 44.6 | 26.2 | Chen et al., [11] |
| | Upper Yellow River | Mean | 339 | 13.1 | 2.8 | 24.5 | 215.6 | 16.1 | 1.2 | 48.4 | 14.8 | Wu et al., [37] |
| | Pearl River | Median | 7.9 | 239 | 2.2 | 10.3 | 117 | Na⁺K⁺ | 4.4 | 32.6 | 5.4 | Zhang et al., [39] |
| | Huai River basin | Mean | 508.6 | 81.4 | 9.5 | 106.9 | 142.6 | 87.3 | 6.7 | 45 | 21.5 | Zhang et al., [32] |
| | Huai River (main channel) | Mean | 214.2 | 22.5 | 3.3 | 27.5 | 86.4 | 24.8 | 3.7 | 27.7 | 10 | Zhang et al., [32] |
| Brahmaputra | Mean | 101 | 1.1 | 10.0 | 58.0 | 3.6 | 3.7 | 3.9 | 14.0 | Gaillardet et al., [7] |
| Ganges | Mean | 182 | 5.1 | 8.0 | 119.0 | 3.6 | 9.6 | 2.6 | 23.2 | Gaillardet et al., [7] |
| Indus | Mean | 302 | 33.1 | 41.9 | 129.9 | 6.5 | 31.5 | 4.4 | 38.3 | Gaillardet et al., [7] |
| Amazon | Mean | 80.3 | 3.9 | 0.6 | 4 | 43.9 | 3.9 | 1.2 | 12 | 1.7 | Stallard and Edmond [40] |

*Major-ion concentrations are the samples from rainy season.
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Supporting Information

Figure S1  Major elements in each subcatchment of the upper Han River basin, China (sampling times in each subcatchment from left to right are June, August, November 2005 and April, June, October 2006).

(TIF)

Author Contributions

Conceived and designed the experiments: SYL, QFZ. Performed the experiments: SYL, XLX, XT. Analyzed the data: SYL. Contributed reagents/materials/analysis tools: SYL, XLX. Wrote the paper: SYL, QFZ.
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