# Effects of land use types on surface water quality across an anthropogenic disturbance gradient in the upper reach of the Hun River, Northeast China

Ruizhao Wang · Tianle Xu · Lizhong Yu · Jiaojun Zhu · Xiaoyu Li

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Abstract Surface water quality is vulnerable to pollution due to human activities. The upper reach of the Hun River is an important water source that supplies 52 % of the storage capacity of the Dahuofang Reservoir, the largest reservoir for drinking water in Northeast China, which is suffering from various human-induced changes in land use, including deforestation, reclamation/farming, urbanization and mine exploitation. To investigate the impacts of land use types on surface water quality across an anthropogenic disturbance gradient at a local scale, 11 physicochemical parameters (pH, dissolved oxygen [DO], turbidity, oxygen redox potential, conductivity, biochemical oxygen demand [BOD<sub>5</sub>], chemical oxygen demand [COD], total nitrogen [TN], total phosphorus [TP],  $\overline{NO_3}^{-}$ -N, and  $\overline{NH_4}^+$ -N) of water from 12 sampling sites along the upper reach of the Hun River were monitored monthly during 2009– 2010. The sampling sites were classified into four groups (natural, near-natural, more disturbed, and seriously disturbed). The water quality exhibited distinct spatial and temporal characteristics; conductivity, TN, and  $NO<sub>3</sub><sup>-</sup>-N$  were identified as key parameters indicating the water quality variance. The forest and farmland cover types played significant roles in determining the

R. Wang  $\cdot$  T. Xu  $\cdot$  L. Yu  $\cdot$  J. Zhu ( $\boxtimes$ )  $\cdot$  X. Li State Key Laboratory of Forest and Soil Ecology, Qingyuan Experimental Station of Forest Ecology, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110016, China e-mail: jiaojunzhu@iae.ac.cn

surface water quality during the low-flow, high-flow, and mean-flow periods based on the results of a stepwise linear regression. These results may provide incentive for the local government to consider sustainable land use practices for water conservation.

Keywords Water quality · Land use · Anthropogenic disturbance . Forest land . Hun River

# Introduction

Surface water is susceptible to pollution from natural processes, such as precipitation inputs and erosion, and from anthropogenic disturbances through agricultural, industrial, and urbanization activities that increase the consumption of water resources (Shrestha and Kazama [2007](#page-10-0); Singh et al. [2004](#page-10-0)). Anthropogenic disturbance has received much attention due to landscape modifications and ecosystem alterations (Maloney and Weller [2011\)](#page-9-0). The change of land use types, including deforestation (Walling and Fang [2003\)](#page-10-0), river channelization and realignment (Tong et al. [2009\)](#page-10-0), and the fragmentation of continuous habitats (Miserendino et al. [2011\)](#page-10-0) has resulted in soil erosion, a decline in aquatic biodiversity or scarcity, and water quality degradation.

Studies have demonstrated that the relationship between land use change and the alteration of water physicochemical characteristics is influenced by numerous factors and varies from local to basin or eco-regional scales (Brion et al. [2011](#page-9-0); Mehaffey et al. [2005;](#page-9-0) Tong and Chen [2002;](#page-10-0) Wear et al. [1998;](#page-10-0) Williams et al. [2005\)](#page-10-0). Tong and Chen ([2002\)](#page-10-0) found a significant relationship between land use and in-stream water quality. They showed much higher concentrations of nitrogen and phosphorus in agricultural and impervious urban land than that in forest land surfaces. Wear et al. [\(1998](#page-10-0)) noted that the level of urbanization was the most relevant factor of water quality degradation along the rural–urban gradient in a southern Appalachian watershed in the United States. Likewise, Brion et al. ([2011\)](#page-9-0) observed that agricultural practices and rapid urbanization had altered the natural hydrologic conditions of rivers and increased the possibility of water quality degradation. Mehaffey et al. ([2005\)](#page-9-0) suggested that total nitrogen (TN) and total phosphorous (TP) are significantly positively related to agricultural land. However, no significant correlations between urban or agricultural lands and TN and TP were found in the Ipswich River watershed (Williams et al. [2005\)](#page-10-0). The different effects of land use types on surface water may reflect different watershed characteristics and pollution sources (Tong and Chen [2002](#page-10-0)).

With its rapid economic and industrial growth, environmental degradation is widespread in many regions of China. Most monitored rivers in China were found to be heavily polluted with ammonium nitrate, permanganate, and petroleum in 2007, reflecting the poor water quality of the rivers (Fu [2008](#page-9-0); Zhang et al. [2010a\)](#page-10-0). Although there have been some studies on the impacts of human activities on water quality within different watersheds in China, such as the catchments of the Fuxian and Qilu Lakes in Yunnan Province (Wu et al. [2008\)](#page-10-0), the Chenqi and Dengzhanhe catchments in Guizhou Province (Zhao et al. [2010\)](#page-10-0), and the Grand Canal in the Taihu watershed (Wang et al. [2011b\)](#page-10-0), studies on the intrinsic relationships of land use and water quality in Northeast China are scarce (Zhang et al. [2009](#page-10-0)). The Hun River is situated in Liaoning Province, Northeast China. The discharge of the upper reach of Hun River is large, contributing more than 52 % of the storage capacity of the Dahuofang Reservoir, which has a maximum storage capacity of 2.2 billion m<sup>3</sup>. As an important source of drinking water, the Dahuofang Reservoir sustains 23 million residents in Liaoning Province, Northeast China (Wang et al. [2011a](#page-10-0)). However, there is great concern about the surface water quality in the upper stream region because of rapidly occurring land-use changes, including deforestation, increased agriculture and mining, and urbanization. Therefore, it is urgent that the effects of land use types on surface water quality, relative to the different

intensities of anthropogenic disturbances, be investigated for safety of use and to identify key factors for the further recovery of the aquatic ecosystem.

This study was performed to explore the effects of land use types relative to the different intensities of anthropogenic disturbances (forest, grassland, farmland, mining industry, and urban expansion) on the physicochemical characteristics of the water in the upper reach of the Hun River. The aims of this study were as follows: (a) to analyze the spatial and temporal distribution characteristics of the surface water quality; (b) to identify the key factors determining the water quality variability during the low-flow, high-flow, and mean-flow periods; and (c) to clarify the effect of land use on water quality across the gradient of anthropogenic disturbance in the upper reach of the Hun River.

### Materials and methods

## Study area and sampling sites

The Hun River, a major tributary of the Liao River, is situated in Liaoning Province, Northeast China. The river, which originates from Qingyuan County, has a length of 415 km and a drainage area of  $11,400$  km<sup>2</sup> (Yao et al. [2011\)](#page-10-0). Known as the "mother river," the Hun River flows through seven cities including the provincial capital Shenyang. The river provides a large amount of water resources for domestic, agricultural, industrial and other purposes. This region is subject to the temperate continental monsoon climate and its annual mean temperature ranges between 4 °C and 8 °C. The average annual precipitation ranges from 700 to 900 mm, and as much as 70–80 % of annual precipitation falls from June to August (Zhang et al. [2009](#page-10-0)). According to the monthly mean precipitation, three distinctive periods were determined: low-flow (April and May), high-flow (June– August), and mean-flow (September and October).

On the basis of Digital Elevation Model (DEM) data, the boundary of the upper reach of the Hun River was extracted using ArcGIS 9.3. The upper reach of the Hun River (from 41°47′52″ to 42°28″25″N, 124°20″06″ to 125°28″58″E) (Fig. [1](#page-2-0)) covers a large area of forest, grassland, farmland, town and copper mining areas in Qingyuan County before discharging into the Dahuofang Reservoir.

Twelve study sites were identified on the riverside along the upper reach of the Hun River to represent

<span id="page-2-0"></span>

Fig. 1 Location of study area and sampling sites in the upper reach of the Hun River, Northeast China

different land use types. Sites S1–S4 were near the headwater region, and sites S5 and S6 were situated at a famous driftage tourism resort. S7 and S8 were located upstream and downstream of Qingyuan County, respectively. S9 and S10 were seated at the confluence of two tributaries, the Yinge and Hong Rivers. S11 and S12 were situated in the copper mining area (Fig. 1).

Water sampling and determination of physicochemical parameters

Water samples were collected at monthly intervals from July 2009 to October 2010 from 12 sampling stations except during the freeze period from November 2009 to March 2010. The turbidity, pH, conductivity, dissolved oxygen (DO), and oxidation reduction potential (ORP) were measured in situ with a HORIBA W-20 series multi-parameter water quality meter probe (Horiba Advanced Techno Co., Ltd, Kyoto, Japan) at approximately 30 cm below the water surface. To quantify the chemical analyses, three polyethylene bottles were used to collect water samples, which were kept at 4 °C and transported to the laboratory for advanced analysis. The chemical parameters were performed following standard methods (State Environment Protection Bureau of China [2002\)](#page-9-0). These parameters included nitrate-nitrogen  $(NO<sub>3</sub><sup>-</sup>-N)$ ,

ammonium nitrogen (NH<sub>4</sub><sup>+</sup>-N), total nitrogen (TN), total phosphorus (TP), biochemical oxygen demand  $(BOD<sub>5</sub>)$ and chemical oxygen demand (COD).

## Land use analysis

Each sampling site was delineated according to the longitude and latitude and circled within a radius of 400 m to decide the land use type. The land use types within the given scope were extracted from Advanced Land Observing Satellite (ALOS) images of 2009 (2.5 m spatial resolution) using ArcGIS 9.3 Desktop GIS software. The five land use categories were forest land, grassland, farmland, mine and built-up. These data were used to calculate Land Use Stress (LUS) scores based on the weighted sum of the percent land cover in forest land (no weighting), grassland (weighting factor=1), farmland (weighting factor=2), mine (weighting factor=3), and built-up (weighting factor=4), according to Collier  $(2008)$  $(2008)$ . The values varied between 0 for sites draining only forest to 400 for sites of entirely urbanized built-up land.

#### Data analysis

Differences in physicochemical parameters for the different sites were tested by a one-way analysis of variance (ANOVA) within the SPSS 16.0 package, depending upon the results of the test for the homogeneity of variances. Factor analysis (FA) and stepwise linear regression were applied to extract the most important physicochemical parameters of the water during the different rainfall periods using the SPSS 16.0 software package. Multiple analyses of variance within cluster analysis (CA) and principal component analysis (PCA) within the PC-ORD 5.0 package (McCune and Mefford [1999](#page-9-0)) were conducted to determine the spatial/temporal variations of water quality across the anthropogenic disturbance gradient. The Monte Carlo permutation test was used to verify the significance.

# Results and discussion

## Land use composition and site similarity

Analysis showed that the proportion of forest land was greater than that of other land-use types at S1–S6, while farmland occupied the largest areas at S7–S12 except for S11 (Fig. 2, Table [1\)](#page-4-0). An obvious feature was that natural landscapes, including forest land and grassland, were dominant at S1–S6, with the sum of proportions varying from 78 % to 100 % (Table [1](#page-4-0)). Conversely, farmland, mine, and built-up areas, the three types of anthropogenic landscapes, dominated at S7–S12; the sum of these three land use types varied from 71 % to 84 % (Table [1\)](#page-4-0).

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The dendrogram from the CA based on the water physicochemical parameters from the 2-year data (total of 432 samples) significantly discriminated the 12 sites into three clusters, with 82.5 % of the variance explained (Fig. [3\)](#page-4-0). Based on the analysis of the LUS scores (Table [1\)](#page-4-0), these three clusters were divided again into four groups. Sites S1–S4 (cluster 1), which were located in the headwater region, formed Group I. S5 and S6 (cluster 2), which were adjacent to the location of famous driftage tourism resort, constituted Group II. Sites S7–S12 (cluster 3) could be divided into two sub-groups. One sub-group, named Group III, consisted of S7, S9 and S10 and had LUS scores below 200. The other sub-group, named Group IV, consisted of S8, S11, and S12 and had LUS scores over 200. Therefore, these 12 sites were divided into four groups representing the increasing intensity of anthropogenic disturbance: Group I (S1–S4, natural landscape), Group II (S5 and S6, near-natural landscape), Group III (S7, S9, and S10, more disturbed), and Group IV (S8, S11, and S12, seriously disturbed).

The results based on the CA indicated that this procedure was useful in offering reliable classification of the surface waters in the upper reach of the Hun River. The procedure made it convenient to further analyze the anthropogenic disturbance gradient in a facile and credible manner. Other reports (Shrestha & Kazama [2007](#page-10-0); Singh et al. [2004\)](#page-10-0) had shown that a similar approach can be successfully applied to water quality programs.

Legend Forest land Grassland Farm land Water area Built-up Mine





#### <span id="page-4-0"></span>Table 1 Proportions of land use types and Land Use Stress (LUS) scores at the 12 sampling sites in the upper reach of the Hun River, Northeast China

# Spatial and temporal variations of physicochemical parameters

The major parameters tend to increase significantly from Group I to Group IV and from upstream to downstream  $(p<0.05, n=432, Fig. 4)$  $(p<0.05, n=432, Fig. 4)$  $(p<0.05, n=432, Fig. 4)$ . The lowest values of conductivity, turbidity, TN, TP,  $NO<sub>3</sub><sup>-</sup>-N$ , and  $NH_4^+$ -N were all found in Group I, while the highest concentrations of these parameters were found in Group IV, except TP (Fig. [4](#page-5-0)). The water samples at Group I and Group II were remarkably better than those of Group III and Group IV, according to the concentrations of TN,  $NO_3^{\pm}$ -N, and NH<sub>4</sub><sup>+</sup>-N. The water quality parameters showed obvious temporal variations. The surface water in the high-flow period had a lower concentration of nutrient-related parameters (TN,  $NO_3$ <sup>-</sup>-N, and  $NH_4$ <sup>+</sup>-N) than that of the lowflow and mean-flow periods (Fig. [4](#page-5-0)). The apparent decline in N-related concentrations in the high-flow period was caused by the dilution effect, and the highest concentrations in the low-flow period most likely indicated inadequate dilution due to the lowest runoffs and slowest flow velocity (Ahearn et al. [2004](#page-9-0); Sigleo and Frick [2007\)](#page-10-0). However, the TP concentration exhibited a different trend, with the lowest value in the low-flow period and the highest value in the meanflow period. The variation of the TP concentration in the rivers may be explained by the trade-off between erosion and the dilution effect in the given rainfall periods. A previous study showed that hydraulic erosion played a major role in determining the concentration of TP when the rainfall and runoff were not abundant in the low- or mean-flow periods (Absalon and Matysik [2007\)](#page-9-0).





<span id="page-5-0"></span>

Fig. 4 Comparison of a conductivity, b turbidity, c TN, d TP, e  $NO_3$ <sup>-</sup>-N, and **f** NH<sub>4</sub><sup>+</sup>-N of different groups during the low-flow, high-flow, and mean-flow periods. Different lowercase letters

on the error bars represent the existence of significant differences among groups at  $p < 0.05$  ( $n = 432$ )

The results of the principal component analysis showed similar trends (Fig. [5\)](#page-6-0). The first three PCs with eigenvalues >1 accounted for 37.8 %, 22.1 %, and 15.2 % of the total variance. From left to right of Axis 1, there was a gradually increasing gradient of anthropogenic disturbance from Group I (S1–S4) to Group II (S5 and S6) and a blending of Group III (S7, S9, and S10) and Group IV (S8, S11, and S12). In addition, Axis 1 showed the sampling locations along the river direction from the headwater region to Qingyuan County and to the copper mining area. Axis I was significantly positively related to  $NO_3^-$ -N ( $r=0.94$ ), conductivity  $(r=0.78)$  and TN  $(r=0.78)$ . From top to bottom of Axis 2, the samples showed an obvious time series from lowflow to high-flow to mean-flow periods. Axis II was significantly negatively related to TP ( $r=-0.86$ ) and DO  $(r=-0.82)$ .

The surface water in the upper reach of the Hun River exhibited good water quality with lower concentration of TN,  $NH_4^+$ -N and TP and lower values of EC (Fig. 4) compared with those of a tributary of the Daliao River in Northeast China (Zhang et al. [2009\)](#page-10-0), the Han River (Li et al. [2009\)](#page-9-0), the Xiangjiang River (Zhang et al. [2010b](#page-10-0)), and the Changjiang River (Liu et al. [2003](#page-9-0)). Due to anthropogenic activities, including agriculture, urbanization, and especially the use of chemical fertilizers and pesticides with abundant nitrogen and phosphorus, the water quality of many rivers in China has been affected by heavy pollution loads. The upper reach of the Hun River is primarily located in a mountainous area and subjected to relatively less anthropogenic disturbance. In this study, the four intensities of anthropogenic disturbance based on the results of LUS scores (Table [1](#page-4-0), Fig. [3\)](#page-4-0) exhibited different water quality levels, in accordance with the clean water quality standard from Collier ([2008](#page-9-0)). In our study, the sites with LUS scores less than 100 were affected by fewer anthropogenic disturbances, whereas LUS scores of more than 200 indicated the sites were suffering serious anthropogenic disturbances. With the increased intensity of disturbance from Group I to Group IV, the concentration of TN,  $NO_3$ <sup>-</sup>-N, and NH<sub>4</sub><sup>+</sup>-N increased.

<span id="page-6-0"></span>Fig. 5 Principal component analysis (PCA) ordination from the physicochemical parameters of the water of the 12 sampling sites in the upper reach of the Hun River. L low-flow period,  $H$  high-flow period, M mean-flow period



○ Group I © Group II ● Group III ● Group IV

Moreover, the surface water had better quality with lower nutrient concentrations (Fig. 5) during the highflow period than the other periods, most likely a result of the diluting effect of rainfall.

Identification of important seasonal water quality parameters

The most important water quality parameters were chosen with an absolute correlation coefficient value >0.95 for the first two factors during the low-, high-, and mean-flow periods in the upper reach of the Hun River (Table [2\)](#page-7-0). In the low-flow period, the mineralrelated parameter of conductivity and inorganic nutrient parameter  $NO<sub>3</sub><sup>-</sup>-N$  were more sensitive to water quality variation than the other parameters. Turbidity and  $NO<sub>3</sub><sup>-</sup>-N$  showed the most variation during the high-flow period. In addition, conductivity, turbidity, and  $NO<sub>3</sub><sup>-</sup>-N$  were key parameters for determining the water quality variation during the mean-flow period. The nutrient-related parameter  $NO<sub>3</sub><sup>-</sup>-N$  was the most sensitive parameter for characterizing the water quality variance throughout the year.

In the present study, among the 11 studied water physicochemical parameters, three parameters (i.e., conductivity, turbidity, and  $NO_3$ <sup>-</sup>-N) exhibited the most variation, and only  $NO<sub>3</sub><sup>-</sup>-N$  always showed the most variation when determining the water quality conditions for all three periods (Table [2](#page-7-0)). The key parameters for determining the water quality variability were not immobile (Table [2](#page-7-0), Fig. 5). One parameter that was more important in one period may not have been important in another, a characteristic consistent with the study of Ouyang et al. [\(2006](#page-10-0)). The key parameters (conductivity, turbidity, and  $NO<sub>3</sub><sup>-</sup>-N$ ) in this study were common indicators of water quality evaluation as described by Pesce and Wunderlin [\(2000](#page-10-0)) and Singh et al. [\(2004](#page-10-0)). Turbidity was associated with suspended material, which can also be bacteriological contaminations (Pronk et al. [2007](#page-10-0)). Conductivity could indicate the presence of mineral acids or similar contaminants discharged to the river (Ouyang et al. [2006\)](#page-10-0).  $NO<sub>3</sub><sup>-</sup>-N$  may be interpreted as representing influences from anthropogenic inputs (Miserendino et al. [2011\)](#page-10-0). The changing trend of the  $NO<sub>3</sub><sup>-</sup>-N$  concentration was correlated with the

<span id="page-7-0"></span>Table 2 Rotated factor correlation coefficients for low-flow, high-flow, and mean-flow periods



Bold numbers indicate an absolute value >0.95

intensity of the anthropogenic disturbance, which could be a good index for monitoring the water quality variance and the intensity of anthropogenic disturbance in the upper reach of the Hun River for all three periods.

Linkage between water physicochemical parameters and the intensity of anthropogenic disturbance

The percentages of forest or farm cover played important roles in determining the variations of water physicochemical parameters in the different rainfall periods on the basis of the results of stepwise multiple regressions (Table [3](#page-8-0)). During the low-flow period, the percentage of forest land cover was negatively correlated to the values of conductivity,  $NO<sub>3</sub><sup>-</sup>-N$  and TN, while farmland and mine land cover were positively correlated with the variation of water quality. This result was in agreement with the studies of Mayer et al. ([2007\)](#page-9-0) and Allan and Castillo [\(2007](#page-9-0)), mainly because forested riparian areas could effectively remove  $NO<sub>3</sub>$ <sup>-</sup> N from the discharges. The common sources of phosphorous included agricultural and industrial sewage and animal waste. Moreover, human-induced disturbance of land vegetation increased erosion resulting in more phosphates being washed out of the soil. The supply of phosphates was constant throughout the year, and there was less discharge to dilute them in the low-flow period. Only farmland played a crucial role in determining the variations of water quality during the high-flow period (Table [3\)](#page-8-0). The proportions of farmland cover were negatively correlated with the nutrient-related parameters  $(NO_3^{\text{-}}-N$  and TN) and positively correlated with the oxygen-related parameters (DO and ORP). Similarly, these key parameters were deeply affected by farmland in the mean-flow period. Our results seemingly disagree with previous studies in which negative relationship was found between farmland and the concentration of  $NO<sub>3</sub><sup>-</sup>-N$  in the high- and mean-flow periods. In the present study, the sites with the greatest proportion of farmland (Fig. [1](#page-2-0), Table [1\)](#page-4-0) were located at the confluence of two tributaries, where the dilution effect lowered the concentration of nutrient related parameters  $(NO_3^-N)$ and TN). In addition, agricultural waste produced by farmland was combined with that from mining and built-up land, which aggravated the deterioration in the less agricultural land. Therefore, this contradictory situation mainly reflects the differences in the specific sampling sites and the watershed characteristics in different studies (Tong and Chen [2002](#page-10-0)). In general, forest land cover played an important role in determining the water quality variations in the low-flow period, while farmland cover had a profound effect on surface water quality in both the high- and mean-flow periods.

Forest land is mostly related to good water quality and it plays an important role in keeping water clean in different watersheds around the world (Lepers et al. [2005](#page-9-0); Neary et al. [2009](#page-10-0); Tu [2011](#page-10-0)). Similar to the previous studies, negative relationships are also found between the percentage of forest land and the key <span id="page-8-0"></span>Table 3 Stepwise multiple gression models for physicochemical parameters in the u reach of the Hun River, No eastern China

Forest, farm, and mine in the models represent the percent of each land use type



parameters (conductivity,  $NO_3$ <sup>-</sup>-N and TN) in this study (Table 3). The lower concentration of nutrient loading may be attributable to the deposition and filtering of forest land, and forest ecosystems are generally effective at controlling and decreasing the sediment pollutants carried in surface runoff (Lowrance et al. [1997](#page-9-0); Neary et al. [2009;](#page-10-0) Tu and Xia [2008\)](#page-10-0).

As one of the essential components of human disturbances, farmland is usually considered an important pollution source that degrades water quality (Filik Iscen et al. [2008](#page-9-0)). Numerous studies have shown significant relationships between the percentages of agricultural or unban land cover and nutrient concentrations in streams and rivers. Lenat and Crawford ([1994\)](#page-9-0) found that agricultural lands worsened water quality and produced the highest nutrient concentrations compared with forested and urban lands in the Piedmont region of North Carolina. Mouri et al.

[\(2011\)](#page-10-0) observed that the urban land type, together with the effects of increased population, domestic water use, and industrial wastewater, was positively associated with increases in water pollution. Similarly, Tu [\(2011\)](#page-10-0) found stronger positive relationships between the percentage of commercial land and the concentration of water pollutants based on the geographically spatial data analysis technique. In our study, the proportions of farmland cover were negatively correlated with nutrient related parameters  $(NO_3^-N$  and TN) and positively correlated with oxygen-related parameters (DO and ORP). The dilution effect played a major role for the sampling sites located at the confluence of two tributaries, and abundant discharge reduced the concentration of N-related parameters in the mean/highflow periods. Although a negative correlation between percentages of agricultural land cover and concentrations of nutrients in the streams was found in the <span id="page-9-0"></span>mean- or high-flow periods, a more detailed investigation would help clarify the relationships. The results also indicate that the pollution source mainly comes from agricultural runoff and less mining industrial effluents.

## Conclusions

In the present study, 12 sampling sites in the upper reach of the Hun River were classified into four groups (Group I: natural, Group II: near-natural, Group III: more disturbed, and Group IV: seriously disturbed) based on the results of CA and LUS scores. The major parameters (conductivity, turbidity, TN, TP,  $NO<sub>3</sub><sup>-</sup>-N$ , and  $NH_4^+$ -N) tend to increase significantly from Group I to Group IV, and from upstream to downstream. With the increased intensity of anthropogenic disturbances, the concentrations of nutrient-related parameters (TN,  $NO_3$ <sup>-</sup>-N, and  $NH_4$ <sup>+</sup>-N) increased from Group I to Group IV. Conductivity, turbidity, and  $NO<sub>3</sub><sup>-</sup>-N$  were identified as the most sensitive parameters in different rainfall periods and only  $NO<sub>3</sub><sup>-</sup>-N$  was always the key parameter in determining the water quality variations for all year. These parameters make it convenient for local authorities to monitor and assess water quality variations quickly through a few simple parameters.

The results of this study provide insight into the associations between the surface water quality and land use types at the local scale in the upper reach of the Hun River. Forest played an important role in maintaining clean water, whereas farmland deteriorated the surface water quality due to non-point agricultural pollutants in the low-flow period. The results of the study show that it is fundamental to preserve sufficient forest land area and to control agriculture to maintain good water quality in the upper reach of the Hun River. Finally, sustainable land use practices and scientific environmental regulations are required for water conservation and management in the upper reach of the Hun River.

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### References

- Absalon, D., & Matysik, M. (2007). Changes in water quality and runoff in the Upper Oder River Basin. Geomorphology, 92, 106–118.
- Ahearn, D. S., Sheibley, R. W., Dahlgren, R. A., & Keller, K. E. (2004). Temporal dynamics of stream water chemistry in the last free-flowing river draining the western Sierra Nevada, California. Journal of Hydrology, 295(1–4), 47– 63.
- Allan, J. D., & Castillo, M. M. (2007). Stream ecology: structure and function of running waters (2nd ed.). New York: Chapman and Hall.
- Brion, G., Brye, K., Haggard, B., West, C., & Brahana, J. (2011). Land-use effects on water quality of a first-order stream in the Ozark Highlands, Mid-Southern United States. River Research and Applications, 27(6), 772–790.
- Bureau, S. E. P. (2002). Methods of monitoring and analysis for water and wastewater (4th ed.). Beijing: Chinese Environment Science Press.
- Collier, K. (2008). Temporal patterns in the stability, persistence and condition of stream macroinvertebrate communities: relationships with catchment land-use and regional climate. Freshwater Biology, 53(3), 603–616.
- Filik Iscen, C., Emiroglu, O., Ilhan, S., Arslan, N., Yilmaz, V., Ahiska, S., et al. (2008). Application of multivariate statistical techniques in the assessment of surface water quality in Uluabat Lake, Turkey. Environmental Monitoring and Assessment, 144(1–3), 269–276.
- Fu, B. (2008). Blue skies for China. Science, 321, 611.
- Lenat, D., & Crawford, J. K. (1994). Effects of land-use on water-quality and aquatic Biota of 3 North-Carolina Piedmont streams. Hydrobiologia, 294(3), 185–199.
- Lepers, E., Lambin, E. F., Janetos, A. C., DeFries, R., Achard, F., Ramankutty, N., et al. (2005). A synthesis of information on rapid land-cover change for the period 1981–2000. Bioscience, 55(2), 115–124.
- Li, S. Y., Gu, S., Tan, X., & Zhang, Q. F. (2009). Water quality in the upper Han River basin, China: the impacts of land use/land cover in riparian buffer zone. Journal of Hazardous Materials, 165(1–3), 317–324.
- Liu, S. M., Zhang, J., Chen, H. T., Wu, Y., Xiong, H., Zhang, Z. F., et al. (2003). Nutrients in the Changjiang and its tributaries. Biogeochemistry, 62(1), 1–18.
- Lowrance, R., Altier, L. S., Newbold, J. D., Schnabel, R. R., Groffman, P. M., Denver, J. M., et al. (1997). Water quality functions of riparian forest buffers in Chesapeake Bay watersheds. Environmental Management, 21(5), 687–712.
- Maloney, K. O., & Weller, D. E. (2011). Anthropogenic disturbance and streams: land use and land-use change affect stream ecosystems via multiple pathways. Freshwater Biology, 56(3), 611–626.
- Mayer, P. M., Reynolds, S. K., McCutchen, M. D., & Canfield, T. J. (2007). Meta-analysis of nitrogen removal in riparian buffers. Journal of Environmental Quality, 36, 1172–1180.
- McCune, B., & Mefford, M. J. (1999). PC-ORD. Multivariate Analysis of Ecological Data.Version 5.0 MjM Software. USA: Gleneden Beach, OR.
- Mehaffey, M. H., Nash, M. S., Wade, T. G., Ebert, D. W., Jones, K. B., Rager, A., et al. (2005). Linking land cover and water

<span id="page-10-0"></span>quality in New York City's water supply watersheds. Environmental Monitoring and Assessment, 107(1–3), 29–44.

- Miserendino, M. L., Casaux, R., Archangelsky, M., Di Prinzio, C. Y., Brand, C., & Kutschker, A. M. (2011). Assessing land-use effects on water quality, in-stream habitat, riparian ecosystems and biodiversity in Patagonian northwest streams. Science of the Total Environment, 409(3), 612–624.
- Mouri, G., Takizawa, S., & Oki, T. (2011). Spatial and temporal variation in nutrient parameters in stream water in a rural– urban catchment, Shikoku, Japan: effects of land cover and human impact. Journal of Environmental Management, 92 (7), 1837–1848.
- Neary, D. G., Ice, G. G., & Jackson, C. R. (2009). Linkages between forest soils and water quality and quantity. Forest Ecology and Management, 258(10), 2269–2281.
- Ouyang, Y., Nkedi-Kizza, P., Wu, Q. T., Shinde, D., & Huang, C. H. (2006). Assessment of seasonal variations in surface water quality. Water Research, 40(20), 3800–3810.
- Pesce, S. F., & Wunderlin, D. A. (2000). Use of water quality indices to verify the impact of Cordoba City (Argentina) on Suquia River. Water Research, 34(11), 2915–2926.
- Pronk, M., Goldscheider, N., & Zopfi, J. (2007). Particle-size distribution as indicator for fecal bacteria contamination of drinking water from karst springs. Environmental Science & Technology, 41(24), 8400–8405.
- Shrestha, S., & Kazama, F. (2007). Assessment of surface water quality using multivariate statistical techniques: a case study of the Fuji river basin, Japan. Environmental Modelling & Software, 22(4), 464–475.
- Sigleo, A. C., & Frick, W. E. (2007). Seasonal variations in river discharge and nutrient export to a Northeast Pacific estuary. Estuarine, Coastal and Shelf Science, 73, 368–378.
- Singh, K. P., Malik, A., Mohan, D., & Sinha, S. (2004). Multivariate statistical techniques for the evaluation of spatial and temporal variations in water quality of Gomti River (India) — a case study. Water Research,  $38(18)$ , 3980– 3992.
- Tong, S. T. Y., & Chen, W. L. (2002). Modeling the relationship between land use and surface water quality. Journal of Environmental Management, 66(4), 377–393.
- Tong, S. T., Liu, A. J., & Goodrich, J. A. (2009). Assessing the water quality impacts of future land-use changes in an urbanising watershed. Civil Engineering and Environmental Systems, 26(1), 3–18.
- Tu, J. (2011). Spatially varying relationships between land use and water quality across an urbanization gradient explored by geographically weighted regression. Applied Geography, 31(1), 376–392.
- Tu, J., & Xia, Z. G. (2008). Examining spatially varying relationships between land use and water quality using geographically weighted regression: I. Model design and

evaluation. Science of the Total Environment, 407(1), 358–378.

- Walling, D. E., & Fang, D. (2003). Recent trends in the suspended sediment loads of the world's rivers. Global and Planetary Change, 39(1–2), 111–126.
- Wang, J. H., Shen, Y. M., Zhen, H., Feng, Y., Wang, Z. X., Yang, X., et al. (2011). Three-dimensional numerical modelling of water quality in Dahuofang Reservoir in China. Science China-Physics Mechanics & Astronomy, 54(7), 1328–1341.
- Wang, X. L., Han, J. Y., Wang, X. L., Han, J. Y., Xu, L. G., Gao, J. F., et al. (2011). Effects of anthropogenic activities on chemical contamination within the Grand Canal, China. Environmental Monitoring and Assessment, 177(1–4), 127–139.
- Wear, D. N., Turner, M. G., & Naiman, R. J. (1998). Land cover along an urban–rural gradient: implications for water quality. Ecological Applications, 8(3), 619–630.
- Williams, M., Hopkinson, C., Rastetter, E., Vallino, J., & Claessens, L. (2005). Relationships of land use and stream solute concentrations in the Ipswich River basin, Northeastern Massachusetts. Water Air Soil Pollution, 161(1–4), 55–74.
- Wu, G., Liu, Y., Shao, G. F., Tang, L., & Wang, G. Z. (2008). Effects of land use on water quality of two high-altitude lakes and catchments in Yunnan Province, China. International Journal of Sustainable Development and World Ecology, 15(6), 534–542.
- Yao, J., He, X., Li, X., Chen, W., & Tao, D. (2011). Monitoring responses of forest to climate variations by MODIS NDVI: a case study of Hun River upstream, northeastern China. European Journal of Forest Research. doi:[10.1007/](http://dx.doi.org/10.1007/s10342-011-0543-z) [s10342-011-0543-z.](http://dx.doi.org/10.1007/s10342-011-0543-z)
- Zhang, Y., Guo, F., Meng, W., & Wang, X. Q. (2009). Water quality assessment and source identification of Daliao river basin using multivariate statistical methods. Environmental Monitoring and Assessment, 152(1), 105–121.
- Zhang, Y. X., Dudgeon, D., Cheng, D. S., Thoe, W., Fok, L., Wang, Z. Y., et al. (2010). Impacts of land use and water quality on macroinvertebrate communities in the Pearl River drainage basin, China. Hydrobiologia, 652(1), 71– 88.
- Zhang, Z., Tao, F. L., Du, J. A., Shi, P. J., Yu, D. Y., Meng, Y. B., et al. (2010). Surface water quality and its control in a river with intensive human impacts — a case study of the Xiangjiang River, China. Journal of Environmental Management, 91(12), 2483–2490.
- Zhao, M., Zeng, C., Liu, Z. H., & Wang, S. J. (2010). Effect of different land use/land cover on karst hydrogeochemistry: a paired catchment study of Chenqi and Dengzhanhe, Puding, Guizhou, SW China. Journal of Hydrology, 388(1–2), 121–130.