



Article Deteriorated Water Quality of Agricultural Catchments in South China by Net Anthropogenic Phosphorus Inputs

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Abstract: Improper anthropogenic phosphorus (P) management is considered a major cause of water quality deterioration, however the relationship between anthropogenic P input and catchment water quality is rarely quantified in China. The study area encompassed eight small catchments with areas ranging from 58.6 to 13,442.4 ha in the subtropical region of South China. On-site observations of P concentrations, stream fluxes, and social investigation of P input were conducted over a 3-year period. The regional variations of net anthropogenic phosphorus inputs (NAPI) and responses of riverine P export were quantitatively analyzed. Results showed that the total NAPI of catchments varied from 11.04 to 40.52 kg P ha⁻¹ year⁻¹, where cropland systems (NAPI_c) were the largest P sources, accounting for 47.7–67.7% in total. Meanwhile, net food and feed P input varied from 3.87 to 30.73 kg P ha⁻¹ year⁻¹, accounting for 35.0–75.8% in total, followed by fertilizer and non-food P input with 4.65–10.48 and 0.63–2.89 kg P ha⁻¹ year⁻¹, respectively. Riverine P export and the soil total P and Olsen–P contents in croplands were all positively related to NAPI (p < 0.05). A simple empirical model was simulated to predict the annual riverine total P fluxes using NAPI_c with greater accuracy than with using NAPI or NAPI for residential land (NAPI_r). Gray relational analysis suggested that livestock density was the most important influencing factor for NAPI. It is concluded from these results that, although the livestock accounted for the largest part of the NAPI, the cropland contributed the greatest to catchment riverine P export. This probably due to recycling of animal manure for plant cropping systems. Therefore, maintaining a reasonable scale of livestock production, and reducing the internal cycle of manure or replacing part of the chemical fertilizer should be a major approach in reducing NAPI and corresponding riverine P export in the study area.

Keywords: phosphorus; eutrophication; NAPI; livestock density; source catchment

1. Introduction

Huge inputs of anthropogenic phosphorus (P) (e.g., through chemical P fertilizer application and feed supplements) are widely considered to be a major cause of water eutrophication and environmental deterioration [1–3]. An integrated anthropogenic P cycling pattern and a quantitative understanding of the factors controlling its input are key issues concerning the protection of water quality and sustainable catchment management practices.

Net anthropogenic P input (NAPI, including the P sources of fertilizer, feed, food, and non-food) was found to be an effective approach to evaluate the P cycle by relating anthropogenic P inputs

China are the basic unit of agricultural production with traditional farming and breeding production models. Thus, it is valuable to understand and characterize the regional variations of NAPI at the catchment scale and its impact on the environment in the subtropical region of China.

Riverine P export and accumulation in soil are the major pathways of NAPI in terms of the environmental impacts. Analysis of NAPI has been proven useful tool for identifying primary P sources and predicting present or future riverine P export [12]. However, relationship between the NAPI and riverine P export usually changes with land use types [13]. The P export from agricultural landscapes to rivers is mainly through surface runoff and leaching processes, particularly for the cropland soils characterized with high P contents, while the P losses from developed land mainly via sewage discharge [11]. Soil is the key interface linking anthropogenic P inputs to riverine P exports, as most P compounds tend to precipitate or be adsorbed onto soil particles before delivery to surface waters [14]. Chen et al. [11] reported that the contents of soil total P (TP)/Olsen-P in surface soils significantly increased over the past 32 years along with an increase in NAPI in the Jiaojiang watershed in Zhejiang province, China. In China, water eutrophication mainly occurs in the humid south. However, few studies on nutrient budgets relating to water environmental protection and soil P accumulation, in particular at the small catchment scale, have been conducted [11].

In this paper, using data from in situ observation and investigation, we (a) explored the characteristics of NAPI in eight sub-catchments in a source catchment and how the characteristics might vary with regional conditions; and (b) separately estimated the NAPI for cropland and developed land (NAPI_c and NAPI_r, respectively) to evaluate their influence on riverine TP export and cropland soil TP/Olsen-P contents. The results will be helpful to understand the P budgets in small catchments and to guide governmental scientific nutrient management and water environmental protection in southern China.

2. Materials and Methods

2.1. Study Area and Data Sources

The selected Jinjing catchment area $(112^{\circ}56'-113^{\circ}36' \text{ E}, 27^{\circ}55'-28^{\circ}40' \text{ N}, \text{ elevation } 43-460 \text{ m})$ is a naturally formed source catchment of Xiangjiang River located at Changsha city, Hunan province, China, covers an area of 134.4 km² (Figure 1). The region represents a typical subtropical humid monsoon climate, with a mean annual precipitation 1200–1400 mm (most of rainfall occurs during from March to June), a mean annual temperature of 17.2 °C, and a frost-free period of 274 days. Cropland (e.g., paddy field, tea garden and dry land), residential land (e.g., rural residential, roads, and industrial), and forest covers 27.3, 2.6 and 67.2% of total catchment area, respectively (Table 1). The main crops are rice (e.g., double-rice and single rice), vegetables, and tea. The paddy field is mainly distributed in valley and flood plains. Vegetable fields and dry land (planting soybean and maize typically) only make up to a very small part of catchment area, and they are mainly distributed adjacent to the local households. Livestock production, particularly pigs, is prevalent throughout the study area. The feeds are mostly purchased from the adjacent town outside the catchment, and partly come from organic waste of crop planting (i.e., rice straw). The poultries in this region are mainly chicken and duck. The catchment contains 15 administrative villages, consisting of approximate 55,000 inhabitants. Based on the land use patterns, livestock husbandry distribution, and water quality observation point distribution, eight representative sub-catchments with areas ranging from 58.6 to 13,442.4 ha were selected (Table 1).



Figure 1. Land use types and the water quality sampling site in the eight catchments in Jinjing region, Hunan province, China, analyzed in this study.

Catchment	Area	Population Density	Livestock Density	Land Use (%)			
	(ha)	(Person ha ⁻¹)	$(AU ha^{-1})$	Cropland	Forest	Tea Garden	Residential Land
Bamaotian (BMT)	58.6	3.1	0.72	24.4	63.8	6.7	2.8
Dongshanqiao (DSQ)	299.6	1.9	1.04	25.0	68.0	4.0	2.0
Guanjia (GJ)	2590.5	1.6	0.21	16.9	80.1	0.1	1.6
Jinjng (JJ)	13,442.4	4.1	0.77	24.9	67.2	2.4	2.6
Jianshan (JS)	5024.1	3.4	0.51	18.5	77.3	0.9	1.7
Shuiba (SB)	263.8	3.1	1.70	37.0	55.0	2.0	4.0
Tuanjia (TJ)	523.9	0.9	0.40	10.0	85.0	0.0	1.0
Tuojiahe (TJH)	5211.6	4.7	0.92	31.7	58.5	4.3	3.3

Table 1. Characteristics of the eight subtropical catchments analyzed in Jinjing region, South China.

The livestock density value (one AU is equivalent to 454 kg of live weight [15]) per unit area of the county. *Livestock Density* = $(\sum_{i=1}^{n} N_i/e_i)/A$, where *A* is the total area of a given catchment (ha), N_i is the annual number of livestock or poultry type *i* raised in a given catchment, and e_i is the equivalent number per AU of livestock or poultry type *i* [4].

2.2. NAPI Estimation

The NAPI (kg P ha⁻¹ year⁻¹) was estimated based on the anthropogenic P inputs and outputs in a certain spatial unit. The P inputs include seed input (*SI*), fertilizer application (*CF*), net imports of food and feed (*NFFI*), and non-food household use of P (*NFI*) (i.e., detergent) [4]. All units are kg P ha⁻¹ year⁻¹.

$$NAPI = SI + CF + NFI + NFFI$$
(1)

$$NFFI = AC + HC - CP - AP \tag{2}$$

where *AC* is the animal consumption (kg P ha⁻¹ year⁻¹), *HC* is the human consumption (kg P ha⁻¹ year⁻¹), *CP* is the crop production (kg P ha⁻¹ year⁻¹), and *AP* indicates animal products (kg P ha⁻¹ year⁻¹).

To more clearly attribute NAPI to particular anthropogenic activities and land uses, the NAPI was divided into two components: cropland and residential land (Figure 2). Cropland (NAPI_c, kg P ha⁻¹ year⁻¹) and residential land (NAPI_r, kg P ha⁻¹ year⁻¹) budget estimations were modified from the standard NAPI method [4,11]:

$$NAPI = NAPI_{c} + NAPI_{r}$$
(3)

$$NAPI_{c} = SI + CF + RM - CP \tag{4}$$

$$NAPI_{r} = NFI + AC + HC - AP - RM$$
(5)

where *RM* refers to recycled human and animal excreta used as manure (NAPI_c, kg P ha⁻¹ year⁻¹).



Figure 2. Conceptual diagram for phosphorus budget including inputs, outputs, and river discharge.

Detailed descriptions of individual P sources and sinks as well as the parameters used in estimating NAPI are available in Table 2. In addition, the annual census (2012–2014) of livestock and poultry numbers was used in this study to estimate livestock density. The number of households surveyed accounted for 10% of the total. The contents of the social survey mainly included population density, land use types and areas, crop yields and sale ratios, livestock density, recycled rural animal and human excreta for fertilizing, and chemical fertilizer varieties and quantities. The total area and land use composition for each catchment were calculated based on digital elevation models in ArcGIS.

Table 2. Summary of data used in the net anthropogenic phosphorus inputs calculation in eight catchments Jinjing region, South China.

Animal and Human P Consumption [16,17]			P Content in Agricultural Crop Products [18]		Non-Food P [19]	
Animal Type	Consumption (P Intake Rate, kg P Capita ⁻¹ Year ⁻¹)	Animal Production (kg P Capita Year ⁻¹)	Сгор Туре	P (g kg ⁻¹)	Туре	kg P Capita ⁻¹ Year ⁻¹
Pigs Cattle	4.59 10.99	1.42 1.21	Paddy Vegetable	1.10 0.30	Detergent	0.63
Chickens Ducks	0.12 0.22	0.06 0.12	Fruits	0.13		

2.3. Estimation of Riverine Net TP Export

To determine the NAPI impacts on catchment surface water quality, a real-time hydrological monitoring system and a regular water quality observation scheme were established at the outlets of eight catchments (Figure 1). The water height at each catchment outlet was measured at 10-min intervals using water pressure transducers connected to data loggers, and the stream fluxes were quantified using the observed flow velocity and the flow cross-section area method due to the large stream cross-section area [20].

Water quality samples were collected using plastic bottles on days of 8, 18 and 28 each month in 2012 to 2014. The collected water samples were immediately transported to the laboratory and stored in a frozen fridge at -18 °C until analysis. Concentrations of total P (TP) were determined were determined using the potassium peroxydisulfate digestion and molybdate colorimetric method [21,22] The annual net export of riverine P (kg ha⁻¹ year⁻¹) was estimated using the following equation:

$$APL = \sum_{m=1}^{12} \overline{C}_m \times RD_m \tag{6}$$

$$RD_m = Q_m / A \tag{7}$$

where *APL* indicates the annual TP export loading of the river (kg ha⁻¹ year⁻¹), \overline{C}_m indicates the mean monthly TP concentration (mg L⁻¹) in stream water in the outlet of a catchment, *RD_m* is the runoff depth (mm year⁻¹), *m* indicates the month, *Q* indicates the observed stream flow flux (m³), and *A* indicates the catchment area (ha) [23].

2.4. Soil P Measurement

Soil samples (total n = 982) were collected from the upper 20-cm layer of croplands (i.e., paddy fields, dryland, and tea gardens) in 2010, supported by the Strategic Priority Research Program—Climate Change: Carbon Budget and Related Issues. Soil samples were air dried, milled, and passed through a 2 mm sieve for chemical analysis. The items of soil P analyzed mainly included 0.5 M NaHCO₃-extractable P (Olsen-P) and TP (H₂SO₄-HClO₄-digested and molybdate colorimetric method).

2.5. Gray Relational Analysis

The gray relational analysis (GRA) was performed to identify the key factors of NAPI. The advantage of this method is that it can quantitatively examine the intrinsic relationships among investigated factors using a limited amount of data [24,25]. For a given reference sequence and a given set of comparative sequences, the gray relational grade (GRG) computed by GRA can identifies the relative associations between the reference and each comparative sequence in the given set. GRA analysis was conducted between the factors (the percentage of different land use, LD, and population density) and NAPI. GRA was analyzed using the GMS v6.0 (Nanjing University of Aeronautics and Astronautics).

3. Results

3.1. NAPI Estimation and Its Constituents

The annual NAPI for the eight catchments averaged over 2012–2014 ranged from 11.04 to 40.52 kg P ha⁻¹ year⁻¹ (Figure 3a). NFFI was the largest individual source of NAPI, accounting for 35.0–75.8% of the net P inputs. The amount of NFFI varied across the eight catchments, ranging from 3.87 (GJ catchment) to 30.73 kg P ha⁻¹ year⁻¹ (SB catchment). Annual CF P inputs ranged from 4.65 to 10.48 kg P ha⁻¹ year⁻¹. The average input of detergent P ranged from 0.63 to 2.89 kg P ha⁻¹ year⁻¹. P inputs by seed and atmospheric deposition were 0.01–0.04 and 0.39 kg P ha⁻¹ year⁻¹, respectively.

In terms of NAPI components, 47.7–67.7% derived from croplands (NAPI_c), while the remaining 32.3–52.3% originated from residential lands (NAPI_r) (Figure 3b). Among the eight catchments, catchment SB, with more than 30% cropland and 1.7 AU ha⁻¹ LD (Table 1), had the highest NAPI_c (20.09 kg P ha⁻¹ yearr⁻¹). Catchment GJ with less than 17% cropland and 0.21 AU ha⁻¹ LD had the lowest NAPI_c (7.08 kg P ha⁻¹ year⁻¹).



Figure 3. (a) Net anthropogenic phosphorus inputs (NAPI) from chemical fertilizer P (CF), net food and feed import (NFFI) (seed input was <0.05% of NAPI and is not individually shown); (b) NAPI to cropland (NAPI_c) and residential land (NAPI_r), and riverine total P (TP) export in the eight catchments. The data are the average values for 3 years (2012–2014).

3.2. Riverine TP Export and Its Correlation with NAPI

The annual riverine TP exports varied widely from 0.33 to 2.95 kg P ha⁻¹ year⁻¹ in the study area (Figure 4b). The highest APL was observed in catchment SB with high LD and cropland proportion, whereas the lowest level was measured in the forest-agricultural catchment GJ with the highest forest land percentage and a lower LD.

A significantly positive correlation was found between riverine TP export and NAPI (p < 0.01), NAPI_c, and NAPI_r (p < 0.05) (Figure 4), suggesting a significant difference in TP delivery efficiency to rivers between NAPI_c and NAPI_r. Among the models with different variables (NAPI, NAPI_c, and NAPI_r), the models that incorporated NAPI_c had the higher accuracy to explain annual riverine TP export ($y = 0.09094e^{0.1833x}$, $R^2 = 0.86$, p < 0.01). The target of the water quality standard is 0.05 mg P L⁻¹ in the study area. Based on the model incorporating NAPI, the critical NAPI was 5.74–13.72 kg P ha⁻¹ year⁻¹ for the eight catchments (Figure 4a).



Figure 4. Relationship between riverine total phosphorus (TP) export and (**a**) net anthropogenic P inputs (NAPI); (**b**) NAPI to cropland (NAPI_c), and (**c**) NAPI to residential land (NAPI_r). The target of water quality standard is 0.05 mg P L⁻¹ in the study area. The critical NAPI was calculated based on the model between riverine TP export and NAPI.

3.3. Correlation between NAPI and Soil P

The contents of soil TP and Olsen–P were significantly different (p < 0.05) among the eight catchments, and mean soil TP and Olsen–P contents ranged from 12.17–23.65 mg kg⁻¹ to 0.56–0.73 g kg⁻¹ (Figure 5). The mean soil Olsen–P in the SB and DSQ catchments with relatively high LDs and cropland percentages were 1.5 times higher than that in the JS, BMT, and GJ catchments (p < 0.05). The mean soil TP was higher in the SB catchment than in that the BMT and GJ catchments (p < 0.05).

Croplands account for 10.0–37.0% of the area of the eight catchments (Table 1) and received 47.7–67.7% of NAPI (Figure 3b). Part of NAPI_c has accumulated in the soil, which is an important mode of P accumulation. We found that NAPI_c was positively correlated with soil TP ($R^2 = 0.44$) and Olsen-P ($R^2 = 0.73$) (Figure 5C).



Figure 5. (**A**) Soil Olsen–phosphorus (P, total n = 982) contents and (**B**) total P (TP, total n = 982) in the upper 20 cm of arable land in the eight catchments in 2014, and (**C**) the relationship between net anthropogenic P inputs to cropland (NAPI_c) and mean TP and Olsen-P values of agricultural soils. Different lowercase letters denote significant differences among catchments for soil TP/Olsen-P (p < 0.05, Duncan's multiple-range test).

3.4. Factor Analysis of NAPI

The GRD values of LD and cropland percentage were greater than 0.9, ranking them as the first and second factors, indicating a marked influence on the changes in NAPI (Table 3). Residential land percentage was the third-ranked factor, with relatively marked GRDs, mainly >0.8. The GRD values for population density were >0.7, indicating its noticeable influence on NAPI. The GRD for forest percentage was relatively low at 0.6–0.7.

Table 3. Gray relational grade (GRG) rankings for net anthropogenic phosphorus input (NAPI) and contributing factors in the eight catchments analyzed.

NAPI	Land Use (%)			Livestock Density	Population Density	
1 1 1 1	Cropland	Residential Land	Forest	$(AU ha^{-1})$	(Person km^{-2})	
GRD ranking	0.9065 2	0.8713 3	0.6513 5	0.9266 1	0.7743 4	

The discrimination coefficient (ρ) is 0.5; AU: animal unit.

4. Discussion

4.1. The Characteristics of NAPI in the Eight Catchments

The NAPI values measured in the eight catchments ($11.04-40.52 \text{ kg P ha}^{-1} \text{ year}^{-1}$), were substantially larger than those measured at provincial (China, 1.9 to 33.4 kg P ha⁻¹ year⁻¹) [9] and national scales (Europe, 0.38 to 11.42 kg P ha⁻¹ year⁻¹) [5], indicating that there is loss of sensitivity when assessments are averaged over and provincial and national scales. Generally, the variation magnitude of NAPI largely depends on the relative intensities of different P sources within a certain

spatial unit [4]. Population density, livestock density, and percentage of agricultural land, as indicators of intensities of P sources, combined explain 93.5% (step-wise linear regression, p < 0.001) of the variability in the NAPI at the study catchment scale, and generally distributed heterogeneously at different spatial scales, the smaller spatial scale the larger heterogeneity. Therefore, the analysis of NAPI at the study catchment scale is more sensitive to capture greater small-scale variation. In addition, the livestock density in eight catchments was 0.4-1.11 AU ha⁻¹, higher than that in most county/national scale. Similar studies in Chesapeake Bay, the annual NAPI of the county with higher livestock density (>0.3 AU ha⁻¹) ranged from 15.80 to 78.46 kg P ha⁻¹ year⁻¹ [4]. The reasons for higher annual NAPI in the eight source catchments could be explained by the above mentioned respects. In terms of NAPI components, 47.7-67.7% was attributed to croplands. The recycled human and animal excreta manure is connection between the NAPI_c and NAPI_r (Equations (4) and (5)), which was found to played crucial role in the ratios during the calculation. The breeding types in study catchments was still family-scale breeding. Compared to the regions with the large-scale intensive breeding, the animal manure generated by family-scale breeding usually utilized more efficiently for the local cropland. However, farmers always apply excessive manure as the supplement to mineral fertilizer and pay little attention to the potential environmental P risk of manure [26]. Numerous research have suggested that there was a higher risk of P losses from cropland soil using the manure than mineral P fertilizers [27,28]. Therefore, the excessive application of manure usually increased potential risk of P losses. Impacts of NAPI on P concentrations in soil and surface water

The fate of NAPI, including soil accumulation and riverine exports, were various in eight catchments. The percentage of riverine exports of NAPI ranged from 2.3 to 7.9%. This estimation consistent with previous studies in the America, Europe, and China (1–14%; [4,7,29]), suggesting that the major part of cumulative NAPI was retained in cropland soils [11,30]. In this study, soil TP and Olsen-P contents exhibited a linear positive correlation with NAPI_c. The soil TP and Olsen-P contents in SB catchment with the highest NAPI_c, was significantly higher than in other seven catchments, suggesting that the large anthropogenic P input could significantly increased soil TP and Olsen-P contents (Figure 5). In addition, the dominant soil type (e.g., Ultisols and Oxisols) and warmer climate could increase soils iron/aluminum oxide/hydroxide contents that could elevates soil P retention capacity [31].

The fate of NAPI determines the P flow and budget balance, which strongly involves with the deterioration of water quality. Previous study found that there was a linear correlation between the NAPI and riverine TP export [5,7]. In this study, riverine TP export was exponentially related to the NAPI ($R^2 = 0.92$, p < 0.01) (Figure 4). This relationship suggests that small increase in NAPI may lead to a relatively great increase in riverine TP export, and therefore induce a higher potential risk of water quality deterioration in catchments. This phenomenon probably comes from the P saturation of watershed storage pools (e.g., soil, riparian buffer, wetland, and sediments) due to the excessive catchment P input [32].

4.2. The Influencing Factors of NAPI and Mitigation Strategies

GRA determined that LD had the greatest impact on the change of NAPI in the eight catchments. NFFI, which was further associated with LD, was the largest individual source of NAPI, accounting for 35.0–75.8% of the net P inputs. This explained why LD had the greatest impact on NAPI of all influencing factors. This result differs from those of previous studies. Other research has shown that population density was the best predictor for singly forecasting NAPI [4,8] in an urbanized region and higher proportions of developed land. Agricultural catchments with higher livestock density require imports of P in feed from outside the region boundaries to meet the high demands that cannot be met by local P reservoirs. Moreover, in contrast to the urbanized region, the animal excreta used as manure is not counted as a net outflow in the calculation of NAPI, but rather a flow between subcomponents. The type of livestock excreta treatment does not remove P from the catchment unless the waste is shipped outside of the boundaries. Thus, compared with population density, LD could be a better

predictor for singly forecasting NAPI than other influencing factors in Chinese traditional agricultural catchments with highly developed livestock production.

Based on our study, specific aspects of catchment management can be recommended to mitigate NAPI and protect water quality in subtropical source catchments in China: first, by finding the critical NAPI based on the model incorporating NAPI and the target of water quality standard and, secondly, by reasonably reducing NAPI based on the critical values, for example, promoting scientific fertilizer application, decreasing the traditional breeding model, and transferring livestock wastes out of the catchment unit. Furthermore, various engineering or agricultural measures should be employed to control P losses associated with soil and water erosion.

5. Conclusions

This study analyzed the spatial characteristic of NAPI in the Jinjing catchment, a source catchment of the Dongting Lake. In eight catchments of Jinjing, NAPI varied from 11.04 to 40.52 kg P ha⁻¹ year⁻¹, and 47.7–67.7% of the net anthropogenic P was added to the croplands. P input from food and feed was the largest source of NAPI, accounting for 35.0–75.8% (3.87–30.73 kg P ha⁻¹ year⁻¹) of the total NAPI, followed by fertilizer and non-food P input. Livestock density and cropland percentage were the most important factors for NAPI. Changing anthropogenic P could amplify P export from landscapes to rivers and increase the contents of Olsen-P and TP in cropland soil. Compared to NAPI, NAPI_c could better predict the riverine TP export in the source agricultural catchments. Thus, improving the management of livestock production and using a reasonable percentage of recycled animal and human excreta for fertilizing have the greatest potential for reducing NAPI and riverine TP export. In addition, to support the improvement of local aquatic environments, additional research should be conducted on livestock carrying capacity within the catchments.

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Abbreviations

APL	Annual Phosphorus Export Loading
GRA	Gray relational analysis
GRG	Gray relational grade
LD	Livestock density
NAPI	Net anthropogenic phosphorus input
NAPIc	NAPI for cropland
NAPI _r	NAPI for residential land
ТР	Total phosphorus

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