Bian Zihao (Orcid ID: 0000-0003-2310-3662)
Tian Hanqin (Orcid ID: 0000-0002-1806-4091)
Lu Chaoqun (Orcid ID: 0000-0002-1526-0513)
You Yongfa (Orcid ID: 0000-0002-8916-2940)

Title: Soil legacy nutrients contribute to the decreasing stoichiometric ratio of N and P loading from the Mississippi River Basin

Running Title: Mechanisms of the decreasing N:P loading

Zihao Bian[1,2,3], Hanqin Tian[1,2]*, Shufen Pan[1,2], Hao Shi[1,4], Chaoqun Lu[5], Christopher Anderson[1], Wei-Jun Cai[6], Charles S. Hopkinson[7], Dubravko Justic[8], Latif Kalin[1], Steven Lohrenz[9], Steven McNulty[10], Naiqing Pan[1,2], Ge Sun[10], Zhuonan Wang[1], Yuanzhi Yao[1,11], Yongfa You[1,2]

Zihao Bian: 0000-0003-2310-3662

Hanqin Tian: 0000-0002-1806-4091

Shufen Pan: 0000-0001-7920-1427

Hao Shi: 0000-0001-8250-0567

Chaoqun Lu: 0000-0002-1526-0513

Christopher Anderson: 0000-0002-0408-6476

Wei-Jun Cai: 0000-0003-3606-8325

Charles S. Hopkinson: 0000-0002-7331-8322

Steven Lohrenz: 0000-0003-3811-2975

Steven McNulty: 0000-0003-4518-5646

Ge Sun: 0000-0002-0159-1370

Zhuonan Wang: 0000-0002-8945-7247

Yuanzhi Yao: 0000-0003-2387-4598

Yongfa You: 0000-0002-8916-2940

[1]International Center for Climate and Global Change Research, and College of Forestry, Wildlife and Environment, Auburn University, Auburn, AL, USA

[2]Schiller Institute for Integrated Science and Society, Department of Earth and Environmental Sciences, Boston College, Chestnut Hill, MA, USA

[3]School of Geography Science, Nanjing Normal University, Nanjing 210023, China

[4]State Key Laboratory of Urban and Regional Ecology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, China

[5]Department of Ecology, Evolution, and Organismal Biology, Iowa State University, Ames, IA, USA

[6]School of Marine Science and Policy, University of Delaware, Newark, DE, USA

[7]Department of Marine Sciences, University of Georgia, Athens, GA, USA

[8]College of the Coast and Environment, Louisiana State University, Baton Rouge, LA, USA

[9]School for Marine Science and Technology, University of Massachusetts Dartmouth, New Bedford, MA, USA

[10]Eastern Forest Environmental Threat Assessment Center, Southern Research Station, U.S. Department of Agriculture Forest Service, Research Triangle Park, NC, USA

[11]School of Geographic Sciences, East China Normal University, Shanghai, China

Correspondence: Hanqin Tian (hanqin.tian@bc.edu; tianhan@auburn.edu)

Abstract: Human-induced nitrogen-phosphorus (N, P) imbalance in terrestrial ecosystems can lead to disproportionate N and P loading to aquatic ecosystems, subsequently shifting the elemental ratio in estuaries and coastal oceans and impacting both the structure and functioning of aquatic ecosystems. The N:P ratio of nutrient loading to the Gulf of Mexico from the Mississippi River Basin increased before the late 1980s driven by the enhanced usage of N fertilizer over P fertilizer, whereafter the N:P loading ratio started to decrease although the N:P ratio of fertilizer application didn't exhibit a similar trend. Here, we hypothesize that different release rates of soil legacy nutrients might contribute to the decreasing N:P loading ratio. Our study used a data-model integration framework to evaluate N and P dynamics and the potential for long-term accumulation or release of internal soil nutrient legacy stores to alter the ratio of N and P transported down the rivers. We show that the longer residence time of P in terrestrial ecosystems results in a much slower release of P to coastal oceans than N. If contemporary nutrient sources were reduced or suspended, P loading sustained by soil legacy P would decrease much slower than that of N, causing a decrease in the N and P loading ratio. The longer residence time of P in terrestrial ecosystems and the increasingly important role of soil legacy nutrients as a loading source may explain the decreasing N:P loading ratio in the Mississippi River Basin. Our study underscores a promising prospect for N loading control and the urgency to integrate soil P legacy into sustainable nutrient management strategies for aquatic ecosystem health and water security.

Keywords: Nitrogen; Phosphorus; Nutrient budget; Stoichiometric ratio; Legacy nutrient; Nutrient loading; Nutrient balance.

1. Introduction

Global nitrogen (N) and phosphorus (P) cycles have been substantially disturbed by anthropogenic activities primarily due to the growing demands for food and energy. Biologically available N and P inputs to the biosphere have more than doubled during the Anthropocene (Bouwman et al., 2009; Smil, 2000), posing considerable risks to the stability and sustainability of the Earth biosphere system (Steffen et al., 2015). Imbalanced inputs of anthropogenic N and P into the biosphere coupled with their unique biogeochemical cycles have resulted in significantly changed stoichiometries of N:P bioavailability over space and time (Peñuelas et al., 2013). The altered environmental N:P ratios have affected organisms' metabolism and growth rates, ecosystem functions and structure, and the global carbon (C) cycle (Peñuelas et al., 2013; Sterner & Elser, 2017).

For aquatic ecosystems, nutrient loading from terrestrial ecosystems, especially agricultural land, has stimulated eutrophication and water quality degradation (Bricker et al., 2008). A stoichiometric perspective can provide valuable insights into the aquatic nutrient imbalance and its effects on the biodiversity and structure of aquatic communities, especially those associated with harmful algal blooms (J. J. Elser et al., 2007; Glibert, 2017). Stoichiometric N:P ratios have been widely used to indicate the nutrient limitation of phytoplankton growth in both freshwater and marine systems (Conley et al., 2009; Justić et al., 1995).

Stoichiometric changes in the terrestrial-aquatic linkage are critical in determining whether nutrients are balanced for supporting aquatic primary production and organic matter decomposition (Bauer et al., 2013; Turner et al., 2006). When nutrient loads differ in stoichiometric proportion to the "Redfield ratio (106 C: 16 N: 1 P)", unbalanced nutrient conditions of receiving water may favor the proliferation of harmful algae and the production of toxins (Glibert & Burkholder, 2011; Van de Waal et al., 2009). Globally, the use of N fertilizer over P fertilizer in agriculture has increased N:P ratios of nutrient loads (Peñuelas & Sardans, 2022). This nutrient imbalance has likely contributed to the proliferation of non-N_2-fixing cyanobacteria in freshwater and a shift towards more dinoflagellates in marine systems (Glibert, 2017). Stoichiometric analysis of nutrient loads and nutrient requirements of aquatic ecosystems can aid in designing strategies to focus management efforts on the most critical nutrient.

The hypoxic bottom water or so-called "dead zone" of the northern Gulf of Mexico is one of the largest hypoxic zones in coastal ecosystems, and the algal blooms and eutrophication are primarily supported by excessive nutrient inputs originating from intensive agricultural activities within the Mississippi River Basin (Dodds, 2006). Comprehensively understanding the intricate nutrient dynamics within the Mississippi River Basin can shed light on nutrient management and water quality control measures applicable to the broader context of watersheds. The examination of water quality monitoring data from stations near the outlet of the Mississippi River showed that the mean annual N:P ratio first increased from the late 1970s to the 1980s, but then declined (S. Stackpoole et al., 2021; Turner et al., 2006) (Fig. 1). The earlier increase in the N:P ratio in riverine nutrient export can be attributed to the impact of anthropogenic nutrient inputs on agricultural land. However, the underlying mechanisms responsible for the recent decline in the N:P ratio, consequent to the decreasing TN and the increasing TP river loads, remain unclear. Understanding why the N:P loading ratio decreases in the Mississippi River Basin can provide valuable insights for managing environmental N:P ratio, given the global increasing N:P imbalance is still a serious concern (Peñuelas & Sardans, 2022).

Legacy nutrients are accumulated nutrients within the watershed (e.g., soil, vadose zone, groundwater, and sediments) due to the anthropogenic nutrient surplus from previous years and have the potential to act as a long-term nutrient source to coastal oceans (Chen et al., 2018). Nevertheless, detecting and monitoring soil legacy nutrient change over time is challenging because of the huge stocks of N and P in soils and the complicated and distinct processes they each involve. There have been some efforts that applied models and mass balance methods to estimate legacy nutrients and their contribution to nutrient loading, and agricultural legacy pools are likely high throughout many parts of the Mississippi River Basin (Sabo, Clark, Gibbs, et al., 2021; S. M. Stackpoole et al., 2019; Van Meter et al., 2018). However, the impact of soil legacy nutrients on N:P loading ratio change has not been thoroughly investigated. Given soil legacy nutrients are an important aquatic nutrient source, in addition to contemporary nutrients, for nonpoint source pollution, we hypothesize that they have contributed to the recent decline in N:P ratios of riverine nutrient export from the Mississippi River Basin.

In this study, we explore the potential reasons for the recent decreased stoichiometric ratio of riverine N and P exports from the Mississippi River Basin. A coupled biogeochemical and hydrological model, Dynamic Land Ecosystem Model (DLEM), in conjunction with long-term anthropogenic nutrient input data, was used to quantify long-term N and P dynamics along the terrestrial-aquatic continuum in the Mississippi River Basin. Our objectives are threefold: (1) estimating the N and P budgets, nutrient accumulation rates, and N:P ratio in contemporary nutrient sources within the basin; (2) investigating the impacts of soil legacy nutrients on riverine exports of N and P (dissolved and particulate forms, organic and inorganic forms) by comparing simulated results in "NORMAL" (i.e., historical conditions) and "LEGACY" (i.e., 100% nutrient use efficiency starting in 1990) scenarios; and (3) discussing the responses of the N:P loading ratio to changes in agricultural nutrient surplus, soil legacy nutrients, and other environmental factors. Our work has the potential to inform nutrient reduction strategies that could lead to more effective management of nutrient loading from the Mississippi River Basin to estuaries and coastal oceans, thereby controlling water quality and ecosystem health.

2. Methods

2.1. Dynamic Land Ecosystem Model.

The DLEM is a process-based biogeochemical model coupling water, C, N, and P cycles across the plant-soil-aquatic continuum (Fig. 2 and Text S1) (Tian et al., 2015; Z. Wang et al., 2020). The model is capable of simulating the long-term dynamics of N and P fluxes and storages in terrestrial and aquatic ecosystems driven by multiple environmental forcings (e.g., climate, atmospheric CO_2 concentration, land use change, synthetic fertilizer, livestock manure, and atmospheric N deposition). Within the modeling framework, nutrients from terrestrial ecosystems enter aquatic ecosystems through surface and subsurface runoff, leaching, erosion, and wastewater discharge, and then are transported from headwaters to mainstreams and finally to coastal oceans (Yao et al., 2021). The DLEM has been developed, calibrated, validated, and applied to estimate century-long dynamics of riverine discharge (Liu et al., 2013), C (Ren et al., 2016), N (Tian et al., 2020), and P (Bian et al., 2022) loading from the Mississippi River Basin into the Gulf of Mexico (Fig. S1). The DLEM-simulated N:P ratio of riverine nutrient exports has been decreasing at a rate of 0.19 yr^{-1} in recent decades, which is close to the observed N:P ratio decrease rate (0.32 yr^{-1}) reported by USGS (Fig. S2). The nutrient budgets estimated in this study are comparable with previous studies (David et al., 2010; S. Stackpoole et al., 2021). The soil legacy effect is represented by the accumulation of nutrients in all soil N and P pools in the model (Fig. 2). The distinct storage and flux characteristics of N and P within and between different pools can reflect the intricate processes governing their transformations, surpassing the scope of empirical inventory studies and highlighting the complexity of their changes over time (Sabo, Clark, Gibbs, et al., 2021). In the DLEM, N is primarily stored in soil organic pools and P is stored in both organic pools and inorganic pools (e.g., secondary mineral P and occluded P). Soil organic matter consists of six pools: autochthonous microbial pool (SMB1), zymogenous microbial (SMB2), soil microbial residues (SMR), native organic matter (NOM), passive soil organic matter (PSOM), and dissolved organic matter (DOM) (Fig. 2). The residence times of C, N, and P in NOM and PSOM pools are much longer than the residence times in other organic pools (Table S1). The residence times of inorganic P pools (Labile P, Secondary Mineral P, Occluded P) were on the order of years to tens of millennia. However, the model oversimplifies nutrient reaction and transport processes in groundwater and river sediments, which may lead to inaccurate simulations of legacy effects caused by these pathways (Donovan et al., 2015; Holman et al., 2008; Jarvie et al., 2005). Therefore, the legacy nutrients in this study mainly refer to soil legacy nutrients.

2.2. Input Datasets

The input datasets of the DLEM include climate, atmospheric CO_2 concentration, land use, river network, soil properties, and N and P inputs. These datasets were collected or developed by combining multiple data sources (Table. 1 and Fig. S3) and were at a spatial resolution of 5×5 arc-min (around 9.2 × 9.2 km at the equator). The long-time series of anthropogenic nutrient input data, including synthetic fertilizer, livestock manure, and atmospheric deposition data, is key for quantifying soil legacy nutrients.

Grid-level fertilizer nutrient dataset during 1960–2018 was developed by down-scaling state-level crop-specific survey data based on annual crop distribution maps and crop rotation maps (Cao et al., 2018). We obtained the time-series crop-area-specific fertilizer data of nine major crops (e.g., wheat, corn, rice, soybean, cotton, sorghum, barley, oats, and peanut) from the US

Department of Agriculture (USDA). The harvest area fraction for each crop in each pixel was calculated based on the spatial distribution of harvest area for each crop in the continental U.S. (Portmann et al., 2010). The crop-weighted fertilizer application amount in each grid during 1960-2018 was calculated by combining the crop-specific fertilizer application amount and the fraction of harvest area for each crop in the specific grid cell. Then, based on cropland area data (Yu & Lu, 2018), the annual total fertilizer application was calculated and compared with the annual FAO and USDA dataset at the country scale. A modification ratio was calculated and used to harmonize the national total fertilizer application amount during 1960-2018. Since state- and national-level synthetic N and P fertilizer data before 1960 are not available through FAO and USDA databases, we filled in data during 1901-1960 by assuming that change rates in N fertilizer followed an estimated historical N fertilizer change in the US (Cao et al., 2018) and P fertilizer change was consistent with the global P fertilizer change rates (Cordell et al., 2009).

Similarly, we generated grid-level manure N and P data by combining county-level livestock survey data and livestock distribution maps (Bian et al., 2021). The county-level manure nutrient data were firstly calculated based on county-level livestock populations, dynamic livestock weights, and excreted-manure-nutrient rate. Data of livestock and poultry population were derived from the USDA census reports from 1930 to 2017. Secondly, the geographically explicit manure N and P production data were developed by down-scaling county-level manure nutrient data according to the livestock distribution maps from the Global Livestock Impact Mapping System (GLIMS) (https://livestock.geo-wiki.org/home-2/). To generate grid-level manure production from 1901 to 1930, we assumed that manure production change rates followed the trend of global manure nutrient production (Holland et al., 2005). The details of manure nutrient data have been provided in our previous study (Bian et al., 2021).

In this study, we assumed that all fertilizer and manure nutrients were applied to agricultural land, which may overestimate the total nutrient input in agricultural ecosystems. Additionally, manure generated in a given land area may not be applied in the same area. Furthermore, other pathways of nutrient fluxes across the system, such as forest harvest and fire emission, were not considered, which may result in biases in estimated nutrient balance and legacy nutrients.

2.3. Simulation experiments.

The DLEM simulation process involved three stages: 1) an equilibrium run was carried out using the 40-year (1861–1900) mean climate datasets to establish the initial state under pre-1900 conditions; 2) a spin-up simulation was conducted to remove any noise resulting from the shift from equilibrium to transient simulation; 3) a transient simulation was performed utilizing 118 years of forcings to generate outcomes. Two simulation scenarios "NORMAL" (representing the actual scenario) and "LEGACY" (depicting a hypothetic scenario without contemporary nutrient surplus) were designed to study the impacts of legacy nutrients on riverine nutrient export. All the simulations started from the same baseline equilibrium state. The NORMAL scenario adopted historical nutrient inputs and outputs during 1901-2018, representing the conditions with both contemporary and legacy nutrient sources. The simulation under the LEGACY scenario was the same as the NORMAL scenario during 1901−1990, but assumed no additional newly added nutrients surplus on agricultural land thereafter, representing 100% nutrient use efficiency of agricultural systems and an equal balance of nutrient inputs (fertilizer, manure, atmospheric deposition, weathering, and BNF) to harvest removal nutrient (Fig. 3). To simulate NUE=100% scenario, all daily nutrient inputs on agricultural ecosystems were set to enter into vegetation production pool within the DLEM (Fig. 2), which would eventually be harvested and removed when "no nutrient surplus" condition began. Under the LEGACY scenario, the soil nutrient stock first increased during 1901-1990 and then became the only dominant nutrient source (aside from the background source) for riverine nutrient export since 1991. Comparing the results of NORMAL and LEGACY scenarios after 1991 can help to assess the impact of legacy nutrients on riverine nutrient exports.

3. Results and discussions

3.1. N and P budgets in the Mississippi River Basin

The legacy nutrients result from the imbalance between the inputs and outputs of N and P during 1901-2018 (Figs. 4 and S4). The N and P outputs in the Mississippi River Basin, including harvest removal, gas emission, and riverine export, increased over the last century following the sharp growth of the anthropogenic N and P inputs (Fig. 4a-b). From the 1960s to the 2010s, the simulated average annual riverine N export increased from 1.05 Tg N yr^{-1} to 1.63 Tg N yr^{-1}, accounting for 8%-9% of all basin N inputs, meanwhile, simulated N gas emissions (N_2, N_2O, NO, and NH_3) also increased due to both enhanced anthropogenic N inputs and climate change (Lu, Yu, et al., 2021), accounting for 18-19% of basin N inputs. In contrast to the relatively stable proportion of N export and gas emissions to N inputs, the proportion of N harvested from agricultural land increased from 35% in the 1960s to 56% in the 2010s, reflecting the increased nutrient use efficiency (NUE) of crops (Sabo, Clark, & Compton, 2021). Similarly, the average annual harvest P in total P inputs increased from around 45% to 68% from the 1960s to the 2010s. Riverine P export increased from 0.11 Tg P yr^{-1} to 0.19 Tg P yr^{-1} from the 1960s to the 2010s, accounting for 6-7% of total basin P inputs. Except for harvest removal of nutrients, the proportion of N leakage (around 26-27% of total N), including loss into the atmosphere and export to the coastal ocean, is much higher than the corresponding proportion of P leakage out of terrestrial ecosystems (around 6-7% of total P inputs). Both N and P balances between inputs and outputs substantially increased from the 1930s to the 1970s, and began to decrease thereafter (Fig. 4c-d). The decline in N and P balances means the accumulation of N and P in terrestrial ecosystems (e.g., soil and vegetation pools) slowed down.

3.2. N:P ratio changes in contemporary nutrient sources

Contemporary nutrient surplus is recognized as the major contributor to nutrient loading in any particular year, aside from legacy nutrients from previous nutrient surplus and background sources from natural systems and urban wastewater (Fig. 3). Synthetic fertilizer and livestock manure are the two most important anthropogenic N and P inputs to agricultural land. The N:P molar ratio of fertilizer increased from around 8.0 to 12.0 from the 1960s to the 1990s, but it became relatively stable after 1990 except from 2008 to 2010, when the price of P fertilizer highly increased, and consumption was constrained (Fig. 5). Meanwhile, the N:P molar ratio of manure slightly decreased from 7.4 to 6.8 from 1960 to 2018. The decreasing N:P ratio of manure was associated with the change in the composition of livestock populations (e.g., increases in the proportions of beef cows and broilers) (Bian et al., 2021), and may make a small contribution to the decreasing N:P ratio of nutrient loading to the Gulf. The contemporary nutrient surplus, which is the primary basis for many statistical methods or lumped watershed models to calculate the nutrient export, can indicate agricultural activities' overall impact on non-point source nutrient supply. The DLEM-simulated nutrient surplus N:P ratio in the Mississippi River Basin didn't exhibit a significant decreasing trend from 1990 to 2018 (Figs. 5 and S5).

Additionally, several nutrient budgets based on survey data showed that the N:P ratio in cropland nutrient surplus has increased over the past three decades in the continental U.S. (Jones & Bruulsema, 2021; Lu, Cao, et al., 2021). The temporal patterns of the N:P river load ratio matched those of the N:P ratio of fertilizer and manure nutrients for the period 1960 to 1990, but after 1990 there was a disconnect. While the N:P river load ratio decreased, the N:P ratio of fertilizer and manure nutrients remained relatively stable, which therefore, may not be the major reason for the decreasing N:P loading ratio.

3.3. Impacts of soil legacy nutrients on N:P loading

In the NORMAL scenario (Fig. 3), simulated riverine exports of total nitrogen (TN) and total phosphorus (TP) to the Gulf increased by 219% and 62%, respectively, from the 1900s to the 1990s. Then DLEM-simulated TN export decreased by 9% while TP export increased by 9% from the 1990s to the 2010s (Fig. 6a-b), which is similar to the 11% decrease in TN export and 17% increase in TP export observed by USGS (Fig. S1). In contrast, simulated riverine TN export decreased by 20%, and TP export increased by 3% from the 1990s to the 2010s in the LEGACY scenario (Fig. 6d-e). Without newly added nutrient surplus on agricultural land, riverine TN export was predicted to decrease substantially, but TP export did not decrease, and dissolved inorganic nutrients were major decreasing components for both N and P export. The proportions of dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) in TN and TP exports decreased from 73% and 31% to 43% and 28%, respectively, from the 1980s to the 2010s, and the reduction in DIN was more substantial than that of DIP under the LEGACY scenario (Fig. 6d-e). After legacy nutrients became the only dominant nutrient source (aside from background sources) in the LEGACY scenario (Fig. 3), the TN:TP molar ratio of nutrient export decreased from 24.0 in 1991 to 11.0 in 2018, which was primarily attributed to the decreasing DIN:DIP molar ratio (changed from 56 to 17) (Fig. 6f). The impact of decreasing DIN on TN is larger than the impact of decreasing DIP on TP because DIN is the major component of TN export, while the proportion of DIP in TP export is less than half.

The DLEM-simulated riverine DIN export in the LEGACY scenario declined more rapidly compared to the results simulated by the ELEMeNT model (Van Meter et al., 2018). The discrepancy between the two models may be due to the exclusion of groundwater legacy N in the DLEM and overestimated net mineralization rates of soil organic nitrogen (SON) in the

ELEMeNT. Given the dominant role of SON in contributing legacy N in the Mississippi River Basin (Van Meter et al., 2017), the different net mineralization rates used in the two models may be the key to explaining the discrepancy in simulated results. In the ELEMeNT model, the N surplus is directly added into soil organic pools without considering the conversion process from inorganic N to organic N, then SON gradually contributes to total N loading through the mineralization process (Van Meter et al., 2017). Since soil inorganic N loss can only occur after the mineralization process in the ELEMeNT model, an overestimated mineralization rate may be adopted. In contrast, the accumulation of SON in the DLEM is controlled by vegetation uptake, litter and residue inputs, immobilization, and mineralization processes. The soil inorganic N loss can occur before it is converted to organic N, and a high mineralization rate would limit the accumulation of SON. Therefore, this study may adopt a relatively low mineralization rate of SON compared to the ELEMeNT model. In the LEGACY scenario of this study, the low mineralization rate and long residence time limited the conversion of SON to inorganic N, as well as DIN loading from land, resulting in the rapid decline of N loading when there was no additional nutrient surplus. Ballard et al. (2019) suggested that recovery time scales simulated by ELEMeNT in the Mississippi River Basin are highly uncertain. Additionally, ELEMeNT outputs for the Mississippi River Basin seem to greatly deviate from other ELEMeNT applications in the Chesapeake Bay and China (Chang et al., 2021; Zhou et al., 2023). Generally, DLEM-simulated N results are squaring more with the 5-15 year response time reported by Chang et al. (2021), Dupas et al. (2020), and S. Stackpoole et al. (2021).

Nitrogen can leave terrestrial ecosystems through gaseous emissions (vertical flux) and water transport (lateral flux), but the major pathway for P loss is the lateral flux to aquatic systems (J. Elser & Bennett, 2011). Molecular forms of N are highly soluble and can convert to gaseous form through volatilization, nitrification, and denitrification processes, whereas P is less mobile and occurs largely in particulate form by attaching itself to clay surfaces, or combining with Fe, Al, Mg, and Ca (McDowell et al., 2004). The higher retention of P in soil than that of N decouples the N and P between soil and water, and the average N:P ratio of riverine export is usually higher than that of soil surplus (Romero et al., 2021). The mean residence time of P in the terrestrial biosphere was estimated to be over 3.5 times that of N (Schlesinger & Bernhardt, 2013; Y. P. Wang et al., 2010). If anthropogenic nutrient surplus was reduced or suspended, soil labile N (inorganic N and organic N with short residence time) was predicted to decline quickly within a decade, and soil legacy organic N with long residence time would serve as a long-term N source but the mineralization rate would limit its contribution to DIN export. Meanwhile, soil labile P was predicted to decrease much slower than N, and P export derived from soil legacy P may also decrease slower than N export from legacy N. Our findings show that soil legacy P is enough to sustain the level of P export even without additional anthropogenic nutrient surplus in the Mississippi River Basin.

In actual conditions (NORMAL scenario), the change in the N:P ratio of nutrient loading is governed by both legacy nutrient sources and contemporary nutrient sources (Fig. 3). If the contemporary nutrient surplus is the dominant source, the N:P loading would follow the change in the N:P ratio of contemporary nutrient surplus. On the contrary, the N:P loading may decline if soil legacy nutrient sources play an important role in contributing to nutrient loading. In the Mississippi River Basin, the use of synthetic fertilizer and livestock manure nutrients remained relatively stable since the 1990s. Meanwhile, crop harvest increased as the agroecosystem NUE improved (Swaney & Howarth, 2019; J. Zhang et al., 2021) (Figs. 4 and S4). With the reduction in newly introduced nutrient surplus (Fig. S5), legacy nutrients have been increasingly important in contributing to riverine nutrient export in recent decades (Fig. 7). While the N:P ratio has remained stable in agricultural nutrient surplus, declining N:P ratio in total nutrient loading can be observed as legacy sources became dominant at one point with cumulative legacy impacts over time (Fig. 7).

3.4. Impacts of other environmental factors on the N:P loading ratio

Aside from agricultural nutrient inputs, the nutrient loading to the Gulf can also be influenced by other environmental factors, such as climate, wastewater discharge, groundwater, dam construction, and land use change. Here, we discussed how these factors act differently on N and P and why these factors may not be the key reasons for the decreasing N:P loading ratio.

The sensitivity of the N:P loading ratio to climate variability largely depends on the difference between the responses of N and P loading to hydrologic variability. The N:P ratio in riverine nutrient export was reported to increase with discharge in subbasins with intensive crop agriculture and high fertilizer application rates but is less predictable in other subbasins of the Mississippi River Basin (Leong et al., 2014). In agricultural land where the leaching of DIN and DIP was the major pathway for nutrients entering aquatic systems, the higher mobility of inorganic N compared with that of inorganic P may make DIN more sensitive to discharge than DIP. The erosion loss of particulate form N and P is another major source of nutrient loading. The more frequent extreme precipitation in the Mississippi River Basin can enhance the erosion rate and the loss of particulate form nutrients (Tan et al., 2021) (Fig. S6). The proportions of different N and P species play a role in changing the N:P loading ratio. Compared with DIN:DIP ratios, PN:PP ratios are much lower (Fig. 6). Thus, if the proportion of particulate nutrient components increases within the total nutrient loading, the TN:TP ratio may decrease. The trade-off between the dynamics in DIN:DIP ratio and the proportion of PN and PP in nutrient loading under changing hydrological conditions may determine the response of TN:TP loading ratio to climate variability. For the entire Mississippi River Basin, where agricultural land is the most important source of total nutrient export, there is a positive relationship between TN:TP ratio and discharge (Leong et al., 2014). However, there has been no significant trend in annual discharge in the Mississippi River Basin in recent decades (Fig. 1). The discharge variability may not be the reason for the decreasing N:P ratio, rather increased extreme precipitation (Fig. S6) and intensified erosion disproportionately favor the mobilization of legacy P and may amplify the declines in the N:P loading ratio (Goyette et al., 2019).

Wastewater production, as the point N and P source delivered to streams and coastal oceans, is associated with urbanization and population. The SPARROW model estimated that N input from wastewater treatment plants (WWTPs) decreased by 4.3% while P input increased by 45% from 2002 to 2012 in the Mississippi River Basin (Robertson & Saad, 2021), indicating that the N:P ratio of point-source input may decrease in a certain period. On the contrary, wastewater treatment facility data from the U.S. Environmental Protection Agency (USEPA) Clean Watershed Needs Survey (CWNS) showed that the average N:P molar ratio in wastewater has increased from 22.8 in 1978 to 52.7 in 2012 in the U.S. (Falcone et al., 2017). The rapid improvements and construction of WWTPs can increase TN:TP ratio in wastewater discharge due to the higher removal efficiency of P over N (Tong et al., 2020). Overall, considering the relatively small proportion of point sources in total nutrient loading (WWTPs contributed 5.4% N and 13.0% P in 2012) (Robertson & Saad, 2021), the impact of point sources on the changes in TN:TP loading ratio may be small.

Nutrient removal occurs during the transport of nutrients through streams, lakes, dam reservoirs, and groundwater systems. The contrasting behaviors of N and P along flow paths can reshape the N:P ratio of nutrient export to coastal oceans. Streams tend to favor the removal of N over P, whereas lakes and reservoirs are sites of relatively high water column P loss through sediment settling (Goyette et al., 2019). Dam construction in basins has increased N:P ratios of delivered material by facilitating the retention of particulate forms of nutrients and preferential removal of P over N in reservoirs (Maavara et al., 2020). In groundwater, DIN converted to gas form is the predominant removal pathway, and DIP is generally removed through sorption or co-precipitation with Al, Ca, or Fe into mineral phases. Removal of P is often more efficient than N in groundwater, resulting in a strong increase of the N:P ratio along flow paths (Fitzgerald et al., 2015; Slomp & Van Cappellen, 2004). Water retention capacities are also influenced by changes in flow rate and landscape (Goyette et al., 2019). The decrease in flow rate favors in-stream sediment deposition or precipitation of mineral phase in groundwater, which plays a more important role in P removal. Changes in land cover, such as wetland conversion to agricultural lands, may cause the loss of water retention capacity and change N:P ratios in downstream waters (Goyette et al., 2019). In the Mississippi River Basin, the increased number of dams likely favored P retention over N (Maavara et al., 2015). Additionally, there is insufficient evidence that long-term average water retention capacities were significantly altered by flow rate and land cover change after the 1990s. Therefore, water retention capacity change is not likely to be the reason for the declining N:P ratio of nutrient loading.

3.6. Implications

Eutrophication in the Mississippi River plume and surrounding coastal waters is the result of nutrient enrichment from runoff within the Mississippi River Basin. The level of eutrophication and resulting hypoxia reflect relative inputs of N, P, and silica (Si) over space and time (Justić et al., 1995; Turner et al., 2006). High N and Si inputs favor the production of large, rapidly sinking phytoplankton species, while higher relative P inputs promote small, slower sinking dinoflagellate communities (Bi et al., 2021; Glibert et al., 2011; Guo et al., 2014). However, how the decreasing N:P loading ratio would impact harmful algal blooms is still unclear and calls for more studies.

An interim target of a 20% reduction of N and P loading from the Mississippi River Basin by 2025 (relative to the 1980-1996 average) has been set by the Hypoxia Task Force (Force, 2015). Our study indicates that reductions in N loading are achievable if we continue controlling the inputs and surplus of N, while P surplus is perpetuating a longer legacy of eutrophication. N is generally identified as the ultimate limiting nutrient of the whole Gulf ecosystem, due to the efficient recycling of P and the loss of N to the atmosphere (Ammerman, 1992; Howarth et al., 2011; Rinker & Powell, 2006). The achievable reduction in N offers opportunities for effectively mitigating harmful algal blooms and hypoxia in the Gulf, presenting promising strategies to address these environmental challenges. Although P loading reductions have little effect on overall primary production in the Gulf, a dual nutrient reduction strategy as the most prudent management approach can reduce the required magnitude of N reduction to achieve target outcomes (Fennel & Laurent, 2018). However, measures to reduce nutrient loading have been degraded by the mineralization/release of legacy P, given that the TP loading from the Mississippi River Basin continued to increase. Future climate change with increased storm density and accelerated hydrologic cycle in the Mississippi River Basin is likely to exacerbate legacy nutrient loss as well (J. Zhang et al., 2022). Nutrient control measures need to better address the challenges of legacy P, to meet nutrient reduction goals.

Soil legacy nutrients serve as a long-term nutrient source for receiving water, but also a potentially important nutrient source for crop production. The nutrient management strategies can include efforts to improve the efficient use of legacy nutrients to satisfy crop demand and thereby reduce nutrient losses to the surface water or atmosphere. Understanding the impacts of soil conditions (soil moisture, temperature, pH, texture, and soil mineral) and crop types on nutrient mineralization and desorption processes is critical to improving current beneficial management practices for mitigating soil legacy nutrient loss. Measures aimed at enhancing soil legacy nutrient utilization by crops may include cultivation, conservation tillage, intercropping, crop breeding, and moisture regulation (Chen et al., 2018). These measures may be suitable for different farming systems, depending on the heterogeneity in soil legacy nutrient forms, soil profile distributions, soil mineralogy and pH, and climate regimes. For example, the adoption of reduced tillage or no-tillage practices enhances the accumulation of organic matter in surface soils, thereby promoting increased mineralization and subsequent release of dissolved nutrients for crop uptake but also for leaching through runoff (Daloğlu et al., 2012; Rodrigues et al., 2016).

The water quality risk should be considered when applying conservation tillage or no-tillage in wet regions. Optimizing the utilization of legacy soil nutrient resources requires information regarding their magnitude, distribution, forms, appropriate timing of application, and efficient accessibility (Rowe et al., 2016). A large-scale rough estimation of legacy P storage has been conducted in the U.S. (Sabo, Clark, Gibbs, et al., 2021). In some farming systems, soil P mining and P-based management programs have successfully resulted in decreased application of P fertilizer and manure (Kleinman et al., 2015). These observations highlight that legacy nutrient mining could be potentially feasible without sacrificing crop yields. Further detailed investigations of background soil nutrient levels in different farming systems and the efficiencies of legacy nutrient utilization practices should be encouraged.

4. Conclusion

This study investigates processes and mechanisms of N and P inputs and remineralization in soils that result in varying ratios of N to P loading to coastal Louisiana from the Mississippi River Basin. We find that relative differences in the long-term accumulation of N relative to P within the basin and their ultimate release following remineralization processes have led to changes in the N:P of loading to the coastal zone that differ from long-term trends in their inputs to the system from anthropogenic activities. According to the N and P budgets across the Mississippi River Basin, the accumulated N and P continued to increase but slowed down in recent decades. Although both soil legacy N and P can serve as long-term sources for nutrient loading, P has a longer residence time and soil labile P declines more slowly than N. If the NUE of agricultural systems became 100% (no additional nutrient surplus), riverine N loading would decrease more rapidly due to the quick loss of soil labile N relative to P. Therefore, the N:P ratio of nutrient loading may decrease over time as the NUE of crops increases and soil legacy nutrients become increasingly important in contributing to nutrient loading. Improvements in the NUE could lead to relatively rapid declines in N loading and facilitate the primary nutrient control goal for the Gulf. However, P loading will persist longer time scale, and mining out legacy P or attenuating the legacy pools with Best Management Practices (BMPs) can potentially satisfy crop demand and contribute to water quality control.

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Data availability statement: The model input datasets are openly available as stated in Table 1. The model-simulated annual nutrient budgets are archived at https://doi.org/10.5281/zenodo.8378286 (Bian et al., 2023).

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Table 1. Model input data and validation data.

Data variables	**Time period/step**	**Reference/source**
Model input data/Environmental Drivers		
Climate (Temperature, Precipitation)	1901–2018/ daily	GRIDMET (1979–2018) (http://www.climatologylab.org/gridmet.html) CRUNCEP (1901–1978) (https://doi.org/10.5065/PZ8F-F017)
Land Cover and Land Use (Crop density /rotation maps)	1901–2016/ yearly	(Yu & Lu, 2018)
N fertilizer	1901-2018/ yearly	(Cao et al., 2018) USDA National Agricultural Statistics Service (https://quickstats.nass.usda.gov/)
P fertilizer	1901–2018/ yearly	USDA National Agricultural Statistics Service
Manure N and P production	1901–2017/ yearly	(Bian et al., 2021)
N deposition rate	1901-2014/ yearly	(Morgenstern et al., 2017; Schwede & Lear, 2014)
P deposition rate	Annual average	(Mahowald et al., 2008)
Model Calibration and Validation data		
River discharge	1979-2018/ monthly	USGS
Water quality	1979-2018/ monthly	USGS
Crop yield and Harvest nutrient	1910-2018/ yearly	USDA- National Agricultural Statistics Service (X. Zhang et al., 2015)

Figure legends

Fig. 1. Interannual variations and trends of riverine (a) N and (b) P fluxes, (c) TN:TP ratio in water column, and (d) flow from 1990 to 2018 at USGS site St. Francisville (USGS 07373420, near the outlet of the Mississippi River Basin). Solid lines in (a) and (b) show the WRTDS flow normalized results, dash lines are regression trend lines, and shaded areas represent the 90% confidence intervals.

Fig. 2. The major N and P pools and fluxes in the DLEM-Terrestrial/Aquatic scheme. Blue arrows and boxes represent unique N processes and orange ones represent unique P processes. Organic matter pools interact with coupled C, N, and P fluxes. Added organic matter pools AOM1 and AOM2 are litter pools with different residence times. Soil organic matter consists of six pools: autochthonous microbial pool (SMB1), zymogenous microbial (SMB2), soil microbial residues (SMR), native organic matter (NOM), passive soil organic matter (PSOM), and dissolved organic matter (DOM).

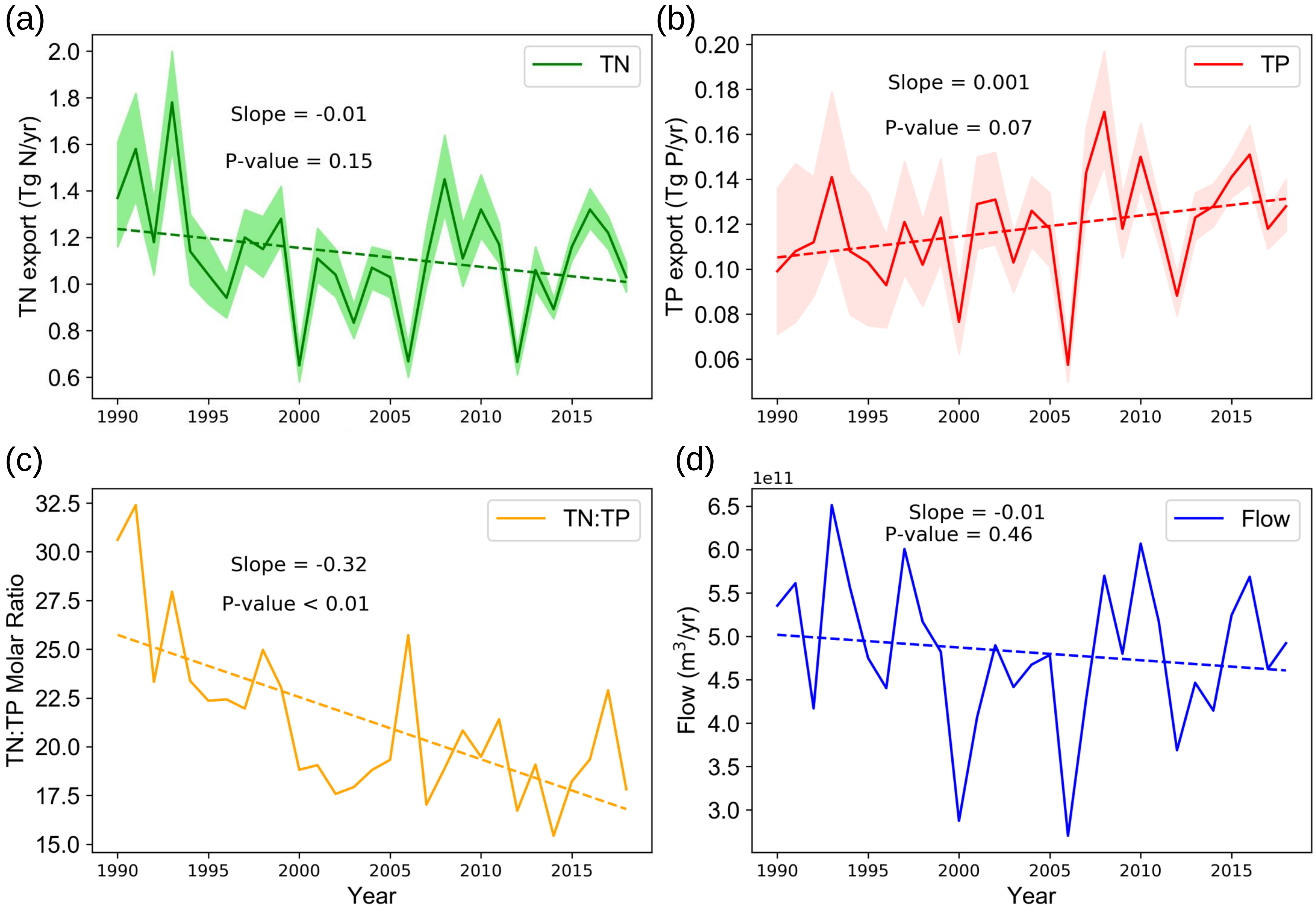
Fig. 3. The N and P inputs and outputs in terrestrial ecosystems under NORMAL and LEGACY (after 1990) scenarios. The major N and P inputs in terrestrial ecosystems include synthetic N and P fertilizer, livestock manure N and P, atmospheric N deposition, and biological N fixation (BNF). Meanwhile, the major N and P outputs include harvest removal of N and P, nitrous gas (NH_3, N_2O, NO, N_2) emissions, and riverine N and P exports. Background source represents nutrients from natural ecosystems and point source represents wastewater nutrient discharge.

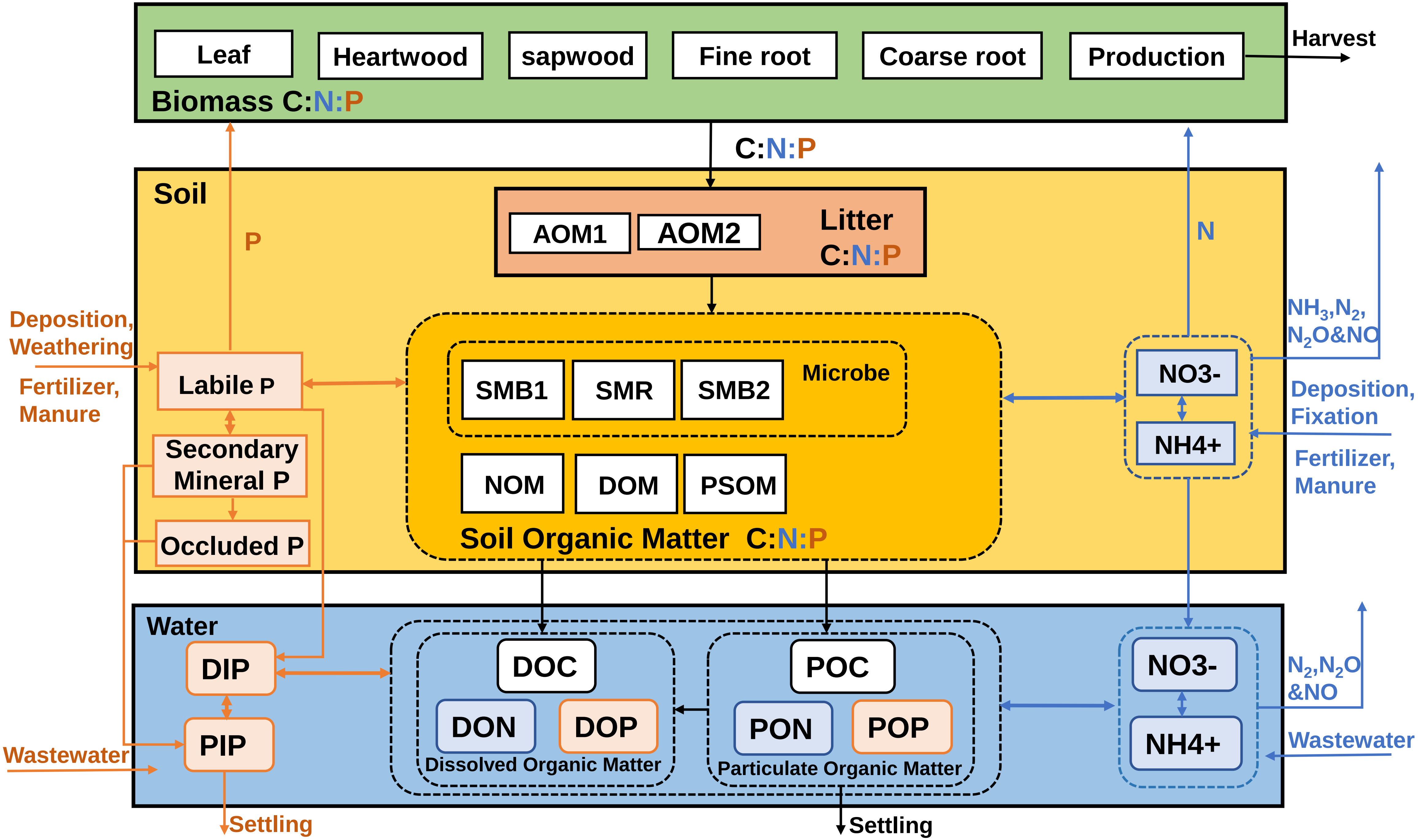
Fig. 4. The annual variations of (a) N and (b) P budgets in the Mississippi River Basin during 1901-2018 (stacked chart). N and P fertilizer, manure N and P, and N deposition are data-based input variables. Biological N fixation (BNF), harvest N and P, NH_3 emission, N_2O emission, N_2 emission, NO emission, and riverine N and P exports are simulated variables. N and P input variables are positive numbers and output variables are set as negative numbers. (c) N and (d) P balances which are the differences between all N or P inputs and all N or P outputs represent the annual accumulated nutrient in terrestrial ecosystems.

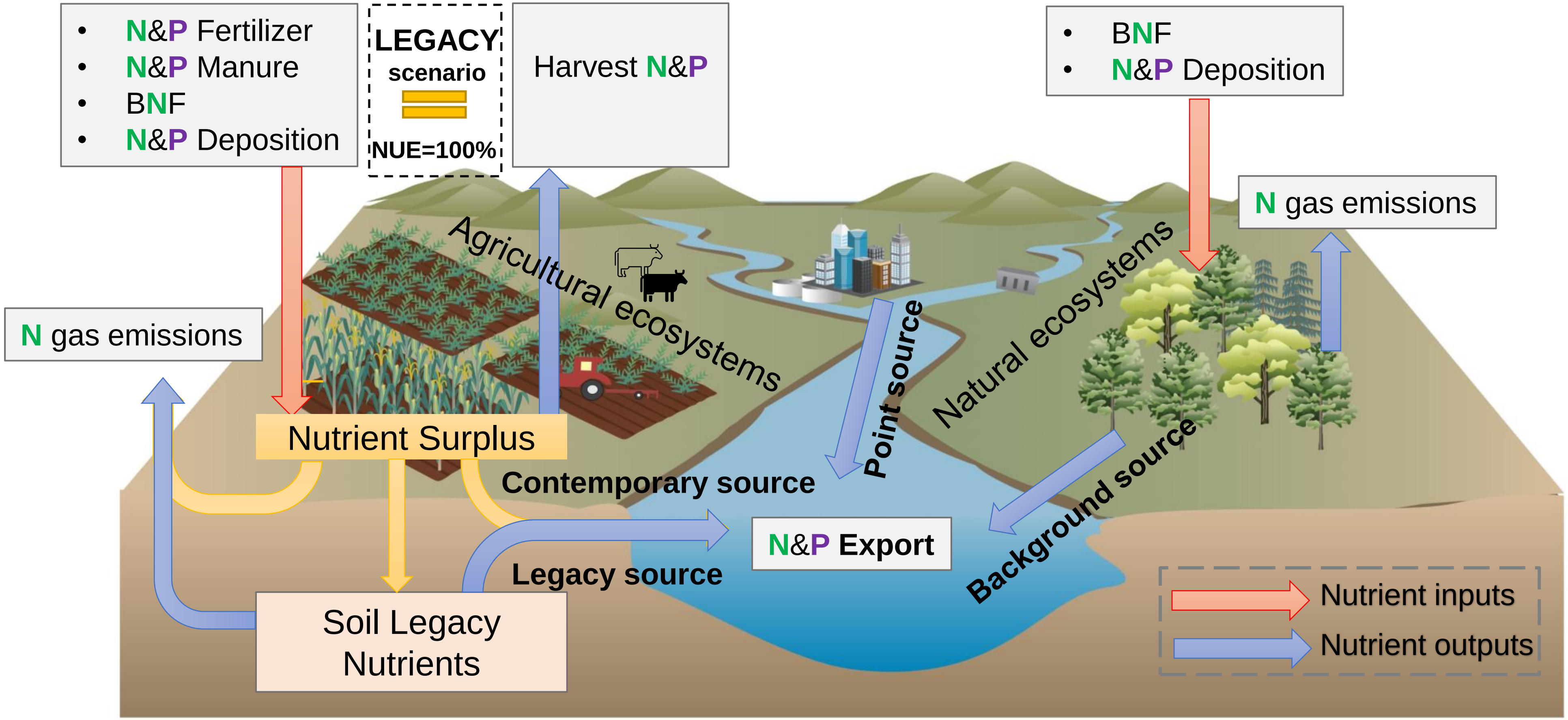
Fig. 5. The interannual variations of fertilizer, manure, and nutrient surplus in the Mississippi River Basin from 1960 to 2018. Nutrient surplus is defined as the difference between total N or P inputs and harvest removal N or P in agricultural systems. Note: the analysis period starts from 1960 when the fertilizer inventory data from USDA are available.

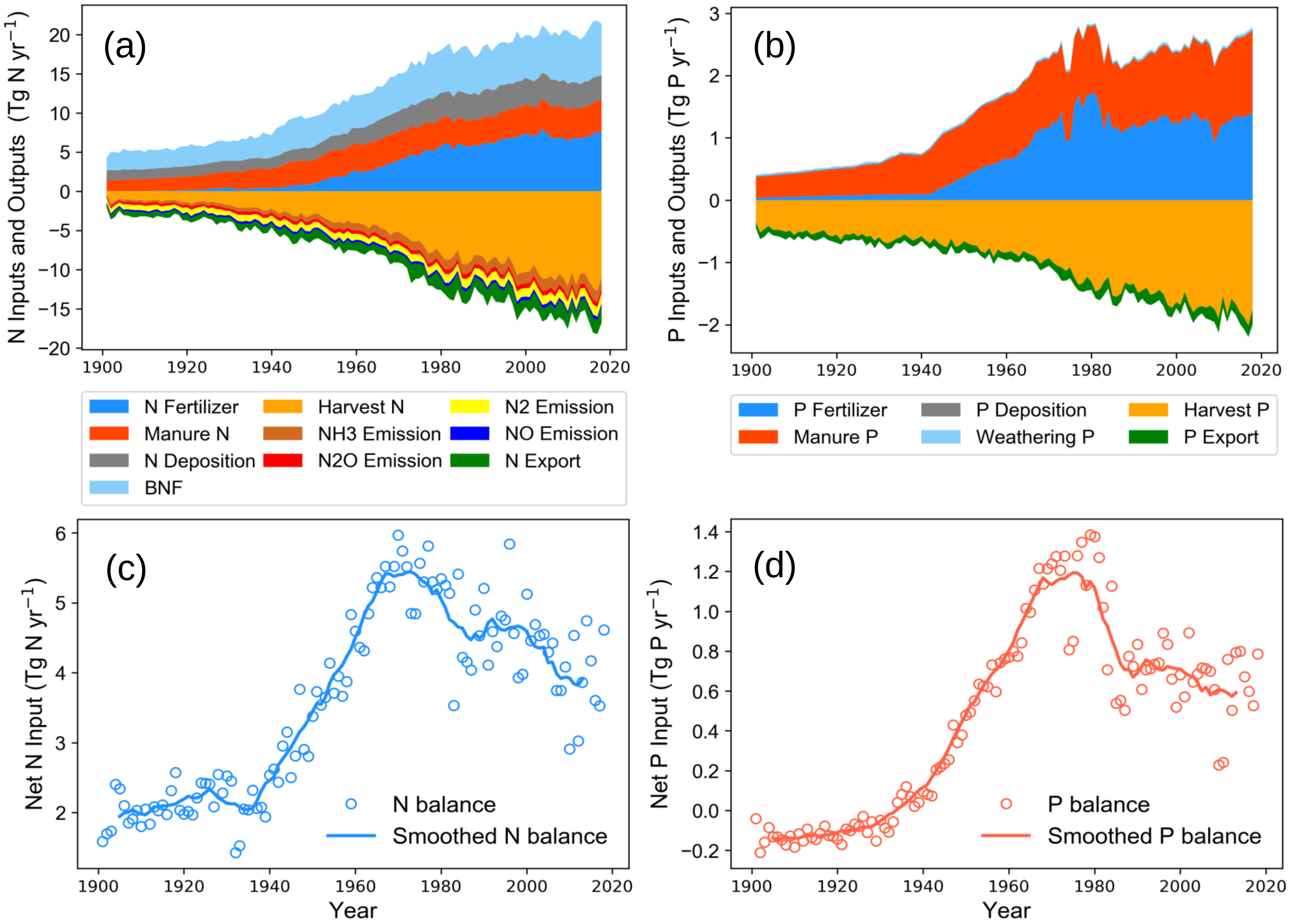
Fig. 6. The interannual variations of (a, d) simulated N exports, (b, d) simulated P exports, and (c, f) simulated TN:TP, DIN:DIP, and PN:PP molar ratio of riverine exports in the NORMAL and LEGACY scenarios during 1901-2018. The TN:TP-USGS in (c) refers to the monitored TN:TP ratio in Mississippi River flow from 1990 to 2018 at USGS site St. Francisville (USGS 07373420). The "no additional nutrient surplus in agricultural systems" condition started in 1991 in the LEGACY scenario. NH_4^+: ammonium; NO_3^-: nitrate; PON: particulate organic nitrogen; DON: dissolved organic nitrogen; DIP: dissolved inorganic phosphorus; PIP: particulate inorganic phosphorus; POP: particulate organic phosphorus; DOP: dissolved organic phosphorus; DIN: dissolved inorganic nitrogen (NH_4^+ and NO_3^-); PN: particulate nitrogen (PON); PP: particulate phosphorus (PIP and POP).

Fig. 7. Schematic representation of the mechanisms of the decline in the N:P loading ratio. Temporal changes in the quantities and N:P ratio of contemporary surplus and soil nutrient pools within terrestrial ecosystems (left panel) have led to corresponding changes in the relative proportions of contemporary and legacy N and P sources in aquatic ecosystems (right panel).


(a)
TN
Slope = -0.01
P-value = 0.15
TN export (Tg N/yr)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
1990
1995
2000
2005
2010
2015
(b)
TP
Slope = 0.001
P-value = 0.07
TP export (Tg P/yr)
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
1990
1995
2000
2005
2010
2015
(c)
TN:TP
Slope = -0.32
P-value < 0.01
TN:TP Molar Ratio
32.5
30.0
27.5
25.0
22.5
20.0
17.5
15.0
1990
1995
2000
2005
2010
2015
Year
(d)
1e11
Flow
Slope = -0.01
P-value = 0.46
Flow (m^3/yr)
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
1990
1995
2000
2005
2010
2015
Year


Leaf
Heartwood
sapwood
Fine root
Coarse root
Production
Harvest
Biomass C:N:P
C:N:P
Soil
P
N
AOM1
AOM2
Litter C:N:P
Deposition, Weathering
Fertilizer, Manure
Labile P
Secondary Mineral P
Occluded P
SMB1
SMR
SMB2
Microbe
NOM
DOM
PSOM
Soil Organic Matter C:N:P
NH_3,N_2, N_2O&NO
NO3-
NH4+
Deposition, Fixation
Fertilizer, Manure
Water
DIP
PIP
Wastewater
Settling
DOC
DON
DOP
Dissolved Organic Matter
POC
PON
POP
Particulate Organic Matter
Settling
NO3-
NH4+
N_2,N_2O &NO
Wastewater


N&P Fertilizer
N&P Manure
BNF
N&P Deposition
LEGACY scenario
NUE=100%
Harvest N&P
BNF
N&P Deposition
N gas emissions
Agricultural ecosystems
Natural ecosystems
Point source
N gas emissions
Nutrient Surplus
Contemporary source
Background source
N&P Export
Legacy source
Soil Legacy Nutrients
Nutrient inputs
Nutrient outputs


(a)
N Inputs and Outputs (Tg N yr^{-1})
20
15
10
5
0
−5
−10
−15
−20
1900
1920
1940
1960
1980
2000
2020
N Fertilizer
Manure N
N Deposition
BNF
Harvest N
NH3 Emission
N2O Emission
N2 Emission
NO Emission
N Export
(b)
P Inputs and Outputs (Tg P yr^{-1})
3
2
1
0
−1
−2
1900
1920
1940
1960
1980
2000
2020
P Fertilizer
Manure P
P Deposition
Weathering P
Harvest P
P Export
(c)
Net N Input (Tg N yr^{-1})
6
5
4
3
2
1900
1920
1940
1960
1980
2000
2020
Year
N balance
Smoothed N balance
(d)
Net P Input (Tg P yr^{-1})
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
−0.2
1900
1920
1940
1960
1980
2000
2020
Year
P balance
Smoothed P balance

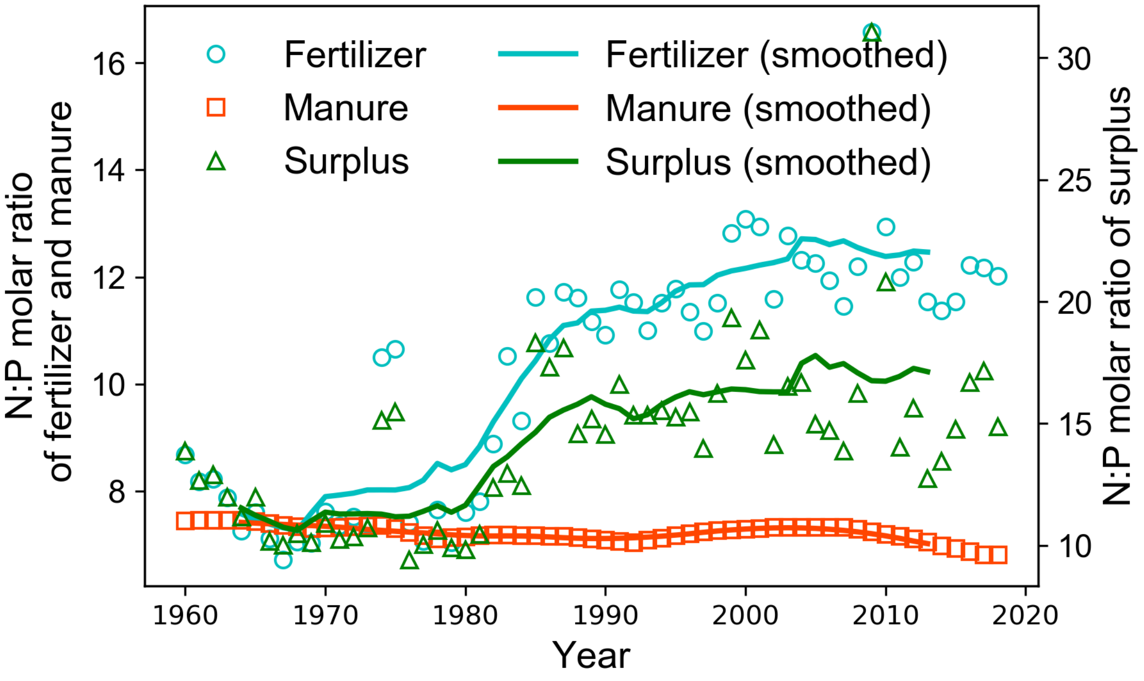
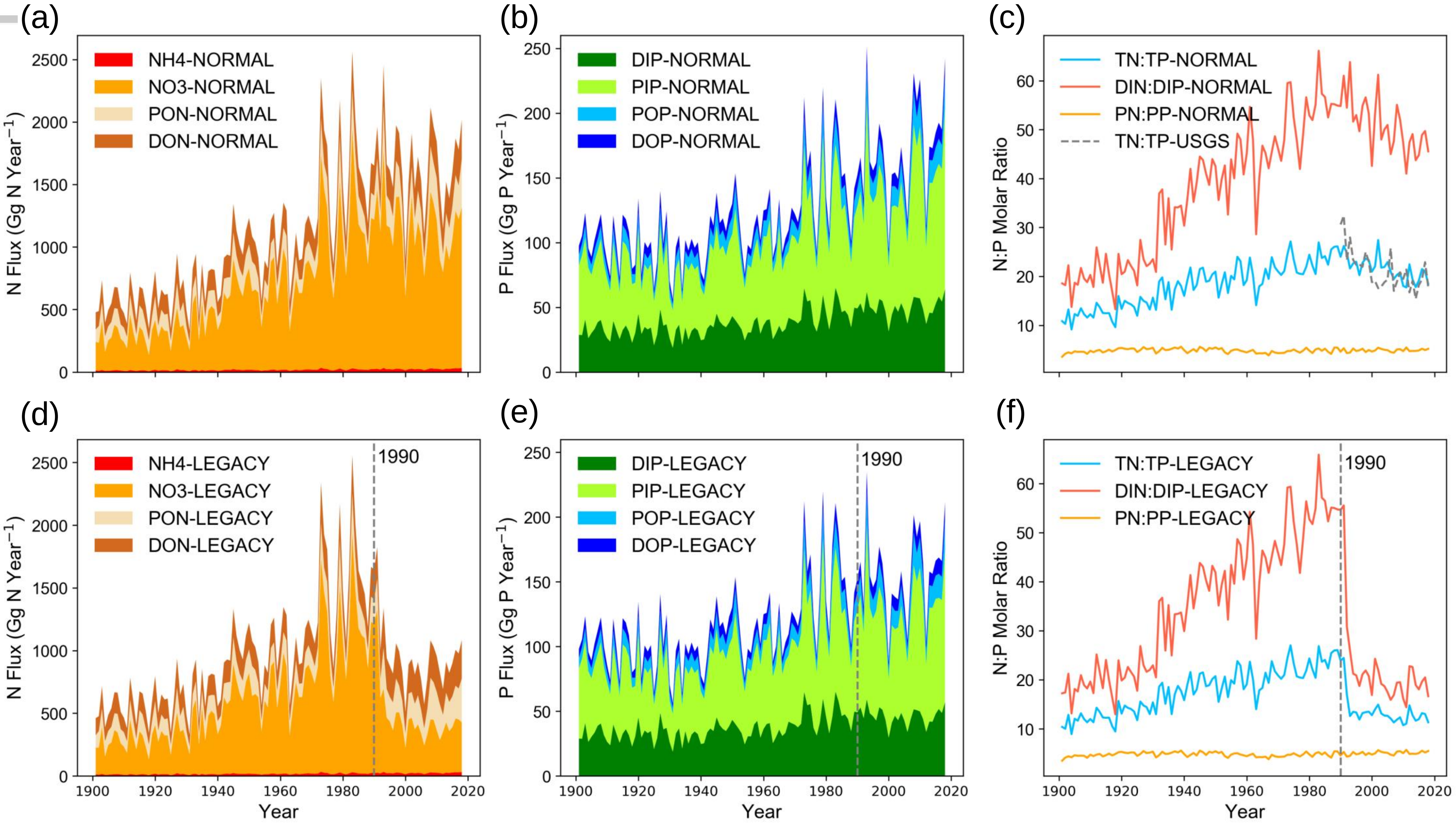
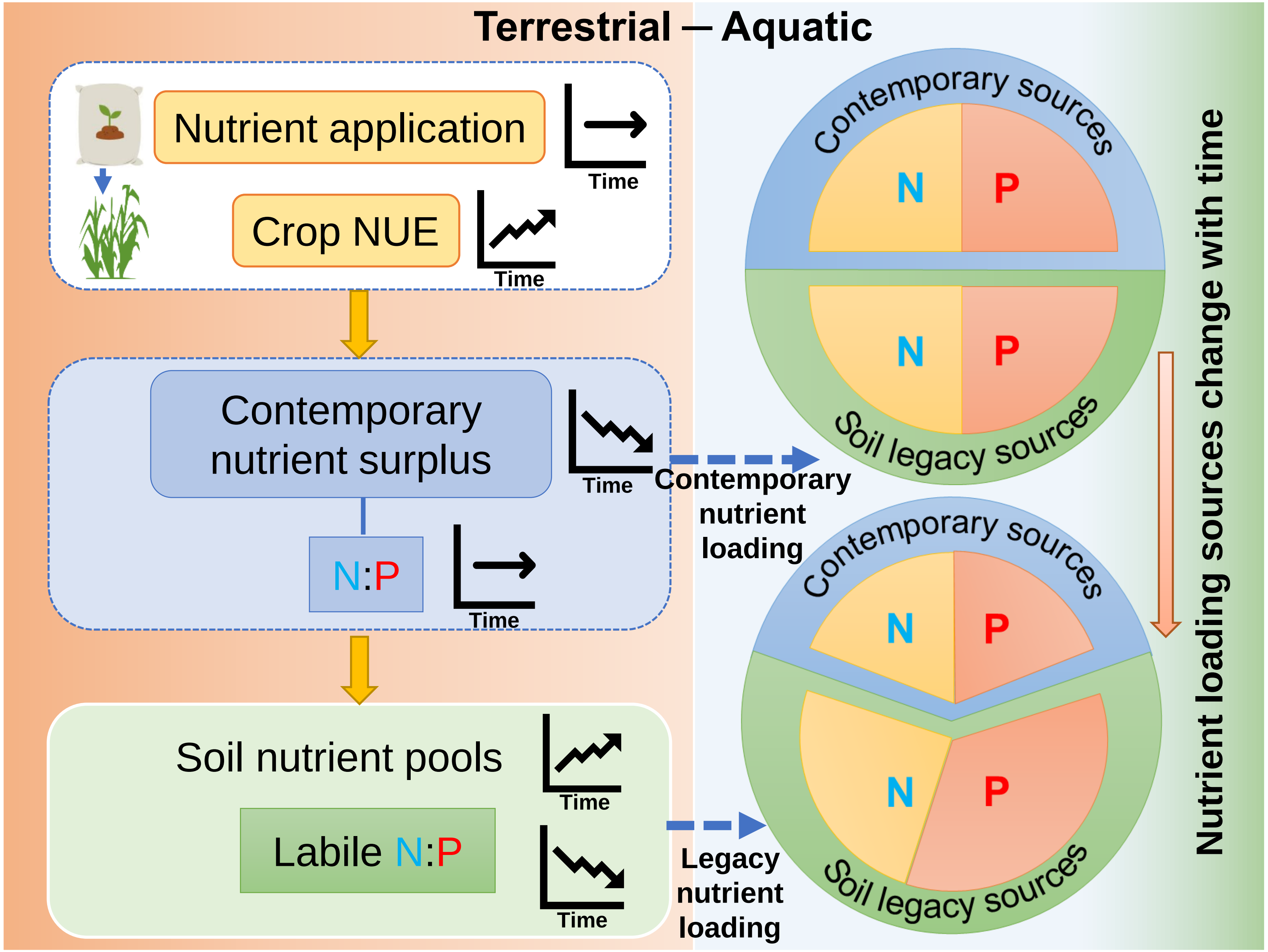

Fertilizer
Manure
Surplus
Fertilizer (smoothed)
Manure (smoothed)
Surplus (smoothed)
N:P molar ratio of fertilizer and manure
N:P molar ratio of surplus
Year
16
14
12
10
8
30
25
20
15
10
1960
1970
1980
1990
2000
2010
2020

Fig5.tif


(a)
NH4-NORMAL
NO3-NORMAL
PON-NORMAL
DON-NORMAL
N Flux (Gg N Year^{-1})
0
500
1000
1500
2000
2500
(b)
DIP-NORMAL
PIP-NORMAL
POP-NORMAL
DOP-NORMAL
P Flux (Gg P Year^{-1})
0
50
100
150
200
250
(c)
TN:TP-NORMAL
DIN:DIP-NORMAL
PN:PP-NORMAL
TN:TP-USGS
N:P Molar Ratio
10
20
30
40
50
60
(d)
NH4-LEGACY
NO3-LEGACY
PON-LEGACY
DON-LEGACY
1990
N Flux (Gg N Year^{-1})
0
500
1000
1500
2000
2500
Year
1900
1920
1940
1960
1980
2000
2020
(e)
DIP-LEGACY
PIP-LEGACY
POP-LEGACY
DOP-LEGACY
1990
P Flux (Gg P Year^{-1})
0
50
100
150
200
250
Year
1900
1920
1940
1960
1980
2000
2020
(f)
TN:TP-LEGACY
DIN:DIP-LEGACY
PN:PP-LEGACY
1990
N:P Molar Ratio
10
20
30
40
50
60
Year
1900
1920
1940
1960
1980
2000
2020


Terrestrial — Aquatic
Nutrient application
Time
Crop NUE
Time
Contemporary nutrient surplus
Time
N:P
Time
Soil nutrient pools
Time
Labile N:P
Time
Contemporary nutrient loading
Legacy nutrient loading
Contemporary sources
N
P
Soil legacy sources
Contemporary sources
N
P
Soil legacy sources
Nutrient loading sources change with time