Water quality assessments and driving factors analysis in a typical headwater catchment, Southeast China

*Kaiyan Zhao[1, 2], Huawu Wu[1, *], Wen Chen[1], Wei Sun[1], Haixia Zhang[1, 2], Weili Duan[3], Bin He[4, 5, *]*

([1]Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing, China, 210008;

[2]University of Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing, China, 100049;

[3]Xinjiang Institute of Ecology and Geography, Chinese Academy of Sciences, Urumqi, China, 830011;

[4]Guangdong Key Laboratory of Integrated Agro-environmental Pollution Control and Management, Guangdong Institute of Eco-environmental Science and Technology, Guangzhou, China, 510650;

[5]National Regional Joint Engineering Research Center for Soil Pollution Control and Remediation in South China, Guangzhou, China, 510650)

First author: Kaiyan Zhao, Email: k.y.zhao@qq.com;

**Corresponding author: Huawu Wu, Email: hwwu@niglas.ac.cn;*

Bin He, Email: bhe@soil.gd.cn.

Abstract: Safety of source water streams is an urgent environmental issue, while protections in monsoon controlled subtropical regions face difficulties because of the lack of small scaled observation and analysis in small source water catchments. Basing on continuous weekly water quality data (2014-2017) in Pingqiao River Catchment, the annual average values of TN, NO_3, NH_4 and TP are 3.36, 1.64, 0.28 and 0.02 (mg/L) respectively. During dry, normal and wet seasons, the variability of parameters is over 35%, which indicates an obvious seasonality. Multiple methods are combined in order to assess the water quality and find the driving factors during dry, normal and wet seasons. This study suggests precipitation and fertilization are the mainly seasonal factors, which can make water quality better in wet season than dry season due to the dilution effect. The mechanism between seasonality and compound of nutrients can also be traced by log(TN:TP), and log(NO_3:NH_4). Among six main land use types (forest, tea plantation, cropland (paddy), urban, bare soil and water), the former three ones are influential mostly during dry and wet season. Tea plantation has the largest nutrients discharge amount per area, which is similar to cropland in dry season. By contrary, forest has the double power in reducing nitrogen release in wet and normal seasons. When transformed into paddies, croplands can lower the phosphorus concentration. Conclusions of this study can be used in southeastern China and similar regions on source water protection and agricultural plans.

Keywords: headwater catchment; water quality assessment; driving factors; spatial and temporal analysis; Southeast China

1. Introduction

Water becomes a global concerned issue in 21st century due to both natural and anthropogenic factors with rising uncertainty, such as climate change and extreme weather, land use and land cover, urbanization and industrialization [1,2,3]. Among all the problems, nonpoint water pollution, usually caused by loss of nutrients, including nitrogen and phosphorus mainly, is a tricky one due to the difficulties in tracing observation, mechanism analysis, and preventive measure [4,5,6]. Therefore maintaining the high water quality in a whole watershed is kind of impossible in an intensive industrialized area, so protecting the source water and keeping safe of drinking water are the vital tasks [7,8].

Situation in China is even severe, since many researches have revealed and demonstrated the decrease of water quality in reservoirs [9,10,11]. For years as subtropical monsoon controlled region, the southeastern China usually has ample precipitation and high forestage coverage in source water areas, which can play a role of mitigate the nonpoint pollution [12,13,14]. However, in the last two decade, with the increasing population pressure and the widely use of chemical fertilizers and pesticides, the quality of source water is challengeable [9,15,16]. Most studies focus on the water quality in reservoirs, but researches lack quantitative analysis on the upstream flows of the reservoirs [10,17]. Pingqiao River catchment is the source water catchment of Taihu Basin, in monsoon controlled subtropical area, which can be an ideal study area for three reasons: (1) there are intensive influences from both natural in temporal scale and anthropic in spatial; (2) the area of the study area is small enough for sampling in one hour and weekly water quality data can be available; (3) as a source water stream, Pingqiao River determine the inflow nutrient discharge into drinking water reservoir and the water quality was degrading during recent decade [9,18]. So doing water quality assessments and driving factors analysis in Pingqiao River Catchment can be a break point for source water protection.

Several methods, both statistic and modelling, are used in water quality assessments and analysis, such as Pearson's correlation coefficients, and stepwise regressions for primary data process. And then sophisticated statistics techniques like hierarchical cluster analysis, discriminant analysis (DA), factor analysis (FA), principal component analysis (PCA) and redundancy Analysis (RDA) [11,19,20,21]. Also index system are developed into water quality assessments, some effective ones are water quality index (WQI) and ratio between different parameters or components like TN:TP and NO_3:NH_4 are used in order to show the situation of eutrophication and seasonality respectively [8,22,23,24].

This study aims at (1) displaying the spatial and temporal distribution of nutrient concentration, and assessing the water quality of flow water in Pingqiao River Catchment, (2) finding the controlling drivers of water quality in different conditions basing on seasons and land use types.

2. Materials and Methods

2.1 Study area

Pingqiao River is one of the three main streams of Shahe Reservoir in Liyang City, Jiangsu Province, China, whose annual discharge is

$8.68*10^6 m^3$. The catchment of Pingqiao River (31.16-31.24N, 119.41-119.47E) covers an area of 16.61 km^2, the total length is 10.24 km and the average width is 1.62 km.

Pingqiao River Catchment is located in a hill area with an average altitude of approximate to 100m, and as shown in **Fig.1a** the hills and mountains cover 2/3 of the catchment especially in the upstream areas and the downstream areas are plains obviously. As in a subtropical monsoon controlled zone, the average temperature is 15.71ºC and annual precipitation is 1166.72mm, which can be divided into three distinctive period (1) wet season (from April to July), (2) normal season (from August to October), and (3) dry season (from November to March next year). The dominate land use/land cover type is forest, covering 72.58% of total land, and about half of which is Mao bamboo (**Fig.1b**). Tea plantations are common in Yangtze Delta area, and in the study area, they distribute in steep hills. Cropland, mainly paddies, and urban areas are mixed in plains (**Fig.1b**) [21]. There is only one town-Pingqiao Community in the downstream of catchment and the total population of whole area is about

7500. Through occupies in a small proportion, bare soils are the most complex type because of different sources, such as deforested areas, abandoned farms, and tea plantations under recovering and demolished constructions. Nearly 4% of land are rivers, lakes, ponds and reservoirs, biggest of which is Shiba Reservoir, located in the sampling site U4 (**Fig.1a**). Other than being the source of domestic and agricultural usage, Shiba Reservoir is also the cut-off point of upstream and downstream.

[Fig.1. is inserted here]

2.2 Water sampling and analytical methods

There are twelve sampling sites in total (**Fig.1a**), divided into three groups: upstream (U1-U4), downstream (D1-D5), and a main tributary (T1-T3). Sampling sites are choosing mainly after the inflow of tributaries and the intervals between neighboring ones are about 1km. Sub-catchments are displayed in **Fig.1a** and they are generally suitable for the principle that the land use types to be homogeneity and the areas to be equal. Water samples are collected weekly from 2014 to 2017, so for each site, there are 125 samples for analyzing.

Seven of parameters are measure including total nitrogen (TN), nitrate nitrogen (NO_3), ammonium nitrogen (NH_4), and total phosphorus (TP). All samples are collected in transparent sampling bottles and preserved in 5°C and tested in less than five days in State Key Laboratory of Lake Science and Environment. The laboratory tests of water samples are following the standard methods in guide book by State Environmental Protection Agency [25,26], which is also global accepted.

Logarithm value of TN:TP and NO_3:NH_4 are calculated as indicators of drivers of water quality [8,23]. Pearson's correlation analysis, stepwise multiple regression, hierarchical cluster analysis and redundancy analysis are calculated and presented by programming on R Studio 3.5. Maps are displayed via QGIS 3.0.

3. Results

3.1 Land use/land cover patterns

Proportion of land use types of twelve sampling sites are shown and compared in **Fig.2** in the sequence from upstream to downstream then to tributary. Excepting T1 and T2, forest is the dominant land use in ten sites, which decreases from U1 (81.23%) to T3 (32.42%) rapidly. On contrary, cropland, mainly paddy increases as a replacement of forest. Two minority land use types (bare soil and water) stay at low rates less than 5%. While tea plantation and urban tend to gather in particular sites like D1, D2 and T1 for tea plantation and D3 and D4 for urban.

[Fig.2. is inserted here]

3.2 Spatial and temporal assessments of water quality

Changing patterns of twelve sampling sites are combined and shown in **Fig.3** on the left side and the spatial hierarchical cluster analysis is displayed on the right side. For each parameter, by comparing the data array of 1,500 values, the linear relationship among sampling sites is distinctive, but the synchronic effect is obvious. Thus in study area, temporal factors are more powerful than spatial ones. The results of cluster analysis shows that the neighboring sites usually have the close values like the upper ones (U1 and U2), middle ones (D2, D1, U3, and U4), and lower ones (D3, D5, and D4). Also the vertical axis of cluster diagram represents lower value at bottom and higher value at top, so form U1 to D4, there is an increase on all parameters as a whole, which means the rising of nutrient concentration in water from upstream to downstream generally.

[Fig.3. is inserted here]

By dividing into three distinctive seasons, values of parameters are displayed in **Fig.4** with violin graph and box graph in order to figure out the temporal distribution. The outer violin graphs show the frequency distribution of data, the inner box graphs show the medium, upper quartile, and lower quartile in black bars and the algorithm mean value with white points. Similar to the regulation revealed in **Fig.3**, water quality parameters share more similarity spatially rather than temporally. According to each parameters, there are three different types: (1) Log(NO_3:NH_4) and TP, having slight differences through three seasons; (2) Log(TN:TP), NH_4, and TN, having similar patterns in dry and wet seasons, but different ones in normal season; (3) NO_3, having different characters among all seasons.

[Fig.4. is inserted here]

3.3 Spatial and temporal driving factors of water quality

By using stepwise multiple regression method, main driving factors of each season are found out and listed in **Table 1**. Cropland (paddy) has great influence on dry season and urban impacts wet season the most. In normal season, it is complicated because several factors work. The decisive indicators (R^2 and sig.) show cropland in dry season is rather strong, while urban in wet season is weak. And in normal season, there are both strong and weak factors. When coming to the positive and negative effects, majority of drivers show positive ones. And the forest shows an effect of reducing TN and NO_3 in wet and normal season, and cropland (paddy) seems to reduce TP in normal season, which needs further discussion. When comparing the coefficients in equations, forest tends to have the double effect of cropland through, and they work on opposite directions.

[Table 1 is inserted here]

Relationships between land use types and water quality parameters during different seasons are presented in **Fig.5** with the red points represent negative correlation, and the blue ones represent positive correlation. Through seasons, dry and wet season are close to each other while normal season is unique. Forest is the only factor having stable reducing effect of water quality parameters, especially in dry and wet season, the effect is strong. On contrary, cropland has strong positive effect in dry and wet season. Two other factors, tea planation and bare soil could increase values of TN, NO_3 and NH_4 in wet season particularly. The relationship of others is fairly weak.

[Fig.5. is inserted here]

3.4 Characters and relationships among driving factors of water quality

Basing on redundant analysis (RDA), relationships among environmental factors (land use types) and species (water quality parameters) are displayed in **Fig.6** along with pots representing sampling sites. From all seasons, two major land use types (forest and cropland) are the most effective ones acting on opposite ways. Tea plantation and bare soil are close to cropland in all seasons with smaller effects. Urban area has weak relationship with cropland and forest. And its effect is close to zero in normal season. According to parameters, two ratios (TN:TP and NO_3:NH_4) are quite influential when compared with other parameters, but the two indicators themselves have weak relationship to each other. For TN:TP, in dry and normal season, it shows positive correlation with TN, and in wet season, the main driver is TP with negative effects. In normal season, NO_3:NH_4 has a positive correlation with NO_3, and in wet season, has a strong negative correlation with NH_4. In all three graphs, TN is close to NO_3 rather than NH_4.

[Fig.6. is inserted here]

4. Discussions

4.1 Driving effect of seasonality on water quality parameters

As revealed and described in Section 3.2, in study area, seasonality has more powerful influence on water quality rather than land use types. Though land use types are the fundamental reason of nutrients input and release, water quality, particular the indexes themselves are strongly controlled by the amount of water when concerning the dilution and concentration effects. Thus in typical subtropical region like Pingqiao River Catchment, precipitation is the main driver of nutrient transport. With the rainfall of 457mm, 700mm, and 925mm in dry, normal, and wet seasons separately, the concentration of nutrients are negative related with rainfalls. Other researches also support the similar theory to view rainfall as the first factor of water quality in monsoon zones [27, 28].

Other than natural events, agricultural activities can also impact water quality seasonally. During the time of late March and late May, fertilizing is taken place in the study area. Obviously, fertilization is the main source of nitrogen and phosphorus in Pingqiao River Catchment, but is not directly linked with nutrient loss. From observed data, combination with fertilization and middle rainfall (5mm to 25 mm per day) can cause high level of nitrogen concentration in stream flow, and the peak time of pollutant is around three days after rainfall. Both small rain (less than 5mm per day) and heavy rain (more than 50mm per day) has less effect on washing out nutrients from soil immediately in study area, and other catchments share the climate region and soil types have the similar phenomenon [29,30].

4.2 Driving effect of land use types on water quality parameters

The land use types and distribution in **Fig.2** are typical in the rural areas with nonpoint pollutions, and the values of TN and TP are close to other studies as well [27,28]. As illustrated in Section 3.3, forest usually plays a role of reducing the nutrient elements leaching, while cropland (paddy) and urban are acted as producers, which is widely accepted by other researchers [29,31,32]. Water bodies, especially reservoir act as a dilution maker, so Shiba Reservoir, located at point U4, can reduce the concentration of nutrients greatly. As a result, there is a clear gap of water quality between U4 and D1. Tea plantation and bare soil are unique but typical in southeastern China, while materials are lack when focusing on these two land use types. In some study areas, tea plantations are included into forest, but in Pingqiao River Catchment, they become an independent type since the intensive activities as irrigation and fertilization [21,32]. In this aspect, tea plantation is more like cropland rather than forest as shown in Section 3.4. Additional, tea plantation often releases more nutrients than cropland in study catchment. Last, as transformed from cropland, tea plantation and built-up areas, bare soil shared their characters with high concentration of nitrogen but this land use type cannot slow down the erosion by rainfall [30,31]. Therefore, the release rate of nutrient is fairly high in bare soil.

According to phosphorus, forest can be a source of phosphorus losses, and the leaching rate in this study area is reasonable [33]. Cropland is truly a source of phosphorus, but in study catchment, it seems to reduce the discharge of phosphorus during normal season interestingly. The explanation is that in normal season, on one hand there is no considerable input of phosphorus, and on the other hand, in Pingqiao River Catchment, more than 80% of croplands are paddies, which can play a role like water bodies to dilute the concentration of TP. This view is also supported by other studies [34,35]. And results in Section 3.3 demonstrate during dry season and wet season, croplands can no longer be a sink of TP because they are transformed into dry land in dry season and in the wet season, the load of phosphorus increases through fertilization. Generally, urban, tea plantation, and bare soil do not have distinctive characters of TP releasing, and one reason is that they all cover small amount of land, and can be easily influenced by forest and cropland. Other reasons remain to be found basing on field experiments. Finally, the waterfowl culture in water bodies during dry season is the first factor to increase the release of phosphorus.

4.3 Evaluation of water quality indicators

Log(TN:TP) is an important parameter to show the quality of water and the eutrophication conditions. In Pingqiao River Catchment, this ratio is generally high during dry season and tends to be lower in normal and wet season. One hypothesis is suitable for this phenomenon that since phosphorus is a minor scale pollutant, it can be easily dissolved in water rather than remain in soil. In other words, TP can stay in water bodies for a long time, but no likely to be washed out from soil immediately. Consequently, TP is not strongly influenced by rainfall but impacted by the amount of water bodies available, among which are not only perennial waters but also seasonal one like paddies [31,33,36].

The ratio between NO_3 and NH_4 indicates the condition of nitrification process and denitrification process. Farmland manure and compound fertilizer are used in cropland and tea plantation, and their major compositions are NH_4 rather than NO_3. During dry and normal seasons, there are weak relationships between NH_4 and cropland or tea plantation, but in wet season, it comes to strong positive. The theory of limit conditions for nitrification process is suitable for this phenomenon because in a harsh situation of high temperature and humidity, the activity of nitrifying bacteria is reduced [30,37]. Moreover, in wet season, because of the heavy rains, nitrifying bacteria do not have enough time for nitrification. But in normal and dry seasons, optimal conditions of both water and temperature can be available for nitrification, which can transform NH_4 to NO_3 [38,39].

5. Conclusion

Basing on the observing water quality data of Pingqiao River Catchment from 2014 to 2017, including parameters: TN, NO_3, NH_4, TP, log(TN:TP), and log(NO_3:NH_4), and analyzing them by multiple statistics methods, this study indicates:

(1) Seasonality is the most influential driver of water quality. Two factors, precipitation and fertilization caused by nature and human beings separately, are mixed during dry, normal and wet seasons. As in a typical monsoon controlled subtropical region, water quality in wet season tends

to be better than dry season due to the dilution effect.

(2) Land use types play an important role on water quality parameters and the dominant land use types usually determine the positive or negative correlation with the water quality. Being detailed, forest is demonstrated as a sink of nitrogen and phosphorus; cropland (paddy) can reduce TP concentration in normal season; and other land use types including tea plantation, urban, bare soil and water, act as a source of nutrients generally.

(3) Radio indexes can suggest the changing patterns of seasonal water bodies (log(TN:TP)) and the nitrification conditions (log(NO_3:NH_4)) which is the main factors of phosphorus and different forms of nitrogen.

Acknowledgement

This research was jointly supported by the GDAS' Project of Constructing Domestic First Class Institution (2020GDASYL-0102), the National Natural Science Foundation of China (41871119, 41471460 and 41701036), the Strategic Priority Research Program of the Chinese

Academy of Sciences (XDA23020102), the Natural Science Foundation of Jiangsu Province (BK20161612). We would like to thank Meng Huifang, Yang Chaojie, Wu Yanjuan, and Liu Xiangnan for their field work.

References

1. Ferrier, R.C.; Edwards, A.C.; Hirst, D.; Littlewood, I.G.; Watts, C.D.; Morris, R. Water quality of Scottish rivers: spatial and temporal-trends. Sci. Total Environ. 2001, 265, 327–342.
2. Wilson, C.O.; Weng, Q. Simulating the impacts of future land use and climate changes on surface water quality in the Des Plaines River watershed, Chicago metropolitan statistical area. Ill. Sci. Total Environ. 2011, 409, 4387-4405.
3. Tu, J. Spatial variations in the relationships between land use and water quality across an urbanization gradient in the watersheds of northern Georgia, USA. Environ Manag. 2013, 51, 1-17.
4. Pieterse, N.M.; Bleuten, W.; Jorgensen, S.E. Contribution of point sources and diffuse sources to nitrogen and phosphorus loads in lowland river tributaries. J. Hydro. 2003, 271, 213-225.
5. Lee, S.W.; Hwang, S.J.; Lee, S.B.; Hwang, H.S.; Sung, H.C. Landscape ecological approach to the relationships of land use patterns in watersheds to water quality characteristics.Landscape.UrbanPlan. 2009, 92, 80–89.
6. Ngoye, E.; Machiwa, J.F. The influence of land use patterns in the Ruvu river watershed on water quality in the river system. Phys.Chem.Earth. 2004, 29, 1161–1166.

7. Carney, E. Relative influence of lake age and watershed land use on trophic state and water quality of artificial lakes in Kansas. Lake and Reservoir Management. 2009, 25, 199-207.

8. Caille, F.; Riera, J.L.; Rosell-Mele, A. Modeling nitrogen and phosphorus loads in a Mediterranean river catchment (La Tordera, NE Spain). Hydrol. Earth Syst. Sci. 2012, 16, 2417-2435.

9. Zhao, G.J.; Gao, J.F.; Tian, P.; Tian, K.; Ni, G.H. Spatial–temporal characteristics of surface water quality in the Taihu Basin, China. Environ Earth Sci. 2011, 64, 809-819.

10. Chen, N.; Wu, J.; Hong, H. Effect of storm events on riverine nitrogen dynamics in a subtropical watershed, southeastern China. Science of the Total Environment. 2012, 431, 357-365.

11. He, G.; Lu, Y.; Mol, A.P.; Beckers, T. Changes and challenges: China's environmental management in transition. Environ. Dev. 2012, 3, 25–38.

12. Liu, J.; Zhang, L.; Zhang, Y.; Hong, H.; Deng, H. Validation of an Agricultural Non-point Source (AGNPS) pollution model for a catchment in the Jiulong River watershed, China. J. Environ. Sci. 2008, 20, 599-606.

13. Li, S.; Gu, S.; Tan, X.; Zhang, Q. Water quality in the upper Han River basin, China: the impacts of land use/land cover in riparian buffer zone. Hazard Mater. 2009, 165, 317-324.

14. Tong, S.T.; Sun, Y.; Ranatunga, T.; He, J.; Yang, Y.J. Predicting plausible impacts of sets of climate and land use change scenarios on water resources. Appl.Geogr. 2012, 32, 477-489.

15. Dunn, S.; Brown, I.; Sample, J.; Post, H. Relationships between climate, water

resources, land use and diffuse pollution and the significance of uncertainty in climate change. J. Hydrol. 2012, 434, 19-35.

16. Burger, G.; Sobie, S.R.; Cannon, A.J.; Werner, A.T.; Murdock, T.Q. Downscaling extremes: an intercomparison of multiple methods for future climate. J. Clim. 2013, 26, 3429-3449.
17. Buck, O.; Niyogi, D.K; Townsend, C.R. Scale-dependence of land use effects on water quality of streams in agricultural catchment. Environment Pollution. 2004, 130, 287-299.
18. Wu, Z.S.; Wang, X, L.; Chen, Y, W.; et al. Assessing river water quality using water quality index in Lake Taihu Basin, China. Science of the Total Environment. 2018, 612, 914-922.
19. Woli, K.P.; Nagumo, T.; Kuramochi, K.; Hatano, R. Evaluating river water quality through land use analysis and N budget approaches in livestock farming areas. Sci. Total Environ. 2004, 329, 61–74.
20. Jarvie, H. P.; Withers, P.J.; Hodgkinson, R.; Bates, A.; Neal, M.; Wickham, H.D.; Harman, S.A.; Armstrong, L. Influence of rural land use on stream water nutrients and their ecological significance. Journal of Hydrology. 2008, 350, 166–186.
21. Yang, C.J.; He, B.; Duan, W.L.; Li, B., Chen, W.; Yang, G.S. Analysing the apatial and temporal variations and influencing factors of the water quality in a typical hilly water source of Lake Taihu Basin: A case study in Pingqiao River Watershed. Resources and Environment in the Yangtze Basin. 2017, 26, 273-281.
22. Schoonover, J.E.; Lockaby, B.G. Land cover impacts on stream nutrients and fecal coliform in the lower Piedmont of West Georgia. J. Hydrol. 2006, 331, 371–382.
23. Chen, N.; Hong, H.; Zhang, L.; et al. Nitrogen sources and exports in an agricultural

watershed in Southeast China. Biogeochemistry. 2008, 87, 169-179.

24. Cherry, K.; Shepherd, M.; Withers, P.; et al. Assessing the effectiveness of actions to mitigate nutrient loss from agriculture: A review of methods. Science of the Total Envionment. 2008, 406, 1-23.

25. SEPA. Water and Wastewater Monitoring Analysis Method. Beijing: China Environmental Science Press. M. 2002, 210-284. (in Chinese)

26. Frost, P. C.; Larson, J.H.; Johnston, C.A.; Young, K.C.; Maurice, P.A.; Lamberti, G.A.; Bridgham, S.D. Landscape predictors of stream dissolved organic matter concentration and physiochemistry in a Lake Superior river watershed. Aquatic Sciences. 2006, 68, 40–51.

27. Abbaspour, K.C.; Rouholahnejad, E.; Vaghefi, S.; Srinivasan, R.; Yang, H.; Kløve, B. A continental-scale hydrology and water quality model for Europe: calibration and uncertainty of a high-resolution large-scale SWAT model. J. Hydrol. 2015, 524, 733-752.

28. Shrestha, S.; Kazama, F. Assessment of surface water quality using multivariate statistical techniques: a case study of the Fuji river basin, Japan. Environmental Modelling & Software. 2007, 22, 464-475.

29. Absalon, D.; Matysik, K. Changes in water quality and runoff in the Upper Oder River Basin. Geomorphology. 2007, 92, 106-118.

30. Galloway, J.N.; Townsend, A.R.; Erisman, J.W.; et al. Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. Science. 2008, 320, 889-892.

31. Solanki, V.R.; Hussain, M.M.; Raja, S.S. Water quality assessment of Lake Pandu Bodhan, Andhra Pradesh State, India. Environmental Monitoring and Assessment.

2010, 163, 411-419.

32. Bu, H.M.; Meng, W.; Zhang, Y.; Wan, J. Relationships between land use patterns and water quality in the Taizi River basin, China. Ecological Indicators. 2014, 41, 187-197.
33. Yan, R.H.; Gao, J.F.; Huang, J.C. WALRUS-paddy model for simulating the hydrological processes of lowland polders with paddy fields and pumping stations. Agr. Water Manag. 2016, 169, 148-161.
34. Vermaat, J.E.; Hellmann, F. Covariance in water-and nutrient budgets of Dutch peat polders: what governs nutrient retention? Biogeochemistry. 2010, 99, 109-126.
35. Uygun, B.S.; Albek, M. Determination effects of impervious areas on urban watershed. Environ. Sci. Pollut. R. 2015, 22, 2272-2286.
36. Frost, P.C.; Kinsman, L.E.; Johnston, C.A.; et al. Watershed discharge modulates relationships between landscape components and nutrient ratios in stream seston. Ecology. 2009, 90, 1631-1640.
37. Gadegast, M.; Hirt, U.; Opitz, D.; et al. Modelling changes in nitrogen emissions into the Oder River System 1875-1944. Regional Environmental Change. 2012, 12, 571-580.
38. Alexander, R.B.; Smith, R.A.; Schwarz, G.E. Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. Nature. 2000, 403, 758-761.
39. Frost, P. C.; Stelzer, R.S.; Lamberti, G.A.; et al. Ecological Stoichiometry of tropic interactions in the Benthos: Understanding the role of C: N: P ratios in Lentic and Lotic Habitats. Journal of the North American Benthological Society. 2000, 21, 515-528.

Captions of Tables and Figures

Table 1 Stepwise multiple regression results between land use types and water quality parameters in Pingqiao River Catchment during dry, normal, and wet seasons. Note: FOR for forest; TEA for tea plantation; CRO for Cropland (paddy); URB for Urban; BAR for bare soil; WAT for water.

Fig.1. Sampling sites (a), DEM (a), and land use/land cover patterns (b) in Pingqiao River Catchment.

Fig.2. Composition of land use/land cover types of sub-catchments of sampling sites in Pingqiao River Catchment. Note: U1 to U4 refer to upstream sampling sites, D1 to D5 refer to downstream sampling sites, and T1 to T3 refer to tributary sites.

Fig.3. Spatial distribution and hierarchical cluster analysis result of water quality parameters in Pingqiao River Catchment. Note: U1 to U4 refer to upstream sampling sites, D1 to D5 refer to downstream sampling sites, and T1 to T3 refer to tributary sites.

Fig.4. Water quality parameters (TN, NO_3, NH_4, TP, log(TN:TP), and log(NO_3:NH_4)) of dry season (November to March next year), normal season (August to October), and wet season (April to July) in different

sampling sites ($p < 0.05$, two tailed).

Fig.5. Pearson's correlation coefficients between land use types and water quality parameters in Pingqiao River Catchment during dry, normal, and wet seasons ($p<0.05$, two tailed).

Fig.6. Relationships between land use types and water quality during different seasons based on redundancy analysis

Table 1 Stepwise multiple regression results between land use types and water quality parameters in Pingqiao River Catchment during dry, normal, and wet seasons. Note: FOR for forest; TEA for tea plantation; CRO for Cropland (paddy); URB for Urban; BAR for bare soil; WAT for water.

	Regression equation	R^2	Sig.
Dry season			
TN	0.352+0.645CRO	0.665	0.001
NO_3	0.590+0.385CRO	0.668	0.001
NH_4	0.060+0.062CRO	0.591	0.004
TP	0.030-0.004URB	0.387	0.031
Log(TN:TP)	1.793+0.092CRO	0.727	<0.001
Log(NO_3:NH_4)	1.209-0.110URB	0.342	0.046
Normal season			
TN	2.062+0.255BAR	0.667	0.001
NO_3	4.176-1.433FOR	0.274	0.081
NH_4	0.130+0.061URB	0.091	0.341
TP	0.050-0.004CRO	0.649	0.002
Log(TN:TP)	1.029+0.225WAT	0.594	0.003
Log(NO_3:NH_4)	0.787+0.105CRO	0.163	0.194
Wet season			
TN	14.198-1.982FOR	0.761	<0.001
NO_3	5.930-1.523FOR	0.445	0.018
NH_4	0.105+0.050BAR	0.564	0.005
TP	0.016+0.005URB	0.211	0.133
Log(TN:TP)	2.414-0.084URB	0.374	0.033
Log(NO_3:NH_4)	1.032-0.073URB	0.542	0.006

($p < 0.05$, two tailed)

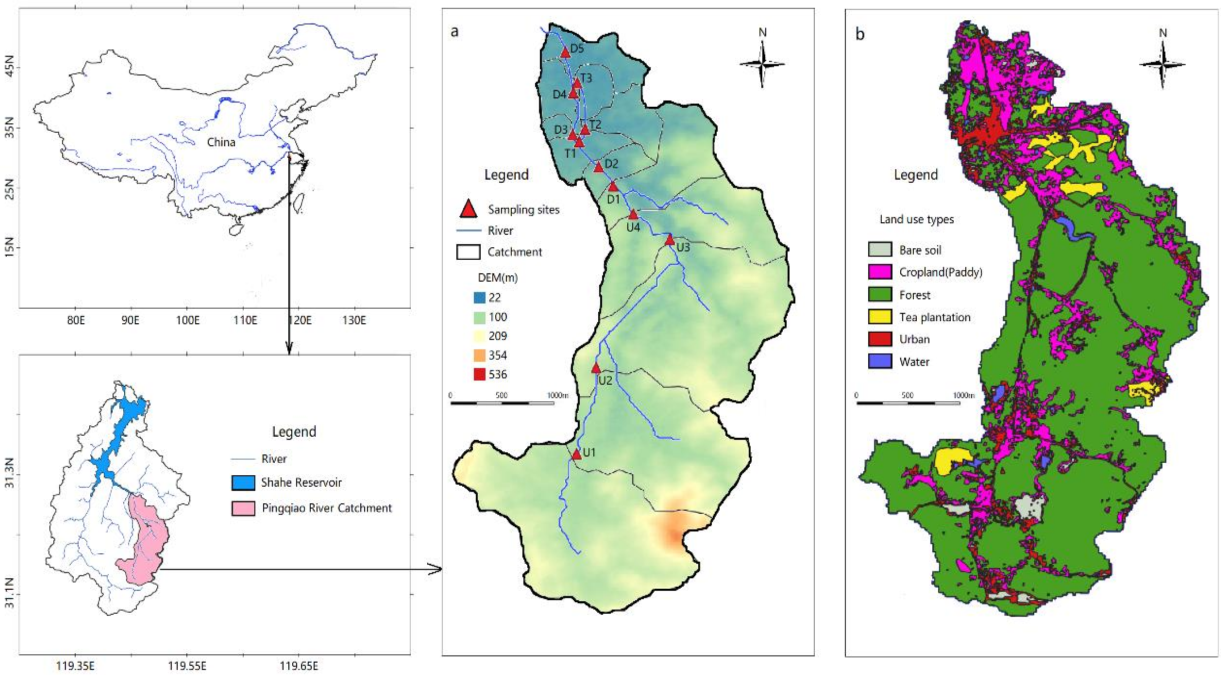

Fig.1. Sampling sites (a), DEM (a), and land use/land cover patterns (b) in Pingqiao River Catchment.

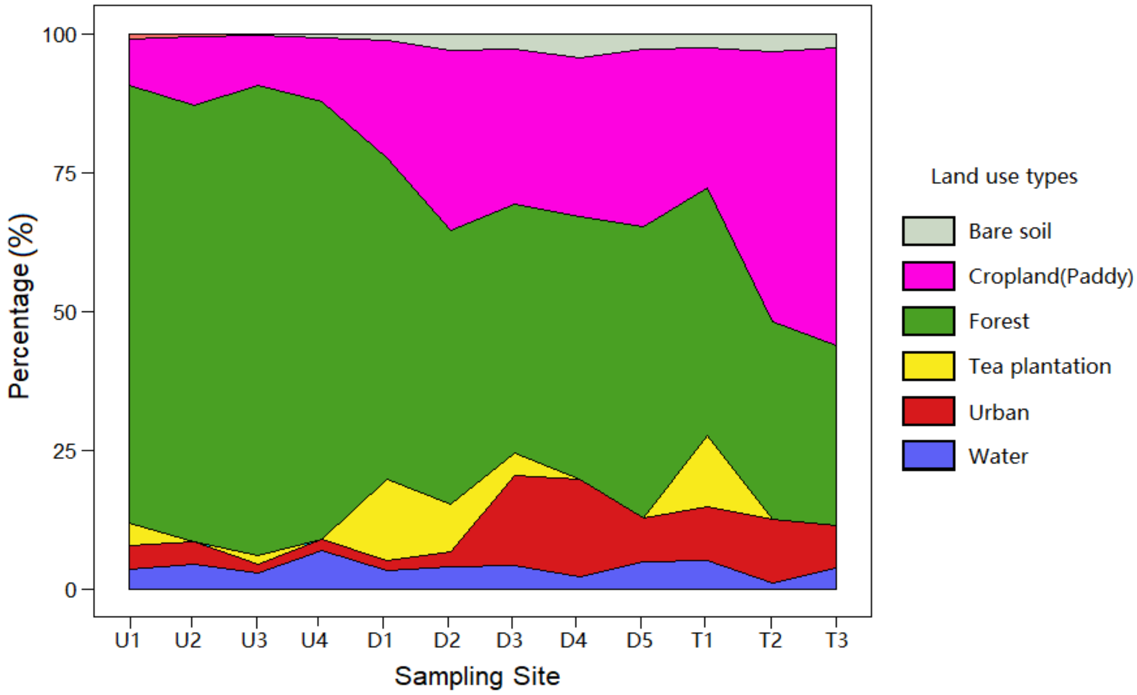

Fig.2. Composition of land use/land cover types of sub-catchments of sampling sites in Pingqiao River Catchment. Note: U1 to U4 refer to upstream sampling sites, D1 to D5 refer to downstream sampling sites, and T1 to T3 refer to tributary sites.

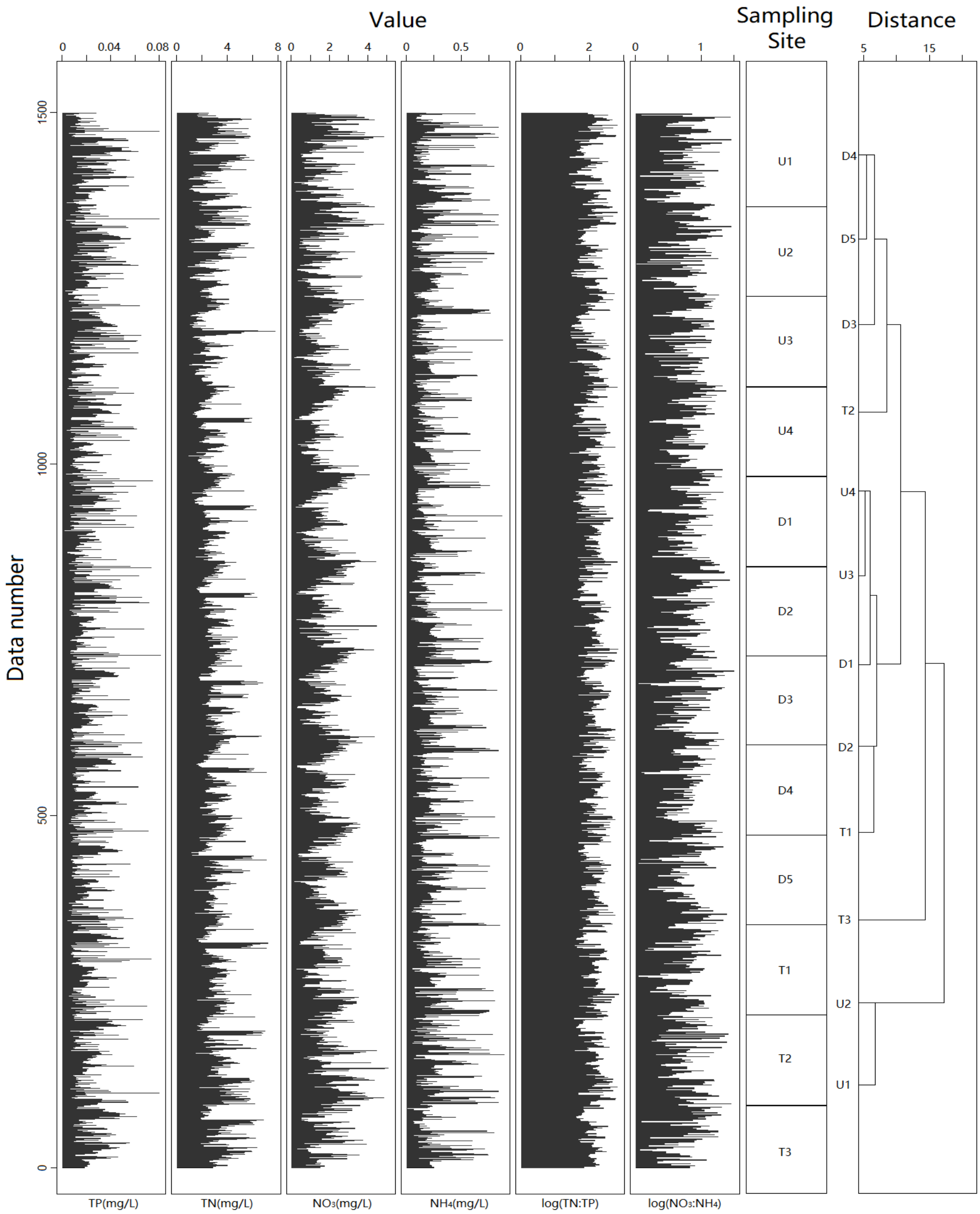

Fig.3. Spatial distribution and hierarchical cluster analysis result of water quality parameters in Pingqiao River Catchment. Note: U1 to U4 refer to upstream sampling sites, D1 to D5 refer to downstream sampling sites, and T1 to T3 refer to tributary sites.

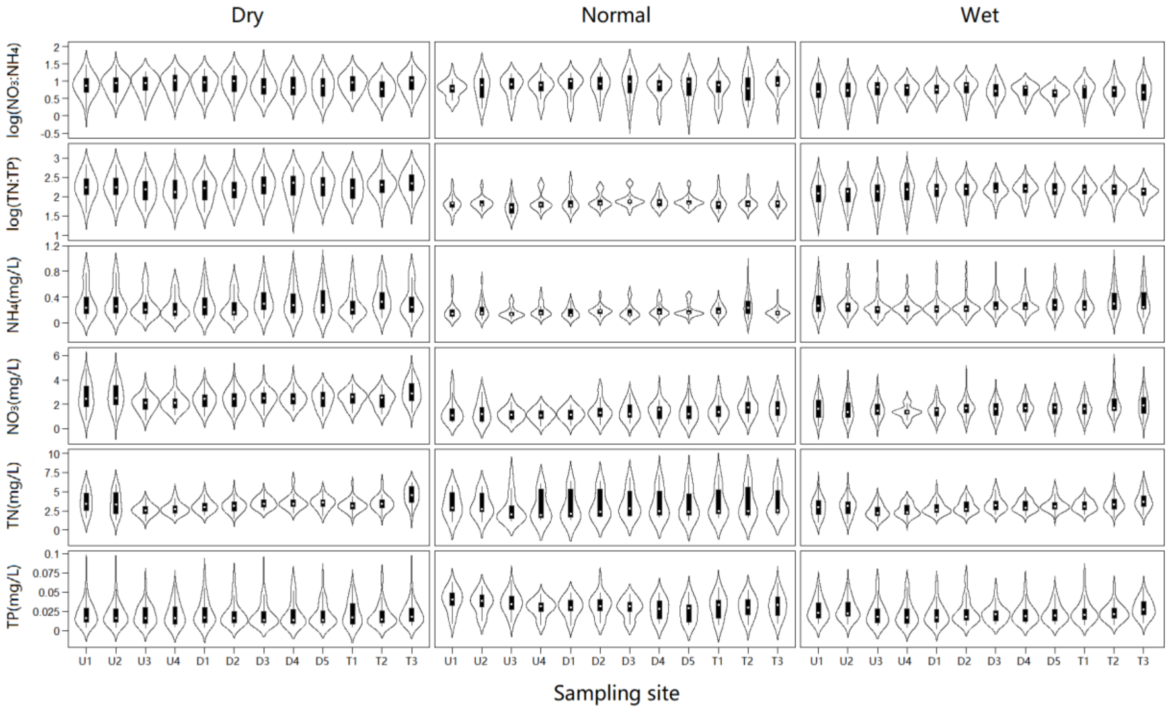

Fig.4. Water quality parameters (TN, NO_3, NH_4, TP, log(TN:TP), and log(NO_3:NH_4)) of dry season (November to March next year), normal season (August to October), and wet season (April to July) in different sampling sites ($p < 0.05$, two tailed).

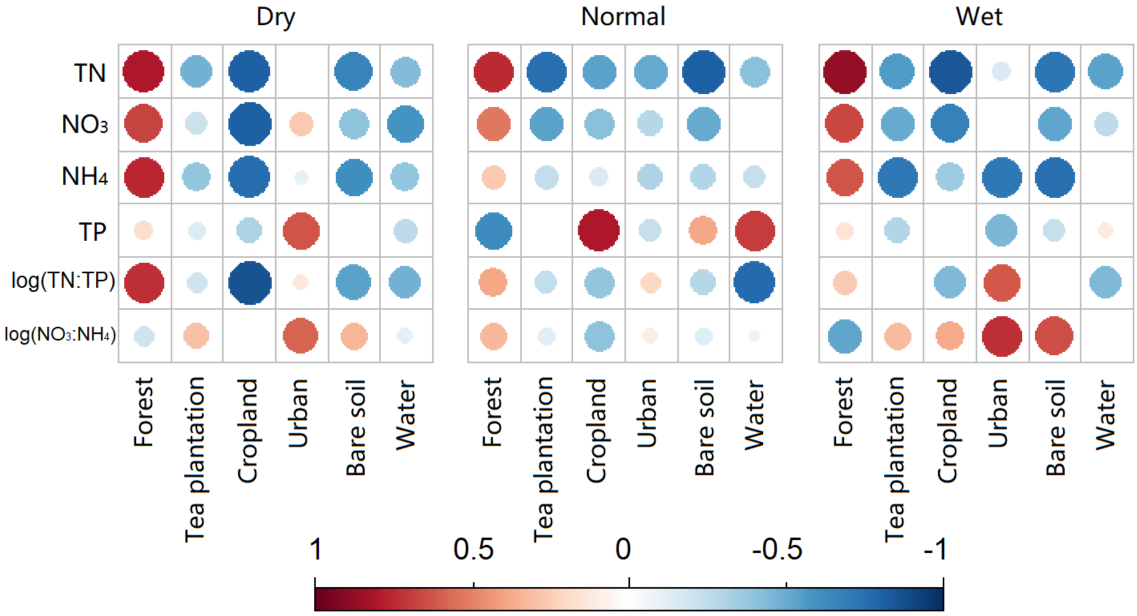

Fig.5. Pearson's correlation coefficients between land use types and water quality parameters in Pingqiao River Catchment during dry, normal, and wet seasons ($p<0.05$, two tailed).

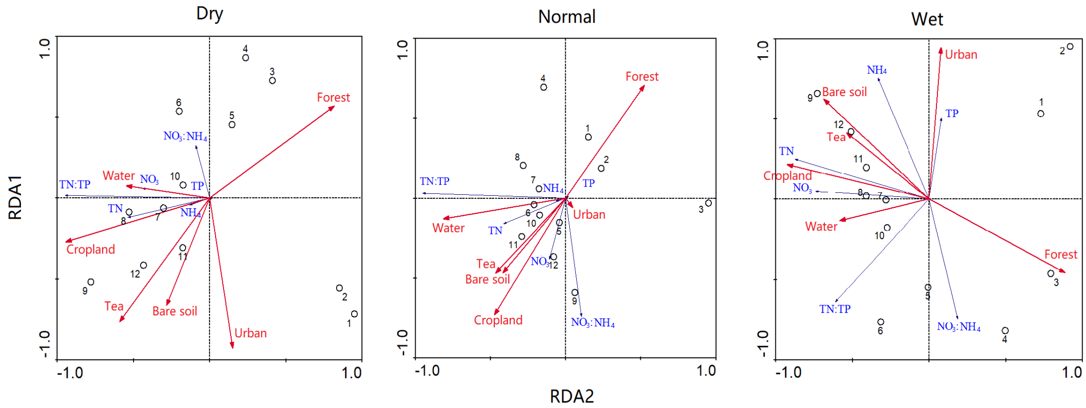

Fig.6. Relationships between land use types and water quality during different seasons based on redundancy analysis.