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Phosphorus Flow Patterns in the Chaohu Watershed from 1978 to 2012

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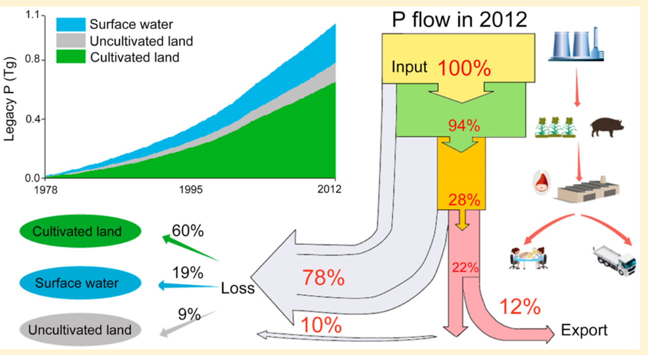
Supporting Information

ABSTRACT: Understanding historical patterns of phosphorus (P) cycling is critical for sustainable P management and eutrophication mitigation in watersheds. This study built a bottom-up model using the substance flow analysis approach to quantify P cycling in the Chaohu watershed during 1978–2012. We found that P flows have been intensified, with a 5-fold increase of annual P inputs to sustain the expanding intensive agriculture. Annually, most P inputs (75%) were stored within the watershed, which caused accelerating buildup of legacy P in cultivated land (from 4.9 Gg to 6.5 × 10^2 Gg), uncultivated land (from 2.1 Gg to 1.3 × 10^2 Gg) and surface water (from 3.7 Gg to 2.6 × 10^2 Gg) during 1978–2012. The main legacy P sources include fertilizer application for cultivated land, phosphogypsum abandonment for uncultivated land, respectively. The animal husbandry contributed about 63–66% of total P inputs to surface water. The contribution of animal food-P increased greatly during 1978–2012, from 7% to 24% and from 1% to 8% for urban and rural residents, respectively. This work demonstrates principle for the buildup of legacy P at the watershed-scale, and advances the knowledge of sustainable P management, such as improving agricultural technologies to reduce fertilizer application.



1. INTRODUCTION

Phosphorus (P) is an important nutrient that sustains ecological and human life and acts as a primary cause of eutrophication.[1,2] Over the past three decades, massive consumption and excessive losses of P have caused serious eutrophication and algal blooms in surface water.[3,4] Great effort has been made in conservation plans in the Taihu watershed, the Chaohu watershed, the Dianchi watershed, the Chesapeake Bay watershed, and the Lake Erie basin,[5−7] but the outcomes have not always been as effective as hoped.[8−11] The increasing external P loads and the chronic release of P from "legacy P" stocks could be major causes.[12,13] The term "legacy P" refers to P accumulated within the land−freshwater continuum that can serve as long-term P sources to surface water.[12] Field measurements have shown that long-term external P loads would cause a continual increase in legacy P,[14,15] of which the chronic release of legacy P could significantly influence the P dynamics in lakes even after external loads have been reduced for more than 20 years.[16,17] Therefore, the status of legacy P in watersheds has drawn more and more attention.[18,19]

Quantifying the historical patterns of P cycling at watershed scale can not only estimate the current P loads but also discover the sources of the legacy P.[13,20] As an effective tool to analyze the pathway of a specific element within a system, substance flow analysis (SFA) has been applied to quantify P flows at global, regional, city, and county levels.[21−25] These studies are carried out using either top-down or bottom-up methods. At the watershed scale, a bottom-up SFA-based model has also been developed to quantify anthropogenic P flows.[26] However, these quantifications consider only part of natural or anthropogenic P flows within a specific year and lack adequate attention to P losses into soil and surface water, which provided insufficient knowledge about the buildup of legacy P.

In this study, we quantify the P flows in Chaohu watershed, located in the southeast China, with refined SFA, to answer the following two questions: (1) how has the P cycling pattern changed, and (2) how and why has legacy P been built up at the watershed level? We first refine the bottom-up P cycle model[26] by integrating the coupled human and natural systems to track the sources and clarify the pathways of P flows. Then, we selected Chaohu watershed (Figure S1), where one of the three most ultraeutrophic lakes in China is located,[27] as the case area to quantify P flows and stocks from 1978 to 2012 and to identify the causes of the buildup of legacy P. Finally, we conduct a scenario analysis to estimate future trends of legacy P and propose suggestions for sustainable P management strategies.

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2. METHOD AND DATA SOURCE

2.1. WPFA Model. To quantify the P flows, we construct a SFA-based watershed phosphorus flow analysis (WPFA) model, which is derived from the SFA-based model developed by Yuan et al.[26] Our improvements include but are not limited to (1) considering more P associated anthropogenic activities and natural processes in the analytical framework, such as the food/feed industry, aquaculture, wind erosion, and atmospheric deposition, (2) dividing the system into six subsystems based on mutual services among these activities, including extraction (mining and P chemical industry), production (crop farming, animal husbandry and food/feed industry), consumption (urban and rural consumption), disposal (wastewater treatment and solid waste disposal), life support (uncultivated land, surface water, and atmosphere), and exchanger (import/export), (3) improving the calculations of P flows. For example, P flows associated with urban sewage and rural wastewater are calculated using independent methods, thus a cross-check can be conducted by balancing inputs and outputs.

The P balances of a system and its subsystems are calculated based on the mass balance principle:

$$\sum_{i}^{n} IN_i = \sum_{j}^{m} OUT_j + \sum_{k}^{o} STO_k$$

where IN_i and OUT_j represent the P input and output, respectively, and STO_k is the P stock in a specific system, or subsystem. The subscripts, i, j, and k represent input, output and stock categories. Because of the data unavailability of product imports and exports at the county level, similar to Yuan et al.[26] and Ma et al.,[28] we assume that local products are in priority to meet local demands, which means only the excess are for export and the shortfall is met by import or export. We divide all of the equations into three types: (1) independent equations, in which P flows are calculated by multiplying activity data by coefficients, (2) dependent equations, in which P flows are calculated relying on other equations, and 3) systemic balance equations, which are used to calculate unknown P flows or stocks by balancing all of the P flows. Among the three equations, independent equations are given priority to reduce the interaction with other flows (see Supporting Information for details).

The legacy P in cultivated land, uncultivated land, and surface water is calculated as follows:

$$\text{legacy}P_{\text{cl/ucl/sw}} = \sum_{i=1}^{n} STO_{\text{cl/ucl/sw}}$$

where, the subscripts cl, ucl, and sw mean cultivated land, uncultivated land, and surface water, and i is the year considered.

2.2. Data Collection. The system boundary is defined as the geographic area of the Chaohu watershed, which covers one city and seven counties (Figure S1, see Supporting Information for details). The temporal scale is from 1978 to 2012. Data sources include P associated activity data and coefficients. The P associated activity data are derived from governmental statistical yearbooks and bulletins, including population, cultivated areas of crops, agricultural inputs such as fertilizer and pesticide, and production of P associated products such as fertilizer, crops, livestock, and aquatic products. The coefficients, such as the P content of products and ratios of byproducts recycled are acquired from questionnaires, face-to-face interviews, and published literature (see Supporting Information for details).

2.3. P Use Efficiency and P Recycling Rate Indicators. The following indicators are used to quantify the P use efficiency (PUE):

$$PUE_{ch} = \frac{\text{chem\_prod\_output}_P}{\text{chem\_Ind\_input}_P} \quad (1)$$

where PUE_{ch} is the PUE of the P chemical industry, $\text{Chem\_Prod\_Output}_P$ refers to P output through P chemical products such as fertilizer, detergent and pesticide, and Chem_Ind_Input_P means P input through P minerals.

$$PUE_{c/a} = \frac{\text{crop/anim\_output}_P}{\text{CF/AH\_input}_P} \quad (2)$$

where $PUE_{c/a}$ is the PUE of crop farming/animal husbandry, $\text{crop/anim\_output}_P$ refers to P output through primary crop products/live animal such as rice, wheat, rapeseed/pig, bovine, sheep, and CF/AH_input_P is the P input into crop farming/animal husbandry, such as fertilizer, manure, feed, fodder, and straw.

$$PUE_{c+a} = \frac{\text{Pr\_output}_P}{\text{Pr\_input}_P} \quad (3)$$

where PUE_{c+a} represents the PUE of production, Pr_output_P is the P output through crop and animal foods such as manufactured rice, flour, and slaughtered animal, and Pr_input_P refers to total P input into production, including fertilizer, seed, pesticide, human manure, atmosphere deposition, feed imported from other regions, fodder, and food residue.

$$PC_c = \frac{\text{CF\_newinput}_{IP}}{\text{cropf\_output}_P} + \frac{\text{CF\_newinput}_{LP}}{\text{cropf\_output}_P} \times \frac{1}{PUE_{ch}} \quad (4)$$

where PC_c is the life-cycle P consumption to delivery 1 kg P in crop product, CF_NewInput_{IP} represents new P input into crop farming (imported), CF_NewInput_{LP} is new P input into crop farming (produced locally), and cropf_output_P means P output through crop product. For crop farming, "new" P include fertilizer P, seed P, pesticide P, and atmospheric P deposition.

$$PC_a = \frac{\text{AH\_newinput}_{IP}}{\text{animf\_output}_P} + \frac{\text{AH\_newinput}_{LP}}{\text{animf\_output}_P} \times PC_c \quad (5)$$

where PC_a is the life-cycle P consumption to delivery 1 kg P in animal food, AH_newinput_{IP} means new P (imported) input into animal husbandry, AH_NewInput_{LP} refers to new P (produced locally) input into animal husbandry, and anim_output_P is P output through animal food. For animal husbandry, "new" P include feed P and fodder P.

$$PC_{a+c} = \frac{\text{Pr\_newinput}_P}{\text{Fd\_output}_P} \quad (6)$$

where PC_{a+c} is the life-cycle P consumption to delivery 1 kg P in food, Pr_NewInput_P presents new P input into production, and Fd_output_P refers to the output of food-P. For production subsystem, "new" P include fertilizer P, seed P, atmospheric P deposition, import of P via feed.

The P recycling rate (PRR) is calculated as follows:

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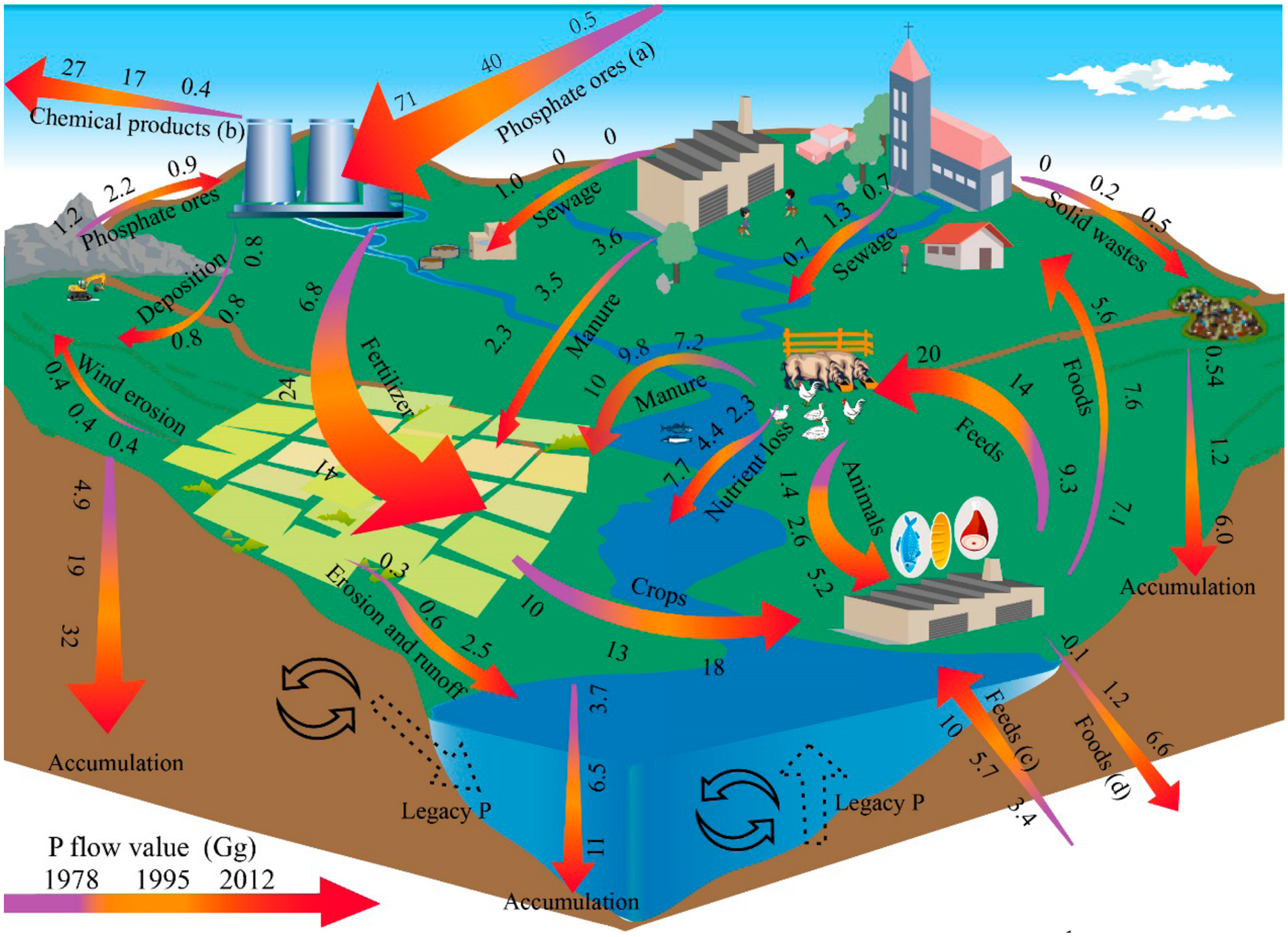

Figure 1. Schematic model of P cycling in the Chaohu watershed (Gg P yr^{-1}). Import/export arrows, including phosphate ores (a), chemical products (b), feeds (c), and foods (d), are shown as net P values.

$$PRR_{cw/aw} = \frac{recycling_{cw/aw}}{CF/AW\_waste_p} \tag{7}$$

where $PRR_{cw/aw}$ is the P recycling rate in crop farming/animal husbandry, $Recycling_{cw/aw}$ refers to P recycled from through straw/manure, and CF/AW_waste_p represents P in crop straw/animal waste.

$$PRR_{uw/rw} = \frac{recycling_{uw/rw}}{UC/RC\_waste_p} \tag{8}$$

where $PRR_{uw/rw}$ represents the P recycling rate in urban/rural consumption, $recycling_{uw/rw}$ is the P recycled through urban/rural waste, and UC/RC_waste_p means P in total urban/rural waste.

2.4. Uncertainty Analysis. The data employed in the bottom-up SFA approach are from different sources with variable data uncertainty. Therefore, we conducted the Monte Carlo (MC) simulation to quantitatively test the sensitivities of parameters, and the propagation of input uncertainty and variability into the final results. We did this by providing a range in all data instead of using a single-point estimate. We do not include uncertainties from activity data as there is no other data source. Parameters are provided with the continuous distributions (triangular, uniform of normal) by taking data quality into account as the possibility of appearance (see Supporting Information for details, Table S1). In general, we assume independence between input data to sample them independently from its distributions.

The MC simulation model is run 10 000 times by randomly selecting values from the input distribution to generate ranges of results. Measurements of uncertainty of the annual main P flows include CVs, 5th, 95th percentiles.

3. RESULTS

3.1. P Production and Utilization in the Chaohu Watershed. The overall depiction of P cycles in the Chaohu watershed over the past 35 years is shown in Figure 1 and Figure S3. In general, P cycling in the Chaohu watershed is no longer a natural dominated loop, but a one-way flow process altered by anthropogenic activities, which was intensified during 1978−2012.

Fabrication, involving industrial processes that transform P ore into phosphate fertilizers, organophosphate pesticides and synthetic detergents, is associated with the most intensive P flows, of which the P inputs increased dramatically from 1.7 Gg in 1978 to 72 Gg in 2012 (Figure 2a). Due to little extraction, the Chaohu watershed has heavily relied on the imports of P ores since the early 1980s, contributing 99% to the total P inputs in 2012. Only about 8% of the total P inputs are made into pesticides and detergents during 1978−2012, which are primarily for export (Figure 2b). The remaining 92% are manufactured into fertilizers, increasing from 1.2 Gg to 64 Gg

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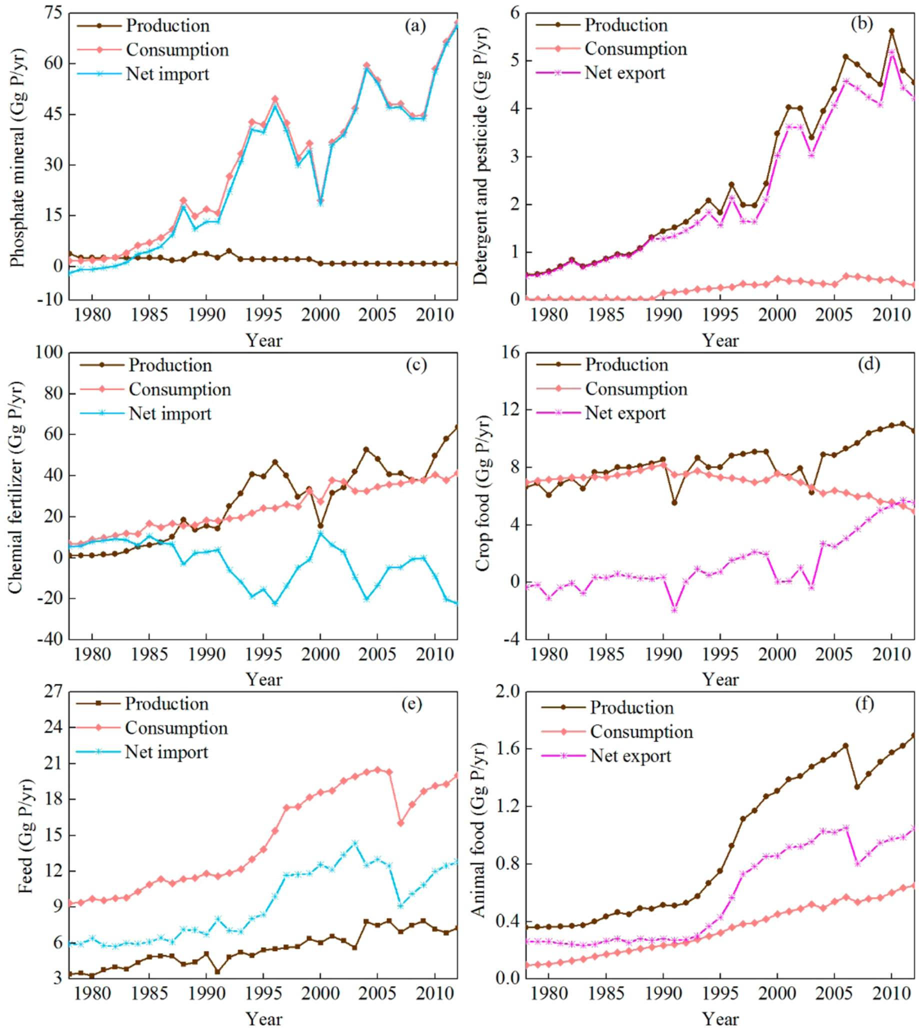

Figure 2. P production and utilization in the Chaohu watershed. (a) P in minerals. (b) P in detergents and pesticides. (c) P in fertilizer. (d) P in crop derived food. (e) P in feed. (f) P in animal derived food. In a specific year, if the production exceeds consumption, the part in excess means P exports. In contrast, the shortage means P imports.

during 1978–2012 (Figure 2c). The development of fertilizer production has made the Chaohu watershed a net fertilizer-P exporter since the early 1990s, except for the periods of 1999–2001 and 2008–2009. The temporal fluctuation during 1999–2001 results from a technical update to produce a cheaper, high efficiency amorphous complex P fertilizer. The fluctuation during 2008–2009 was caused by the price decline of fertilizers in China.

The P input into crop farming through fertilizer has been boosted 6-fold over the past 35 years (Figure 2c). During the same period, the P output through crops has also increased, from 10 Gg to 18 Gg (Figure 1). Then, the P in crops is earmarked for the food/feed industry, where 60% is converted to food annually. The Chaohu watershed has become a crop food-P exporter since 1984 thanks to the expansion of crop production, of which the net export has increased to 53% of the total production in 2012 (Figure 2d). The P in feeds approximately doubled between 1978 and 2012, all of which was consumed locally (Figure 2e).

The amount of P inputs into animal husbandry has increased from 12 Gg in 1978 to 23 Gg in 2012 (Figure 2e). During the entire period, the largest share of P in feeds (varying between 79% and 88%) is "new" feed-P. The main sources of P in feeds are soybean cake, corn, and wheat imported from northeast China, accounting for 55–72% of new feed-P input annually. Along with the P intake by animals, the output of P in live animals has increased 4-fold between 1978 and 2012 (Figure 1). While only approximately 20% of the P in live animals has been converted to animal-derived food (e.g., pork, beef, mutton, and poultry), most of P is stored in the inedible bone, blood, and hair of animals in the form of hydroxyapatite,[29] and abandoned to landfill or other land. The massive production makes the Chaohu watershed an important animal food-P exporter, of which the net exports comprise 53–73% of production annually (Figure 2f). The falling price of animal products and the outbreak of animal disease contributed to the sudden decrease of both feed-P consumption and animal food-P production in 2007 (Figure 2e, 2f).

Regarding P inputs into human consumption, there is a slight decline, from 7.1 Gg in 1978 to 5.8 Gg in 2012, of which 98% is food-P (Figure S5). Similarly, the food-P consumption per capita has decreased from 0.71 to 0.46 kg for urban residents and from 1.1 to 0.69 kg for rural residents during 1978–2012. The proportion of diet derived from animal food increased

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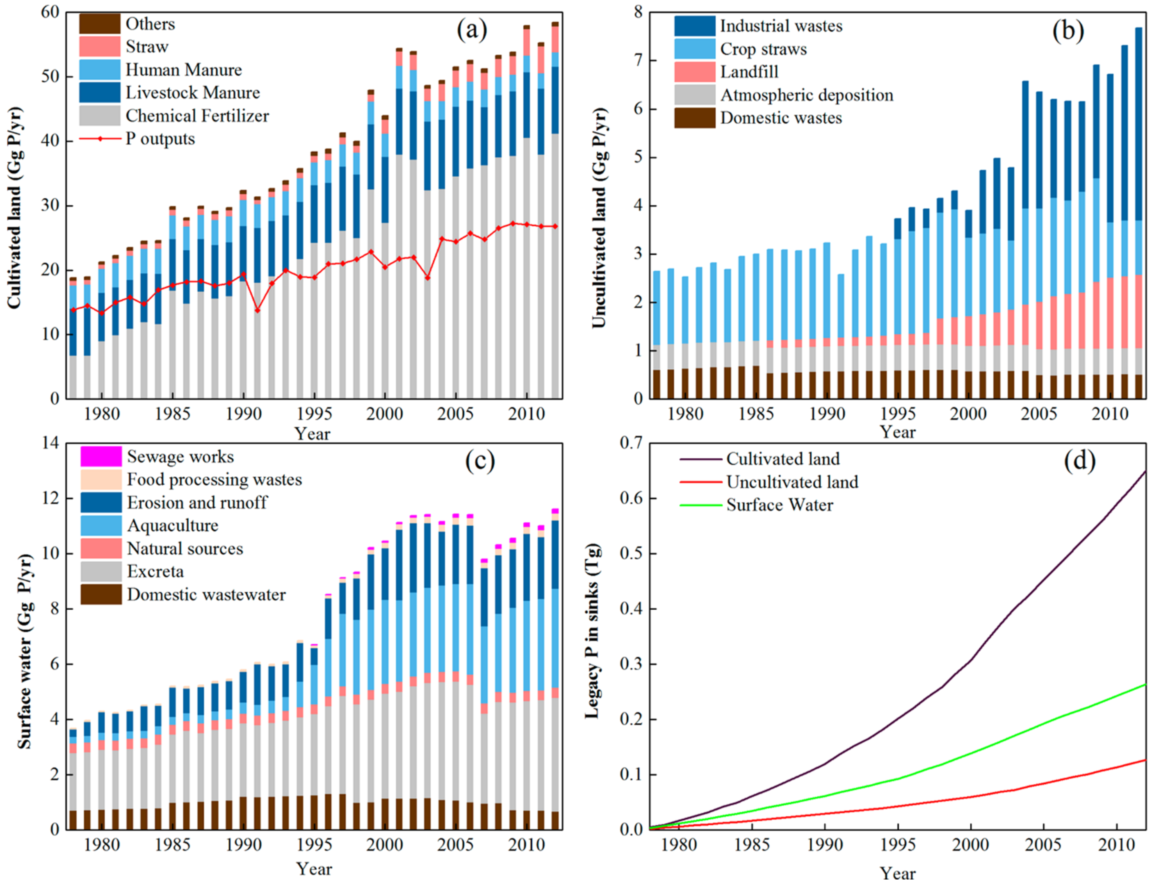

Figure 3. P inputs and outputs and legacy P in the environment. (a) P inputs and outputs in cultivated land. (b) P inputs in uncultivated land. (c) P inputs in surface water. (d) Legacy P in sinks. Here, sinks includes cultivated land, uncultivated land and surface water. Surface water includes all of the ditches, streams, and rivers, lakes and underwater bed sediments in the Chaohu watershed. Uncultivated land means land excluding cultivated land.

from 7% to 24% for urban residents and from 1% to 8% for rural residents between 1978 and 2012.

3.2. P Use Efficiency and P Recycling Rate. The use efficiency in the P chemical industry (PUEch) was high (~98%) before 2000 because only a few quantities of P was lost in the form of dust during the production of single superphosphate (a dominant P fertilizer in Chaohu watershed before 2000) (Table S5). After that, the PUE_{ch} decreased slightly to ~94%, resulting in massive P losses through phosphogypsum in the complex process of manufacturing ammonium phosphate. In 1978, the PUE_c and PUE_a were 54% and 12%, respectively. Toward the end of the period, the PUE_c decreased to 32% as the PUE_a increased to 22%. A major reason for the decreasing PUE_c is the overuse of P fertilizer. The improved PUE_a is associated with advanced P management in animal production. Considering the crop farming, animal husbandry and food/feed industries together, PUE_{a+c} decreased from 34% in 1978 to 18% in 2012. To produce 1 kg-P in crop food, the life-cycle P consumption (PC_c) was 1.1 kg in 1978, and increased to 2.2 kg in 2012. In contrast, PC_a decreased from 28 to 18 kg kg^{-1}. Currently, only one-fifth of P in minerals and feeds reaches food as the PC_{a+c} increased to 5.2 kg kg^{-1} in 2012, whereas it was 2.4 kg kg^{-1} in 1978.

The popularity of straw burning in fields contributed to an increase of PRR_{cw} (from 54% to 80% in 2012). However, field burning is one of the worst ways to reuse straw, and may be responsible for the air pollution in China.[30] Moreover, recycling as fodder, the most effective way to reuse P in straw declined to 8% in 2012 from 32% in 1978 (Figure S6). As for P in wastes generated in animal husbandry, our results suggest a relatively large decrease in recycling rate (76% in 1978 to 59% in 2012). In urban areas, the PRR_{uw} decreased sharply from 46% to 4% between 1978 and 2012. In contrast, it is still popular in rural areas to use excreta as organic fertilizer, thus the decline in PRR_{rw} is slight (82% in 1978 to 78% in 2012).

3.3. P Losses into the Environment. Total P losses into cultivated land increased more than 5 times, from 5.0 Gg in 1978 to 32 Gg in 2012 (Figure 4a). The fertilizer is the most important P source, which contributed from 36% of P input in 1978 to 71% in 2012, followed by livestock and human excreta, and straw (Figure 3a). Compared with other sources, P input through human manure started to decline after 1989. The reasons are complex and may include (1) Cheaper and high-efficiency fertilizer is provided by the quick development of fertilizer industry. (2) Large transfer distances boost transport costs. (3) The waste treatment facilities constructed in urban areas lack a P recovery function. Total P outputs were 14 Gg in 1978 and 27 Gg in 2012, mainly through crop uptake.

Total P losses into landfill increased from 2.1 Gg in 1978 to 7.1 Gg in 2012 (Figure 4b). Straw was the single largest source of P before 2002, and declined from 57% of total P input in 1978 to 15% in 2012 (Figure 3b). Nonetheless, the absolute amount shows a slightly downward trend (1.5 Gg-P in 1978 and 1.1 Gg-P in 2012) resulting from the reduced use of straw

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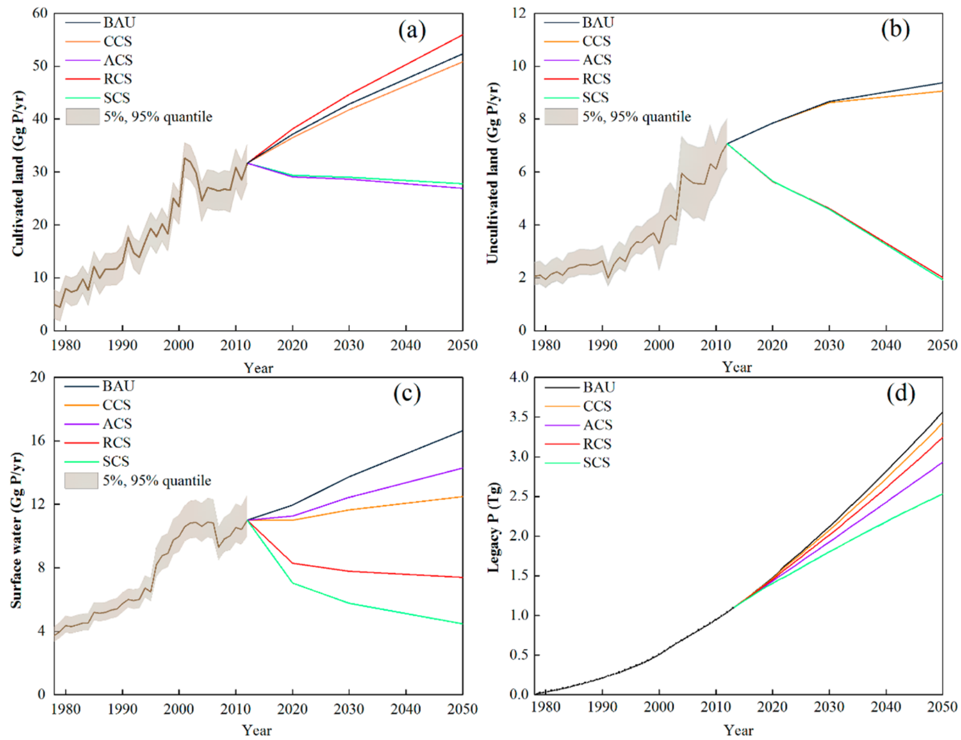

Figure 4. P losses and legacy P under different scenarios. (a) Annual P losses into cultivated land. (b) Annual P losses into uncultivated land. (c) Annual P losses into surface watershed. (d) Legacy P in Chaohu watershed. Dash area in panels (a), (b), and (c) represents the uncertainties. BAU, CCS, ACS, RCS, and SCS represent the scenarios.

Table 1. Comparison of Results in Different Countries and Areas[a]

		plant production			animal production	food chain	food consumption		
country/area	year	PIN	DOC	PUEc	PUEa	PCc+a	PCA	AFP	RAW
U.S.[31]	2007	68	70%	82%	22%	5.1	0.97	47%	
Netherlands[32]	2005	44	38%	61%	39%	2.3	1.13	61%	49%
Austria[33]	2004–2008	35	35%	77%	25%	2.5	1		69%
UK[34]	2009	44	27%	81%	17%	2.9	0.6		86%
France[35]	2002–2006	25	43%	68%	21%	5	1.24	80%	64%
Malaysia[36]	2007	30	95%	34%	25%		1.31		
Turkey[37]	2001	10	86%	80%	20%	2	0.7	16%	
Busia District, Uganda[38]	2010	39	2%	39%	12%		0.59	22%	
Harare District, Zimbabwe[39]	2001	22	23%	15%			0.85	6%	
Phoenix[40]	2005–2010	62	37%	83%	16%		1.02		44%
Thachin Basin, Thailand[41]	2006	75	89%	32%	25%		0.44		88%
Dianchi watershed, China[42]	2000	165	64%	29%	7%				41%
Beijing area China[28]	1978	81	79%	30%	4%	5.1	0.7	4%	
	2008	154	76%	24%	10%	4	0.7	27%	
Chaohu watershed China	1978	36	42%	54%	12%	2.4	1.1	1%	73%
	2012	142	62%	32%	22%	5.2	0.61	12%	83%
China[43]	1984	82	57%	64%	21%	2.8	0.9	5%	62%
	2008	102	72%	60%	33%	4.2	1.1	10%	85%

[a]P input intensity (PIN, kg ha^{-1}) is calculated by dividing total P input into crop farming by cultivated land areas. DOC is the percentage of chemical fertilizer in total P inputs to crop farming. Per capita (PCA, kg P cap^{-1} yr^{-1}) is annual P consumption per capita in diet. PC_{c+a} (kg kg^{-1}) means life-cycle P consumption to delivery 1 kg P in food chain. AFP is the percentage of P in the diet derived from animal products. RAW is the percentage of P from agriculture in total P inputs to surface water.

as biomass fuel. The increase of P input through phosphogypsum is significant, from 11% of total P input in 1995 to 52% in 2012. The amount of P in landfill wastes, following the same trend, has increased from 0.16 Gg in 1986 to 1.5 Gg in 2012, whereas the P input in abandoned domestic wastes starts to decline during the same period resulting from the gradual improvement of solid waste treatment systems in urban areas.

Total P losses into surface water were 3.8 Gg in 1978 and 11 Gg in 2012 (Figure 4c). This change was been highly driven by the expansion of animal husbandry and the low use efficiency of fertilizer. The contribution of P from livestock excreta, the largest source, has declined from 56% of total P input in 1978 to 40% in 2012. However, the absolute amount has increased almost 2-fold between 1978 and 2012, from 2.1 Gg to 4.1 Gg

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(Figure 3c). P loss from aquaculture was 0.23 Gg in 1978 and dramatically increased to 3.6 Gg in 2012, especially after 1993, when the size of aquaculture suddenly expanded. In contrast, P input through domestic wastewater decreased after 1997, benefiting from the improved treatment of sewage in urban areas. Compared with these sources, natural P losses, referring to runoff from uncultivated land and atmospheric deposition are relatively stable and as low as 0.40 Gg P annually.

3.4. Legacy P in the Chaohu Watershed. At the watershed scale, total P inputs have increased 6-fold, from 13 Gg in 1978 to 82 Gg, with only 25% of annual P inputs exported outside directly. As massive amounts of P are consumed and then lost to the watershed, the buildup of legacy P is accelerated, with annual growth rates of 15%, 12%, and 13% in cultivated land, uncultivated land, and surface water, respectively (Figure 3d). During the entire period, the largest share of legacy P storage is in cultivated land (varying between 42 and 69%), followed by surface water (varying between 22 and 38%), and uncultivated land (varying between 8 and 20%). The absolute amounts were 6.5×10^2 Gg, 2.6×10^2 Gg, and 1.3×10^2 Gg for each sinks in 2012, whereas it was 5.0 Gg, 3.7 Gg and 2.1 Gg in 1978, respectively. For uncultivated land, only 12% of the legacy P were stored in landfill, and the rest was carelessly disposed and abandoned around fertilizer plants or rural settlements.

4. DISCUSSION

4.1. Reliability and Uncertainty of the Results. Our result that agriculture is the largest contributor to P input into surface water is consistent with those from the literature across the world (Table 1). For PIN in crop farming, our results are mostly within the range of results in China, but are much higher than the situations in other countries. It is reasonable as China has to feed more people with less cultivated land than other countries, particularly in the Chaohu watershed where the national agriculture base is located. The high DOC in this research corresponds to the results conducted in China, but is relatively lower than in most developed countries. Our results for PUE_c and PUE_a are on the lower end of the range of the results conducted at country level, but is consistent with that conducted at region level. We note that our result about PCA in recent years is on the lower end of the range of the results in other research. The reason may be our calculation only includes some primary processed food (grain, meat, poultry, etc.), but fruit, bread, wine, cake, and other highly processed food are excluded due to unavailable data. It affects the reliability of our results and it should be paid more attention in future research. However, the RAW in this study, also in China, is lower than that in developed countries.

There are uncertainties associated with the study in aspects of flow quantification model and data sets. To reduce the uncertainties in the quantification model, we conducted interactive crosschecks among alternative calculation methods for each P flow to determine the most appropriate one. Meanwhile, efforts are made to ensure the accuracy of parameters by setting series selection criteria (see Supporting Information for details).

The sensitivity analysis shows only a few parameters contribute to more than 95% variance of the results (Figure S9). More specially, P content in rice, ratio of straw used as fuel, and P content in fish feed contributed to 58%, 72%, and 52% variance of P losses into cultivated land, uncultivated land and surface water in 2012, respectively. The Monte Carlo simulation shows the aggregated uncertainties of annual P losses into cultivated land, uncultivated land and surface water are within the value ranges of 16−17%, 18−22%, and 9−13%, respectively (Figure 4a−c). In the year 2012, for instance, the result of P losses into cultivated land was a distribution of the density of results over time, ranging from 24 to 40 Gg (Figure S10). In general, our model is relatively robust against such changes. In particular, when the model is used in other watersheds, efforts conducted to reduce variance in parameters mentioned above can largely reduce uncertainty in results.

4.2. Environmental Implications. To our best knowledge, our study, for the first, determines the magnitude of the legacy P sink in watershed over long time. In cultivated land, 6.5×10^2 Gg P are accumulated, equivalent to increase total P in topsoil (30 cm) by approximately 305 mg/kg over the past 35 years. It needs decades or more to reduce high soil P concentration to levels that have a lower potential to enrich runoff by ceasing P applications. Thus, it is necessary to mobilize soil P for plant to access it to shorten the process, which may reduce the risk of P loss to nearby water bodies. Surface-water body is another legacy P sink in the Chaohu watershed, with 2.6×10^2 Gg P accumulated during 1978−2012. As there are 10 inflow rivers and only 1 outflow rivers (Figure S1), Chaohu Lake is recognized as standing water, which is weak at reducing legacy P by downstream transport. As a result, the legacy P built up can become an important source of P and potential risk for water quality.

4.3. Driving Forces of P Cycling Changes. The P flows have been intensified rapidly, driven by population growth, living standard improving, agriculture expansion and changes in waste treatment system. First, the rapid growth of population and living standard are key drivers. The population has increased by 43% during 1978−2012, and the gross domestic product (GDP) and consumption expenditure per-capita have increased by 25 and 8 times, respectively (Figure S4). This has promoted the change of diets toward more animal proteins. As we mention above, the PC_a is much higher than PC_c, thus higher animal food diet means more P may be consumed to produce these food. We calculated the virtual phosphorus requirement for food consumption (VPRF) (see Supporting Information for details). The results show that, in 1978, VPRF was 3-fold higher than P in food consumed directly in urban areas, whereas it was 1-fold higher in rural areas (Figure S7). Toward the end of the period, the gap increased to 6-fold and 4-fold for urban and rural areas, respectively. Additionally, the animal derived P accounted for 72% and 41% of VPRF in urban areas and rural areas, respectively, in 2012, in contrast with 24% and 8% for the ratio in direct food-P consumption (Figure S8). This implies that a higher proportion of diets rich in animal proteins contributes to the rapid increase of mineral P consumed to produce these food, and the impact is more appreciable in urban areas.

At the same time, major obstructions to the expansion of modern agriculture have been removed. Mao's Commune system has given way to the Household Responsibility System, and the planned economy has been replaced by a free market economy since the early 1980s.[44] The farmers are encouraged to develop intensive crop farming and animal husbandry to obtain more income since the reform. With the support of a series of policies, for example, the "Fish for Wealth Project" and "the exemption from agricultural taxation", intensive agriculture has rapidly expanded, resulting in more P inputs through minerals and crop feeds. However, most farms are small scale,

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thus agricultural management practices are poor. Farmers are lacking in valid guidance for the scientific fertilizer application and reasonable breeding methods, and there are a lack of funds to introduce advanced farm technologies. This has led to a continuous decrease of P use efficiency and the increase of P losses from agricultural production. Both the policy change and unsustainable agricultural practices are the dominant drivers making agriculture the direct driver of the intensified P flows.

Furthermore, the unsustainable and incomplete waste treatment systems accelerated the changes. For one thing, the large transport distances prevent P in manure recycling back into crop farming, and contributes to the transformation of the agricultural mode from the traditional mixed crop-animal production system to mineral-consuming production, where more new P inputs are required for agricultural production. For another, to alleviate eutrophication in Chaohu Lake, 18 municipal sewage plants and 8 landfills in urban areas have been constructed by 2012. However, these facilities are simply "collecting-storing" P rather than "collecting-recycling" it, leading to the continuous decline of PRR_{uw}. In vast rural areas, it is even less common to have a simple storage facility, without which all P in domestic wastewater is discharged to surface water and causes serious eutrophication in numerous rivers near settlements.

4.4. Prediction of Legacy P. According to the above analysis, changes of P cycling are mainly influenced by the growth of population, changes in dietary structure, expansion of intensive agriculture, unsustainable agricultural practices, and a lack of recycling systems. We then conducted a scenario analysis to predict the legacy in the Chaohu watershed by 2050. The following scenarios are used: (1) business as usual (BAU) is set as the worst-case scenario; (2) controlling population and optimizing diets (CCS) is set as a scenario, where population and dietary structure are controlled moderately; (3) improving agricultural practices scenario (ACS) is set where PUE in agriculture is raised on the basis of that in BAU; (4) constructing multiple recycling systems (RCS) is a scenario referring to improved treatment and recycling rates of P in wastes; (5) integrated sustainable management scenario (SCS) is set by considering all of the scenarios above (see Supporting Information for details). The results show that legacy P will surge to 3.6 Tg by 2050 in BAU, which is more than triple the amount in 2012 (Figure 4d). However, in CCS, ACS, and RCS, legacy P will be 4%, 18%, and 9% lower than that in BAU by 2050. Annual P losses in cultivated land have the largest decrease in scenario ACS (49% lower than that in BAU in 2050) (Figure 4a). As for annual P losses in surface water and uncultivated land, the largest decrease is in scenario RCS, being 56% and 78% lower than that in BAU in 2050 (Figure 4b,c). In SCS, legacy P will reduce legacy P by 29% of relative to that in BAU by 2050, and can reduce annual P losses into all P sinks.

4.5. Policy Implications. The P flows are dominated by agricultural production and the trend has been accelerating, as the Chaohu watershed plays a more important role on producing food. The challenge confronting sustainable P management is to minimize mineral P inputs and losses as pollution, while still maintaining agricultural production. For crop farming, an effective way to mitigate P losses is to reduce the application of chemical fertilizer. As farmers usually apply fertilizer according to experience and are more concerned about crop production rather than the environment, it may be feasible to reduce mineral P input by improving farming technologies, such as precision fertilization, using low P-containing fertilizer, adopting P-efficient genotype, rhizosphere management, and rotation/intercropping with legumes, which can also help to recover legacy P. Furthermore, paddy field accounts for more than 80% of the cultivated land in this region. Thus, controlling surface drainage from paddy field by intermittent irrigation and providing guidance for reasonable draining time is also important to reduce P losses. Numerous small-scale livestock farms in the region contribute massive P loss in animal husbandry. Thus, merging these small farms into large ones can help introduce advanced breeding technologies to improve feed efficiency and can also help to recycle manure to cultivated land by cutting transportation costs. In addition, optimizing food consumption patterns and cutting down on food waste are also helpful to mitigate P flows. To do this, high protein crop food, including tofu, sweet corn, peanuts, etc., are recommended to meet demand for protein rather than consuming more animal-derived food.

A common practice to treat phosphogypsum is to store it in the vicinity without any prior treatment. It was not merely a threat to water quality because of the transferability of hazardous elements, but also a waste of P resource.[45] The appropriate disposal approach is to produce low-P containing fertilizer, which can also be helpful to reduce fertilizer application.

In the future, we expect the way P cycles through the system can be characterized by a high reliance on P recycling from domestic waste, animal manure, and even legacy in cultivated soil and underwater bed sediment. To achieve this goal, the challenge is to activate practitioners who directly affect P cycling (e.g., residents, farmers, and waste disposal plant officials). High cost of the recovery techniques is another impediment. Thus, if recycling P is worth conducting, it is worthy of consideration. Affordability of the fee is another problem. Cost-benefit analysis may be a solution to balance economic cost and environment benefit.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b03202.

Detailed description of the WPFA and data source for calculating P flows in Chaohu watershed, uncertainty analysis and scenario analysis. Table S1−S4, main parameters; Table S5, P use efficiency and P recycling rate indicators; Table S6−S9, uncertainties; Table S10−S13, parameters in scenario analysis; Figure S1, location of Chaohu watershed; Figure S2 hierarchical structure of WPFA; Figure S3, aggregate chart of P cycling in Chaohu watershed; Figure S4, socioeconomic status in Chaohu watershed; Figure S5, P consumption by residents; Figure S6, utilization of crop straw; Figure S7−S8, comparison with VPRF and food-P consumed directly; Figure S9, sensitivity analysis of parameters; Figure S10, aggregated uncertainties in 2012. Figure S11, projection of the BAU factors (DOC)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Elser, J.; Bennett, E. Phosphorus cycle: a broken biogeochemical cycle. *Nature* **2011**, *478* (7367), 29−31.

(2) Schindler, D. W.; Hecky, R. E.; Findlay, D. L.; Stainton, M. P.; Parker, B. R.; Paterson, M. J.; Beaty, K. G.; Lyng, M.; Kasian, S. E. Eutrophication of lakes cannot be controlled by reducing nitrogen input: results of a 37-year whole-ecosystem experiment. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105* (32), 11254−11258.

(3) Oliveira, M.; Machado, A. V. The role of phosphorus on eutrophication: a historical review and future perspectives. *Environ. Technol. Rev.* **2013**, *2* (1), 117−127.

(4) Khan, M. N.; Mohammad, F. Eutrophication: Challenges and Solutions. In *Eutrophication: Causes, Consequences and Control*; Ansari, A. A., Gill, S. S., Eds.; Springer: Netherlands, 2014; pp 1−15.

(5) State Environmental Protection Administration. *Water pollution control plan on "Three river" and "Three river"*; China Environmental Science Press: Beijing, 2000; in Chinese.

(6) Sharpley, A.; Richards, P.; Herron, S.; Baker, D. Case study comparison between litigated and voluntary nutrient management strategies. *J. Soil Water Conserv.* **2012**, *67* (5), 442−450.

(7) USEPA. *Guidance for Federal Land Management in the Chesapeake Bay Watershed*; USEPA, Office of Wetlands, Oceans, and Watersheds: Washington, DC, 2010; http://water.epa.gov/polwaste/nps/chesbay502.cfm. (accessed May 15, 2015).

(8) Villa, P.; Duan, H.; Loiselle, S. Using remote sensing to assess the impact of human activities on water quality: Case study of Lake Taihu, China. In *Advances in Watershed Science and Assessment*; Younos, T., Parece, T. E., Eds.; Springer International Publishing, 2015; Vol. 33, pp 85−110.

(9) Yang, L.; Lei, K.; Meng, W.; Fu, G.; Yan, W. Temporal and spatial changes in nutrients and chlorophyll-α in a shallow lake, Lake Chaohu, China: An 11-year investigation. *J. Environ. Sci.* **2013**, *25* (6), 1117−1123.

(10) Huang, C.; Wang, X.; Yang, H.; Li, Y.; Wang, Y.; Chen, X.; Xu, L. Satellite data regarding the eutrophication response to human activities in the plateau lake Dianchi in China from 1974 to 2009. *Sci. Total Environ.* **2014**, *485−486*, 1−11.

(11) Zhang, Y.; Ma, R.; Duan, H.; Xu, J. Cyanobacteria blooms in Lake Chaohu observed from time-series MODIS images. In *Lakes: the mirrors of the earth, Italy*; Biscarin, C., Piwelwoni, A., Nasellt-flores, L., Eds.; Science4Press: Italy, 2014; pp 134−137.

(12) Sharpley, A.; Jarvie, H. P.; Buda, A.; May, L.; Spears, B.; Kleinman, P. Phosphorus legacy: overcoming the effects of past management practices to mitigate future water quality impairment. *J. Environ. Qual.* **2013**, *42* (5), 1308−1326.

(13) Jarvie, H. P.; Sharpley, A. N.; Spears, B.; Buda, A. R.; May, L.; Kleinman, P. J. Water quality remediation faces unprecedented challenges from "legacy phosphorus. *Environ. Sci. Technol.* **2013**, *47* (16), 8997−8998.

(14) Zhang, H.; Shan, B. Historical distribution and partitioning of phosphorus in sediments in an agricultural watershed in the Yangtze-Huaihe region, China. *Environ. Sci. Technol.* **2008**, *42* (7), 2328−2333.

(15) Xie, L.; Xie, P. Long-term (1956−1999) dynamics of phosphorus in a shallow, subtropical Chinese lake with the possible effects of cyanobacterial blooms. *Water Res.* **2002**, *36* (1), 343−349.

(16) Seo, D.; Canale, R. Analysis of sediment characteristics and total phosphorus models for Shagawa Lake. *J. Environ. Eng.* **1999**, *125* (4), 346−350.

(17) Søndergaard, M.; Bjerring, R.; Jeppesen, E. Persistent internal phosphorus loading during summer in shallow eutrophic lakes. *Hydrobiologia* **2013**, *710* (1), 95−107.

(18) Cheng, Y.; Li, P.; Xu, G.; Li, Z.; Cheng, S.; Gao, H. Spatial distribution of soil total phosphorus in Yingwugou watershed of the Dan River, China. *CATENA*, **2015**, http://dx.doi.org/10.1016/j.catena.2015.02.015. (In press).

(19) Liu, E.; Shen, J.; Yang, X.; Zhang, E. Spatial distribution and human contamination quantification of trace metals and phosphorus in the sediments of Chaohu Lake, a eutrophic shallow lake, China. *Environ. Monit. Assess.* **2012**, *184* (4), 2105−2118.

(20) Haygarth, P. M.; Jarvie, H. P.; Powers, S. M.; Sharpley, A. N.; Elser, J. J.; Shen, J.; Peterson, H. M.; Chan, N.-I.; Howden, N. J. K.; Tim Burt, F. W.; Zhang, F.; Liu, X. Sustainable phosphorus management and the need for a long-term perspective: the legacy hypothesis. *Environ. Sci. Technol.* **2014**, *48* (15), 8417−8419.

(21) Liu, Y.; Villalba, G.; Ayres, R. U.; Schroder, H. Global phosphorus flows and environmental impacts from a consumption perspective. *J. Ind. Ecol.* **2008**, *12* (2), 229−247.

(22) Liu, Y.; Mol, A. P. J.; Chen, J. Material flow and ecological restructuring in China. *J. Ind. Ecol.* **2004**, *8* (3), 103−120.

(23) Li, S.; Yuan, Z.; Bi, J.; Wu, H. Anthropogenic phosphorus flow analysis of Hefei City, China. *Sci. Total Environ.* **2010**, *408* (23), 5715−5722.

(24) Yuan, Z.; Sun, L.; Bi, J.; Wu, H.; Zhang, L. Phosphorus flow analysis of the socioeconomic ecosystem of Shucheng County, China. *Ecol. Appl.* **2011**, *21* (7), 2822−2832.

(25) Yuan, Z.; Shi, J.; Wu, H.; Zhang, L.; Bi, J. Understanding the anthropogenic phosphorus pathway with substance flow analysis at the city level. *J. Environ. Manage.* **2011**, *92* (8), 2021−2028.

(26) Yuan, Z.; Wu, H.; He, X.; Liu, X. A bottom−up model for quantifying anthropogenic phosphorus cycles in watersheds. *J. Cleaner Prod.* **2014**, *84* (1), 502−508.

(27) Chen, X.; Yang, X.; Dong, X.; Liu, Q. *Nutrient dynamics linked to hydrological condition and anthropogenic nutrient loading in Chaohu Lake (southeast China)*, 2011, *661*, (1), 223−234.

(28) Ma, L.; Guo, J.; Velthof, G. L.; Li, Y.; Chen, Q.; Ma, W.; Oenema, O.; Zhang, F. Impacts of urban expansion on nitrogen and phosphorus flows in the food system of Beijing from 1978 to 2008. *Global Environ. Change* **2014**, *28*, 192−204.

(29) Combs, D. Hair analysis as an indicator of mineral status of livestock. *J. Anim. Sci.* **1987**, *65* (6), 1753−1758.

(30) Qu, C.; Li, B.; Wu, H.; Giesy, J. P. Controlling air pollution from straw burning in China calls for efficient recycling. *Environ. Sci. Technol.* **2012**, *46* (15), 7934−7936.

(31) MacDonald, G. K.; Bennett, E. M.; Carpenter, S. R. Embodied phosphorus and the global connections of United States agriculture. *Environ. Res. Lett.* **2012**, *7* (4), 1−13.

(32) Smit, A. L.; van Middelkoop, J. C.; Dijk, W. v.; Reuler, H. v.; de Buck, A. J.; van de Sande, P. A. C. M. *A Quantification of Phosphorus Flows in the Netherlands through Agricultural Production, Industrial Processing and Households*; Plant Research International, Business Unit Agrosystems: Wageningen, The Netherlands, 2010.

(33) Egle, L.; Zoboli, O.; Thaler, S.; Rechberger, H.; Zessner, M. The Austrian P budget as a basis for resource optimization. *Resour. Conserv. Recycl.* **2014**, *83*, 152−162.

(34) Cooper, J.; Carliell-Marquet, C. A substance flow analysis of phosphorus in the UK food production and consumption system. *Resour. Conserv. Recycl.* **2013**, *74*, 82−100.

(35) Senthilkumar, K.; Nesme, T.; Mollier, A.; Pellerin, S. Conceptual design and quantification of phosphorus flows and balances at the country scale: The case of France. *Global Biogeochem. Cycles* **2012**, *26* (2), 1−14.

(36) Ghani, L.; Mahmood, N. Balance sheet for phosphorus in Malaysia by SFA. *Aust. J. Basic Appl. Sci.* **2011**, *5* (12), 3069−3079.

(37) Seyhan, D. Country-scale phosphorus balancing as a base for resources conservation. *Resour. Conserv. Recycl.* **2009**, *53* (12), 698−709.

(38) Lederer, J.; Karungi, J.; Ogwang, F. The potential of wastes to improve nutrient levels in agricultural soils: A material flow analysis case study from Busia District, Uganda. *Agric., Ecosyst. Environ.* **2015**, *207*, 26−39.

(39) Gumbo, B.; Savenije, H.; Kelderman, P. Ecologising societal metabolism: The case of phosphorus. In *Proc. 3rd Int. Conf. Environmental Management*, 2002; pp 27−30.
(40) Metson, G. S.; Hale, R. L.; Iwaniec, D. M.; Cook, E. M.; Corman, J. R.; Galletti, C. S.; Childers, D. L. Phosphorus in Phoenix: a budget and spatial representation of phosphorus in an urban ecosystem. *Ecol. Appl.* **2011**, *22* (2), 705−721.
(41) Schaffner, M.; Bader, H. P.; Scheidegger, R. Modeling the contribution of point sources and non-point sources to Thachin River water pollution. *Sci. Total Environ.* **2009**, *407* (17), 4902−4915.
(42) Liu, Y.; Chen, J.; Mol, A. P. J.; Ayres, R. U. Comparative analysis of phosphorus use within national and local economies in China. *Resour. Conserv. Recycl.* **2007**, *51* (2), 454−474.
(43) Ma, D.; Hu, S.; Chen, D.; Li, Y. The Temporal Evolution of Anthropogenic Phosphorus Consumption in China and Its Environmental Implications. *J. Ind. Ecol.* **2013**, *17* (4), 566−577.
(44) Gulati, A.; Fan, S.; Dalafi, S. *The dragon and the elephant: Agricultural and rural reforms in China and India*; International Food Policy Research Institute, 2005; http://ageconsearch.umn.edu/bitstream/59826/2/mtidp87.pdf (accessed May 17, 2015).
(45) Tayibi, H.; Choura, M.; Lopez, F. A.; Alguacil, F. J.; Lopez-Delgado, A. Environmental impact and management of phosphogypsum. *J. Environ. Manage.* **2009**, *90* (8), 2377−2386.

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Environ. Sci. Technol. 2015, 49, 13973−13982