Contents lists available at ScienceDirect





# Science of the Total Environment

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

# The effects of land use on water quality of alpine rivers: A case study in Qilian Mountain, China



Hui Wang <sup>a,c</sup>, Xiong Xiong <sup>a,\*</sup>, Kehuan Wang <sup>a,c</sup>, Xin Li <sup>a</sup>, Hongjuan Hu <sup>a</sup>, Quanliang Li <sup>b</sup>, Hengqing Yin <sup>b</sup>, Chenxi Wu <sup>a</sup>

<sup>a</sup> State Key Laboratory of Freshwater Ecology and Biotechnology, Institute of Hydrobiology, Chinese Academy of Sciences, Wuhan 430072, China

<sup>b</sup> Qinghai Service Guarantee Center of Qilian Mountain National Park, Xining 810000, China

<sup>c</sup> University of Chinese Academy of Sciences, Beijing 100049, China

# HIGHLIGHTS

# GRAPHICAL ABSTRACT

- Scale and region affect the impact of land use on water quality in alpine rivers.
- Land use in buffer zone scale affects water quality in alpine river headwaters areas.
- Large spatial scale land use affects water quality in the mainstream of alpine rivers.
- Natural land surface affects water quality in the headwaters area of alpine rivers.
- Water quality in the mainstream is influenced by human-related land use.

# ARTICLE INFO

Editor: Ouyang Wei

Keywords: Land use Scale Water quality Predict River Alpine



# ABSTRACT

Land use influences the variation of river water quality. This effect varies depending on the region of the river and the spatial scale at which land use is calculated. This study investigated the influence of land use on river water quality in Qilian Mountain, an important alpine river region in northwestern China, on different spatial scales in the headwaters and mainstem areas. Redundancy analysis and multiple linear regression were used to identify the optimal scales of land use for influencing and predicting water quality. Nitrogen and organic carbon parameters were more influenced by land use than phosphorus. The impact of land use on river water quality varied according to regional and seasonal differences. Water quality in headwater streams was better influenced and predicted by land use types on the natural surface at the smaller buffer zone scale, while water quality in mainstream rivers was better influenced and predicted by land use types on water quality differed with regional and seasonal variations, while the impact of land types associated with human activities on water quality parameters mainly resulted in elevated concentrations. The results of this study suggested that different land types and spatial scales needed to be considered to assess water quality influences in different areas of alpine rivers in the context of future global change.

and agricultural development (Akasaka et al., 2010). The water quality of

rivers is an essential factor limiting the ability of rivers to perform various functions (Caissie, 2006). River water quality is influenced by a combina-

tion of natural and anthropogenic factors (Mouri et al., 2011) The most intuitive manifestation of these factors at the watershed scale is land use, which appears on the earth's surface (Mouri et al., 2011). Natural surfaces

include forests, grasslands, shrublands, etc.(Lei et al., 2021), while

# 1. Introduction

As an important surface water resource, rivers play key roles in economic and social development, public health, environmental protection,

\* Corresponding author at: Donghu South Road #7, Wuhan 430072, China. *E-mail address:* xxiong@ihb.ac.cn (X. Xiong).

http://dx.doi.org/10.1016/j.scitotenv.2023.162696

Received 15 December 2022; Received in revised form 11 February 2023; Accepted 3 March 2023 Available online 9 March 2023 0048-9697/© 2023 Elsevier B.V. All rights reserved. industrial and agricultural activities and urbanization processes often happened on anthropogenic surfaces (Mouri et al., 2011). Although many studies have been conducted to reveal the effects of land use on river water quality (Ding et al., 2016; Wang et al., 2022a; Yu et al., 2016), there are still many questions to be addressed regarding differences in regions and scales.

The effects of land use on river water quality are diverse. Due to the fixation and adsorption effects of plants, the total phosphorus (TP) and total nitrogen (TN) levels in the watershed tend to decrease as the area of vegetation land increases (Cheng et al., 2022; Wang et al., 2022a). However, Ouyang et al. (2014) find that forests contribute to the non-point source (NPS) of nutrient loading. Poorer water quality is also associated with higher patch densities of grassland in the upper Dan River basin (Shi et al., 2017). The proportions of surfaces affected by anthropogenic factors, such as farmlands and urban areas, are positively correlated with water pollution (Zhang et al., 2019b; Zhang et al., 2014). As more lands are reclaimed for agriculture, the nutrients in the water bodies in the watershed increase (Mouri et al., 2011). Urban impervious surfaces enhance surface runoff, soil erosion, and non-point source pollution, which deteriorates the aquatic environment (Ding et al., 2016). However, the effects of land use on water quality in rivers mentioned above are often regional. Factors such as climate, topography, soils, and anthropogenic activity intensity in different regions influence the processes that drive river water quality by land use through their influence on surface runoff (Lei et al., 2021; Yin et al., 2017; Yu et al., 2016).

In addition to regional differences, there are also spatial scale differences in the effects of land use on river water quality. Shi et al. (2017) find that land use types on the riparian scale predict water quality better than those on the catchment scale, while some other studies have opposite conclusions (Ding et al., 2016). Landscape metrics that affect water quality also vary with spatial scale extent (Xu et al., 2022). Cheng et al. (2022) have found that agricultural land use has opposite effects on water quality at small-scale and large-scale buffers. The spatial scale variation in the impacts of land use on river water quality is related to the geographical location of the river (Guo et al., 2010). Therefore, for understanding the influence of land use on river water quality, it is essential to study the effects at different regions in various spatial scales.

Alpine rivers are located in a special region characterized by high elevation and harsh climatic conditions (Wang et al., 2022b). These rivers are sensitive to human activities and natural environmental change (Jasper et al., 2004; Yin et al., 2017). Understanding the impact of land use on the water quality of alpine rivers is critical for protecting the water security and ecological health of this ecologically sensitive area. However, few studies have focused on the relationship between water quality and land use patterns in alpine rivers. The role of regional differences and spatial scales in assessing and predicting the effects of land use on water quality in alpine rivers needs to be further revealed. Qilian Mountain is an important source of endorheic rivers in northwestern China. The water quality of alpine rivers in Qilian Mountain profoundly affects the water for living, agriculture, and ecology in the watersheds. The watersheds of Qilian Mountain have unique climatic, topographic, and soil characteristics (Yang et al., 2018). There is also a strong spatial heterogeneity of various natural and anthropogenic elements within Qilian Mountain (Guan et al., 2018; Sun et al., 2016). In this study, we investigated the effect of land use on water quality at different spatial scales in the headwater and mainstream of alpine rivers in Qilian Mountain. Through this study, we hope to reveal the impact of land use on different areas of alpine rivers, identify the role of spatial scale on the above impacts, and provide guidance for water quality protection of alpine rivers.

# 2. Materials and methods

#### 2.1. Study area

Qilian Mountain ( $35^{\circ}50'12''N \sim 39^{\circ}58'15''N$ ,  $93^{\circ}33'27''E \sim 103^{\circ}53'43''$ E) is in northwest China. It is far from the ocean and at the intersection of the Qinghai-Tibet Plateau, Mongolian Plateau, and Loess Plateau (Fig. 1a). The elevation of the Qilian Mountain area ranges from 2000 to 5800 m. As a typical alpine frigid and subhumid mountain climate zone, Qilian Mountain has an average annual temperature of 4 °C and an annual precipitation ranging from 150 mm to 800 m, which is mainly concentrated from May to September (Sun et al., 2016). The vegetation in this area includes mountain grasslands, temperate scrubs, mountain forests, subalpine scrubs, alpine subglacial sparse vegetation, and other types. There are 2748 mountain glaciers developed in the range of Qilian Mountain (Liu et al., 2015). River systems originating from these glaciers and other sources develop in the Qilian Mountain watersheds. They constitute important endorheic water sources in northwestern China for natural ecosystems and human activities (Sun et al., 2016). The local economy mainly comes from animal husbandry, mining, and tourism.

#### 2.2. Field sampling and laboratory analysis

The study area contained the headwater areas and mainstream areas of major rivers within Oilian Mountain, including Hei River (including its tributaries: Babao River and Tuole River), Datong River (including its tributaries), Shiyang River (headwaters area), and Shule River (Fig. S1). We set up 40 sampling sites in the study area and sampled them in June and September 2021, which represented spring and autumn in Qilian Mountain, respectively (Fig. 1a). Sample sites within 30 km of the river sources were classified as the headwater group (HW, n = 20), while the other sample sites were the mainstream group (MS, n = 20). The river status was presented in the supplementary material (Fig.S2). The water samples were collected into polyethylene sample bottles, kept in dark and at 4 °C, and brought back to the laboratory. TP, TN, soluble reactive phosphorus (SRP), nitrate nitrogen (NO<sub>3</sub>-N), nitrite nitrogen (NO<sub>2</sub>-N), and ammonia nitrogen (NH<sub>3</sub>-N) of water samples were measured according to the Chinese national standard method (SEPA, 2002a). Total organic carbon (TOC) was analyzed using an Elementar vario TOC select TOC analyzer (Langenselbold, Germany).

#### 2.3. Spatial data resources

The digital elevation model (DEM) data were obtained from the ASTER GDEM 30 M product of the geospatial data cloud platform of the Computer Network Information Center of the Chinese Academy of Sciences (http:// www.gscloud.cn). The land use data used the 30 m resolution global surface coverage product Globeland30 (www.globeland30.org) in 2020 which had a total accuracy of 85.72 % and a Kappa coefficient of 0.82. Globeland30 data includes ten surface cover types, while there are only nine types in study areas, including cultivated land, forest, grassland, shrubland, water bodies, wetlands, artificial surface, bare land, and permanent snow and ice.

#### 2.4. Multi-scale land use metrics

The Hydrology module of ArcGIS was used to extract the watersheds of rivers and the buffer zones of sites at different scales based on the DEM data. The land use types were derived from three spatial scales (Fig. 1b, c, and d): Catchment: the entire upstream catchment of each site; Subcatchment: the sub-catchment between the sampling site and the adjacent upstream sampling site; Buffer zone: upstream area with 500 m of radius from each site.

# 2.5. Statistical analysis

The Mann-Whitney test was used to compare the difference in water quality between water body types and seasons due to the non-normal distribution of the data. Redundancy analysis (RDA) was performed to assess the impact of land use on water quality at different scales. The hierarchical partitioning and variation partitioning of the RDA results were performed to obtain the contribution (%) of the individual (group) explanatory



Fig. 1. The sample sites and land use types in the study area (a) and 3 diagrams illustrating the three scales used in this study: (b) catchment, (c) sub-catchment, and (d) buffer zone.

variables in the RDA analysis by averaging the distribution of the commonly explained components (Lai et al., 2022). The explanatory variables with negative contributions will be removed and reanalyzed until all explanatory variables have a positive contribution. Adj.r<sup>2</sup> was the proportion of total variance explained by all canonical axes after correction, which showed the degree of explanation of all significant explanatory variables for overall water quality (Lai et al., 2022). A Monte Carlo permutation test (499 permutations) was used to determine the statistical validity of the RDA, models with p > 0.05 are regarded as invalid models and will not be presented as final results. Multiple linear regression (MLR) modeling was used to select the optimal factors and scales that could predict a single water quality parameter. The optimal model was selected using the stepwise method with reference to (Ding et al., 2016). The water quality data were transformed as Log (x + 1) to reduce the asymmetric distribution of the dependent variables in the models before MLR (Basnyat et al., 1999). The adjusted determination coefficient (Adj.R<sup>2</sup>) was used as a model fit indicator to measure the predictive power of the MLR model (Legendre and Legendre, 2012). The standard partial regression coefficient (B) was chosen to compare the relative importance of the different predictors on the response. A higher value of B indicated a greater effect of the predictors on the response variables (Bring, 1994). The variance inflation factor (VIF) was the collinearity indicator, if the VIF of each predictor was <10, there was no covariance among predictors (Bring, 1994). The measured versus predicted values were used to do a simple linear regression analysis, and the slope and  $R^2_{adj}$  were used to show the predictive power of the prediction model. The statistical analysis and plotting were performed in SPSS 25.0 (IBM Company, Armonk, New York, USA) and R 4.1.0 (R Development Core Team, 2018) within the "ggplot2", "rdacca. hp", and "vegan" package.

# 3. Results

#### 3.1. Land use pattern among different spatial scales

The overall land use distribution in the study area was dominated by grasslands. Permanent snow and ice, bare ground, and forests were also common land use types. The proportions of cultivated land, shrubland, wetlands, water bodies, and artificial surfaces were low, except for relatively high proportions of wetlands, water bodies, and cultivated land in the buffer zone scale for MS. For HW, the proportions of the forest, cultivated land, wetland, and water bodies increased with the increasing spatial scales, while the proportions of shrubland and bare land decreased. For MS, as the spatial scales decreased, the proportions of cultivated land, wetland, and water bodies increased, while the proportion of shrubland and artificial surfaces decreased (Fig. 2).

# 3.2. Temporal and spatial variations of water quality in Qilian Mountain

Most of the sample sites in the alpine rivers of Qilian Mountain had good water quality based on nutrient concentrations (Fig. 3). The TP levels were generally below 0.2 mg/L, with most of them even below 0.1 mg/L in June. The SRP levels were mostly around 0.01 mg/L, indicating that the majority of the phosphorus in the rivers was present in particulate form. TN concentrations were mostly <1.5 mg/L, particularly in June when they were below 1 mg/L. NO<sub>3</sub>-N was the main component of nitrogen, while the NH<sub>3</sub>-N levels were generally below 0.5 mg/L. TOC levels in these rivers were typically below 5 mg/L. According to China's environmental quality standards for surface water (SEPA, 2002b), these alpine rivers in Qilian Mountain met or better than the requirements of Class III for TP and NH<sub>3</sub>-N.

Considering spatial differences, only the SRP of the MS group was significantly higher than that of the HW group in June (p < 0.05), and NO<sub>3</sub>-N of the MS group was significantly lower than that of the HW group in September (p < 0.05) (Fig. 3). For the HW group, TP, SRP, TN, and NO<sub>3</sub>-N were all significantly higher in September than in June (p < 0.01), while NH<sub>3</sub>-N was significantly lower in September than in June (p < 0.05). For the MS group, only TP and NH<sub>3</sub>-N showed significant temporal differences (p < 0.05), which were higher in June than in September. The water quality parameters of the MS group tend to have more outliers than those of the HW group in boxplots (Fig. 3). TP in rivers was mainly composed of NO<sub>3</sub>-N and the proportion of NH<sub>3</sub>-N was low.

#### 3.3. Relationship between land use and water quality

In June, only land use at the buffer zone scale in the HW group and at the catchment scale in the MS group could explain the variation in river water quality parameters in the RDA (Table 1, p < 0.05). While in September, river water quality parameters of the HW group could be explained by the land use at the catchment and buffer zone scale, while those of the MS group could only be explained by the land use at sub-catchment scales in RDA (Table 1, p < 0.05). For the HW group in September, the optimal



Fig. 2. Average land use proportions in the catchment, sub-catchment, and 500 m buffer scales in headwater (HW) and mainstream (MS) groups.



**Fig. 3.** Spatial and temporal variation of water quality parameters in headwater (HW) and mainstream (MS). \*: p < 0.05; \*\*: p < 0.01.

scale for land use to explain water quality variation was buffer zone (Adj.  $r^2 = 0.38$ ).

Except for TP of the MS group in September, land use was mainly sufficient in explaining the variation in TOC, TN, and NO<sub>3</sub>-N in all RDA results (Fig. 4). For the HW group in June, TOC concentrations increased with increasing grassland cover at the buffer zone scale, while TN and NO<sub>3</sub>-N followed the same trend as forest cover and bare land at that scale (Fig. 4a). However, TN and NO<sub>3</sub>-N concentrations of the MS group at the same time increased with increasing anthropogenic activity-related land use types (artificial surface and cultivated land) and water bodies at the catchment scale (Fig. 4b). In September, increases in TN and NO<sub>3</sub>-N concentrations in the HW group were accompanied by increases in land use types associated with low vegetation cover (bare land and permanent snow and ice) and decreases in land use types associated with high vegetation cover

#### Table 1

The redundancy analysis (RDA) results for the percentage of overall water quality variance explained by land use types.

Туре	Scales	Р	Adj r <sup>2</sup>	Explanatory variables (contribution %)
Jun. HW	Buffer zone	0.001	0.51	Grassland (66.73), Forest (17.81)
MS	Catchment	0.008	0.54	Cultivated land (14.30),
Sept.				
HW	Catchment	0.007	0.35	Permanent snow and ice (71.94), Grassland (9.3)
MS	Sub-catchment	0.002	0.64	Artificial Surfaces (49.72), Water bodies (25.09)
HW	Buffer zone	0.006	0.38	Shrubland (39.84), Forest (26.55)

Only significant models (P < 0.05) are listed; the highest Adj.r<sup>2</sup> model among scales are in bold.



**Fig. 4.** Triplot of the water quality parameters (blue lines), land use types (red lines), and sample sites (green dots) in the study area according to the redundancy analysis (RDA). Only results that pass the Monte Carlo permutation test (p < 0.05) were shown here. The RDA was conducted separately for the headwater (HW) group and the mainstream (MS) group at different scales. (a): HW at the buffer zone in June; (b): MS at catchment in June; (c) HW at the catchment scale in September; (d) MS at the sub-catchment scale in September; (e) HW at buffer zone in September.

at the catchment scale and buffer zone scale (Fig. 4c and e). TOC concentrations in the September HW group trended opposite to permanent snow and ice at both the catchment scale and the buffer zone scale and grassland at the buffer zone scale but trended the same as wetland at the catchment scale and forest and cultivated land at the buffer zone scale (Fig. 4c and e). The effects of land use on the variation of TN and NO<sub>3</sub>-N in the September MS group were the same as in June, although their scales of action changed. Whereas the increase in TP and TOC was mainly accompanied by an increase in cultivated land and a decrease in forest and permanent snow and ice (Fig. 4d).

Except for TOC and SRP in the HW group in June, SRP and  $NH_3$ -N in the MS group in June, and TP and  $NH_3$ -N in the September MS group, all other water quality parameters could be predicted by MLR based on land use (Table 2 and Table S1). However, considering the fitting results between predicted and measured values (Fig. 5 and Table S2), in June, only NO<sub>3</sub>-N in the HW group and TP in the MS group could be well predicted by land use, while TP, NO<sub>3</sub>-N, and TOC in the HW group and TN, NO<sub>3</sub>-N, TOC, and SRP in the MS group could be well predicted in September.

In June, NO<sub>3</sub>-N in the HW group was co-predicted by forest (B = 0.48) and shrubland (B = -0.43) at the buffer zone scale, while TP in the MS group was co-predicted by artificial land surface (B = 0.68) and wetland (B = 0.45) at the catchment scale. In September, TP in the HW group was co-predicted by permanent snow and ice (B = 1.32), grassland (B = -0.94), cultivated land (B = 0.57), and bare land (B = -0.39) at the catchment scale,  $NO_3$ -N was co-predicted by shrubland (B = -0.66) and grassland (B = -0.37) at the buffer zone scale, while TOC was copredicted by permanent snow and ice (B = -1.001), grassland (B = -0.78), and wetland (B = 0.409) at the catchment scale. In the MS group in September, artificial surfaces were involved in the prediction of both TN (B = 1.09) and NO<sub>3</sub>-N (B = 1.08) at the catchment scale, while forests (B = 0.3) were involved in the prediction of TN, and cultivated land (B = -0.35) and wetlands (B = -0.17) were involved in the prediction of NO<sub>3</sub>-N. TOC and SRP in the September MS group were predicted by water bodies (B = 0.58) and shrublands (B = -0.43) at the sub-catchment scale and permanent snow and ice (B = 0.63) at the sub-catchment scale, respectively.

## 4. Discussion

## 4.1. Effects of land use on riverine water quality in Qilian Mountain

Due to the low anthropogenic activity, nitrogen in the headwaters area was mainly determined by land use types associated with natural features of the surface such as vegetation cover and snow and ice cover. It was similar to the factors influencing nitrogen in previous studies of rivers in remote areas or protected areas (Balestrini et al., 2013; Hood et al., 2003). Bare land contributed positively to river nitrogen levels in both surveys. Bare land often implied strong erosion (Duan et al., 2017). The contribution

#### Table 2

The relative importance of the significant predictors in the best models.

of nitrogen from surface runoff to rivers through erosion was also found in a previous study (Wolka et al., 2021). Previous studies of glacier-feeding streams indicated opposite trends in dissolved inorganic nitrogen concentrations of streams and changes in glacier cover (Elser et al., 2020). It contradicted the positive effect of permanent snow and ice on TN concentrations in the headwaters area of Qilian Mountain in September. Considering the low precipitation in the study area in September (Zhang et al., 2018), permanent snow and ice would be a major source of river recharge in watersheds (Korup and Montgomery, 2008). The nitrogen deposited by the atmosphere in snow and ice could be a non-negligible source of nitrogen in the rivers of the source area (Niu et al., 2022). Forests contributed positively to nitrogen levels in the headwaters area in June, while all vegetation cover-related land use types contributed negatively to nitrogen levels in September. As important producers in alpine regions, plant litter could provide nutrients to water bodies (Hao et al., 2022). On the other hand, vegetation has a mitigating and purifying effect on the nitrogen input from surface runoff (Ding et al., 2016; Shi et al., 2017). Unlike the headwaters area, river nitrogen in the mainstem area was mainly influenced by land use types related to anthropogenic activities. Both anthropogenic nitrogen pollution and low permeable surfaces in constructed urban areas led to increased nitrogen input to the river (Shi et al., 2017; Zhang et al., 2019b). It indicated that in areas where human activities existed, they could still have a large impact on the nitrogen of alpine rivers.

Permanent snow and ice and vegetation were also the primary factors affecting TOC in water in the headwaters area. The effect of reduced snow and glacier cover on the increase of organic carbon in both headwaters and mainstems was consistent with previous studies (Elser et al., 2020). The increasing effect of vegetation cover on TOC in headwaters was contributed by grassland and forest in the buffer zone scale in June and September, respectively. The difference in sources may also be the reason for the difference in the mechanism of forest and grassland influence on TOC in the headwater rivers. The contribution of grasslands to organic carbon was mainly from litter, while the contribution of grasslands to organic carbon input could also include livestock feces and soil microbial activity (Chang et al., 2021; Wang et al., 2020). Cultivated land would increase productivity in the originally infertile mountain soils (Glaser, 2007). It could be the reason for the promotion of TOC in water bodies by cultivated land in the mainstream area of rivers in Qilian Mountain.

Although the variation of phosphorus in the headwaters area of Qilian Mountain could not be well explained by land use in the RDA, TP in the headwaters area in September could be predicted by permanent snow and ice, grassland, cultivated land, and bare land together. It suggested that TP in the headwaters area was influenced by a combination of multiple natural land use types. TP in the rivers of Qilian Mountain is mainly dominated by particulate phosphorus, which mainly originated from erosion and atmospheric deposition in the watershed under natural conditions (Gao et al., 2017; Han et al., 2021). Particulate phosphorus deposition on snow

Season	Response	HW			MS		
		Best model	Significant predictors(B)	Adj.R <sup>2</sup>	Best model	Significant predictors(B)	Adj.R <sup>2</sup>
Jun.	LogTP	Buffer zone	Forest (0.62)	0.34	Catchment	Artificial Surfaces (0.68), Wetland (0.45)	0.55
	LogTN	Sub-catchment	Forest (-0.52)	0.22	Catchment	Water bodies (0.51)	0.21
	LogNO3-N	Buffer zone	Forest (0.48), Shrubland (-0.43)	0.41	Catchment	Forest (-0.55)	0.26
	LogTOC	-	-	-	Catchment	Artificial Surfaces (0.52)	0.23
	LogSRP	-	-	-	-	-	-
	LogNH <sub>3</sub> -N	Buffer zone	Shrubland (0.77)	0.56	-	-	-
Sept.	LogTP	Catchment	Permanent snow and ice $(-1.32)$ , Grassland	-	-	-	-
			(-0.94), Cultivated land (0.57). Bare Land $(-0.39)$				
-	LogTN	Buffer zone	Shrubland (-0.48)	0.19	Catchment	Artificial Surfaces (1.09), Forest (0.3)	0.86
	LogNO <sub>3</sub> -N	Buffer zone	Shrubland ( $-0.66$ ), Grassland ( $-0.37$ )	0.56	Catchment	Artificial Surfaces (1.08), Cultivated land ( $-0.35$ ), wetland ( $-0.17$ )	0.9
	LogTOC	Catchment	Permanent snow and ice $(-1.001)$ , Grassland $(-0.78)$ , Wetland $(0.409)$	0.57	Sub-catchment	Water bodies (0.58), Shrubland $(-0.43)$	0.4
	LogSRP	Sub-catchment	Water bodies (0.58), Shrubland $(-0.43)$	0.19	Sub-catchment	Permanent snow and ice (0.63)	0.36
	LogNH <sub>3</sub> -N	Buffer zone	Wetland (0.57)	0.29	-	-	-



Fig. 5. Scatter plots of measured and fitted values based on the final models of individual water quality parameters. The dotted and solid lines present the 1:1 line and linear fitting line between measured and fitted values, respectively.

and ice, interception of surface runoff by grasslands, and the phosphoruspoor nature of the bare land all affected TP in the headwater area (Ding et al., 2016; Zhang et al., 2019a). In addition, the role of human activities, especially agricultural practices, on riverine phosphorus was also evident in different areas of Qilian Mountain, as human daily life and agricultural production activities involved large amounts of phosphorus use (Wang et al., 2021).

#### 4.2. Spatial scale differences in the impact of land use

For the alpine rivers in Qilian Mountain, water quality variations in the headwaters were better explained and predicted by land use at the small scale, while water quality variations in the mainstem were more dependent on land use at the large scale. It could be related to a variety of factors such as the size, morphology, and flow of the river. Land use on small scale was more important for the variation of water quality in smaller streams (Buck et al., 2004; Ding et al., 2016). Headwater area watersheds tended to have steeper slopes. Surface runoff in the headwater area was likely to be more intense and more likely to carry material from small-scale areas into the river (Hayashi, 2020). These materials could quickly affect the water quality of headwater rivers due to their smaller flows (Alexander et al., 2007). Whereas for the mainstream, the greater volume of water quality. It suggested that including a larger area was required to account for more distant sources of matters in the mainstream (Pratt and Chang, 2012).

For the mainstream, the scale was reduced to the sub-catchment level in September compared to the good explanation of water quality variations by land use types at the catchment scale in June. June was the beginning of the wet season in Qilian Mountain (Zhu et al., 2022). The increase in precipitation led to an increase in the flow of rivers and more matter from the catchment into the rivers (Pokharel et al., 2020). It implied that impacts on river water quality could occur on a larger scale. In September, with lower precipitation and flow, the area that could affect the water quality of the river was reduced. For the headwaters, better predictions for nitrogen occurred for land use types at the small scale, while better predictions for phosphorus and TOC occurred for land use types at the large scale. It might be due to the fact that phosphorus and organic carbon were inherently deficient within the watershed of the headwaters in the alpine region (Qin et al., 2021), and that small-scale sources of phosphorus and organic carbon were not sufficient to affect the concentrations in the river.

# 4.3. Potential impacts of future land use changes on river water quality in Qilian Mountain

Climate change and human activities are important drivers of land use change (Lu et al., 2009), which could affect the water quality of alpine rivers in Qilian Mountain. From the 1960s to 2020, the glacier area in the major river watersheds of Qilian Mountain decreased by 16.7–61.7 % and this trend is projected to continue due to climate change (Liu et al., 2021). The warmer and wetter climate and ecological restoration projects in Qilian Mountain region from 2000 to 2019 (Peng et al., 2021). Based on the results of our study, the decrease in glaciers will lead to an increase in TP and TOC in HW and a decrease in SRP in mainstreams in September. The increase in vegetation cover will be accompanied by the increase in NO<sub>3</sub>-N of headwaters in June and in TN of mainstreams in September. On account of the important role played by headwater in biodiversity and ecosystem service function (Alexander et al., 2007), it is urgent to take measures to address the effects of climate change on water quality.

Human activities often led to expanding cultivated land and artificial surfaces and reducing vegetation covers (Qian et al., 2019). This trend could lead to an increase in TP and TOC in June and an increase in TN, NO<sub>3</sub>-N, and TOC in September in mainstreams based on our results. In recent years, human activities within the Qilian Mountain National Park have been restricted as conservation practices are strengthened (Peng et al., 2021), which would benefit the water quality of the alpine rivers in Qilian Mountain. However, as the human footprint continues to expand in the Qinghai-Tibet Plateau (Hua et al., 2022), anthropogenic threats to Qilian Mountain still need attention. Therefore, it is still urgent to strengthen ecological protection in Qilian Mountain, strictly control the expansion of cultivated land and urban area, and maintain sustainable

#### H. Wang et al.

development of the ecosystem by considering the impact of driving factors and local conditions.

#### 5. Conclusion

Our study illustrated significant differences in the effects of land use and spatial scale on water quality in the headwaters and mainstream rivers in Qilian Mountain. The land use at the buffer zone scale in both surveys could well explain the variation of river water quality parameters in headwaters of Qilian Mountain, while the optimal scale for land use to explain the variation of water quality in mainstreams was the catchment scale in June and the sub-catchment scale in September. The land use types that influence water quality parameters of headwaters and mainstreams were mainly nature surfaces and anthropogenic activity-related surfaces, respectively. Nitrogen and TOC are the water quality parameters that are more significantly influenced by land use. The impact of natural land use types on water quality differed with regional and seasonal variations, while the impact of land types associated with human activities on water quality parameters mainly resulted in elevated concentrations. Although more research is needed in the future to characterize the generality of land use impacts on water quality in alpine rivers, our results still suggested that the proposed watershed management measures should consider the spatial and temporal impacts of land use on water quality on different scales for alpine rivers.

#### CRediT authorship contribution statement

Hui Wang: Writing – Investigation; Methodology; Original draft preparation and Visualization.

Xiong Xiong: Writing – Conceptualization; Review & editing; Project administration.

Kehuan Wang: Investigation.

Xin Li: Methodology; Data Curation.

Hongjuan Hu: Investigation.

Quanliang Li: Investigation; Project administration.

Hengqing Yin: Project administration.

Chenxi Wu: Supervision.

# Data availability

Data will be made available on request.

# Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgments

This work is supported by the Second Tibetan Plateau Scientific Expedition and Research Program (STEP, 2019QZKK0304), the State Key Laboratory of Freshwater Ecology and Biotechnology, Qinghai Provincial Forestry and Grassland Administration, and the Youth Innovation Promotion Association CAS (2021339).

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.scitotenv.2023.162696.

#### References

Akasaka, M., Takamura, N., Mitsuhashi, H., Kadono, Y., 2010. Effects of land use on aquatic macrophyte diversity and water quality of ponds. Freshw. Biol. 55 (4), 909–922. https://doi.org/10.1111/j.1365-2427.2009.02334.x.

- Alexander, R.B., Boyer, E.W., Smith, R.A., Schwarz, G.E., Moore, R.B., 2007. The role of headwater streams in downstream water quality JAWRA. J. Am. Water Resour. Assoc. 43 (1), 41–59. https://doi.org/10.1111/j.1752-1688.2007.00005.x.
- Balestrini, R., Arese, C., Freppaz, M., Buffagni, A., 2013. Catchment features controlling nitrogen dynamics in running waters above the tree line (central Italian Alps). Hydrol. Earth Syst. Sci. 17 (3), 989–1001. https://doi.org/10.5194/hess-17-989-2013.
- Basnyat, P., Teeter, L.D., Flynn, K.M., Lockaby, B.G., 1999. Relationships between landscape characteristics and nonpoint source pollution inputs to coastal estuaries. Environ. Manag. 23 (4), 539–549. https://doi.org/10.1007/s002679900208.
- Bring, J., 1994. How to standardize regression-coefficients. American Statistician 48 (3), 209–213. https://doi.org/10.2307/2684719.
- Buck, O., Niyogi, D.K., Townsend, C.R., 2004. Scale-dependence of land use effects on water quality of streams in agricultural catchments. Environemtal Pollution 130 (2), 287–299. https://doi.org/10.1016/j.envpol.2003.10.018.
- Caissie, D., 2006. The thermal regime of rivers: a review. Freshw. Biol. 51 (8), 1389–1406. https://doi.org/10.1111/j.1365-2427.2006.01597.x.
- Chang, J., Ciais, P., Gasser, T., Smith, P., Herrero, M., Havlík, P., Obersteiner, M., Guenet, B., Goll, D.S., Li, W., 2021. Climate warming from managed grasslands cancels the cooling effect of carbon sinks in sparsely grazed and natural grasslands. Nat. Commun. 12 (1), 1–10. https://doi.org/10.1038/s41467-020-20406-7.
- Cheng, C., Zhang, F., Shi, J., Kung, H.-T., 2022. What is the relationship between land use and surface water quality? A review and prospects from remote sensing perspective. Environ. Sci. Pollut. Res. 29 (38), 56887–56907. https://doi.org/10.1007/s11356-022-21348-x.
- Ding, J., Jiang, Y., Liu, Q., Hou, Z., Liao, J., Fu, L., Peng, Q., 2016. Influences of the land use pattern on water quality in low-order streams of the Dongjiang River basin, China: a multi-scale analysis. Sci. Total Environ. 551–552, 205–216. https://doi.org/10.1016/j. scitotenv.2016.01.162.
- Duan, J., Yang, J., Tang, C., Chen, L., Liu, Y., Wang, L., 2017. Effects of rainfall patterns and land cover on the subsurface flow generation of sloping ferralsols in southern China. PLoS One 12 (8). https://doi.org/10.1371/journal.pone.0182706.
- Elser, J.J., Wu, C., Gonzalez, A.L., Shain, D.H., Smith, H.J., Sommaruga, R., Williamson, C.E., Brahney, J., Hotaling, S., Vanderwall, J., Yu, J., Aizen, V., Aizen, E., Battin, T.J., Camassa, R., Feng, X., Jiang, H., Lu, L., Qu, J.J., Ren, Z., Wen, J., Wen, L., Woods, H.A., Xiong, X., Xu, J., Yu, G., Harper, J.T., Saros, J.E., 2020. Key rules of life and the fading cryosphere: impacts in alpine lakes and streams. Glob. Chang. Biol. 26 (12), 6644–6656. https://doi. org/10.1111/gcb.15362.
- Gao, Y., Hao, Z., Yang, T., He, N., Wen, X., Yu, G., 2017. Effects of atmospheric reactive phosphorus deposition on phosphorus transport in a subtropical watershed: a Chinese case study. Environ. Pollut. 226, 69–78. https://doi.org/10.1016/j.envpol.2017.03.067.
- Glaser, B., 2007. Prehistorically modified soils of Central Amazonia: a model for sustainable agriculture in the twenty-first century. Philos. Trans. R. Soc. B-Biol. Sci. 362 (1478), 187–196. https://doi.org/10.1098/rstb.2006.1978.
- Guan, Q., Yang, L., Pan, N., Lin, J., Xu, C., Wang, F., Liu, Z., 2018. Greening and browning of the hexi corridor in Northwest China: spatial patterns and responses to climatic variability and anthropogenic drivers. Remote Sens. 10 (8), 1270. https://doi.org/10.3390/ rs10081270.
- Guo, Q., Ma, K., Yang, L., He, K., 2010. Testing a dynamic complex hypothesis in the analysis of land use impact on Lake water quality. Water Resour. Manag. 24 (7), 1313–1332. https://doi.org/10.1007/s11269-009-9498-y.
- Han, X., Xiao, J., Wang, L., Tian, S., Liang, T., Liu, Y., 2021. Identification of areas vulnerable to soil erosion and risk assessment of phosphorus transport in a typical watershed in the Loess Plateau. Sci. Total Environ. 758, 143661. https://doi.org/10.1016/j.scitotenv.2020.143661.
- Hao, X., Ouyang, W., Zhang, K., Wan, X., Cui, X., Zhu, W., 2022. Enhanced release, export, and transport of diffuse nutrients from litter in forested watersheds with climate warming. Sci. Total Environ. 837. https://doi.org/10.1016/j.scitotenv.2022.155897.
- Hayashi, M., 2020. Alpine hydrogeology: the critical role of groundwater in sourcing the headwaters of the world. Groundwater 58 (4), 498–510. https://doi.org/10.1111/ gwat.12965.
- Hood, E.W., Williams, M.W., Caine, N., 2003. Landscape controls on organic and inorganic nitrogen leaching across an alpine/subalpine ecotone, Green Lakes Valley, Colorado Front Range. Ecosystems 6 (1), 31–45. https://doi.org/10.1007/s10021-002-0175-8.
- Hua, T., Zhao, W., Cherubini, F., Hu, X., Pereira, P., 2022. Continuous growth of human footprint risks compromising the benefits of protected areas on the Qinghai-Tibet Plateau. Glob. Ecol. Conserv. 34, e02053. https://doi.org/10.1016/j.gecco.2022.e02053.
- Jasper, K., Calanca, P., Gyalistras, D., Fuhrer, J., 2004. Differential impacts of climate change on the hydrology of two alpine river basins. Clim. Res. 26 (2), 113–129. https://doi.org/ 10.3354/cr026113.
- Korup, O., Montgomery, D.R., 2008. Tibetan plateau river incision inhibited by glacial stabilization of the Tsangpo Gorge. Nature 455 (7214), 786–789. https://doi.org/10.1038/nature07322.
- Lai, J., Zou, Y., Zhang, J., Peres-Neto, P.R., 2022. Generalizing hierarchical and variation partitioning in multiple regression and canonical analyses using the rdacca.Hp R package. Methods Ecol. Evol. 13 (4), 782–788. https://doi.org/10.1111/2041-210x.13800.
- Legendre, P., Legendre, L., 2012. Numerical Ecology. Elsevier.
- Lei, C., Wagner, P.D., Fohrer, N., 2021. Effects of land cover, topography, and soil on stream water quality at multiple spatial and seasonal scales in a German lowland catchment. Ecol. Indic. 120. https://doi.org/10.1016/j.ecolind.2020.106940.
- Liu, G., Chen, R., Li, K., 2021. Glacial Change and Its Hydrological Response in Three Inland River Basins in the Qilian Mountains, Western China. Water 13. https://doi.org/10. 3390/w13162213.
- Liu, S., Yao, X., Guo, W., Xu, J., Shangguan, D., Wei, J., Bao, W., Wu, L., 2015. The contemporary glaciers in China based on the second Chinese glacier inventory. Acta Geograph. Sin. 70 (1), 3–16.
- Lu, L., Li, X., Veroustraete, F., Kang, E., Wang, J., 2009. Analysing the forcing mechanisms for net primary productivity changes in the Heihe River basin, north-West China. Int. J. Remote Sens. 30 (3), 793–816. https://doi.org/10.1080/01431160802438530.

#### H. Wang et al.

- 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. J. Environ. Manag. 92 (7), 1837–1848. https://doi.org/10.1016/j. jenvman.2011.03.005.
- Niu, H., Kang, S., Sarangi, C., Zhang, G., Chen, M., Zhang, Y., Qin, H., 2022. Source apportionment and elevational gradient of dissolved organic matter over the Tibetan Plateau. Catena 216, 106372. https://doi.org/10.1016/j.catena.2022.106372.
- Ouyang, W., Song, K., Wang, X., Hao, F., 2014. Non-point source pollution dynamics under long-term agricultural development and relationship with landscape dynamics. Ecol. Indic. 45, 579–589. https://doi.org/10.1016/j.ecolind.2014.05.025.
- Peng, Q., Wang, R., Jiang, Y., Li, C., 2021. Contributions of climate change and human activities to vegetation dynamics in Qilian Mountain National Park, Northwest China. Glob. Ecol. Conserv. 32, e01947. https://doi.org/10.1016/j.gecco.2021.e01947.
- Pokharel, B., Wang, S.Y.S., Meyer, J., Marahatta, S., Nepal, B., Chikamoto, Y., Gillies, R., 2020. The east-west division of changing precipitation in Nepal. Int. J. Climatol. 40 (7), 3348–3359. https://doi.org/10.1002/joc.6401.
- Pratt, B., Chang, H., 2012. Effects of land cover, topography, and built structure on seasonal water quality at multiple spatial scales. J. Hazard. Mater. 209, 48–58. https://doi.org/ 10.1016/j.jhazmat.2011.12.068.
- Qian, D.W., Cao, G.M., Du, Y.G., Li, Q., Guo, X.W., 2019. Impacts of climate change and human factors on land cover change in inland mountain protected areas: a case study of the Qilian Mountain National Nature Reserve in China. Environ. Monit. Assess. 191 (8). https://doi.org/10.1007/s10661-019-7619-5.
- Qin, D., Ren, J., Yao, T., Ding, Y., 2021. Introduction to Cryospheric Science. Springer Nature. SEPA, 2002. Water and Wastewater Monitoring and Analysis Methods. China Environmental Science Press, Beijing, pp. 210–213.
- SEPA, 2002. Environmental Quality Standards for Surface Water (GB 3838-2002). State Environmental Protection Administration of China, Beijing.
- Shi, P., Zhang, Y., Li, Z., Li, P., Xu, G., 2017. Influence of land use and land cover patterns on seasonal water quality at multi-spatial scales. Catena 151, 182–190. https://doi.org/10. 1016/j.catena.2016.12.017.
- Sun, F., Lyu, Y., Fu, B., Hu, J., 2016. Hydrological services by mountain ecosystems in Qilian Mountain of China: a review. Chin. Geogr. Sci. 26 (2), 174–187. https://doi.org/10. 1007/s11769-015-0791-9.
- Wang, L., Han, X., Zhang, Y., Zhang, Q., Wan, X., Liang, T., Song, H., Bolan, N., Shaheen, S.M., White, J.R., Rinklebe, J., 2022a. Impacts of land uses on spatio-temporal variations of seasonal water quality in a regulated river basin, Huai RiverChina. Science of The Total Environment 857 (Pt 2), 159584. https://doi.org/10.1016/j.scitotenv.2022.159584.
- Wang, R., Wang, Q., Dong, L., Zhang, J., 2021. Cleaner agricultural production in drinkingwater source areas for the control of non-point source pollution in China. J. Environ. Manag. 285, 112096. https://doi.org/10.1016/j.jenvman.2021.112096.

- Wang, S., Shen, M., Liu, W., Ma, Y., Shi, H., Zhang, J., Liu, D., 2022b. Developing remote sensing methods for monitoring water quality of alpine rivers on the Tibetan Plateau. GISci. Remote Sens. 59 (1), 1384–1405. https://doi.org/10.1080/15481603.2022.2116078.
- Wang, S., Wang, X., He, B., Yuan, W., 2020. Relative influence of forest and cropland on fluvial transport of soil organic carbon and nitrogen in the Nen River basin, northeastern China. J. Hydrol. 582. https://doi.org/10.1016/j.jhydrol.2019.124526.
- Wolka, K., Biazin, B., Martinsen, V., Mulder, J., 2021. Soil and water conservation management on hill slopes in Southwest Ethiopia. I. Effects of soil bunds on surface runoff, erosion and loss of nutrients. Sci. Total Environ. 757, 142877. https://doi.org/10.1016/j. scitotenv.2020.142877.
- Xu, Q., Yan, T., Wang, C., Hua, L., Zhai, L., 2022. Managing landscape patterns at the riparian zone and sub-basin scale is equally important for water quality protection. Water Res. 119280. https://doi.org/10.1016/j.watres.2022.119280.
- Yang, W., Wang, Y., Webb, A.A., Li, Z., Tian, X., Han, Z., Wang, S., Yu, P., 2018. Influence of climatic and geographic factors on the spatial distribution of Qinghai spruce forests in the dryland Qilian Mountains of Northwest China. Sci. Total Environ. 612, 1007–1017. https://doi.org/10.1016/j.scitotenv.2017.08.180.
- Yin, Z., Feng, Q., Yang, L., Wen, X., Si, J., Zou, S., 2017. Long term quantification of climate and land cover change impacts on streamflow in an Alpine River catchment, northwestern China. Sustainability 9 (7). https://doi.org/10.3390/su9071278.
- Yu, S., Xu, Z., Wu, W., Zuo, D., 2016. Effect of land use types on stream water quality under seasonal variation and topographic characteristics in the Wei River basin, China. Ecol. Indic. 60, 202–212. https://doi.org/10.1016/j.ecolind.2015.06.029.
- Zhang, F., Yushanjiang, A., Jing, Y., 2019a. Assessing and predicting changes of the ecosystem service values based on land use/cover change in Ebinur Lake wetland National Nature Reserve, Xinjiang, China. Sci. Total Environ. 656, 1133–1144. https://doi.org/10. 1016/j.scitotenv.2018.11.444.
- Zhang, J., Li, S., Dong, R., Jiang, C., Ni, M., 2019b. Influences of land use metrics at multispatial scales on seasonal water quality: a case study of river systems in the Three Gorges Reservoir area, China. J. Clean. Prod. 206, 76–85. https://doi.org/10.1016/j.jclepro. 2018.09.179.
- Zhang, L.N., Jiang, Y., Zhao, S.D., Jiao, L., Wen, Y., 2018. Relationships between tree age and climate sensitivity of radial growth in different drought conditions of Qilian Mountains, northwestern China. Forests 9 (3). https://doi.org/10.3390/f9030135.
- Zhang, Y., Li, F., Zhang, Q., Li, J., Liu, Q., 2014. Tracing nitrate pollution sources and transformation in surface- and ground-waters using environmental isotopes. Sci. Total Environ. 490, 213–222. https://doi.org/10.1016/j.scitotenv.2014.05.004.
- Zhu, G., Wang, L., Liu, Y., Bhat, M.A., Qiu, D., Zhao, K., Sang, L., Lin, X., Ye, L., 2022. Snowmelt water: an important water source for Picea crassifolia in Qilian Mountains. J. Hydrol. 613, 128441. https://doi.org/10.1016/j.jhydrol.2022.128441.