Sources and routes from terrestrial exogenous pollutants affect phytoplankton biomass in reservoir bays

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ABSTRACT

Reservoir bays, the boundary of terrestrial and water where water fluidity slows down and self-purification ability turn weak, hence they are especially sensitive to terrestrial exogenous pollutants, even resulting in eutrophication. According to N:P, water nutrients types can be divided into N limited, P limited and N + P limited classes. Phytoplankton biomass is represented by chlorophyll a, which is one of the sensitive indicators of water eutrophication. Comprehensively traced non-point pollution from terrestrial exogenous pollutants (fertilizer, soil release, anthropogenic discharge) to water nutrients that happen in reservoir bays is of great significance. This paper identified the dominant environmental variables and nutrients limited types of reservoir bays at storage and discharge periods, constructed partial least squares structural equation model (PLS-SEM) to explore the impacts of terrestrial exogenous pollutants. Results showed that in storage period water contamination mainly came from residential discharge and soil endogenous release, the total contribution rate reached 61%. In discharge period, with the increase of rainfall – runoff erosion, the explanatory ability of land use, topography and landscape pattern to water quality increased, up to 58%. The dominant nutrients limited types of reservoir bays were P limited (35%–47%) and N + P limited (35%–59%) at both stages, N limited situations less than 20% and generally appeared in storage period. Whatever the nutrients limited type was, phosphorus always had a higher effect on phytoplankton biomass. In N limited situation, nitrogen mainly from soil release (total effect = 0.6) and phosphorus from fertilizer (total effect = 0.22) and soil release (total effect = 0.17). In P limited situation, all three sources had almost high effects on nitrogen, phosphorus, and phytoplankton biomass. In N + P limited situation, the anthropogenic discharge was the main source of nutrients and the primary threaten factor for phytoplankton biomass. The approaches employed in this study could be generalized to the other basin and the results were significant to early warning and controlling water eutrophication.

Key words | chlorophyll-a, nonpoint pollution, N:P ratio, partial least squares structural equation model PLS-SEM)

HIGHLIGHTS

- The dominant nutrients limited types of reservoir bays were P limited and N + P limited at both stages.
- Whatever the nutrients limited type was, phosphorus always had higher effect on phytoplankton biomass.
The effects and contributes of fertilizer, soil release and anthropogenic discharge to water nutrients and phytoplankton biomass were calculated.

GRAPHICAL ABSTRACT

INTRODUCTION

Hydraulic engineering has been greatly prevented and alleviated nature disasters caused by floods and droughts and plays a vital role in water supply, irrigation, power generation, etc (Chen et al. 2016). Until now there have been more than 50,000 dams height over 15 meters all over the world (Lehner et al. 2011), however, reservoir operation has changed the natural hydraulic mechanism of the river even water connectivity is prevented, which caused water self-purification capacity to decline and river ecological environment changed (Gao et al. 2018; Li et al. 2021; Xiang et al. 2021). These changes will further threaten water quality.

Reservoir bays, semi-enclosed water bodies at terrestrial and water boundaries, affected by its morphological characteristics, water mobility turned down in this place. Because they adjoin with land, make they become the most sensitive places to overland pollutants (Li et al. 2020). There have been quite a lot of reports of water eutrophication events in reservoir bays (Yang et al. 2018; Chuo et al. 2019; Huang et al. 2020) which have aroused extensive concern. What caused the nature of eutrophication in water is phytoplankton blooms, therefore, the key to controlling eutrophication is to inhibit the growth of phytoplankton in water.

Studies on water eutrophication showed that the input of nitrogen, phosphorus, and other nutrients was the vital inducement for algae outbreak and water quality deterioration (Paerl et al. 2017; Mamun et al. 2020). According to Liebig’s law of the minimum, the required nutrients for plant growth were provided by the external environment, if the amount of a certain nutrient approaches the lower bound, then this nutrient was the limiting factor for plant growth (Chen et al. 2013). The ratio of N:P could serve as an index that represents the nutrient limitation for phytoplankton growth when compared with the average composition of nutrients assimilated in algae (C106:N16:P1) (Fujimoto et al. 1997). Early experimental research established that a high concentration of P and a low N:P supply ratio (<29:1) were favorable for the production of algae blooms (Smith 1985). There had been some successful practices that reducing phosphorus (P) inputs based on the premise that P universally limits primary productivity but not all (Elser et al. 2007; Lewis et al. 2011). The theory they based on was that nitrogen flow into the water could be degraded to gas form through denitrification and other biochemical processes, then circulated at the water-gas interface. However, phosphorus had no gas form in
nature, so it was difficult for phosphorus to be degraded in the water. As the water flow slowed down, phosphorus was deposited in the water and became a part of internal pollution. Therefore, the accumulation rate of phosphorus in the water was higher than nitrogen. Many traditional views thought that water eutrophication could only control the input of phosphorus, thus ignoring the limitation of nitrogen (Schindler et al. 2008). Lately, researchers in China, America, Africa, and Europe had been discovered that many lakes exhibit varying nutrient limiting and cycling patterns, including periods of P or N limitation, as well as periods of N and P act in concert to facilitate biomass production (Conley et al. 2009; Harpole et al. 2011; Paerl et al. 2011; Chen et al. 2015). Therefore, the management strategy of eutrophication water bodies should overall consider different situations of nutrient limitation, not only one.

Nutrients enriched in lakes or reservoirs are mainly considered to source from overland flow, soil release, domestic and industrial sewage discharge (Santos et al. 2017; Zhou et al. 2017). When overland runoff erodes the underlying surface, sediments and contamination will flow into the river then afflux into the lake or reservoir (Chen et al. 2018). The concentration and category of pollutants influenced by hydrometeorology, land use, and land cover, soil property, landscape pattern in a watershed (Shi et al. 2013; Yan et al. 2013; Ai et al. 2015; Li et al. 2020). As the extensive management of agricultural, nitrogen and phosphorus fertilizer used in crops always surpass than it practical utilized, meanwhile fertilization activity tended to be coincidence with the rainy season, thus it was inevitable that part of the superfluous fertilizer will erode into surface water, part of which will enrichment or infiltration into the soil (Gao et al. 2004; Menció et al. 2011; Lacher et al. 2019; Xie et al. 2019). Apart from the artificially added nutrients, soil inherent contains nitrogen, phosphorus, organic matter, and so on nutrients, which will also increase the contamination flow into the water in dissolved or particle states (Tong & Chen 2002; Neary et al. 2009; Zhou et al. 2012; Lacher et al. 2019). Besides nonpoint pollution, residential and industrial wastewater discharge constructed another pollutant source. Studies in Xiamen Bay – Jiulong River Basin showed that increasing anthropogenic discharge and agricultural fertilizer loads over the past 30 years were the main causes of high P loadings in water (Chen et al. 2015). Dirk et al. used the geospatial statistical methods to discover the response relationships between landuse and water quality factors under different spatial scales, the results showed that human activities mainly affected the types and concentrations of water pollutants through large-scale urbanization, and the expansion of agricultural activities, the natural landuse mainly affected the variation of water quality in small scale (Vrebos et al. 2017). Excessive nitrogen inputs from sources such as fertilizer from farmland or domestic wastewater from residential areas have been identified as major contributors to stream nitrogen loading (Berka et al. 2001; Jiang et al. 2014; Zhou et al. 2017; Yi et al. 2020). Previous studies have focused on clarifying the sources and contributions to a certain high loading water nutrient, however, the category of water pollutants tends to be different in different situations, such as flood or dry season, land use and land cover, landscapes, etc… Therefore, under different nutrients limited types, exploring the sources and routes from terrestrial exogenous pollutants affecting phytoplankton biomass in reservoir bays remains an unsolved problem. This study aims at clarify the dominant nutrients limited types of reservoir bays and the restrict factors to the concentration of Chl a, and based on the priori assumption of: terrestrial exogenous input (agricultural non-point pollution, domestic sewage discharge, soil release) - water nutrients concentration (nitrogen and phosphorus nutrients) - water phytoplankton biomass (the concentration of Chl a) to construct the path model, further identify the sources and transport routes of water pollution from environment background.

Human construct reservoir because of its indispensable roles in water resource supply, regulation and storage flood, agriculture irrigation, entertainment and so on, we should discover the hidden risk of non-pollution immediately and make scientific guidelines. In this work, we choose reservoir bays as the study area for its special morphological characteristics which made it the most sensitive place for the convergence of non-point pollution. Based on the priori causal path of terrestrial exogenous input – water nutrients concentration – water phytoplankton biomass, structural equation model were built to identify non-point pollution sources form terrestrial exogenous pollutants to water nutrients in both reservoir storage period and discharge period. The major objectives of this study were: (i) to identify the
temporal and spatial distribution of chlorophyll-a concentration in storage and discharge periods of reservoir bays, (ii) to extract the dominant environmental variables that mainly contribute to water contamination, (iii) to elaborate the influence paths and effects across terrestrial exogenous input—water nutrients—phytoplankton biomass in Danjiang-Kou reservoir bays. The results will help researchers and local decision-makers to understand the source and dynamics of Chl a, therefore, it's essential to control the input of nonpoint pollution and eutrophication effectively.

MATERIALS AND METHODS

Study area

Danjiangkou (DJK) reservoir (32°36′–33°48′N, 110°59′–111°49′E) is located on the upstream of Han River, the largest tributary of Yangtze River, and is the water source for the Middle Route Project under the South-to-North Water Transfer Scheme initiated to overcome the spatial unevenly distributed water resource in China (Ai et al. 2015). The area of the DJK reservoir is around 1,023 km² and the watershed of the reservoir is about 17,916 km². The study area contains the DJK reservoir bays and their catchments, covers an area of 689 km² (Figure 2). The crest elevation increased from 162 to 176.6 m in 2012, and in 2014 the project was officially opened to water supply over 20 cities along the line. After the dam was raised, the ecological environment around the reservoir greatly changed, and water quality became an important concern for local and national policymakers. It is because the critical role of water supply and the high sensitivity for water quality security that we choose the DJK reservoir as a representative place to study the causes and sources of water quality variance.

The elevation of the study area ranges from 0 to 957 m, high and steep in the northwest, low and gentle in the southeast. This area has a typical subtropical monsoon climate,
rain and hot during the same period. The average yearly temperature is $-16 \, ^\circ C$, and the average annual precipitation between 800 and 1,000 mm, most of which falls during the monsoon season (June to October), thus lead to higher intensity rainfall and overland flow afflux into the reservoir. According to the hydrometeorological rules and flood control requirements, the reservoir usually discharged water from June to October and stored water from May to November of the following year. Based on the regulation of reservoir operation, May was deemed to be the storage period, September was deemed to be the discharge period. According to the Chinese soil classification system, the major soil types include yellow-brown soil, limestone soils and purple soil (National Soil Survey Office 1998), which correspond respectively to Alfisols, Entisols and Entisols in the USA Soil Taxonomy (Soil Survey Staff 1999). The main land-use type in this watershed is forest, nearly 70%. Farmland and residential areas are concentrated along the river. The major crops are corn (Zea mays L.) and wheat (Triticum aestivum L.).

Stream water sampling and analysis

Reservoir bays were divided based on the digital elevation model (DEM) with a resolution of 25 m by 25 m. Using Geography Information System (GIS) technology practiced in hydrological analysis module, according to the threshold of the catchment area 500 ha to extract bay catchment areas. Follow the rules of homogeneity and universality, we choose 62 reservoir bays which overall considered altitude, slope and land use types.

We sampled water at reservoir bays from 2015 to 2019 in May (storage period) and September (discharge period). Laid three sample points at every bay, respectively boundary, center and mouth, the distance between points over 200 m. Water temperature(Temp), pH, dissolved oxygen
(DO), turbidity (NTU) and the concentration of Chl a were measured in situ using a YSI EXO2 (YSI Inc., Yellow Springs, Ohio, USA) water quality multiparameter analyzer (Li et al. 2021), other water quality indexes were tested at the laboratory. The concentration of the total nitrogen (TN) was determined using the method of Alkaline potassium persulfate digestion -ultraviolet spectrophotometry (CSEPB 2002). The concentration of total phosphorus (TP) was tested by ammonium molybdate spectrophotometry (CSEPB 2002). The Nitrate nitrogen (NO\textsubscript{3}-N) and ammoniacal nitrogen (NH\textsubscript{4}-N) concentration were measured by AA3 flow analyzer (FLAstar 5,000 Analyzer). We collected water 10 m away from the shore, depth between 0 and 20 cm, then filled it into a 500 mm polythene plastic bottle, add H\textsubscript{2}SO\textsubscript{4} until pH less than 2, cold storage at 2–5 °C, analyze within 24 hours. The total water quality indexes and analysis methods were shown in Table 1.

Environmental variables

The primary data used in this study included Digital Elevation Model (DEM) in the DJK reservoir watershed with a resolution of 25 m by 25 m that was purchased from the National Geomatics Center of China. Climate data were available from 9 meteorological stations located within or close to the watersheds. The soil type map (1:100,000 scale) with related soil properties that were derived from the Soil Survey Office of Hubei Province. The drone orthophoto map was obtained from the Chang Jiang River Water Resources Commission, with a special resolution of 0.5 m by 0.5 m. The land-use map was based on the orthophoto map via visual interpretation in ArcGIS 10.4.

Topographical variables include elevation, slope, slope length and soil erosion modulus were calculated based on DEM within ArcGIS 10.4. Soil variables contained SOM, STN, STP, SNO\textsubscript{3}-N, SNH\textsubscript{4}-N. Land-use type comprised water bodies, forestland, shrubland, grassland, garden land, paddy field, dry land, urban land, rural land and unused land, which could be reclassified into water, natural vegetation (forestland, shrubland, grassland), farmland (garden land, paddy field, dry land) and residential area (urban land, rural land).

The application amounts of nitrogen and phosphorus fertilizer of dry land, paddy field and garden land were from the agricultural statistical datum. The pollutant
export coefficient (the loads of TN or TP that were exported from each source per unit time, per unit area, in reservoir bays) from individual agricultural sources were using the output coefficient method to calculate (Li 2010) (Table 2).

\[ L = \sum_{i=1}^{n} E_i[A_i(I_i)] + P \]  

The export coefficient \((E_i)\) describes the pollutant load exported from each land use type per unit area per unit time \((t/km^2 \cdot yr)\) in the catchment. where \(L\) is the loss of nutrients \((t)\), \(A_i\) is the area of the catchment occupied by land-use type \(i\) \((km^2)\), or the number of livestock type \(i\), or people, \(I_i\) is the input of nutrients to source \(i\) \((t)\), and \(P\) is the input of nutrients from precipitation \((t)\).

### Table 1 | Water quality indexes and analysis methods

| Water quality index      | Abbr. | Unit | Assay method                                      |
|--------------------------|-------|------|---------------------------------------------------|
| Water temperature        | Temp  | °C   | YSI6600V2 multiparameter water quality monitor    |
| Potential of hydrogen    | pH    | –    |                                                   |
| Dissolved oxygen         | DO    | mg/kg| Alkaline potassium persulfate digestion-ultraviolet spectrophotometry |
| Turbidity                | NTU   | NTU  |                                                   |
| Chlorophyll a            | Chl a | μg/L |                                                   |
| Total nitrogen           | TN    | mg/L |                                                   |
| Total phosphorus         | TP    | mg/L | Ammonium molybdate spectrophotometry              |
| Nitrate nitrogen         | NO₃-N | mg/L | AA3 flow analyzer                                 |
| Ammoniacal nitrogen      | NH₄-N | mg/L | AA3 flow analyzer                                 |
| Permanganate nitrogen    | COD₅₀ | mg/L | Acidic potassium permanganate titration           |
| Total organic carbon     | TOC   | mg/L | Total organic carbon analyzer                     |

Landscape variables were obtained from the land-use map calculated by the software FRAGSTATS 4.1, which is widely accepted for landscape metrics quantification (McGarigal 2002). The landscape index used in this study included landscape shape index \((LSI)\), Contagion \((CON)\), Shannon’s diversity index \((SHDI)\). Abbreviations and descriptions of the selected variables for the environmental characteristics were shown in Table 3.

### Table 2 | The pollutant export coefficients adopted in this study for TN and TP of fertilization and anthropogenic wastewater

| Nutrient source     | TN   | TP    | Unit              |
|---------------------|------|-------|-------------------|
| Paddy field         | 2,625| 182   | kg·km⁻²·a⁻¹       |
| Dry land            | 1,921| 79    | kg·km⁻²·a⁻¹       |
| Garden land         | 1,234| 98    | kg·km⁻²·a⁻¹       |
| Residential area    | 636  | 36    | kg·km⁻²·a⁻¹       |
| Population          | 19,547| 2,142 | kg·(ca·10⁴)⁻¹·a⁻¹ |

### Statistical analysis

To analysis the distribution of concentration of Chl a in different stages we used the descriptive statistical analysis method to map the distributions of Chl a concentration by ArcGIS 10.4. To figure out the source and contribution of water contamination from the environmental background, we used the redundancy analysis method, which coupled the principal component analysis (PCA) with Multiple Linear Regression (MLR) has been widely used in water quality research (Santos et al. 2017). The results included the relationship between environmental variables and the ordination axis, what’s more, the quantitative decomposition of the independent variables at the ordination axis due to the influence of environmental variables, which showed the relative contribution of explaining variables to predictive variables.
According to the various sources from terrestrial exogenous pollutants – water nutrients – phytoplankton biomass, the PLS-SEM model was built. The first step of PLS-SEM was to propose a conceptual model to reflect the mechanism according to the research problem and the existing understanding of nonpoint pollution. The path routes were built based on the following hypothesis (proven results). (1) Nutrients in the water of reservoir bays were mainly derived from exogenous inputs from the environmental background, including agricultural fertilizer, soil endogenous release and anthropogenic discharge (Onderka et al. 2012; Pratt & Chang 2012; Ai et al. 2015; Pearce et al. 2017). (2) Exploring the influence of water nutrients on Chl a: A multivariate statistical model analysis pollutant concentration can be viewed as the linear sum of the elemental contributions from pollution sources (Helena et al. 2000; Singh et al. 2005). (3) According to the ratio of N:P, reservoir bays could be divided into different nutrients limited classes (N limited, P limited, N + P limited), which results in the major difference for the

| Variables                        | Abbr. | Description                                                                 |
|---------------------------------|-------|-----------------------------------------------------------------------------|
| Topographical variables         | Topo. | Average elevation of a reservoir bay                                        |
| elevation                       | Ele   | Average elevation of a reservoir bay                                        |
| Slope gradient                  | Slope | Average slope gradient of a reservoir bay                                   |
| Soil erosion modulus            | Ero   | Average soil erosion modulus of a reservoir bay                             |
| Soil variables                  | Soil. |                                                                             |
| Soil organic matter             | SOM   | Organic matter component of the soil                                        |
| Soil total nitrogen             | STN   | The total nitrogen component of the soil                                    |
| Soil total phosphorus           | STP   | Total phosphorus component of the soil                                      |
| Soil nitrate-nitrogen           | SNO₃  | The total nitrate-nitrogen component of the soil                            |
| Soil ammonium nitrogen          | SNH₄  | The total ammonium nitrogen component of the soil                           |
| Land use composition            | LU.   |                                                                             |
| Natural vegetation              | Vege  | Percent of the area covered by natural vegetation                          |
| Farmland                        | Farm  | Percent of the area covered by farmland                                     |
| Residential area                | Resi  | Percent of the area covered by residential area                             |
| landscape pattern index         | LSI   | The landscape boundary and total edge within the landscape divided by the total area, adjusted by a constant for a square standard |
| Contagion                       | CON   | The tendency of the patch types to be aggregated                            |
| Shannon's diversity index       | SHDI  | An index based on information theory that indicates the patch diversity in a landscape |

According to the ratio of N:P, reservoir bays could be divided into different nutrients limited classes (N limited, P limited, N + P limited), which results in the major difference for the pollution sources and route effects contribute to phytoplankton (Paerl et al. 2017; Rattan et al. 2017).

The structural equation model (SEM) is a statistical tool based on the established theory of causality hypothesis, which can calibrate and validate the fitness of a model. Wright (1934) first introduced the method in biological population research, and it has been expanded to a wide range of research areas, including social sciences, psychology, chemistry, and biology (Hung et al. 2007; Kashy et al. 2008). SEM combining factor analysis with route analysis contains the relationships of observed variables, potential variables, reveal the direct effect, indirect effect and total effect of independent variables on dependent variables. SEM comprises two basic models, the measurement model and the structural model. The measurement model is composed of potential variables and observed variables, which is the linear function of observed variables, it is usually represented by a rectangular shape. Potential variables are the abstract concept of observed variables, cannot be measured.
but can be reflected by observed variables, it is usually represented by an ellipse shape. The structural model declares the causality of variables if variables represent the reason called exogenous latent variables, in this study are the terrestrial exogenous pollutants. If variables represent the results called endogenous latent variables, such as the concentration of nutrients and the biomass of phytoplankton in water.

In structural model (Inner model), the linear relationships between the latent variables $\xi_j$ is written as:

$$\xi_j = \sum_{i \neq j} \beta_{ji} \xi_i + \zeta_j$$  

(2)

$\beta_{ji}$ is the route coefficients of the latent variables $\xi_j$. Where $\zeta_j$ is a random error.

In measurement model (Outer model), each latent (unobservable) $\xi_j$ variable is described by a linear combination of the manifest variable $x_{jh}$:

$$x_{jh} = \lambda_{jh} \xi_j + \epsilon_{jh}$$  

(3)

$\lambda_{jh}$ is the coefficients of column vector $\xi_j$, $\epsilon_{jh}$ is random error. PLS modeling standardizes each latent variable to get a unit variance, $\text{Var}(\xi_j) = 1$, for achieving scales for unambiguity.

In the structural model the direct effects are illustrated by the corresponding path coefficients ($\beta_{ji}$). Indirect effects between potential variables are those pathways that including intermediary variables, The total effects describe the overall relationships from one causative latent variable to another resultative variable which are the sum of the direct and indirect effects. The model calculation was conducted using R and the R package ‘plspm’ (ver. 0.4.7, Sanchez 2013).

**RESULTS AND DISCUSSION**

Temporal and spatial dynamic change of Chl a concentration

The box chart (Figure 4) drew upon the statistical analysis of the concentration of Chl a from eight times sampling data. The results showed that the range in May (storage period) was always larger than that in September (discharge period), partly because the rainfall was lighter in May, during this period the water mobility was weak in bays, thus made a dispersion distribution of $\rho$ (Chl a). In turn, in September with the increase of precipitation, water mobility increased and caused a more evenly distributed of $\rho$ (Chl a). Besides, with the increase of exogenous input, the median and average of $\rho$ (Chl a) were generally higher than that in May.

To better understand how the concentration of Chl a distributed in spatial we mapped the mean concentration of Chl a in two periods within ArcGIS 10.4 (Figure 5). The results showed that in the storage period (May) the high-value zones were distributed scattered. Conversely, it turned to distribute in high-value groups interval with low-value groups at discharge period (Sep.). Demonstrated that the increase of runoff and the regulation of reservoirs changed the mobility of water and raised the diffusion ability of pollutants. This results indicate that the increase of rainfall-runoff erosion in rainy season is the driving force of non-point pollution. On the one hand, it increases the total amount of exogenous pollutants input into water, on the other hand, the increase of water fluidity enhances the ability of pollutant migration and diffusion in the water (Ai et al. 2015; Zhou et al. 2017; Xie et al. 2019).

Dominant environmental variables that mainly influence water quality in reservoir bays

Using redundancy analysis to perform multivariant regression should eliminate the influence of redundancy
Figure 5  |  Spatial distribution of Chl a concentration of reservoir bays in storage (a) and discharge (b) period.
variables. We use the forward selection method to pick out environmental variables and validating through the Monte Carlo method, the result is presented in Table 4. The slope in topography factors, residential area and natural vegetation in land-use types, STN, SNO$_3$-N, SNH$_4$-N in soil variables were the dominant environmental variables that influence water quality in the storage period, while landscape pattern indexes were not so significant in this period. In discharge period, elevation, slope length, soil erosion modulus among topography factors, residential area and vegetation among land-use types, LSI, CONTAG, SHDI among landscape pattern variables could strongly explain the variance of water quality.

In the RDA ordination graph (Figure 6), the proportion of variance explained by the environment variables were shown in Table 4. The results showed that all of the water quality indexes were positively correlated with Chl a, what’s more, there were two groups of the cluster in water quality indexes, one was water physical indexes another was water nutrients indexes. Among the environmental background variables, the residential area accounted for the largest variation, covering 39% and had a higher correlation with TOC, Chl a, COD$_{Mn}$ and DO. Indicated that the residential sewage discharge was the dominant factor that contributed to the increase of water nutrients and the phytoplankton biomass, which led to the enrichment of organic pollutants in reservoir bays (Zhou et al. 2022). Soil endogenous nutrients release was another important source (Pearce et al. 2017), STN, SNO$_3$-N, SNH$_4$-N together with slope length contributed 22%. Natural vegetation negatively affected water pollutants, consistent with previous researches (Xiao & Ji 2007), it’s proved that vegetation can increase surface roughness and intercept pollutants from overland flow.

As it showed in Figure 6, in the discharge period pH was negatively correlated with the other water quality factors. Indicated that with the increase of external input and the change of water dynamic mechanism, water acidity increased and pH turned down. In this stage, water contamination is mainly attributed to land use, topography and landscape pattern. Residential discharge still accounted for a large part of external input, covering 30%. The contribution of topography factors was quite sophisticated, slope length and soil erosion modulus were positively correlated with water contamination contributed 19%, while elevation effect in opposite which coincidence with CONTAG in landscape pattern (Pratt & Chang 2012; Vrebos et al. 2017). With the increase of altitude, the interference of human activities turned down and mainly distributed continuously of vegetation, which could effectively retain nonpoint pollution (Sliva & Dudley Williams 2001). From the perspective of the landscape, vegetation play the role of ‘sink’, so the large area of continuously distributed vegetation affect negatively on non-point pollution. Landscape indexes LSI and SHDI represent the categories and abundance of patches in a unit area that were positive to water contamination. With the increase of fragmentation and connectivity in the landscape, the fluidity of surface pollutants will increase and the concentration of nonpoint pollution will aggravate (Uuemaa et al. 2005). Soil endogenous release was not so influential in this period.

### Table 4 Forward selection analysis and Monte Carlo test of environmental factors effect on water quality factors at different stages

| Environmental variables | Storage period | | | Discharge period | | |
|---|---|---|---|---|---|---|
| | p-value | R-value | | p-value | R-value | |
| Ele | 0.134 | – | | 0.050* | – | – | 0.10 |
| Slope | 0.131 | – | | 0.145 | – | |
| SI | 0.009** | 0.04 | | 0.035* | 0.16 | |
| Ero | 0.142 | – | | 0.043* | 0.03 | |
| Farm | 0.131 | – | | 0.709 | – | |
| Resi | 0.002** | 0.39 | | 0.014* | 0.30 | |
| Vege | 0.020* | – | | 0.050* | – | – | 0.03 |
| LSI | 0.072 | – | | 0.045* | 0.04 | |
| CON | 0.119 | – | | 0.042* | – | – | 0.03 |
| SHDI | 0.113 | – | | 0.043* | 0.05 | |
| SOM | 0.120 | – | | 0.143 | – | |
| STN | 0.014* | 0.10 | | 0.190 | – | |
| STP | 0.093 | – | | 0.179 | – | |
| SNO$_3$ | 0.016* | 0.05 | | 0.164 | – | |
| SNH$_4$ | 0.018** | 0.03 | | 0.134 | – | |
| Total | – | 0.65 | – | | 0.74 | |

*Abbreviations for the environmental variables are defined in Table 3.

**p < 0.01, *p < 0.05; p-value represents the significance level, R-value represents the percentage of variance explained by the environment variable.
The sources and effects of nonpoint pollution in reservoir bays

The well-established results for nutrients limited study in inland hydrostatic water indicated that when the ratio of N:P concentration is higher than 23, the limiting nutrient referred to P, when the ratio of N:P concentration is lower than 9 that was tend to N limited, besides, the nutrients were N + P limited (Paerl et al. 2017). According to this prior classify criteria, the nutrients limited level could be divided into N-limited, P-limited and N + P limited (Figure 7). Different nutrients limited types determine the kinds and amount of nutrients available to phytoplankton, which caused the difference in the biochemical process.

Figure 6 | RDA ordinations of water quality factors and environment variables in the storage (a) and discharge (b) period. Black arrows point to independent variables, red arrows point to dependent variables.

Figure 7 | The distribution of the nutrients limited classes of reservoir bays. The pie charts showed statistics of the occurrence frequency of three types of nutrients limited classes in storage and discharge period.
between phytoplankton and water environmental factors. Therefore, it is necessary to establish a path analysis model based on the nutrients limited classes from the sources of nitrogen and phosphorus.

The results of nutrients limited classification during both periods (Figure 7) showed that the most commonly distributed types were P-limited (35%–47%) and N + P limited (35%–59%), while N-limited situations appeared quite rarely, accounted for less than 20%. In the storage period, P limited (47%) was the dominant distribution type, meanwhile, the N limited situations up to the most in this stage (18%). In the discharge period, the pervasively distributed situations were N + P limited (59%), with rainfall increasing, nutrients transported to reservoir bays with surface runoff became more comprehensively, thus quite a lot of reservoir bays converted to N and P joint limited (Paerl et al. 2017; Li et al. 2020).

One source of nutrients concentrated in reservoir bays was from the endogenous release of sediment and another was from the exogenous input of the terrestrial environment. Considering that there existed a water level fluctuation zone between the high and low water level period, part of the external input of the terrestrial environmental background were released from the submerged soil (Shan et al. 2014; Wu et al. 2017). The amount of pollutants confluence in reservoir bays with surface flow relied on the types of land cover via along the way. For the application of fertilizer in agricultural practices and the discharge of domestic and industrial wastewater in human activities, the agricultural and residential land uses played the role of ‘source’ for non-point pollution and led to the positive contribution to pollutants concentration (Zhao et al. 2019). To clarify the sources and effects input from exogenous pollution, agricultural fertilizer, soil release and anthropogenic discharge were considered as the exogenous latent variables for PLS-SEM. It was because the external input of nitrogen and phosphorus added the concentration of nitrogen and phosphorus in water, and then influenced the biomass of phytoplankton in reservoir bays. Based on these theories pollutants transport routes model PLS-SEM was built (Figure 8).

In PLS-SEM, the available nutrients for phytoplankton depended on nitrogen salt and phosphorus salt in water, the exogenous sources of N and P in reservoir bays mainly

![Figure 8](http://iwaponline.com/ws/article-pdf/doi/10.2166/ws.2021.148/889304/ws2021148.pdf)
came from fertilizer, soil release and artificial discharge. N and P fertilizer mainly from dry land, paddy field and garden land uses. The soil release of N was related to the STN, SNH4, SNO3. While, the soil release of P was considered to STP, SAP. The artificial discharge of N and P was concerned with rural and urban land uses (Hua et al. 2019). PLS-SEM were constructed based on N limited, P limited, N + P limited classes respectively. The total effect, direct effect and indirect effect of the results PLS-SEM were shown in Table 6.

The results of PLS-SEM (Figure 9) showed that whatever the nutrients limited classes were, the higher effect on phytoplankton biomass was all phosphorus salt. This phenomenon was especially obvious when N and P joint limited (Effect of PS = 0.62). While the effect of nitrogen salt was higher than the other nutrients limited types if it was N-limited.

The results of fertilizer, soil release, anthropogenic discharge effects on nitrogen salt, phosphorus salt and phytoplankton biomass were distinctive among three nutrients limited types (Figure 9). In N limited reservoir bays, nitrogen salt mainly came from soil release (total effect = 0.6) and nitrogen fertilizer (total effect = 0.43), of which the indirect effect from fertilizer to soil release was 0.3. The sources of phosphorus salt showed a subtle difference that the effect of fertilizer (total effect = 0.22) was a little

| Latent variables | Measured variables | Description | Unit |
|------------------|-------------------|-------------|------|
| Fer_N | Dryland | Nitrogen fertilizer applied to dry land | kg·km⁻²·a⁻¹ |
| Paddy | Nitrogen fertilizer applied to paddy field | kg·km⁻²·a⁻¹ |
| Garden | Nitrogen fertilizer applied to garden land | kg·km⁻²·a⁻¹ |
| SR_N | STN | Soil total nitrogen content in the hydro-fluctuation belt around reservoir bays | g/kg |
| SNO3 | Soil nitrate-nitrogen content in the hydro-fluctuation belt around reservoir bays | mg/kg |
| SNH4 | Soil ammonium nitrogen content in the hydro-fluctuation belt around reservoir bays | mg/kg |
| AD_N | Urban | Nitrogen discharged from urban sewage | kg·(ca·10⁴)⁻¹·a⁻¹ |
| Rural | Nitrogen discharged from rural sewage | kg·(ca·10⁴)⁻¹·a⁻¹ |
| Fer_P | Dryland | Phosphate fertilizer applied to dry land | kg·km⁻²·a⁻¹ |
| Paddy | Phosphate fertilizer applied to paddy field | kg·km⁻²·a⁻¹ |
| Garden | Phosphate fertilizer applied to garden land | kg·km⁻²·a⁻¹ |
| SR_P | STP | Soil total phosphorus content in the hydro-fluctuation belt around reservoir bays | g/kg |
| SAP | Soil available phosphorus content in the hydro-fluctuation belt around reservoir bays | mg/kg |
| AD_P | Urban | Phosphorus discharged from urban sewage | kg·(ca·10⁴)⁻¹·a⁻¹ |
| Rural | Phosphorus discharged from rural sewage | kg·(ca·10⁴)⁻¹·a⁻¹ |
| NS | TN | Total nitrogen content in water of reservoir bays | mg/l |
| NO3-N | Nitrate nitrogen content in water of reservoir bays | mg/l |
| NH4-N | Ammonium nitrogen content in water of reservoir bays | mg/l |
| PS | TP | Total phosphorus content in water of reservoir bays | mg/l |
| Phy. | Chl a | Chlorophyll a content in water of reservoir bays | μg/l |
bit higher than soil release (total effect = 0.17). And the contributions of fertilizer and soil release (total effect = 0.15) were the same as the biomass of phytoplankton. That means when it comes to N limited situation, fertilizer was the main source that should be paid attention to, what’s more, a part of superfluous fertilizer may infiltrate into the soil and provide for phytoplankton growth through overland flow and submerged soil release (Chen et al. 2021; Han et al. 2021).

In P limited reservoir bays, all of the three sources almost act higher on nitrogen salt, phosphorus salt and phytoplankton biomass. Fertilizer to nitrogen salt (total effect = 0.62) and anthropogenic discharge to phosphorus salt (total effect = 0.5) were contribution most. In P limited reservoir bays, governance strategies should be overall consideration the three sources of contamination.

The results of PLS-SEM in $N+P$ limited reservoir bays showed that the effects of anthropogenic discharge were much higher than the other two sources on nitrogen salt (total effect = 0.66), phosphorus salt (total effect = 0.6) and phytoplankton biomass (total effect = 0.43), which was the dominant causes for the deterioration of water quality. Thus the major practices to alleviate water pollution in this type of reservoir bays should focus on the discharge of residential and industrial wastewater (Ai et al. 2015).

**CONCLUSION**

In this study we choose the study area as reservoir bays gave a new suggestion for reservoir water quality research as it combines the influence from both natural and artificial, water and land surface. The results of the distribution of Chl a showed the spatial discrepancy during two stages which represent two different water dynamic mechanisms. The results of water quality factors respond to external input indicated that the water pollutants in the storage period mainly originated from domestic sewage and soil release, while in the discharge period with the increase of precipitation and surface flow, the disturbance from the environment background added topography and landscape pattern. Surface pollutants were easily delivered and transported in complex and broken landscapes but diluted and sedimented by continuous vegetation. To further made out the nutrient sources and contributions in different types of reservoir bays from terrestrial environment background, PLS-SEM statistical analysis method was used. The main findings were that phosphorus always affected higher on phytoplankton biomass, whatever the nutrients limited types

| Table 6 | Total effect direct effect and indirect effect in the PLS-SEM |
|---------|-----------------|-----------------|
| **N limited** | Direct effect | Indirect effect | Total effect |
| Fer_N -> NS | 0.12 | 0.31 | 0.43 |
| Fer_N -> SR_N | 0.51 | 0 | 0.51 |
| SR_N -> NS | 0.6 | 0 | 0.6 |
| AD_N -> NS | 0.21 | 0 | 0.21 |
| Fer_P -> PS | 0.13 | 0.09 | 0.22 |
| Fer_P -> SR_P | 0.50 | 0 | 0.50 |
| SR_P -> PS | 0.17 | 0 | 0.17 |
| AD_P -> PS | 0.07 | 0 | 0.07 |
| NS -> Phy. | 0.16 | 0 | 0.16 |
| PS -> Phy. | 0.36 | 0 | 0.36 |
| **P limited** | Direct effect | Indirect effect | Total effect |
| Fer_N -> NS | 0.33 | 0.29 | 0.62 |
| Fer_N -> SR_N | 0.54 | 0 | 0.54 |
| SR_N -> NS | 0.54 | 0 | 0.54 |
| AD_N -> NS | 0.54 | 0 | 0.54 |
| Fer_P -> PS | 0.24 | 0.14 | 0.38 |
| Fer_P -> SR_P | 0.34 | 0 | 0.34 |
| SR_P -> PS | 0.42 | 0 | 0.42 |
| AD_P -> PS | 0.5 | 0 | 0.5 |
| NS -> Phy. | 0.02 | 0 | 0.02 |
| PS -> Phy. | 0.18 | 0 | 0.18 |
| **N + P limited** | Direct effect | Indirect effect | Total effect |
| Fer_N -> NS | 0.13 | 0.05 | 0.18 |
| Fer_N -> SR_N | 0.46 | 0 | 0.46 |
| SR_N -> NS | 0.1 | 0 | 0.1 |
| AD_N -> NS | 0.66 | 0 | 0.66 |
| Fer_P -> PS | 0.14 | 0 | 0.14 |
| Fer_P -> SR_P | 0.40 | 0 | 0.46 |
| SR_P -> PS | 0.07 | 0 | 0.07 |
| AD_P -> PS | 0.6 | 0 | 0.6 |
| NS -> Phy. | 0.09 | 0 | 0.09 |
| PS -> Phy. | 0.62 | 0 | 0.62 |

The effects were calculated using standardized path coefficients.
were. However, it was also necessary to take measures to control both sources of nutrients. The prevention of eutrophication should emphasize controlling fertilization and anthropogenic discharge first, then the transfer of the nutrients from the overland flow and infiltration to soil and water cannot be neglected also. This study hoped to propose a new solution to the research on the sources and potential risk warning of eutrophication in reservoirs and expect to provide scientific guidance for the controlling of non-point pollution.

PLS-SEM provides an effective solution to assess the coupled relationships between predictors and water quality characteristics. Nevertheless, for promoting the knowledge of the sources and routes of water nutrients from terrestrial exogenous pollutants that affecting water pollution, the PLS-SEM used in this study could be improved by considering more environmental factors and the sources of pollutants such as the pollution loads from the livestock production in driving water quality changes on different temporal and spatial scales. We expect that the methods presented in this paper will be useful for hydroecologist wishing to apply PLS-SEM.

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DATA AVAILABILITY STATEMENT

Data cannot be made publicly available; readers should contact the corresponding author for details.

REFERENCES

Ai, L., Shi, Z. H., Yin, W. & Huang, X. 2015 Spatial and seasonal patterns in stream water contamination across mountainous watersheds: linkage with landscape characteristics. Journal of Hydrology 523, 398–408.
Berka, C., Schreier, H. & Hall, K. 2001 Linking water quality with agricultural intensification in a rural watershed. Water Air and Soil Pollution 127 (1), 389–401.
Chen, N., Peng, B., Hong, H., Turyahaya, N., Cui, S. & Mo, X. 2013 Nutrient enrichment and N:P ratio decline in a coastal
bay-river system in southeast China: the need for a dual nutrient (N and P) management strategy. *Ocean & Coastal Management* **81**, 7–13.

Chen, J., Shi, H., Sivakumar, B. & Peart, M. R. 2016 Population, water, food, energy and dams. *Renewable and Sustainable Energy Reviews* **56**, 18–28.

Chen, L., Dai, Y., Zhi, X., Xie, H. & Shen, Z. 2018 Quantifying nonpoint source emissions and their water quality responses in a complex catchment: a case study of a typical urban-rural mixed catchment. *Journal of Hydrology* **559**, 110–121.

Chen, W., Nover, D., Xia, Y., Zhang, G., Yen, H. & He, B. 2021 Assessment of extrinsic and intrinsic influences on water quality variation in subtropical agricultural multipond systems. *Environmental Pollution* **276**, 116689.

Chuo, M., Ma, J., Liu, D. & Yang, Z. 2019 Effects of the impounding process during the flood season on algal blooms in Xiangxi Bay in the Three Gorges Reservoir, China. *Ecological Modelling* **392**, 236–249.

Conley, D. J., Paerl, H. W., Howarth, R. W., Boesch, D. F., Seitzinger, S. P., Havens, K. E., Lancelot, C. & Likens, G. E. 2009 Controlling eutrophication: nitrogen and phosphorus. *Science* **323** (5917), 1014–1015.

CSEPB 2002 *Environmental Quality Standards for Surface Water (GB3838-2002)*. State Environmental Protection Administration, Beijing, China.

Elser, J. J., Bracken, M. E. S., Cleland, E. E., Gruner, D. S., Harpole, W. S., Hillebrand, H., Ngai, J. T., Seabloom, E. W., Shurin, J. B. & Smith, J. E. 2007 Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine and terrestrial ecosystems. *Ecology Letters* **10** (12), 1135–1142.

Fujimoto, N., Sudo, R., Sugiuara, N. & Inamori, Y. 1997 Nutrient-limited growth of Microcystis aeruginosa and Phormidium tenue and competition under various N:P supply ratios and temperatures. *Limnology and Oceanography* **42** (2), 250–256.

Gao, C., Zhu, J. G., Zhu, J. Y., Gao, X., Dou, Y. J. & Hosen, Y. 2004 Nitrogen export from an agriculture watershed in the Taihu Lake area, China. *Environmental Geochemistry & Health* **26** (2/3), 199–207.

Gao, Q., He, G., Fang, H., Bai, S. & Huang, L. 2018 Numerical simulation of water age and its potential effects on the water quality in Xiangxi Bay of Three Gorges Reservoir. *Journal of Hydrology* **566**, 484–499.

Han, J., Xin, Z., Han, F., Xu, B., Wang, L., Zhang, C. & Zheng, Y. 2021 Source contribution analysis of nutrient pollution in a P-rich watershed: implications for integrated water quality management. *Environmental Pollution* **279**, 116885.

Harpole, W. S., Ngai, J. T., Cleland, E. E., Seabloom, E. W., Borer, E. T., Bracken, M. E. S., Elser, J. J., Gruner, D. S., Hillebrand, H. & Shurin, J. B. 2021 Nutrient co-limitation of primary producer communities. *Ecology Letters* **14** (9), 852–862.

Helena, B., Pardo, R., Vega, M., Barrado, E., Fernandez, J. M. & Fernandez, L. 2000 Temporal evolution of groundwater composition in an alluvial aquifer (Pisuerga River, Spain) by principal component analysis. *Water Research* **34** (3), 807–816.

Hua, L., Li, W., Zhai, L., Yen, H., Lei, Q., Liu, H., Ren, T., Xia, Y., Zhang, F. & Fan, X. 2019 An innovative approach to identifying agricultural pollution sources and loads by using nutrient export coefficients in watershed modeling. *Journal of Hydrology* **571**, 322–331.

Huang, Y., Li, Y., Ji, D., Nwankwegu, A. S., Lai, Q., Yang, Z., Wang, K., Wei, J. & Norgbey, E. 2020 Study on nutrient limitation of phytoplankton growth in Xiangxi Bay of the Three Gorges Reservoir, China. *Science of the Total Environment* **723**, 138062.

Hung, N. T., Asaeda, T. & Manatunge, J. 2007 Modeling interactions of submersed plant biomass and environmental factors in a stream using structural equation modeling. *Hydrobiologia* **583** (1), 183–193.

Jiang, R., Hatano, R., Zhao, Y., Kuramochi, K., Hayakawa, A., Woli, K. P. & Shimizu, M. 2014 Factors controlling nitrogen and dissolved organic carbon exports across timescales in two watersheds with different land uses. *Hydrological Processes* **28** (19), 5105–5121.

Kashy, D. A., Donellan, M. B., Burt, S. A. & McGue, M. 2008 Growth curve models for indistinguishable dyads using multilevel modeling and structural equation modeling: the case of adolescent twins’ conflict with their mothers. *Developmental Psychology* **44** (2), 316–329.

Lacher, I. L., Ahmadisharaf, E., Fergus, C., Akre, T., McShea, W. J., Benham, B. L. & Kline, K. S. 2009 Scale-dependent impacts of urban and agricultural land use on nutrients, sediment, and runoff. *Science of the Total Environment* **652**, 611–622.

Lehner, B., Liermann, C. R., Revenga, C., Vörösmarty, C., Fekete, B., Crouzet, P., Döll, P., Endeljan, M., Frenken, K., Magome, J., Nilsson, C., Robertson, J. C., Rödel, R., Sindorf, N. & Wisser, D. 2011 High-resolution mapping of the world’s reservoirs and dams for sustainable river-flow management. *Frontiers in Ecology and the Environment* **9** (9), 494–502.

Lewis, W. M., Wurtsbaugh, W. A. & Paerl, H. W. 2011 Rationale for control of anthropogenic nitrogen and phosphorus to reduce eutrophication of inland waters. *Environmental Science & Technology* **45** (24), 10300–5.

Li, L. 2010 *Integrative Assessment of Ecological Environment at Different Scale in Water Source Region of the Middle Route Project Under South-to-North Water Diversion*. PhD thesis, College of resources & environment, Huazhong Agricultural University, Wuhan, China.

Li, N. X., Xu, J. F., Yin, W., Chen, Q. Z., Wang, J. & Shi, Z. H. 2020 Effect of local watershed landscapes on the nitrogen and phosphorus concentrations in the waterbodies of reservoir bays. *Science of the Total Environment* **716**, 137132.

Li, N., Wang, J., Yin, W., Jia, H., Xu, J., Hao, R., Zhong, Z. & Shi, Z. 2021 Linking water environmental factors and the local watershed landscape to the chlorophyll a concentration in reservoir bays. *Science of the Total Environment* **758**, 143617.

Mamun, M., Kwon, S., Kim, J.-E. & An, K.-G. 2020 Evaluation of algal chlorophyll and nutrient relations and the N:P ratios along with trophic status and light regime in 60 Korea reservoirs. *Science of the Total Environment* **741**, 140451.
McGarigal, K. 2002 Fragstats: Spatial Pattern Analysis Program for Categorical Maps. Computer software program produced by the authors at the University of Massachusetts, Amherst. Available from: http://www.umass.edu/landeco/research/fragstats/fragstats.html.

Menciò, A., Boy, M. & Mas-Pla, J. 2011 Analysis of vulnerability factors that control nitrate occurrence in natural springs (Osona Region, NE Spain). Ene of the Total Environment 409 (16), 3049–3058.

National Soil Survey Office 1998 Chinese Soils. Agricultural Press, Beijing, China.

Neary, D. G., Ice, G. G. & Jackson, C. R. 2017 Hydrogeologic and landscape controls of dissolved inorganic nitrogen (DIN) and dissolved silica (DSi) fluxes in heterogeneous catchments. Journal of Hydrology 450–451, 36–47.

Paerl, H. W., Xu, H., McCarthy, M. J., Zhu, G., Qin, B., Li, Y. & Gardner, W. S. 2011 Controlling harmful cyanobacterial blooms in a hyper-eutrophic lake (Lake Taihu, China): the need for a dual nutrient (N & P) management strategy. Water Research 45 (5), 1973–1983.

Paerl, H. W., Scott, J. T., McCarthy, M. J., Newell, S. E. & Wurtsbaugh, W. A. 2017 It takes two to tango: when and where dual nutrient (N & P) reductions are needed to protect lakes and downstream ecosystems. Environmental Science & Technology 50, 10805–10813.

Pearce, A. R., Chambers, L. G. & Hasenmueller, E. A. 2017 Characterizing nutrient distributions and fluxes in a eutrophic reservoir, Midwestern United States. Science of the Total Environment 581–582, 589–600.

Pratt, B. & Chang, H. 2012 Effects of land use, topography, and built structure on seasonal water quality at multiple spatial scales. Journal of Hazardous Materials 209–210, 48–58.

Rattan, K. J., Corriére, J. C., Brua, R. B., Culp, J. M., Yates, A. G. & Chambers, P. A. 2017 Quantifying seasonal variation in total phosphorus and nitrogen from prairie streams in the Red River Basin, Manitoba Canada. Science of the Total Environment 575, 649–659.

Sanchez, G. 2013 PLS Path Modeling with R. Trowchez Editions, Berkeley.

Santos, R. M. B., Sanches Fernandes, L. F., Cortes, R. M. V., Varandas, S. G. P., Jesus, J. J. B. & Pacheco, F. A. L. 2017 Integrative assessment of river damming impacts on aquatic fauna in a Portuguese reservoir. Science of the Total Environment 601–602, 1108–1118.

Schindler, D. W., Hecky, R. E., Findlay, D. L., Stainton, M. P., Parker, B. R., Paterson, M. J., Beatty, K. G., Lyng, M. & Kasián, S. E. M. 2008 Eutrophication of lakes cannot be controlled by reducing nitrogen input: results of a 37-year whole-ecosystem experiment. Proceedings of the National Academy of Sciences of the United States of America 105 (32), 11254–8.

Shan, N., Ruan, X.-H., Xu, J. & Pan, Z.-R. 2014 Estimating the optimal width of buffer strip for nonpoint source pollution control in the Three Gorges Reservoir Area, China. Ecological Modelling 276, 51–63.

Shi, Z. H., Ai, L., Li, X., Huang, X. D., Wu, G. L. & Liao, W. 2013 Partial least-squares regression for linking land-cover patterns to soil erosion and sediment yield in watersheds. Journal of Hydrology 498, 165–176.

Singh, K. P., Malik, A. & Sinha, S. 2005 Water quality assessment and apportionment of pollution sources of Gomti river (India) using multivariate statistical techniques – a case study. Analytica Chimica Acta 538 (1), 355–374.

Sliva, L. & Dudley Williams, D. 2001 Buffer zone versus whole catchment approaches to studying land use impact on river water quality. Water Research 35 (14), 3462–3472.

Smith, V. H. 1983 Low nitrogen to phosphorus ratios favor dominance by blue-green algae in lake phytoplankton. Science 221 (4611), 669.

Soil Survey Staff 1999 Soil Taxonomy. USDA-NRCS, US Gov. Print. Office, Washington, DC.

Tong, S. T. Y. & Chen, W. 2002 Modeling the relationship between land use and surface water quality. Journal of Environmental Management 66 (4), 377–393.

Uuemaa, E., Roosaare, J. & Mander, Ü. 2005 Scale dependence of landscape metrics and their indicator value for nutrient and organic matter losses from catchments. Ecological Indicators 5 (4), 350–369.

Vrebos, D., Beauchard, O. & Meire, P. 2017 The impact of land use and spatial mediated processes on the water quality in a river system. Science of the Total Environment 601–602, 365–373.

Wright, S. 1954 The method of path coefficients. The Annals of Mathematical Statistics 5 (3), 161–215.

Wu, Y., Liu, J., Shen, R. & Fu, B. 2017 Mitigation of nonpoint source pollution in rural areas: from control to synergies of multi ecosystem services. Science of the Total Environment 607–608, 1376–1380.

Xiang, R., Wang, L., Li, H., Tian, Z. & Zheng, B. 2021 Water quality variation in tributaries of the Three Gorges Reservoir from 2000 to 2015. Water Research 195, 116993.

Xiao, H. & Ji, W. 2007 Relating landscape characteristics to non-point source pollution in mine waste-located watersheds using geospatial techniques. Journal of Environmental Management 82 (1), 111–119.

Xie, H., Dong, J., Shen, Z., Chen, L., Lai, X., Qiu, J., Wei, G., Peng, Y. & Chen, X. 2019 Intra- and inter-event characteristics and controlling factors of agricultural nonpoint source pollution under different types of rainfall-runoff events. Catena 182, 104105.

Yan, B., Fang, N. F., Zhang, P. C. & Shi, Z. H. 2015 Impacts of land use change on watershed streamflow and sediment yield: an assessment using hydrologic modelling and partial least squares regression. Journal of Hydrology 484, 26–37.

Yang, Z., Cheng, B., Xu, Y., Liu, D., Ma, J. & Ji, D. 2018 Stable isotopes in water indicate sources of nutrients that drive algal blooms in the tributary bay of a subtropical reservoir. Science of the Total Environment 634, 205–213.
Yi, Q., Zhang, Y., Xie, K., Chen, Q., Zheng, F., Tonina, D., Shi, W. & Chen, C. 2020 Tracking nitrogen pollution sources in plain watersheds by combining high-frequency water quality monitoring with tracing dual nitrate isotopes. *Journal of Hydrology* **581**, 124439.

Zhao, W., Jia, L., Daryanto, S., Chen, L. & Liu, Y. 2019 Source–Sink Landscape. In: *Encyclopedia of Ecology*, 2nd edn (B. Fath ed.). Elsevier, Oxford, pp. 467–473.

Zhou, T., Wu, J. & Peng, S. 2012 Assessing the effects of landscape pattern on river water quality at multiple scales: a case study of the Dongjiang River watershed, China. *Ecological Indicators* **23**, 166–175.

Zhou, Y., Xu, J. F., Yin, W., Ai, L., Fang, N. F., Tan, W. F., Yan, F. L. & Shi, Z. H. 2017 Hydrological and environmental controls of the stream nitrate concentration and flux in a small agricultural watershed. *Journal of Hydrology* **545**, 355–366.

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