1. Introduction

Stream water chemistry is controlled by numerous natural and anthropogenic factors (Ahearn et al., 2005). Their effects on hydrochemistry can either be diffuses (e.g., runoff from urban and crop cultivation, interflow through organic rich soils) or point pollutants (e.g., industrial effluents) (Sliva and Williams, 2001; Li et al., 2008). Also, watershed characteristics including topography and surficial geology can influence surface water quality (Sliva and Williams, 2001). In recent years there is a rapid declining availability of usable freshwater in terms of water quality and quantity due to unsustainable land use practices (Ngoye and Machiwa, 2004).

Water quality is generally linked to land use/land cover (LULC) in catchment (Ahearn et al., 2005), and studies have been focusing on their relationships with water quality variables such as dissolved salts, suspended solid, and nutrients (Hill, 1981; Allan et al., 1997; Johnson et al., 1997; Osborne and Wiley, 1988; Smart et al., 1998; Sliva and Williams, 2001; Turner and Rabalais, 2003; Ahearn et al., 2005). They conclude that agricultural land use strongly influences nitrogen (Johnson et al., 1997; Smart et al., 1998; Ahearn et al., 2005), phosphorus (Hill, 1981), and sediments (Allan et al., 1997; Johnson et al., 1997; Ahearn et al., 2005) in stream water. Urban land use has influenced water nutrients as well (Osborne and Wiley, 1988; Sliva and Williams, 2001).

In 2002, China implemented three-route (East, Middle and West) South to North water transfer Project (SNWTP) with a capacity of transferring a total of 44.8 billion m³ of water annually from the Yangtze River and its tributaries to drought North China and Northwest China (Zhang, 2005). The Han River is the water source area of its Middle Route supplying 13.8 billion m³ of water annually to the North China including Tianjin and Beijing City for domestic, industrial and irrigation purposes (Li et al., in press). Since late 1980s, diffuse sources have been dramatically increasing due to intensive anthropogenic activities (Wang et al., 2006) and the Han River has become one of the most nitrogen-contaminated tributaries of the Yangtze River (Liu et al., 2003; Li et al., in press) with moderate metal contamination (Li et al., 2008). The study presents the spatio-temporal variability of physico-chemicals and the impact of LULC on water quality, and it would help water conservation in the upper Han River basin for the interbasin water transfer project.

2. Study area

The Han River, the largest tributary of the Yangtze River, originates from Ningqiang County of Shaanxi province, and covers approximately 159 × 10³ km² with a total length of 1577 km (Yang et al., 1997; Shen and Liu, 1998). Its upper reaches (31°20’–34°10’ N, 106°–112° E; 210–3500 m a.s.l) are located in the mountainous region, with
drainage area of approximately $95.2 \times 10^3 \text{ km}^2$ and 925 km long (Shen and Liu, 1998; Fig. 1). The upper basin is located in the north sub-tropic monsoon climatic region. Annual mean precipitation is 700–1800 mm, of which about 80% falls in the time period from May to October (Yang et al., 1997). The annual mean runoff is $41.1 \times 10^9 \text{ m}^3$, accounting for 70% of the total runoff of the whole basin with large annual and interannual variability (Jin and Guo, 1993; Yang et al., 1997). The discharge from the Reservoir is about $23.0 \times 10^9 \text{ m}^3/\text{year}$ after the SNWTP, and the peak discharge reaches about 14,000 m$^3$/s in 2005 in the past 30 years.

![Fig. 1. The location of sampling sites, DEM, river network, and land use and land cover of the upper Han River, China (Zone 1—Laoguan River, Zone 2—Dan River, Zone 3—South of the Qinling Mountains, Zone 4—Ziwu River, Zone 5—Hanzhong Plain, Zone 6—North of the Daba Mountains, Zone 7—Ankang Plain, Zone 8—Du River, and Zone 9—Danjiangkou Reservoir).](image-url)
The vegetation in the basin is dominated by coniferous, deciduous forest, mixed coniferous and broad-leaved forest, shrub and herb (Shen et al., 2006). Agricultural lands concentrates in low elevation, i.e., Hanzhong plain (zone 5; Fig. 1; Shen et al., 2006). The main crops include maize (Zea mays Linn), wheat (Triticum aestivum Linn), rice (Oryza sativa Linn), cassava (Manihot esculenta), vegetables including radish (Raphanus sativus L var. radiculus Pers.), cucumber (Cucumis sativus L.), tabasco (Capsicum L.) and citrus (Citrus). A very small area is utilized for human settlements ranging from small towns to villages (Shen et al., 2006), while human population is sparse in uplands. Large cities including Shangluo, Shiyian, Hanzhong and Ankang city are located along the Han River corridor. Soil is composed of yellow brown soil and cinnamon soil (Cai et al., 2000), mapping to Ferric Luvisol and Haplic Greyxems respectively by FAO (1971).

3. Methods

3.1. Water sampling and analysis

Six field surveys were conducted in June, August and November 2005, and April, June and October 2006. Of which, August and November in 2005 and October in 2006 are rainy season, and the rest is dry season. A total of 252 grab samples were collected in the 42 sites of the upper Han River basin (Fig. 1). All sampling bottles were soaked for 48 h in 15% nitric acid and subsequently rinsed twice in distilled water prior to use. Water samples were collected at a depth of approximate 10 cm using previously acid-washed high density polyethylene (HDPE) 1 l bottles. The containers were rinsed thrice with sample water on site. A 500 ml subsample was filtered through a previously acid-washed 0.45 μm pore Millipore nitrocellulose membrane filter and the filters were stored in HDPE bottles. Acid-cleaned polyethylene gloves were used while handling all plastic and glass ware.

Water temperature (T), dissolved oxygen (DO), pH, oxidation–reduction potential (ORP), electrical conductivity (EC), turbidity, total dissolved solids (TDS), nitrate–nitrogen (NO₃–N) and ammonium–nitrogen (NH₄–N) were determined on site using YSI 6920. The instrument was calibrated at 0 and 100% oxygen saturation before and after usage for DO measurement. The pH sonde was calibrated at 7 and 10, turbidity sonde at 123 and 0, and the nitrogen sondes were both calibrated at 100 mg l⁻¹ and 1 mg l⁻¹ before sampling. The membranes used for filtration were dried at 63 °C to constant mass, and suspended particulate matter (SPM) was calculated from the difference in the filter paper weights before and after filtering. Biochemical oxygen demand (BOD) and potassium permanganate index (Jₕₐₙ) were analyzed using dilution and seeding method and potassium permanganate index method, respectively (CSEPB, 2002). Dissolved phosphorus (DP) was detected by inductively coupled plasma atomic emission spectrometer (ICP-AES) (IRIS Intrepid II XSP DUO, USA). Quality control procedures, including internal quality control using reference materials and regular participation in interlaboratory comparisons, were employed to monitor the validity of the test results.

3.2. Land use and land cover analysis

Landsat Thematic Mapper imagery from 2000 was used to map LULC in the basin (Shen et al., 2006). The five land cover categories are (1) vegetated land, including coniferous, deciduous forest, mixed coniferous and broad-leaved forest, thickets and herb; (2) agriculture, including paddy field and dry land; (3) urban, including industrial and residential areas; (4) waters, including rivers, wetland and sandy beach; and (5) bare lands, including gravels, bare ground and bare rocks. ArcGIS 8.3 Desktop GIS software was used to determine the composition of LULC.

3.3. Statistical analyses

Because the upper Han River basin has a large land area of 95,000 km², and the 42 water sampling sites were located across a range of land uses, geology types, and stream orders in the entire upper Han River (Fig. 1). Thus, the upper basin was first delineated into subwatersheds using DEM (O’Callaghan and Mark, 1984; Gu et al., 2007). Considering their similarity of land use and land cover (Shen et al., 2006), water quality, and human activities, the delineated subwatershed were consequently clustered into 9 zones (Table 1, Fig. 1). Analyses in this study were conducted in the zonal level. Relationships among the considered variables were tested using Pearson’s correlation with statistical significance set priori at p<0.05. Analysis of variance (ANOVA) was used to compare variations in water quality under different land uses with significance set at p<0.05 (least-significance difference, LSD). All the statistical analyses were performed using SPSS 13.0 for windows.

4. Results

4.1. Land use and land cover distribution

Vegetated land was the dominant land cover type in the basin (Fig. 2) and it covered from 71.2% (zone 9, Danjiangkou Reservoir) to 4.1% (zone 8 and 9).

**Table 1**

<table>
<thead>
<tr>
<th>Zone</th>
<th>Sub watershed</th>
<th>Watershed characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Laoguan River</td>
<td>Intensive human influence including agriculture in buffer zone and mineral exploration, belongs to the Dan River basin</td>
</tr>
<tr>
<td>2</td>
<td>Dan River</td>
<td>The highest bare land type and large landscape variation</td>
</tr>
<tr>
<td>3</td>
<td>South of the Qinling Mountains</td>
<td>A forested area with lowest urbanization</td>
</tr>
<tr>
<td>4</td>
<td>Ziwu River</td>
<td>A forest area including coniferous upland with little human influences, showing granite geology</td>
</tr>
<tr>
<td>5</td>
<td>Hanzhong Plain</td>
<td>The primary agricultural area, and cultivation like rice and maize is carried out 10–100 m from rivers, with higher urbanization (Hanzhong city)</td>
</tr>
<tr>
<td>6</td>
<td>North of the Daba Mountains</td>
<td>A primary area for minerals with relative higher agricultural land area compared to the South of the Qinling Mountains</td>
</tr>
<tr>
<td>7</td>
<td>Ankang Plain</td>
<td>The highest agriculture land use area, with intensive cultivation in buffer zones; rivers with dam discharge water before flood season</td>
</tr>
<tr>
<td>8</td>
<td>Du River</td>
<td>The largest catchment in the upper Han River basin with serial impoundments for hydropower</td>
</tr>
<tr>
<td>9</td>
<td>Danjiangkou Reservoir</td>
<td>An industrial area (Shiyian city) where industrial effluents drain into the rivers, impacting the water quality directly in the Reservoir</td>
</tr>
</tbody>
</table>

**Fig. 2.** The composition of land use and land cover in the upper Han River basin, China (the area is 4180 km² for zone 1, 11,300 km² for zone 2, 15,700 km² for zone 3, 4030 km² for zone 4, 18900 km² for zone 5, 9230 for zone 6, 8880 km² for zone 7, 12,500 km² for zone 8 and 9940 km² for zone 9, respectively).
95.7% (zone 4, Ziwu River) of its respective land area (Fig. 2). Although agricultural widely distributed across the basin but it mainly concentrated in zones 5–9, comprising from 13.5% to 21.1% of its land area. Urban occupied less than 1% of the watershed area except in zone 5 (i.e., Hanzhong Plain) with 1.2%. Bare land had higher percentage in zones 1, 2, and 9 and it ranged from 5.9% to 9.2% (Fig. 2).

4.2. Physical–chemical water quality in the upper Han River basin

Spatial and temporal variations of physico-chemicals were shown in Fig. 3. Nitrogen, ORP, I_{MN} and turbidity generally displayed higher values in the rainy season, while higher values for T, BOD, DP, EC, TDS, SPM, pH and DO in the dry season. Most water quality

Fig. 3. The physical-chemicals (mean±SEM) in the upper Han River basin, China (the different letters indicate statistical difference of total averages among zones at p<0.05; LSD test).
parameters except T, DO, \( I_{\text{Mn}} \), BOD, and DP showed significant spatial variations (\( p<0.05 \)). The lower values of pH and higher concentration of DP occurred in zones 5 and 9, where large cities Hanzhong and Shiyan were located. Also, zone 9 displayed the highest \( \text{NH}_4^+ - \text{N} \) concentration. EC, TDS and \( \text{NO}_3^- - \text{N} \) had the lowest values in zone 4, an area with the highest vegetation cover (Fig. 2).

### Table 2

Pearson correlation coefficients between LULC and water quality parameters in the upper Han River basin, China

<table>
<thead>
<tr>
<th>Vegetation</th>
<th>Agriculture</th>
<th>Urban</th>
<th>Waters</th>
<th>Bare land</th>
<th>Area (km(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>-0.747(^a)</td>
<td>0.354</td>
<td>0.118</td>
<td>0.405</td>
<td>0.745(^a)</td>
</tr>
<tr>
<td>pH</td>
<td>0.457</td>
<td>-0.394</td>
<td>-0.731</td>
<td>-0.543</td>
<td>-0.055</td>
</tr>
<tr>
<td>EC</td>
<td>-0.522</td>
<td>0.256</td>
<td>0.169</td>
<td>-0.059</td>
<td>0.621</td>
</tr>
<tr>
<td>TDS</td>
<td>-0.521</td>
<td>0.255</td>
<td>0.169</td>
<td>-0.059</td>
<td>0.621</td>
</tr>
<tr>
<td>Turbidity</td>
<td>-0.042</td>
<td>0.442</td>
<td>-0.489</td>
<td>-0.166</td>
<td>-0.394</td>
</tr>
<tr>
<td>SPM</td>
<td>-0.210</td>
<td>0.633</td>
<td>-0.285</td>
<td>-0.161</td>
<td>-0.359</td>
</tr>
<tr>
<td>DO</td>
<td>-0.459</td>
<td>0.572</td>
<td>0.627</td>
<td>-0.021</td>
<td>0.035</td>
</tr>
<tr>
<td>ORP</td>
<td>0.239</td>
<td>-0.186</td>
<td>0.317</td>
<td>-0.468</td>
<td>-0.059</td>
</tr>
<tr>
<td>( I_{\text{Mn}} )</td>
<td>-0.738(^a)</td>
<td>0.788(^b)</td>
<td>0.034</td>
<td>0.419</td>
<td>0.163</td>
</tr>
<tr>
<td>BOD</td>
<td>0.104</td>
<td>-0.219</td>
<td>-0.215</td>
<td>0.172</td>
<td>0.056</td>
</tr>
<tr>
<td>( \text{NH}_4^- - \text{N} )</td>
<td>-0.762(^a)</td>
<td>0.213</td>
<td>0.143</td>
<td>0.811(^b)</td>
<td>0.810(^b)</td>
</tr>
<tr>
<td>( \text{NO}_3^- - \text{N} )</td>
<td>-0.772(^a)</td>
<td>0.219</td>
<td>0.251</td>
<td>0.299</td>
<td>0.882(^b)</td>
</tr>
<tr>
<td>DP</td>
<td>-0.531</td>
<td>0.450</td>
<td>0.808(^b)</td>
<td>0.505</td>
<td>0.122</td>
</tr>
</tbody>
</table>

\(^a\) Significance at 0.05 probability level.
\(^b\) Significance at 0.01 probability level.

### Table 3

Stepwise multiple regression models for physico-chemicals and LULC in the upper Han River basin, China

<table>
<thead>
<tr>
<th>Physico-chemicals</th>
<th>Independent variables</th>
<th>Regression equations</th>
<th>( R^2 )</th>
<th>Adjusted ( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>Vegetation</td>
<td>-0.080(\times)VEG</td>
<td>0.558(^b)</td>
<td>0.495(^b)</td>
</tr>
<tr>
<td>pH</td>
<td>Urban</td>
<td>-0.267(\times)URB</td>
<td>0.535(^b)</td>
<td>0.468(^b)</td>
</tr>
<tr>
<td>SPM</td>
<td>Agriculture Urban</td>
<td>-0.219(\times)AGR +0.434(\times)GR +0.408(\times)URB</td>
<td>0.740(^b)</td>
<td>0.653(^b)</td>
</tr>
<tr>
<td>( I_{\text{Mn}} )</td>
<td>Agriculture</td>
<td>0.838(\times)AGR +0.047(\times)GR +0.161(\times)URB</td>
<td>0.622(^b)</td>
<td>0.568(^b)</td>
</tr>
<tr>
<td>BOD</td>
<td>Urban</td>
<td>0.156(\times)WAT +0.032(\times)BAR</td>
<td>0.853(^b)</td>
<td>0.804(^b)</td>
</tr>
<tr>
<td>( \text{NH}_4^+ - \text{N} )</td>
<td>Bare lands</td>
<td>1.000(\times)BAR</td>
<td>0.778(^b)</td>
<td>0.747(^b)</td>
</tr>
<tr>
<td>( \text{NO}_3^- - \text{N} )</td>
<td>Bare lands</td>
<td>0.001(\times)URB</td>
<td>0.650(^b)</td>
<td>0.600(^b)</td>
</tr>
</tbody>
</table>

The water quality parameters without regression models are not listed.

\(^a\) Significance at 0.05 probability level.
\(^b\) Significance at 0.01 probability level.
4.3. Linking land use/land cover and river water quality

Correlation and regression analyses by analyzing the average values of the water quality parameters and land use patterns revealed that urban was significantly correlated to pH and DP, while agriculture to $hm_n$ and vegetated land cover was negatively related to T, $hm_n$, and nitrogen. Bare ground and rocks had strong positive correlation with nitrogen and $T$ (Table 2). Stepwise multiple linear regression demonstrated that no single land cover type was able to describe the overall water quality, but most water physico-chemicals could be sufficiently predicted using one or two land use/land cover types (Table 3). PH and DP could be predicted by urban area, $NO_3^-$ by bare lands ($R^2=0.747, p<0.01$), $hm_n$ by agriculture ($R^2=0.568, p<0.05$), SPM by agriculture and urban ($R^2=0.653, p<0.05$), and $NH_4^+$-N by water and bare lands ($R^2=0.804, p<0.01$), respectively.

5. Discussions

The overall concentrations of SPM, nitrogen and DP have increased since 2000 (Chen at al., 2000; Liu et al., 2003), which is associated with population increase and economic growth in the Han River basin (Liu et al., 2003; Wang et al., 2006). However, high vegetated land cover (Fig. 2) and low population density in few subwatersheds, such as Laoguan River, south of the Qinling Mountains and Ziwu River, are contributable to the lower concentrations of SPM, nitrate and DP respectively (Fig. 3; Chen at al., 2000; Liu et al., 2003).

Studies have shown that the percentage of agriculture at watershed scale is a primary predictor for nitrogen and phosphorus (Hill, 1981; Johnson et al., 1997; Smart et al., 1998; Ferrier et al., 2001; Ahearn et al., 2005), and there are elevated nitrate concentrations in the streams of urbanized areas (Osborne and Wiley, 1988; Sliva and Williams, 2001). This study indicates that nitrogen concentrations varies among zones (Fig. 3) and in general have a negative correlation with vegetated coverage perhaps by the reduction of nitrogen loss from soil (Table 2; Stark and Hart, 1997). However, bare lands coverage is the primary variable to predict nitrogen concentrations (Tables 3; Hunsaker and Levine, 1995), that implies a great influence of weathering of bare rocks and gravels on nitrogen contents in the riverine network (Holloway et al., 1998; Sliva and Williams, 2001).

In the Han River basin, DP has significant positive correlation with urban and could be predicted using urban area (Tables 2, 3), which is consistent with other reports (Osborne and Wiley, 1988; Ferrier et al., 2001; Sliva and Williams, 2001). Meanwhile, relatively higher DP concentrations are observed in zones 5 and 9 where large cities Hanzhong and Shiyan are respectively located (Fig. 3), that also indicates the impacts of industrial wastes and sewages on P concentration. However, the difference in DP among zones is not statistically significant regardless of the difference in land use and land cover (Figs. 2, 3), that implies that natural processes may have played an important role in determining DP in the basin (Sliva and Williams, 2001).

Urban areas and cultivated lands are primarily located along the river networks in the Han River basin (Fig. 1), and their impacts on the water quality in streams were expected. Our study indicates that agriculture and urban have dominant control on SPM and the highest SPM values occurs in the Ankang plain (zone 7) where cultivated land occupy 21.1% of the land area (Table 3; Fig. 2; Allan et al., 1997; Johnson et al., 1997; Ahearn et al., 2005). Although higher nutrients concentrations are observed in zone 9 where Shiyan city is located (Fig. 3), yet the influences of urban and agriculture on nutrients concentration in streams are relatively limited in the Han River (Tables 2, 3). Perhaps the small percentage may have caused the underestimate of their impacts on water quality (Fig. 2).

At subwatershed scale, much higher levels in the rainy season indicate the major source of diffuses for $hm_n$ (Fig. 3; Zhao et al., 1998), which is also reflected by its strong correlations with agriculture ($R=0.79$, $p<0.05$) and vegetation ($R=0.74$, $p<0.05$) (Table 2). No significant correlations between BOD and LULC (Table 2) and peak values in different seasons (Fig. 3) indicate the mixed and irregular influences including point source and diffuses (Chen et al., 2000). PH, corresponding to urban (Table 2; $R=0.731$, $p<0.05$), displays lower values in the Hanzhong plain and Danjiangkou Reservoir, due to industrial effluents. EC and TDS show lower values in the rainy season (Fig. 3), which is primarily due to the dilution by precipitation (Dai, 1997). Their significant difference among zones implies the different geology and weathering process across the basin (Zhang et al., 1996). Their lowest constituents in the Ziwu River catchment are associated to its highest vegetation coverage and granite lithology.

The watershed delineation of the study area is variable, so different results about linkages between water quality parameters and LULC may be obtained in different subwatershed scale. Meanwhile, water quality variations in different temporal level increase the uncertainties. While total means analysis of water quality variables can give us general information about the impacts of LULC on water quality. Also, the results can determine the types of LULC controlling water quality, and seasonal and spatial patterns of water quality reflect their sources and polluted areas, which is very important for water quality conservation, i.e., sewage treatment plants construction and revegetation. SNWTP will submerge more than 370 km$^2$ land at low asl and introduce a migration of more than 250,000 people (Berkoff, 2003), which will impact land use patterns controlling water quality in the basin (Table 3). For example, the decrease of vegetated land area and urbanization caused by migration will increase $hm_n$ and nutrients.

6. Conclusions

All the water quality variables demonstrate spatial variations except T, DO, $hm_n$, BOD, and DP at subwatershed scale. Of which, nitrogen, ORP, $hm_n$, and turbidity generally display higher contents in the rainy season, while higher concentrations for T, BOD, DP, EC, TDS, SPM, pH and DO in the dry season. The stretches of the river in vegetated areas have lower levels of nutrients compared to areas close to degraded land use type. Bare lands were significantly correlated to concentrations of nitrogen, and urban to pH and DP, while agriculture to SPM and $hm_n$.

In the upper Han River basin, urban and agriculture are primarily distributed in riparian, therefore, the effects of land use in riparian on water quality and relationships between buffer landscape and stream water quality will be the subjects of our further study. We expect further land cover changes declining water quality due to agricultural development and population increase; also, the global climate changes introducing the increase of temperature and evaporation, the decrease of rainfall, serious soil erosion caused by high frequency of flooding and the changes of biochemical cycles, may further offset theses effects. It is recommended that efforts to reduce waste discharges into fluvial system should be taken in urban (e.g., Danjiangkou Reservoir) and in agricultural areas. Additionally, land use in buffer zone in the upper Han River basin and planned urban settlements should be emphasized.

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Letters to Editor.


