Journal of Hazardous Materials 165 (2009) 317–324

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Water quality in the upper Han River basin, China: The impacts of land use/land cover in riparian buffer zone

Siyue Li[a], Sheng Gu[a], Xiang Tan[a,b], Quanfa Zhang[a,*]

[a] Laboratory of Aquatic Botany and Watershed Ecology, Wuhan Botanical Garden, the Chinese Academy of Sciences, Wuhan 430074, China
[b] Graduate School of the Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:
Received 10 July 2008
Received in revised form
15 September 2008
Accepted 29 September 2008
Available online 11 October 2008

Keywords:
Water quality
Riparian
Land use and land cover
Han River
Physico-chemicals

ABSTRACT

Vegetated riparian zones adjacent to rivers and streams, can greatly mitigate nutrients, sediment from surface through deposition, absorption and denitrification, yet, human activities primarily land use practices have dramatically reduced the capacity. In this study, 42 sampling sites were selected in the riverine network throughout the upper Han River basin (approximately 95,200 km^2) of China. A total of 252 water samples were collected during the time period of 2005–2006 and analyzed for physico-chemical variables and major ions. Correlation analysis, principal components analysis and stepwise least squares multiple regression were used to determine the spatio-temporal variability of water quality variables and in particular their correlations with land use/land cover in the 100 m riparian zone along the stream network. The basin in general has a better water quality in the dry season than the rainy season, indicated by the primary pollutants including COD$_{Mn}$ and nitrogen. Major ion compositions display large spatial and seasonal differences and are significantly related to land use and land cover in the riparian zone, while riparian landscape could not explain most of the water quality variability in T, pH, turbidity, SPM and COD$_{Mn}$. The research could provide help develop sustainable land use practice of the riparian zone for water conservation in the basin.

1. Introduction

Surface waters are controlled by both the natural processes, i.e. precipitation inputs, erosion, weathering, and the anthropogenic activities via point sources, such as industrial effluents and wastewater treatment facilities, and diffuse, such as runoffs from urban area and farming land [1–4]. Studies demonstrate that surface water quality has deteriorated noticeably in many countries in the past decades due to poor land use practices (e.g. [1,5]), indicating by the strong relationships between declining water quality and increasing agricultural development at catchment scale [1,6]. Therefore, researchers have been paying more attentions to the effect of land use on water quality, in particular the key contributors of agricultural activities to nutrients and suspended particulate matter [1,6,7]. Other findings note that urban land development greatly influence water quality as well [2,8].

Riparian buffers, especially undisturbed vegetated riparian zones situated adjacent to river and streams, can greatly mitigate nutrients, sediment from surface and groundwater flow through the processes of deposition, absorption and denitrification [9,10]. Past findings highlight the importance of the riparian zones for water quality (e.g. [11,12]), while its extent and the scale of the influences on water physicochemistry are still under debate [2,7,13]. For instance, Sliva and Williams [2] and Hunsaker and Levine [13] find that land use and land cover at catchment level are a better indicator of water quality than those in the buffer zones, while other studies show the opposite [7].

The upper Han River is the water source area of China's South-to-North Water Transfer Project which will transfer water to North China including Beijing and Tianjin for domestic, industrial and irrigational usages [14]. Studies have reported increasing nitrogen concentration and heavy metal contaminations in the Han River [3,5,14,15]. Diffuse pollutants due to land use practices have been increasingly becoming the key contributors to the declining water quality, and pollution prevention requires a better understanding of water quality and the impact by land use and land cover in the basin. Previous study has demonstrated the relationships between water quality and basin-wide land use and land cover [16]. This study presents the spatio-temporal variability of physico-chemicals and particularly the impacts of land use in riparian zone on water quality in order to develop sustainable land use practice for water conservation in the basin and ultimately for the interbasin water transfer project.

---

* Corresponding author. Tel.: +86 27 87510702; fax: +86 27 87510251.
E-mail address: qzhang@wbgcas.cn (Q. Zhang).

0304-3894/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2008.09.123

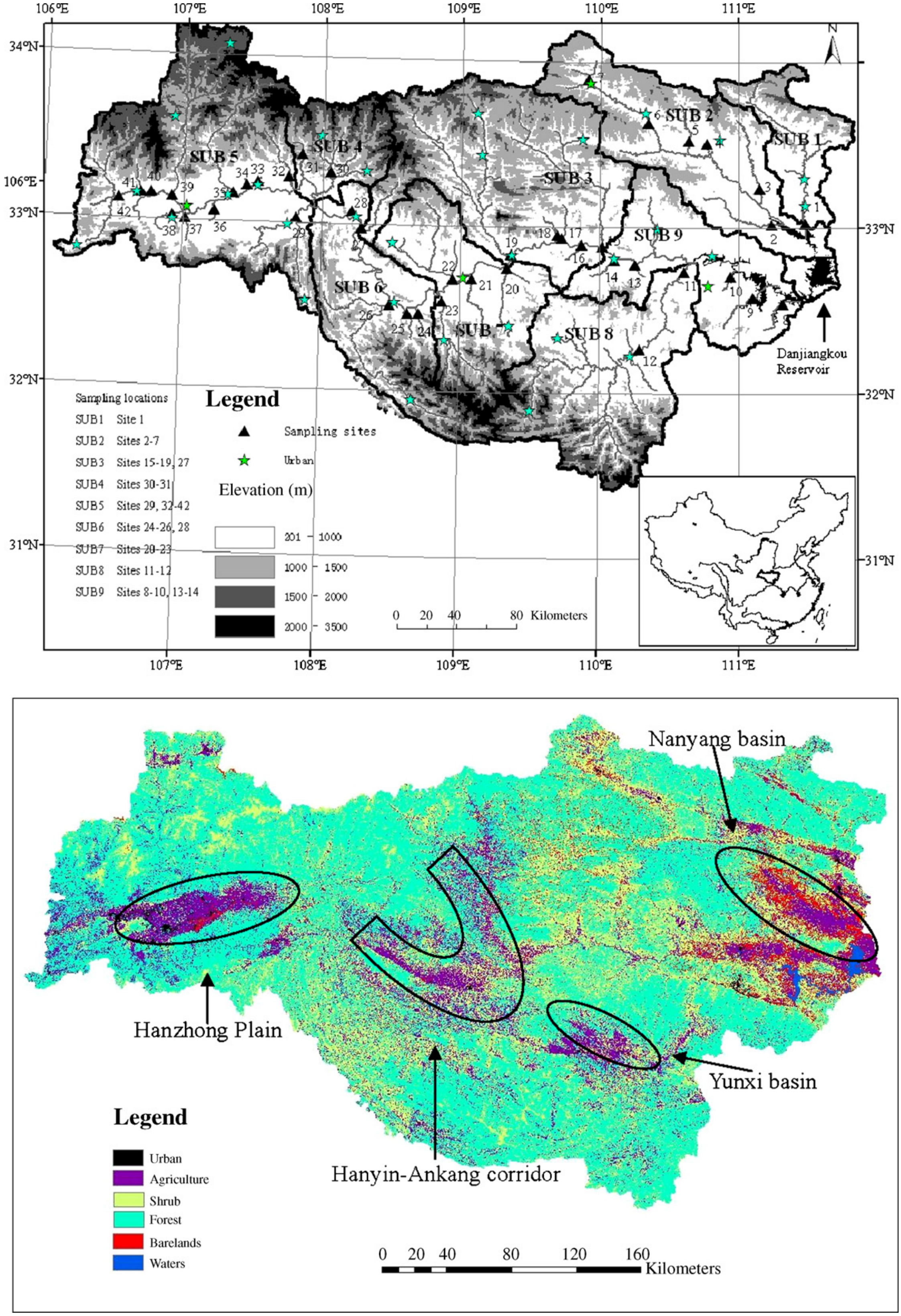

Fig. 1. The upper Han River basin showing the water sampling sites, DEM, drainage system and LULC, China (SUB1, Laoguan River; SUB2, Dan River; SUB3, the South of the Qinling Mountain; SUB4, Ziwu River; SUB5, Hanzhong Plain; SUB6, the North of the Daba Mountains; SUB7, Ankang Plain; SUB8, Du River; SUB9, Danjiangkou Reservoir; [16]).

2. The study area

The upper Han River basin (31–34°N, 106–112°E; 210–3500 m *a.s.l.*) has a drainage area of 95,200 km^2 and is approximately 925 km long (Fig. 1). The basin drains a region of north subtropic monsoon climate, and its annual mean temperature ranges between 12 and 16 °C [14]. Average annual precipitation is from 700 to 1800 mm, and as much as 80% of annual precipitation falls in the period from May to October. The runoff is about 41.1×10^9 m^3/year, accounting for 70% of the total runoff of the entire basin with large annual and interannual variability [14,16].

The principle vegetation in the basin includes coniferous, deciduous forest, mixed coniferous and broad-leaved forest, shrub and herb [16]. Cultivation is mainly located in the Hanzhong Plain, Hanyin-Ankang corridor, Nanyang and Yunxi basins (Fig. 1; [16]). The major crops include maize, wheat, rice, cassava, vegetables and citrus. A very small area is utilized for human settlements ranging from small towns to villages, while human population is sparse in uplands. There are larger cities such as Shangluo, Danjiangkou, Shiyan, Hanzhong and Ankang city locating along the Han River corridor. Soil is characterized by yellow brown soil and cinnamon soil [16], and the surficial lithology in the basin is controlled by carbonates [4].

3. Methods

3.1. Water sampling and analysis

A total of 252 grab samples were collected in 42 sites throughout the upper Han River (Fig. 1) in 6 field surveys, carried out 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 rests are dry season. 15% (v/v) nitric acid was added to all sampling bottles for 24 h and then rinsed with Milli-Q water prior to usage. Water sampling proceeding and analysis for water temperature (*T*), pH, electrical conductivity (EC), turbidity, suspended particulate matter (SPM), dissolved oxygen (DO), nitrate-nitrogen (NO_3^--N), ammonium-nitrogen (NH_4^+-N) and dissolved phosphorus (DP) were following Li et al. [16]. The spatial and temporal variations of the above physico-chemicals have been demonstrated in the previous study [16].

HCO_3^- was titrated by HCl on the sampling day, and chemical oxygen demand (COD_{Mn}) was analyzed by potassium permanganate index method [18]. Major cations (Na, K, Ca and Mg) were determined using Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) (IRIS Intrepid II XSP DUO, USA). Anions (Cl^- and SO_4^{2-}) were measured 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 the range of ±10%.

To avoid the repetition of basic-data exhibition, this study only reported the major ions, i.e. K, Ca, Na, Mg, Cl^-, SO_4^{2-} and HCO_3^-.

3.2. Land use and land cover analysis

Land use composition within the 100 m buffer zones along streams were extracted from the land use and land cover map interpreted from 2000's Landsat TM and +ETM imageries using ArcGIS 8.7 Desktop GIS software. The five land cover categories were (1) forest land, including coniferous, deciduous forest, mixed coniferous and broad-leaved forest; (2) shrub, including thickets and herb; (3) agriculture, including paddy field and dry land; (4) urban, including industrial and residential areas; and (5) bare lands, including gravels, bare ground and bare rocks [16]. The land use composition was calculated based on the nine subwatersheds delineated using DEM, landscape and stream characteristics for comparison between buffer zonal and subcatchment landscape influences on water quality (Fig. 1; [16,17]).

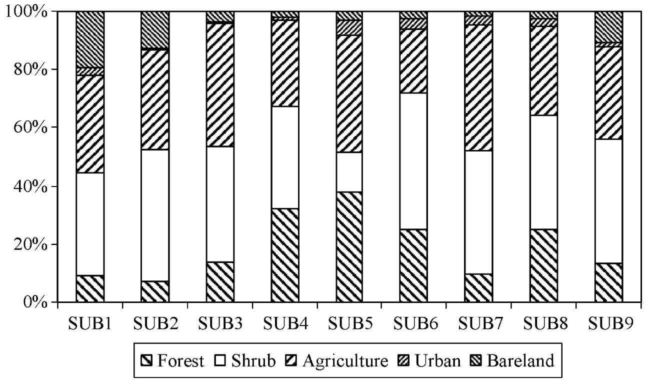

Fig. 2. The land use and land cover composition within 100 m riparian buffer zone along the streams of the nine subwatersheds in the upper Han River basin, China.

3.3. Statistical analyses

Relationships among the considered variables were tested using Pearson's correlation with statistical significance at $p < 0.05$. Principal components analysis (PCA) was conducted to assess patterns of water quality variables among the nine delineated subwatersheds (Fig. 1). Stepwise least squares multiple regression with water quality variables as dependent variables was carried out to assess relations among the land use composition within the 100 m riparian buffer zone and water physicochemistry. Final models were selected when none of the variables outside the model had significant F statistics and every variable in the model was significant. All the statistical analyses were performed using SPSS 15.0 for windows [16].

4. Results

4.1. Land use and land cover composition in the riparian zone

Analysis shows that vegetated lands, including forest and shrub, are the dominant land cover types in the riparian buffer zone (Fig. 2). Of which, shrub ranges from 13.8% in SUB5 (the Hanzhong Plain) to 47.0% in SUB6 (the North of the Daba Mountains), while from 7.1% in SUB2 (the Dan River) to 37.8% in SUB5 (the Hanzhong Plain) for forest. Agriculture in riparian zones is comprised from 21.9% to 43.4% of the total area in the respective subwatershed. Urban ranges from 0.5% (SUB3, the North of the Qinling Mountain) to 5.0% (SUB5, the Hanzhong Plain), and bareland from 1.7% in SUB7 (the Ankang Palin) to 19.2% in SUB1 (the Laoguan River) of its respective land area (Fig. 2).

4.2. Physical–chemicals in the upper Han River basin

Major ions tend to show higher values in the dry season except Mg (Fig. 3). All the water physico-chemical variables show large spatial differences, and the lowest values of EC, NO_3^--N, anions (Cl^-, SO_4^{2-}, HCO_3^-), Ca and Mg occur in SUB4 (the Ziwu River). The lower value of pH, higher concentrations of DP, and the highest concentrations of NH_4^+-N, Cl^- and SO_4^{2-} ([16]; Fig. 3) occur in SUB9 (Shiyan city, the mobile-industry area with a population of more than 500,000) (Fig. 1).

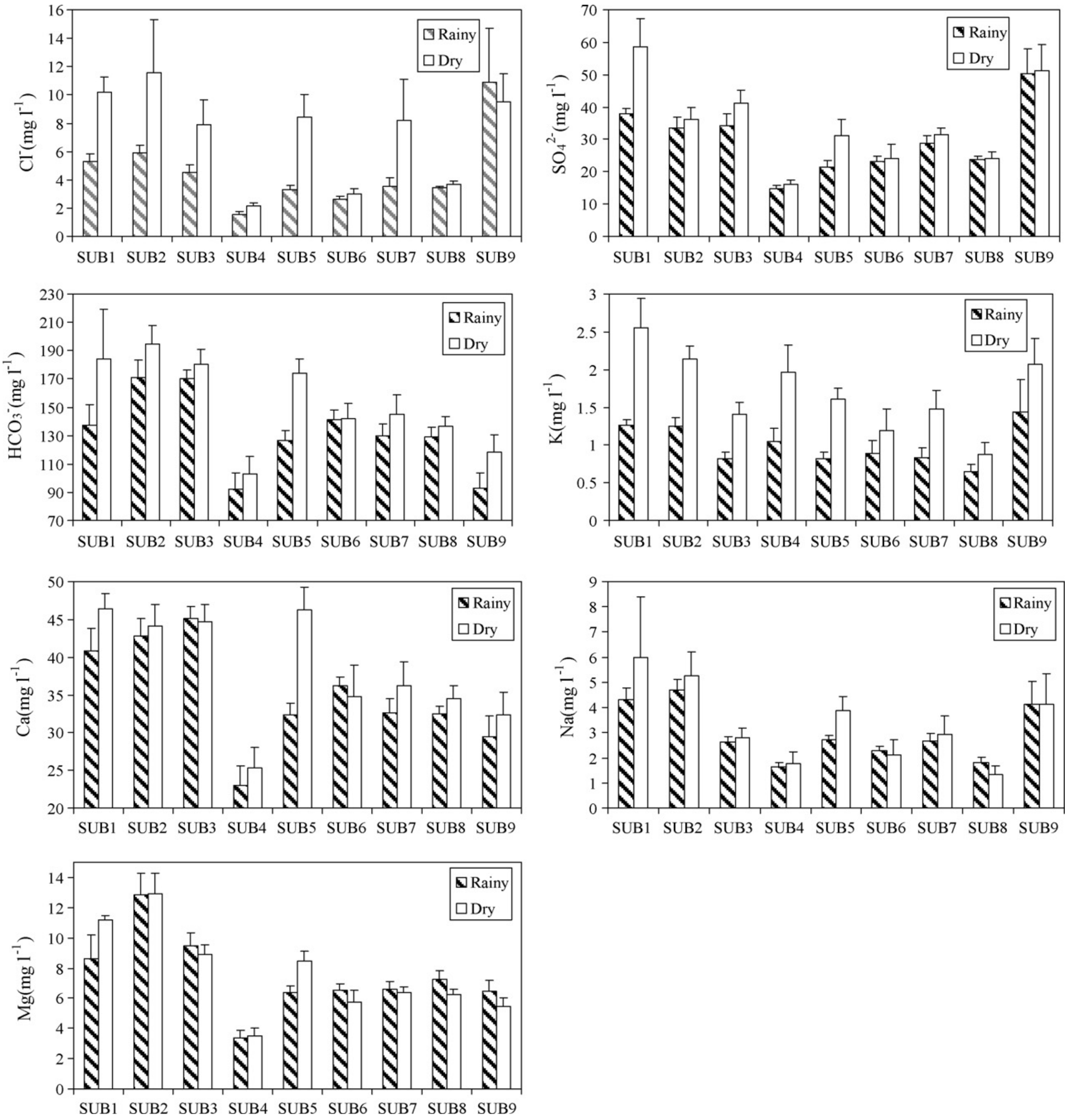

Fig. 3. The physical–chemicals (mean ± S.E.M.) in the upper Han River basin, China (water quality parameters including *T*, pH, EC, turbidity, SPM, DO, COD_{Mn}, NO_3^--N, NH_4^+-N and DP exhibited in [16]).

Correlation analysis for water physico-chemicals indicates that the dominant ions, including HCO_3^-, Ca and Mg have significant positive relationships in both rainy and dry seasons (Table 1). EC always shows positive correlations with HCO_3^-, Ca, Na and Mg in both seasons. NO_3^--N significantly corresponds with NH_4^+-N, Cl^-, SO_4^{2-}, K and Na, respectively in the rainy season, while it tends to be correlated with major cations (K, Ca, Na and Mg), Cl^- and HCO_3^- in the dry season (Table 1).

Principal components analysis (PCA) of the water quality variables extracts six components with eigenvalue >1.0 and they are accounting for 74.2% of the total variances (Table 2). The first two components are mainly comprised by EC, Cl^-, SO_4^{2-}, HCO_3^-, K, Ca, Mg and DP. The third and fifth components were mainly controlled by COD_{Mn} and SPM, and nitrogen, respectively.

4.3. Liking land use/land cover in the riparian zone and stream hydrochemistry

Correlation and regression analyses between the land use/land cover in riparian zone and stream hydrochemistry are shown in Tables 3 and 4. In the rainy season, forest is significantly correlated to EC, NO_3^--N, SO_4^{2-} and Na, and bare land has strong positive correlation with K and Na, and also contributes to nitrogen, Cl^-, SO_4^{2-}, Ca and Mg. In the dry season, bare land has strong positive correlation with EC, NO_3^--N, Cl^-, SO_4^{2-}, K and Na, while vegetation is negatively correlated to EC, NO_3^--N, major anions (Cl^-, SO_4^{2-}, HCO_3^-) and major cations (Ca, Na and Mg).

Stepwise multiple linear regression indicates that EC, NO_3^--N, SO_4^{2-} and Mg are controlled by forest in the riparian zone, while K

Table 1
Pearson correlation coefficients among the water physicochemistry for both rainy and dry season in the upper Han River basin, China.

	pH	EC	Turbidity	SPM	DO	COD_{Mn}	NH_4^+-N	NO_3^--N	DP	Cl^-	SO_4^{2-}	HCO_3^-	K	Ca	Na	Mg
(a) Rainy season																
pH	1.00	−0.14	0.18	−0.01	−0.47	0.05	−0.23	−0.24	−0.51	−0.55	−0.52	0.22	−0.14	0.00	−0.33	−0.04
EC		1.00	0.30	0.15	−0.23	0.45	0.42	0.70	−0.20	0.43	0.60	**0.83**[b]	0.24	**0.94**[b]	**0.70**[a]	**0.94**[b]
Turbidity			1.00	**0.95**[b]	0.11	**0.75**[a]	−0.29	−0.13	−0.24	−0.20	−0.08	0.52	**−0.67**[a]	0.38	−0.37	0.26
SPM				1.00	0.35	0.66	−0.34	−0.22	−0.11	−0.17	−0.05	0.32	**−0.72**[a]	0.22	−0.46	0.07
DO					1.00	0.09	−0.31	−0.18	0.49	0.10	0.18	−0.32	−0.28	−0.18	−0.25	−0.48
COD_{Mn}						1.00	0.18	0.37	0.21	0.21	0.25	0.45	−0.29	0.37	0.08	0.41
NH_4^+-N							1.00	**0.90**[b]	0.22	**0.87**[b]	**0.76**[a]	−0.04	**0.80**[b]	0.11	**0.79**[a]	0.46
NO_3^--N								1.00	0.20	**0.86**[b]	**0.87**[b]	0.25	**0.73**[a]	0.45	**0.91**[b]	0.65
DP									1.00	0.34	0.17	−0.35	0.02	−0.32	0.11	−0.23
Cl^-										1.00	**0.94**[b]	−0.13	**0.72**[a]	0.14	**0.74**[a]	0.33
SO_4^{2-}											1.00	0.07	0.66	0.37	**0.78**[a]	0.44
HCO_3^-												1.00	−0.23	**0.93**[b]	0.27	**0.84**[b]
K													1.00	0.02	**0.79**[a]	0.22
Ca														1.00	0.50	**0.87**[b]
Na															1.00	**0.68**[a]
Mg																1.00
(b) Dry season																
pH	1.00	0.13	0.03	0.10	0.03	−0.06	−0.28	0.37	−0.61	0.07	0.01	0.25	0.39	0.03	0.20	0.35
EC		1.00	−0.26	−0.13	**0.68**[a]	−0.05	0.05	**0.81**[b]	0.20	**0.85**[b]	**0.75**[b]	**0.93**[b]	0.42	**0.94**[b]	**0.83**[b]	**0.93**[b]
Turbidity			1.00	0.50	−0.23	0.14	−0.06	−0.36	−0.40	−0.38	−0.32	−0.17	−0.51	−0.22	−0.39	−0.32
SPM				1.00	−0.24	**0.74**[a]	0.33	−0.19	−0.28	0.07	−0.13	−0.09	−0.28	−0.11	−0.18	−0.18
DO					1.00	−0.25	−0.31	**0.72**[a]	0.05	0.45	0.33	**0.71**[a]	0.08	**0.69**[a]	0.50	**0.77**[a]
COD_{Mn}						1.00	**0.80**[b]	0.07	0.07	0.34	0.31	−0.26	0.25	−0.19	0.22	−0.19
NH_4^+-N							1.00	0.06	0.39	0.49	0.51	−0.26	0.38	−0.17	0.35	−0.15
NO_3^--N								1.00	0.15	**0.76**[a]	0.66	**0.72**[a]	**0.71**[a]	**0.68**[a]	**0.92**[b]	**0.87**[b]
DP									1.00	0.41	0.16	0.08	0.29	0.21	0.38	0.11
Cl^-										1.00	**0.78**[b]	**0.69**[a]	0.59	**0.71**[a]	**0.89**[b]	**0.78**[a]
SO_4^{2-}											1.00	0.46	0.62	0.55	**0.81**[b]	0.55
HCO_3^-												1.00	0.22	**0.96**[b]	0.64	**0.95**[b]
K													1.00	0.21	**0.82**[b]	0.43
Ca														1.00	0.66	**0.87**[b]
Na															1.00	**0.78**[a]
Mg																1.00

Bold values represent correlation with significance.

[a] Significance at the 0.05 probability level.

[b] Significance at the 0.01 probability level.

Table 2
Principal components analysis (PCA) for physical–chemicals at watershed scale of the upper Han River basin, China.

	1	2	3	4	5	6
T	0.00	−0.04	−0.13	**0.88**	−0.15	−0.06
pH	−0.04	−0.51	−0.16	0.27	−0.01	**0.63**
EC	**0.89**	0.31	−0.06	0.16	0.22	−0.06
Turbidity	−0.01	−0.14	**0.89**	−0.01	0.01	−0.02
SPM	−0.02	0.10	**0.71**	−0.27	−0.16	0.06
DO	−0.07	0.05	−0.01	−0.21	−0.07	**0.87**
COD_{Mn}	−0.23	0.06	**0.79**	0.13	0.24	−0.16
NH_4^+-N	0.05	0.40	0.07	0.05	**0.78**	−0.11
NO_3^--N	0.26	−0.01	−0.02	−0.04	**0.84**	0.01
DP	−0.12	**0.68**	−0.03	−0.10	0.00	−0.21
Cl^-	0.32	**0.56**	0.00	0.38	0.22	−0.02
SO_4^{2-}	0.32	**0.54**	−0.01	0.33	0.06	0.12
HCO_3^-	**0.87**	0.00	−0.07	−0.24	0.09	0.04
K	0.24	**0.71**	0.01	0.09	0.20	0.08
Ca	**0.89**	0.10	−0.02	0.21	0.10	−0.05
Na	0.22	0.42	0.03	**0.72**	0.30	−0.11
Mg	**0.79**	0.06	−0.11	0.10	0.05	−0.06
Eigenvalue	4.81	2.39	1.84	1.37	1.16	1.05
Cumulative %	20.21	33.89	45.57	56.77	66.62	74.21

Bold values represent strong and moderate loadings.

and Na are predictable by bare lands in the rainy season. In the dry season, EC, Cl^-, HCO_3^-, Ca, and Mg are controlled by vegetation, while NO_3^--N, SO_4^{2-} and K by bare lands, DP by shrub ($R^2 = 0.31$), and Na by bare land and vegetation ($R^2 = 0.87$), respectively. In general, physico-chemicals in streams are primarily controlled by forest cover and vegetated land (including forest and shrub) within the 100 m riparian zone for the rainy season and dry season, respectively.

5. Discussions

5.1. Overall chemical status

Waters in the basin are of Ca and HCO_3 type with low mineralization (reflected by low EC), low hardness and sub-alkalinity ([16]; Fig. 3). In general, water quality in the basin is relatively better with lower nutrient concentrations compared to other tributaries

Table 3
Pearson correlation coefficients between LULC in the 100 m riparian and water physicochemistry of the upper Han River basin, China.

	Rainy season						Dry season					
	FOR	SHR	AGR	URB	BAR	VEG	FOR	SHR	AGR	URB	BAR	VEG
T	−0.45	0.12	−0.14	0.33	**0.68**[a]	−0.42	−0.50	0.32	0.26	−0.47	0.20	−0.26
pH	0.07	0.44	−0.33	−0.28	−0.38	0.56	−0.51	0.49	−0.05	−0.55	0.32	−0.09
EC	**−0.73**[a]	0.32	0.27	−0.28	0.56	−0.55	−0.53	−0.14	0.44	0.04	**0.67**[a]	**−0.81**[b]
Turbidity	−0.17	0.46	0.09	−0.07	−0.50	0.29	−0.02	0.46	−0.31	0.31	−0.42	0.48
SPM	−0.11	0.32	0.23	0.00	−0.55	0.21	−0.32	0.23	0.48	0.16	−0.36	−0.14
DO	0.13	−0.33	0.40	0.42	−0.26	−0.19	−0.23	−0.13	0.02	0.30	0.51	−0.42
COD_{Mn}	−0.33	0.44	0.10	0.13	−0.26	0.08	−0.43	0.14	0.35	0.10	0.12	−0.38
NH_4^+-N	−0.57	0.33	0.03	−0.47	0.56	−0.34	−0.43	0.17	0.23	−0.13	0.27	−0.35
NO_3^--N	**−0.73**[a]	0.36	0.12	−0.32	0.65	−0.50	−0.53	−0.07	0.14	0.02	**0.89**[b]	**−0.73**[a]
DP	0.31	−0.58	0.36	0.54	−0.16	−0.25	0.33	−0.63	0.20	0.31	0.11	−0.28
Cl^-	−0.54	0.24	0.07	−0.30	0.58	−0.41	−0.66	−0.08	0.56	−0.11	**0.69**[a]	**−0.89**[b]
SO_4^{2-}	**−0.73**[a]	0.32	0.18	−0.33	0.66	−0.55	−0.65	0.03	0.28	−0.13	**0.82**[b]	**−0.77**[a]
HCO_3^-	−0.43	0.21	0.28	−0.15	0.15	−0.30	−0.39	−0.17	0.45	0.07	0.45	**−0.67**[a]
K	−0.47	0.22	−0.19	−0.40	**0.79**[a]	−0.33	−0.40	−0.08	0.07	−0.28	**0.82**[b]	−0.58
Ca	−0.59	0.23	0.28	−0.19	0.42	−0.47	−0.29	−0.35	0.52	0.22	0.44	**−0.74**[a]
Na	**−0.70**[a]	0.16	0.15	−0.21	**0.88**[b]	**−0.69**[a]	−0.55	−0.13	0.26	−0.02	**0.89**[b]	**−0.81**[b]
Mg	−0.66	0.29	0.24	−0.32	0.51	−0.49	−0.52	−0.06	0.34	−0.08	0.66	**−0.71**[a]

FOR, forest; SHR, shrub; AGR, agriculture; URB, urban; BAR, bareland; VEG, vegetated lands (forest and shrub). Bold values represent correlation with significance.

[a] Significance at the 0.05 probability level.

[b] Significance at the 0.01 probability level.

of the Changjiang River [5], also indicating by the dominant water parameters such as EC and major ions (Table 2). Comparing with the World Health Organization [19] and Chinese State Standards (CSS) [20] for drinking water (Table 5), variables including pH, HCO_3 and Ca are less than the maximum permissible levels. Concentrations of COD_{Mn}, nitrogen and DP also exceed standards by CSS (Fig. 3; Table 5). Thus, COD_{Mn} and nitrogen are the key factors impairing the water quality of the basin, and DP is the potential nutrient pollutant. There are great possibility of the increase in organic materials and nutrients beyond the recommended limit due to increasing anthropogenic activities in the basin [21].

5.2. *Spatial and temporal variations of physico-chemicals*

The upper Han River basin has a large area (95,200 km^2) with varying landscape setting, and understandably there is spatial variability in its water quality. The results of this study indicate that physico-chemicals show large differences among subcatchments ([16]; Fig. 3), that may have been contributable to different land use practices at subwatershed and riparian levels (Figs. 1 and 2; [1,14,16]). As for major pollutants, such as COD_{Mn} and nitrogen, the present data highlight higher values in different catchments [16], implying their variable sources, i.e. industrial effluents in Danjiangkou Reservoir (an industrial area), while agriculture and urban domestics in Ankang Plain, and soil erosion in Dan River ([14,16]; Fig. 1). This result has also been supported by the correlations among water quality parameters (Table 1).

The water quality is relatively better in the dry season which is also indicated by DO, pH, turbidity, COD_{Mn} and nitrogen [16]. This is almost certainly a consequence of rain runoff and consequent diffuse environmental pollutants, i.e. agricultural runoff [1,14]. The largest seasonal difference for SPM is recorded in the Ankang Plain, probably due to anthropogenic activities including agriculture and urbanization (Figs. 1 and 2; [16]). In the Southern part of the Qinling Mountains and Ankang Plain, COD_{Mn} demonstrates larger seasonal differences and its highest concentrations are observed in the high and low flows period, which is largely due to intense agricultural activity ([16]; Figs. 1 and 2). Relatively higher

Table 4
Stepwise multiple regression models for physico-chemicals and LULC in the 100 m riparian of the upper Han River basin, China.

Hydrochemicals	Independent variables	Regression equations	R^2	Adjusted R^2
Rainy season				
EC	Forest	335.588 – 3.678FOR	0.540[b]	0.474[b]
NO_3^--N	Forest	3.671 – 0.051FOR	0.534[b]	0.467[b]
SO_4^{2-}	Forest	43.198 – 0.700FOR	0.534[b]	0.467[b]
K	Bareland	0.788 + 0.033BAR	0.616[b]	0.562[b]
Na	Bareland	1.980 + 0.157BAR	0.774[b]	0.742[b]
Mg	Forest	10.522 – 0.157FOR	0.436[a]	0.356[a]
Dry season				
EC	Vegetation	610.140 – 5.615VEG	0.657[b]	0.608[b]
NO_3^--N	Bareland	0.724 + 0.102BAR	0.784[b]	0.753[b]
DP	Shrub	0.075 – 0.001SHR	0.398[a]	0.312[a]
Cl^-	Vegetation	26.414 – 0.337VEG	0.798[b]	0.769[b]
SO_4^{2-}	Bareland	23.449 + 1.783BAR	0.674[b]	0.627[b]
HCO_3^-	Vegetation	288.543 – 2.374VEG	0.450[b]	0.372[b]
K	Bareland	1.248 + 0.069BAR	0.680[b]	0.635[b]
Ca	Vegetation	73.288 – 0.613VEG	0.551[b]	0.487[b]
Na	Bareland Vegetation	6.591 + 0.158BAR – 0.075VEG	0.903[b]	0.871[b]
Mg	Vegetation	21.168 – 0.236VEG	0.502[b]	0.430[b]

The water quality variables without regression models are not listed.

[a] Significance at the 0.1 probability level.

[b] Significance at the 0.05 probability level.

Table 5
Range in values of water quality variables in waters and WHO (2006) and Chinese State Standard (CSS) for drinking water (unit: mg/l except pH, *T* in °C, EC in µs/cm, and turbidity in NTU).

Parameters	Upper Han River (range)	Mean	WHO (2006)		CSS
			Max desirable	Max permissible	
T	12.2–35.7	21.3	25		
pH	6.6–9.3	8.2	7.0–8.5	6.5–9.2	6.5–8.5
EC	111.4–604.1	285.6	750	1500	
Turbidity	0–712.7	31.2		5	1
SPM	0.15–721.2	26.8			
DO	3.75–18.44	10.5			6[a]
COD_{Mn}	0.8–9.2	2.5			3
NH_4^+-N	0.04–6.99	0.3			0.5
NO_3^--N	0.2–15.3	1.6	10	10	10
DP	nd–1.43	0.03			0.1[a]
Cl^-	0.7–70.7	6.3	250	600	250
SO_4^{2-}	1.2–161.9	32.1	250	600	250
HCO_3^-	36.6–342.2	148.0	300	600	
K	0.2–7.3	1.3	100	250	
Ca	13.4–84.0	38.1	75	250	
Na	0.3–16.3	3.3	50	200	200
Mg	1.9–25.9	7.9	30	150	

[a] Values come from limits for level II of Chinese Surface Water Standard.

nitrogen concentrations of rainy season in the Dan River and Danjiangkou Reservoir are attributable to increase in agricultural runoff in high flows and urban domestics [14], and lower forest coverage (Fig. 2; Tables 3 and 4). The variables with weak correlations in different hydrological regimes also demonstrate their combined sources (Tables 1 and 3).

The results of this study suggest vegetated land use and bare land are the most important predictors for water quality variability and major ions. Compared to the rainy season, more variables in the dry season can be predicted by landscape settings in the riparian zone (Table 4), indicating that present buffer construction cannot significantly mitigate pollutant loads to fluvial systems during high flows (i.e. storm runoff). The other reason is point sources from cities, such as the Danjiangkou Reservoir and Hanzhong Plain (Fig. 1). DO and *T* in both hydrological regimes could not be explained by landscape factors (Tables 3 and 4), which have been caused by the range of sampling times ranging from early morning to afternoon, since the two variables follow diurnal cycles.

Previous studies report that land use practices have been able to change nutrient and SPM loads to the fluvial systems [1,2,11,12,16], such as higher concentrations of nitrogen in Dan River and Danjiangkou Reservoir, DP in Hanzhong Plain and Danjiangkou Reservoir, and SPM in Ankang Plain (Fig. 3). The multiple statistical analyses indicate no significant relationships between water quality variables except NO_3^--N and land use types in 100 buffer strips (Tables 3 and 4), yet at subcatchment scale the impacts of agricultural and urban land on water quality were observed in the basin [16]. Thus, water quality has a stranger relationship with the land use and land cover in the 100 m buffer landscape than that at subcatchment scale, similar to results of many studies (e.g. [2,13]) and opposite to the result by Johnson et al. [7]. The influence of buffer land use/land cover compositions in our study may be underestimated due to the low resolution of digitized data used. This indicates the difficulty in determining the desirable width of a riparian buffer effectively mediating pollutant loads to river systems [12,23]. Also, the vegetation type within a buffer strip is important in determining its effectiveness retaining nutrients [2].

Previous reports have found the determinant of major ion compositions by rock weathering in the Han River [4,22,24]. Thus, their spatial and seasonal variations are a consequence of different geology and ecological background. Their good correlations with geochemistry (Tables 1 and 2) demonstrate that chemical weathering is the major source for the important impacts of vegetation and bareland (Tables 3 and 4). Our results imply fewer variables could be predicted by landscape in the rainy season (Table 4), which is due to the contribution of large amounts of precipitation. Also, higher concentrations of Cl^- and SO_4^{2-} in some catchments (i.e. SUB9) imply anthropogenic inputs, similar to the increasing water acidification trend in the Yangtze River [22].

6. Conclusions

(1) The waters in the upper Han River basin are of Ca-HCO_3 type with low mineralization and moderate alkalinity. COD_{Mn} and nitrogen are the main pollutants impairing water quality of the basin.

(2) The basin has a relative better water quality in dry season. Major ion compositions are controlled by geology and ecological background with lower concentrations in high flows because of dilution of precipitation. Water variables, especially the main pollutants have high concentrations in the urban and agricultural production areas. Water conservation effort should concentrate in the reservoir region, Hanzhong and Ankang Plains.

(3) Major ion compositions are significantly correlated with riparian land use/land cover. Nitrogen could be predicted by landscape setting in buffer strip, thus, restoration of riparian ecosystems should be a high priority for water resource conservation in particular along the shorelines of the Danjingkou Reservoir and the two plains where there are intensive agricultural activities.

Acknowledgements

The research is supported by “Hundred-talent Project” of the Chinese Academy of Sciences (O629221C01) and the National Key Technology R&D Program of China (2006BAC10B02). We would like to thank Yiping Wang, Jia Li, Lianfa Li and Sha Mu for their assistance with field sampling, and Hongyin Han for major ions analysis. We also thank comments and suggestions from three anonymous reviewers.

References

[1] S.R. Carpenter, N.F. Caraco, D.L. Correll, R.W. Howarth, A.N. Sharpley, V.H. Smith, Non-point pollution of surface waters with phosphorus and nitrogen, Ecological Applications 8 (3) (1998) 559–568.

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

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

[4] S. Li, Q. Zhang, Geochemistry of the upper Han River basin, China. 1. Spatial distribution of major ion compositions and their controlling factors, Applied Geochemistry 23 (2008) 3535–3544.

[5] S. Liu, J. Zhang, H. Chen, Y. Wu, H. Xiong, Z. Zhang, Nutrients in the Changjiang and its tributaries, Biogeochemistry 62 (1) (2003) 1–18.

[6] O. Buck, D.K. Niyogi, C.R. Townsend, Scale-dependence of land use effects on water quality of streams in agricultural catchments, Environmental Pollution 130 (2004) 287–299.

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

[8] L.L. Osborne, M.J. Wiley, Empirical relationships between land-use cover and stream water-quality in an agricultural watershed, Journal of Environmental Management 26 (1988) 9–27.

[9] W.T. Peterjohn, D.L. Correll, Nutrient dynamics in an agricultural watershed: observations on the role of a riparian forest, Ecology 65 (1984) 1466–1475.

[10] Q. Zhang, Z. Xu, Z. Shen, S. Li, S. Wang, The Han River Watershed Management Initiative for the South-to-North Water Transfer Project (middle route) of China, Environmental Monitoring and Assessment 148 (2009) 369–377.

[11] C.P. Cirmo, J.J. McDonnell, Linking the hydrological and biogeochemical controls of N transport in near stream zones of temperate afforested catchments: a review, Journal of Hydrology 199 (1997) 88–120.

[12] R.P. Smart, C. Soulsby, M.S. Cresser, A.J. Wade, J. Townende, M.F. Billett, S. Langan, Riparian zone influence on stream water chemistry at different spatial scales: a GIS-based modeling approach, an example for the Dee, NE Scotland, The Science of the Total Environment 280 (2001) 173–193.

[13] C.T. Hunsaker, D.A. Levine, Hierarchical approaches to the study of water quality in rivers, Bioscience 45 (1995) 193–203.

[14] S. Li, W. Liu, S. Gu, X. Cheng, Z. Xu, Q. Zhang, Spatio-temporal dynamics of nutrients in the upper Han River basin, China, Journal of Hazardous Materials 162 (2009) 1340–1346.

[15] J. Chen, X. Gao, D. He, X. Xia, Nitrogen contamination in the Yangtze River system, China, Journal of Hazardous Materials 73 (2) (2000) 107–113.

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

[17] J.F. O'Callaghan, D.M. Mark, The extraction of drainage networks from digital elevation data, Computer Vision, Graphics and Image Processing 28 (1984) 323–344.

[18] Chinese State Environment Protection Bureau (CSEPB), Water and Wastewater Monitoring Analysis Methods, 4th ed., Chinese Environment Science Press, Beijing, China, 2002.

[19] WHO, Guidelines for Drinking-Water Quality, 3rd ed., Volume 1 (2006)-Recommendations, Word Health Organization, Geneva.

[20] Chinese Ministry of Health, P.R. China, Chinese State Standards (CSS) for Drinking Water Quality (GB5749-2006), 2006.

[21] J. Wang, W. Yan, X. Jia, Modeling the export of point sources of nutrients from the Yangtze River basin and discussing countermeasures, Acta Scientiae Circumstantiae 24 (4) (2006) 658–666.

[22] J. Chen, F. Wang, X. Xia, L. Zhang, Major element chemistry of the Changjiang (Yangtze River), Chemical Geology 187 (2002) 231–255.

[23] W.N. Xiang, GIS-based analysis: injection of geopraphic information into landscape planning, Landscape Urban Planning 34 (1995) 1–10.

[24] M. Hu, R.F. Stallard, J.M. Edmond, Major ion chemistry of some large Chinese rivers, Nature 298 (1982) 550–553.