Spatio-temporal dynamics of nutrients in the upper Han River basin, China

Siyue Li, a,b Wenzhi Liu, a,b Sheng Gu, a,b Xiaoli Cheng, a Zhifang Xu, c Quanfa Zhang a,*

a Center for Watershed Ecology, Wuhan Botanical Garden, The Chinese Academy of Sciences, Wuhan 430074, China
b Graduate School of Chinese Academy of Sciences, Beijing 100049, China
c Institute of Geology and Geophysics, The Chinese Academy of Sciences, Beijing 100029, China

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ABSTRACT

The upper Han River basin with an area of approximately 95,000 km², is the water source area of the Middle Route of China’s South to North Water Transfer Project. Thus, water quality in the basin’s river network is of great importance. Nutrients including dissolved inorganic nitrogen (DIN), NO3⁻–N, NH4⁺–N, and dissolved phosphorus (DP) were analyzed in 41 sites during the period of 2005–2006. Cluster analysis (CA), analysis of variance (ANOVA) and general linear models (GLM) were performed to explore their spatio-temporal variations in the basin. The results revealed that the DIN, NO3⁻–N and NH4⁺–N increased over the 2 year study period, and their concentrations in the wet season was higher than those in the dry season. The seasonal variation in nitrogen was strongly associated with seasonal pattern of precipitation and there was a negative relationship between DP concentration and river flow. Cluster analysis indicated high nutrient contents in the urban and agricultural production areas. The research will help articulate water resource management strategy for the interbasin water transfer project.

1. Introduction

Excessive loading of nitrogen (N) and phosphorus (P) often results in eutrophication [1,2], impairing both the physical and biologic integrity of the fluvial systems [3–5]. It causes undesirable algal blooming, reduced water transparency, anaerobic hypolimnions, taste and odor problems, and increasing cost of water treatment [3]. Studies have reported that human activities have increasingly caused nutrient pollution of surface waters, and N and P management for water quality conservation will surely be of utmost importance [6–11].

Nutrients in a river mainly come from industrial and municipal wastewater, runoff from urban and agricultural areas, mining practices, septic tanks and atmospheric deposition via rainfall [4,12]. Catchment characteristics such as topography and surficial geology can influence the quality of surface water as well [13]. At present, diffuse sources such as agricultural runoff have increasingly been recognized as a major source of nutrients as control of point discharge increases [12].

The Han River, the water source area of the Middle Route of the South to North Water Transfer Project, will supply water to the North China Plain including Tianjin and Beijing City for domestic, industrial and irrigation purposes [14,15]. Thus, water quality in the basin is of great importance. Previous studies have reported that the Han River is one of the most nitrogen-contaminated tributaries in the Yangtze River [7], and recently point and diffuse sources have increased dramatically due to intensive anthropogenic activities [16]. A number of studies have reported on water quality issues in the upper Han River (e.g., [7,17–19]), yet there is a lack of information on the concentrations and distributions of nutrients in the basin.

The objectives of this study are therefore three-fold: (1) to determine the concentrations of nitrogen and phosphorus; (2) to quantify and assess nutrient pollution; (3) to identify their spatio-temporal pattern in the upper Han River basin. It will help articulate water resource management strategy and conservation policies for the interbasin water transfer project.

2. Materials and methods

2.1. Study site

The Han River, originating from Ningqiang county of Shaanxi province, is the largest tributary in the middle stream of the Yangtze River with a drainage area of approximately 159 × 10³ km² and total length of 1577 km [20,21]. Its upper reaches (31°20′–34°10’ N, 106°–112° E; 210–3500 m a.s.l.) [22] is the water source area of the interbasin water transfer project with a drainage area of about 95.2 × 10³ km² and 925 km long (21, Fig. 1). The region belongs to north sub-tropic monsoon climatic region. The annual mean tem-
Temperature is 12–16 °C with the highest and the lowest temperature of 43 °C and −13 °C, respectively [20]. Annual mean precipitation is 700–1800 mm, of which 80% concentrates in the time period from May to October [20]. The annual mean runoff of the upper Han River basin is $41.1 \times 10^9$ m$^3$, accounting for 70% of the total runoff of the whole basin with large interannual variability [20,23].

The vegetations in the upper Han River basin have a typical gradient with deciduous forest, mixed deciduous and conifer forest, coniferous forest and sub-alpine meadow from low to high elevation, and forest cover is approximately 77% (Fig. 1, [22,24]). Cultivated lands occupy about 15% of the total areas [22]. Urban and agriculture lands are distributed along the river networks (areas

**Fig. 1.** Locations of the sampling sites with DEM and land use/land cover data in the upper Han River basin, China.
Fig. 2. Mean values with standard deviation (mean ± S.D.) of nutrients in the upper Han River basin during 2005–2006, China: (a) DIN, (b) nitrate-N, (c) ammonium-N, and (d) DP.

with lower elevation), i.e., the Hanzhong Plain in the headwater, the Ankang Plain in the middle section and industrial centers in the Danjiangkou Reservoir region ([22], Fig. 1). The soil is composed of umber soil and fuscous soil, and the bedrock including sandstones, shales and schist contains appreciable nitrogen concentrations [24].

2.2. Sampling and analysis

Six field surveys were conducted in June, August and November 2005, and April, June and October 2006 from 41 sites locating throughout the upper Han River basin (Fig. 1). All sampling bottles were soaked for 48 h in 15% nitric acid and subsequently double rinsed in distilled water prior to use. Water samples (1 l) were collected at an approximate depth of 10 cm using previously acid-washed high density polyethylene (HDPE) containers. The containers were rinsed three times with sample water before sampling. A separate 100 ml sample was filtered through a previously acid-washed 0.45 μm pore Millipore nitrocellulose membrane filter and the filters were acidified then stored in HDPE bottles for DP analysis. Acid-cleaned polyethylene gloves were used while handling all plastic and glassware. Immediately after returning to the laboratory, all samples were stored in the dark at 4 °C for analysis in the next day.

Nitrate-nitrogen (NO3−-N), ammonium-nitrogen (NH4+-N) and ammonia-nitrogen (NH3-N) were measured on site using YSI multiparameter water quality sondes (YSI Model 6920, USA) calibrated at 100 mg l−1 and 1 mg l−1 before sampling. Dissolved inorganic nitrogen (DIN) was calculated as the total of NO3−-N, NH4+-N and NH3-N. Total phosphorus (TP) was analyzed from a persulphate-digested split of raw water samples in an autoclave at 120 °C for 40 min. The digested sample was measured with the ammonium molybdate method using a Spectrulabs 752S spectrophotometer with a detection limit of 0.01 mg l−1 [25]. Because TP concentrations of most samples were below or accessible to the detection level, so only dissolved phosphorus (DP) was detected using an inductively coupled plasma atomic emission spectrometer (ICP-AES) (IRIS Intrepid II XSP DUO, USA) in the study. Quality control pro-
Table 1
Pearson correlations of inner-group for N parameters in the five clusters

<table>
<thead>
<tr>
<th></th>
<th>Cluster 1</th>
<th>Cluster 2</th>
<th>Cluster 3</th>
<th>Cluster 4</th>
<th>Cluster 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIN</td>
<td>-N</td>
<td>NO3-N</td>
<td>NH4-N</td>
<td>DIN</td>
<td>NO3-N</td>
</tr>
<tr>
<td>NO3-N</td>
<td>1</td>
<td>0.803</td>
<td>0.980</td>
<td>1</td>
<td>0.955</td>
</tr>
<tr>
<td>NH4-N</td>
<td>0.137</td>
<td>0.916</td>
<td>0.496</td>
<td>1.000</td>
<td>0.884</td>
</tr>
<tr>
<td>DIN</td>
<td>NO3-N</td>
<td>NH4-N</td>
<td>DIN</td>
<td>NO3-N</td>
<td>NH4-N</td>
</tr>
</tbody>
</table>

Characters in bold text highlight significant (p < 0.001, *p < 0.01, and **p < 0.05) correlation values according to t-test.

2.3. Data treatment and multivariate statistical analysis

Cluster analysis (CA) was applied on experimental data (984 observations) standardized through z-scale transformation in order to avoid misclassification due to wide differences in data dimensionality. A 2-factor analysis of variance (ANOVA) and general linear models (GLM) were performed to analyze spatio-temporal differences in NO3–N, NH4+–N, DIN and DP. Relationships among the considered variables were tested using the Pearson R coefficient with significance set at p < 0.05. Statistical analyses were performed using SPSS 13.0 for Windows.

Fig. 3. Annual and seasonal variations of nutrient concentrations (mean ± S.D.) (Wet–Wet season, including August, November 2005 and October 2006; Dry–Dry season, including June 2005, April and June 2006) in the upper Han River basin, China (DP concentrations are unavailable in April 2006).
3. Results

DIN and NO$_3^-$-N show large spatial variability with the maximum of 7.64, 6.17 mg l$^{-1}$ and the minimum of 0.53, 0.40 mg l$^{-1}$, respectively, while NH$_4^+$-N and DP are relatively stable with few exceptions (Fig. 2). In general, NO$_3^-$-N is significantly higher ($p < 0.05$) than NH$_4^+$-N, and all the N parameters are significantly higher ($p < 0.05$) than DP (Fig. 2). The average concentrations of nitrogen and phosphorus increase from 2005 to 2006, and the increase is also observed by comparing their concentrations measured in the same time between the two years (i.e., June 2005 and June 2006, and November 2005 and October 2006). Nitrogen has a relative higher concentration in the wet season than the dry season, while phosphorus is the opposite (Fig. 3).

Cluster analysis groups the 41 sampling sites into five statistically significant clusters at ($D_{\text{link}}/D_{\text{max}}$) $\times 100 < 60$ (Fig. 4). NO$_3^-$-N accounts for more than 80% of the DIN except the cluster 2 (site 10) with 49.1%. NO$_3^-$-N is significantly correlated to DIN in all clusters except in cluster 2, and NH$_4^+$-N is highly positively correlated with DIN in clusters 2 and 3 (Table 1). All N parameters have the maximum values in the wet season but in the dry season for DP (Fig. 5). Spatial differences are large and clusters 2 and 3 have significantly high nitrogen concentrations (Fig. 5). The season and interaction of season x cluster are also highly significant ($p < 0.001$) with the largest values in the wet season for DIN and NO$_3^-$-N (Fig. 5), while significant differences exist among clusters only for NH$_4^+$-N. There are significant differences ($p < 0.001$) for DP among the cluster (Table 2), with an average concentration (0.21 mg l$^{-1}$) in cluster 2 and 0.0075 mg l$^{-1}$ in cluster 5 (Fig. 5). Overall, cluster 2 (site 10) and cluster 3 (sites 6, 8 and 9), cluster 1 (sites 1, 2, 4 and 5) and cluster 4 (sites 21, 29, 33, 34, 36, 38–40), and cluster 5 (the rest sites) correspond to very high, moderate, and low pollution regions, respectively.

4. Discussion

The interannual variations of nitrogen (Fig. 3), as revealed in other studies, may be due to a recent increase in point sources and intensive human activities in the basin [16]. Though this result may be uncertain due to such a short-time (2 year) data, however, month-time scale comparisons (June in 2005 and 2006, Nov. 2005 and Oct. 2006, Fig. 3) can elaborate the interannual changes of increasing nitrogen concentrations. Geologic formations are a large source of nitrate to surface waters, and such a “geological” nitrogen may be especially significant given that nitrate contamination at very low levels can contribute to surface water eutrophication [26]. This research shows that the concentrations of nitrogen in the wet season are relatively higher than that in the dry season (Fig. 3), which is consistent with the previous results of the Dan River [27]. It implies that diffuse N inputs including runoff from agriculture, mining and urban areas contribute to the N concentrations in the basin [11,28,29].

DP increases from 2005 to 2006 with higher values in the dry season (Figs. 3 and 5), which probably due to the interaction of industrial effluents and diffuse sources [3,9,29]. Previous studies have reported that land use practices, especially a decrease in riparian belts have changed nutrient loads to the fluvial systems [30], and P loading to the basin would be double due to increased urbanization in a watershed [28], indicated by the highest DP concentrations in cluster 2 (Fig. 2), an area with intensive anthropogenic activities, high population densities and developed industry (Fig. 1).

Spatial variations of nutrients depend on land use practices and urban development [1,28], and higher nitrogen and phosphorus concentrations usually occur in areas of urban and agricultural activities [1]. In this study, sites in the Reservoir region (clusters 2 and 3) display obvious spatio-temporal changes with significant higher nitrogen and phosphorus ($p < 0.01$) (Figs. 1 and 5). Shiyian City, with more than half a million in population and home of a motor manufacturer, is located in the upper stream of site 10 (cluster 2) (Fig. 1). It may have contributed large amount of nitrogen and phosphorus into the water [9,10,16,29]. Sites 6, 8 and 9 (cluster 2) showed significant difference in nutrient concentrations among the seasons, which may be related to intensive urbanization and agricultural activities [28].

![Fig. 4. Cluster analysis of the nutrient concentrations in the upper Han River basin, China.](image)

Table 2

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Season</th>
<th>Cluster x season</th>
<th>Adjusted $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIN</td>
<td>$p = 0.000$</td>
<td>$p = 0.004$</td>
<td>$p = 0.000$</td>
</tr>
<tr>
<td>F = 16.693</td>
<td>F = 8.567</td>
<td>F = 5.807</td>
<td></td>
</tr>
<tr>
<td>$M^2 = 0.095$</td>
<td>$M^2 = 0.2243$</td>
<td>$M^2 = 0.15206$</td>
<td></td>
</tr>
</tbody>
</table>

| NO$_3^-$-N | $p = 0.000$ | $p = 0.002$ | $p = 0.000$ | 0.253 |
| F = 15.443 | F = 9.545 | F = 5.966 |
| $M^2 = 0.058$ | $M^2 = 0.15235$ | $M^2 = 0.09709$ |

| NH$_4^+$-N | $p = 0.000$ | $p = 0.129$ | $p = 0.058$ | 0.291 |
| F = 24.913 | F = 2.325 | F = 2.311 |
| $M^2 = 0.064$ | $M^2 = 0.6448$ | $M^2 = 0.0644$ |

| DP      | $p = 0.000$ | $p = 0.071$ | $p = 0.997$ | 0.058 |
| F = 5.253 | F = 0.138 | F = 0.037 |
| $M^2 = 0.0095$ | $M^2 = 0.002$ | $M^2 = 0.001$ |

* Mean square calculated from Type III sums of squares.
3) are located in the agricultural production areas (Fig. 1), additionally, chemical extraction of medical materials from *Dioscoreae zingiberensis* (Chinese yam production) may have made a contribution as well [31].

Nitrogen and phosphorus in the Dan River and headwaters (clusters 1 and 4) exhibit higher concentrations at low flows (dry season), reflecting the greater effects of anthropogenic inputs [9]. Nutrient concentrations in the middle section of the study area (cluster 5) show small differences between seasons (Figs. 1 and 5), implying that this area has a mix of diffuse sources, base-flow and natural runoff [16]. Both natural and anthropogenic factors, including weathering of the rock and natural runoff of the drainage basin, and agricultural runoff, urban domestics and industrial effluents, can promote the evidenced spatial variation of nutrients of the waters in the examined stream sector. With the great effort on the reduction of point source nutrient loads into the basin for the interbasin water transfer project, diffuse sources caused by storm water runoff will increasingly become a large source of nutrient loads into the basin [27,32].

Algae blooms occurred in 1992, 1998, 2000 and 2003 in the middle and lower reaches of the Hanjiang River and phosphorus has been considered the limiting factor for algal production [33]. Previous studies have obtained the critical N:P ratios from 10:1 to 32:1 in the environment [34–39]. This study shows that the average DIN:DP ratio is 63:1 (Fig. 3), similar to the Yangtze River [39], suggesting that P is the limiting factor for algae production in the upper Han River as well. However, the N:P ratio is 22 and 19 for the Danjiangkou Reservoir region (cluster 2) and headwater (clusters 4), respectively (Fig. 5), and increase in nitrogen and phosphorus is observed over the sampling period (Fig. 3). Thus, there is possibility of algae blooming in the future considering that the interbasin water transfer project will enlarge the water storage capacity and dramatically slow down the water velocity. The efforts to prevent eutrophication should focus primarily on reducing nutrients loading into the fluvial system by adopting proper agricultural practices in the upper basin [3].

5. Conclusions

(1) The DIN, NO$_3^-$-N and NH$_4^+$-N concentrations has increased respectively from 1.79±1.10 to 2.05±2.42, 1.56±1.03 to 1.63±1.82, and 0.21±0.27 to 0.40±0.83 mg l$^{-1}$ in the time period of 2005–2006, and their higher concentrations occur in the wet season. The DP increases from 0.020±0.02 to 0.045±0.21 mg l$^{-1}$ as well, but with higher concentration in the dry season. It reflects that the nitrogen load is diffuse-input dominated, while DP comes from point inputs, such as urban sources and industrial wastewaters.

(2) Spatial pattern of nutrients are evident in the basin. Generally, high nutrient contents occur in the urban and agricultural production areas, and their seasonal variation was strongly associated with seasonal pattern of precipitation, reflecting the
combined effects of diffuses and industrial effluents. Water conservation effort should concentrate in the reservoir region where there are higher nutrients concentrations.

(3) High N:P ratios reveal that P is the limiting factor for algal production in the study area. With frequent algal blooms in the lower reaches of the Han River in recent years, proper agricultural practices should be developed and adopted to reduce nutrients into the riverine system of the upper Han River basin.

Acknowledgements

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