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Principles, Modeling, and Implications

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Legacy Nutrient Dynamics at the Watershed Scale: Principles, Modeling, and Implications

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Abstract

Legacy nutrient accumulation from excess anthropogenic inputs has become a serious environmental issue in many watersheds worldwide. In this review, we provide a systematic overview of sources, legacy nutrient pools, watershed-scale water quality models, and agronomic and environmental implications of legacy nitrogen and phosphorus pools. Hydrological, biogeochemical, and anthropogenic factors exert interacting controls on legacy nutrient dynamics in soils, sediments, and vadose zone/groundwater. Most current watershed models do not effectively incorporate legacy

nutrient dynamics, while models that consider legacy effect often have high uncertainty in their treatment of legacy nutrient dynamics. In many intensively managed watersheds, legacy nutrients are a dominant and long-term (>10 years) source of nutrients to receiving waters, as well as a potentially important nutrient source for crop production. Many existing beneficial management measures have limitations for reducing legacy nutrient losses to surface waters due to appreciable differences in legacy nutrient forms, watershed storage locations, and temporal dynamics compared to those of contemporary nutrient inputs. Recognizing the importance of legacy nutrients is necessary for developing sustainable watershed nutrient management plans for future food, bioenergy, and water security. These plans require strategies to maximize use of legacy nutrient resources to minimize their loss to the atmosphere (e.g., N₂O emissions) and surface waters. Finally, this synthesis identified future research needs for improving the understanding, utilization, and mitigation of watershed legacy nutrient pools.



1. INTRODUCTION

Nitrogen (N) and phosphorus (P) are essential elements for all forms of life and critical for producing food, fiber, forage, and bioenergy (Billen et al., 2013; Gruber and Galloway, 2008; Sattari et al., 2012). Without anthropogenic N and P additions, the enormous rise in food and energy production that sustained the threefold growth in global population over the past century would not have been possible (Billen et al., 2013; Bouwman et al., 2010; Galloway et al., 2004; Gruber and Galloway, 2008). However, anthropogenic nutrient inputs have greatly exceeded nutrient uptake by crop and animal products. Estimated nutrient recovery efficiencies for global crop production decreased from 68% to 47% for N between 1960 and 2010, and from 60% to 44% for P between 1950 and 2000 (Bouwman et al., 2013; Lassaletta et al., 2014). Nutrient recovery efficiencies by livestock production were even lower for N (<15%) and P (<10%) between 1950 and 2000 (Bouwman et al., 2013). Coupled with increased N deposition from fossil fuel combustion ($\sim 40 \text{ TgN year}^{-1}$, Fowler et al., 2013), such inefficient utilization of nutrient resources results in surplus nutrients in various ecosystems. As nutrients surplus in watersheds, there is considerable potential for nutrient losses to waters (rivers and groundwater) and the atmosphere that may result in a wide range of negative environmental and ecological impacts (e.g., eutrophication, drinking water risk, biodiversity loss, climate change, tropospheric ozone production, etc., Bouwman et al., 2013; Erisman et al., 2013; Fowler et al., 2013; Gruber and Galloway, 2008; Tomich et al., 2016).

Surplus nutrients are subjected to long transit times (ranging from years to decades) through watersheds due to interactions within hydrological and biogeochemical cycles (Fowler et al., 2013; Hamilton, 2012; Meals et al., 2010). As a result, there is a continuous built-up of legacy nutrients within the watershed (Sharpley et al., 2013; Van Meter et al., 2016). Legacy nutrients are the surplus anthropogenic nutrient inputs from previous years that are temporarily stored within the watershed (e.g., soil, vadose zone, groundwater, and sediments) and have the potential to contribute nutrients to the atmosphere, biomass, and waters (Chen et al., 2015a; Sharpley et al., 2013; Van Meter et al., 2016). At the global scale, net P accumulation rates (deducing P loss to waters via runoff) in cropland soils increased from 1 TgP year⁻¹ in 1950 to 8 TgP year⁻¹ in 2000 with cumulative accumulation of about 210 TgP between 1970 and 2010 (Bouwman et al., 2013; Sattari et al., 2012). In addition, the global P accumulation rate in riverine sediments associated with massive dam-building rose from 0.68 TgP year⁻¹ in 1970 and 1.32 TgP year⁻¹ in 2000 (Maavara et al., 2015). Although watershed N inputs are somewhat balanced by denitrification and ammonia volatilization, growing evidence indicates net N accumulation occurring in soils, vadose zone, and groundwater. Compared to current levels of anthropogenic N inputs (i.e., ~220 TgN year⁻¹), some studies suggest that global terrestrial N sequestration may be on the order of 20–100 TgN year⁻¹ (Fowler et al., 2013; Galloway et al., 2004; Zaehle, 2013). In the Mississippi River Basin, 25–70 kgN ha⁻¹ year⁻¹ (a total of 3.8 ± 1.8 GgN year⁻¹) accumulated as soil organic N (SON) in croplands and 508 ± 237 kg ha⁻¹ in groundwater during the 1957–2010 period (Van Meter et al., 2016). Legacy nutrients are of increasing concern due to their considerable magnitude and more dispersive spatial distributions compared to current anthropogenic nutrient additions, and they have significant environmental and agronomic implications (Chen et al., 2015a; Meals et al., 2010; Powers et al., 2016; Rowe et al., 2016; Van Meter et al., 2016).

Legacy N or P can be released and remobilized, acting as a continuing source to downstream waterbodies for years, decades, or even centuries (Chen et al., 2014b; Haygarth et al., 2014; Meals et al., 2010; Sanford and Pope, 2013; Sharpley et al., 2013; Van Meter et al., 2016). Nutrient fluxes contributed from legacy sources are increasingly recognized as a major cause of limited water quality improvement after implementation of long-term nutrient management reduction measures in many watersheds. Examples include the Mississippi River, Chesapeake Bay, North Sea, Baltic Sea, and the Lake Erie basin, where conservation practices were

implemented 20–30 years ago to mitigate nutrient pollution and eutrophication (Bouraoui and Grizzetti, 2014; Dubrovsky and Hamilton, 2010; Haygarth et al., 2014; Jarvie et al., 2013; Van Meter and Basu, 2017; Worrall et al., 2009). Apparent failure of water quality initiatives due to legacy nutrient contributions in many watersheds has led to public questioning of the necessity for significant economic investments in water quality improvement programs and regulatory agency reevaluation of nutrient management standards, measures, and guidelines (Jarvie et al., 2013; Sanford and Pope, 2013; Sharpley et al., 2013). Furthermore, field and laboratory experiments both indicate that cropland soils receiving long-term (>10 years) N fertilization from manure or urea (especially those with high application rates) had substantially larger cumulative N₂O emissions than those with no historical N inputs (LaHue et al., 2016; Pearce, 2016). Although legacy nutrient pools can serve as a long-term source to waters and the atmosphere, those residing in the soil zone have a considerable potential for supporting crop growth. Many long-term field studies indicated that crops can recover legacy P from long-term overapplication of fertilizer and manure P with no reduction in crop yields for several years to decades after cessation of P fertilization (Jarvie et al., 2013; Rowe et al., 2016; Sharpley et al., 2013). An isotopic tracing study in France also observed that 61%–65% of the ¹⁵N fertilizer applied in 1982 was taken up by sugar beets and wheat in the following 30 years (Sebilo et al., 2013). From the perspective of human impacts on the environment, legacy nutrient release or remobilization has the potential to contribute considerable future nutrient fluxes to waters and the atmosphere (Chen et al., 2014b). Given the expected rising demands for food and energy due to increasing population, changing human diets, and standard of living (Lassaletta et al., 2014), global requirements for nutrient resources are destined to increase in the future (Gruber and Galloway, 2008). Future availability of P fertilizers poses a particular challenge as rock phosphate resources may be depleted in the next century (Maavara et al., 2015; Sattari et al., 2012). Therefore, minimizing legacy nutrient losses to the environment and maximizing recovery from soils for future food, bioenergy, and environment security are critical issues requiring informed management of legacy nutrients.

This chapter presents an overview of legacy N and P dynamics at the watershed scale from both environmental and agronomic perspectives. The primary objectives of this work are to: (1) explore the principles of legacy nutrient dynamics, including storage pools, sources, and magnitudes,

as well as controls for accumulation and release/remobilization; (2) present available watershed modeling approaches for quantifying legacy nutrient dynamics; (3) demonstrate agronomic and environmental implications of legacy nutrient pools, including recovery for food production and potential impacts on nutrient pollution; and (4) highlight future research needs for improving the understanding, utilization, and mitigation of legacy nutrient pools. This synthesis provides agronomic and resource managers with important information on an often overlooked aspect for managing nutrient dynamics at the watershed scale.



2. PRINCIPLES OF LEGACY NUTRIENT DYNAMICS AT THE WATERSHED SCALE

2.1 Drivers of Building Up Legacy Nutrient Pools

For a given watershed, the nutrient magnitudes of transport, transfer, storage, and removal within and among various landscapes through the terrestrial–aquatic continuum are dependent on nutrient input–output balance and regulated by a range of hydrologic and biogeochemical processes (Figs. 1 and 2). Therefore, built-up of legacy nutrient pools in various landscapes is mainly resulted from excessive anthropogenic nutrient inputs, hydrologic, and biogeochemical legacy effects.

2.1.1 Excessive Anthropogenic Nutrient Inputs

To meet the energy and food demands of a growing and increasingly urbanized population, anthropogenic nutrient inputs have been dramatically increased (Fowler et al., 2013; Galloway et al., 2008) with low nutrient use efficiencies in many regions (Bouwman et al., 2013; Elser and Bennett, 2011; Fageria and Baligar, 2005). Studies conducted for many watersheds across the world (Cui et al., 2013; Goyette et al., 2016; Grizzetti et al., 2012; Howarth et al., 2012; Swaney et al., 2012; Van Meter et al., 2017) indicated that synthetic fertilizer application and fossil fuel combustion are major sources for total anthropogenic N inputs. Fates of anthropogenic N input usually include denitrification (e.g., 35%–44% in soils and 11%–20% in rivers, Groffman, 2012; Seitzinger et al., 2006), loss via riverine export (average 25%, Howarth et al., 2012), and storage (10%–20%) in landscapes. The synthesis of N mass balance studies for watersheds across the world shows a mean N retention of approximately 50 (1.1–229) kgN ha⁻¹ year⁻¹ during 1940–2008 period (Van Meter et al., 2016). Studies also demonstrated a growing N saturation responds

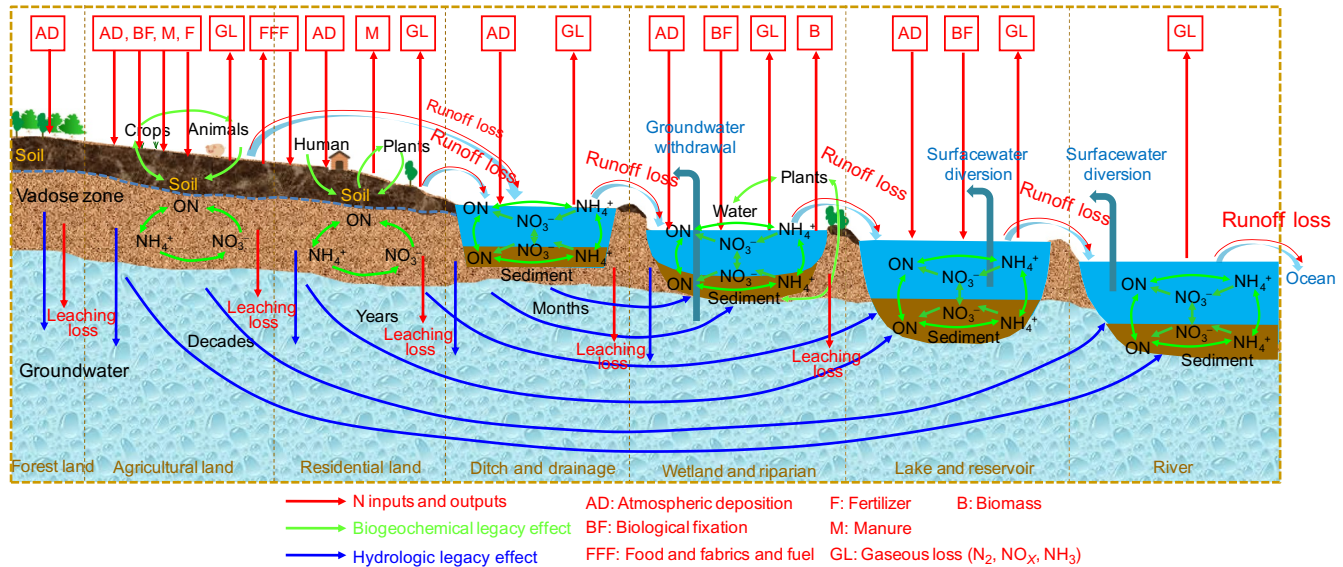


Fig. 1 Conceptual representation of anthropogenic factors, hydrologic and biogeochemical processes influencing legacy nitrogen dynamics in various landscapes at the watershed scale.

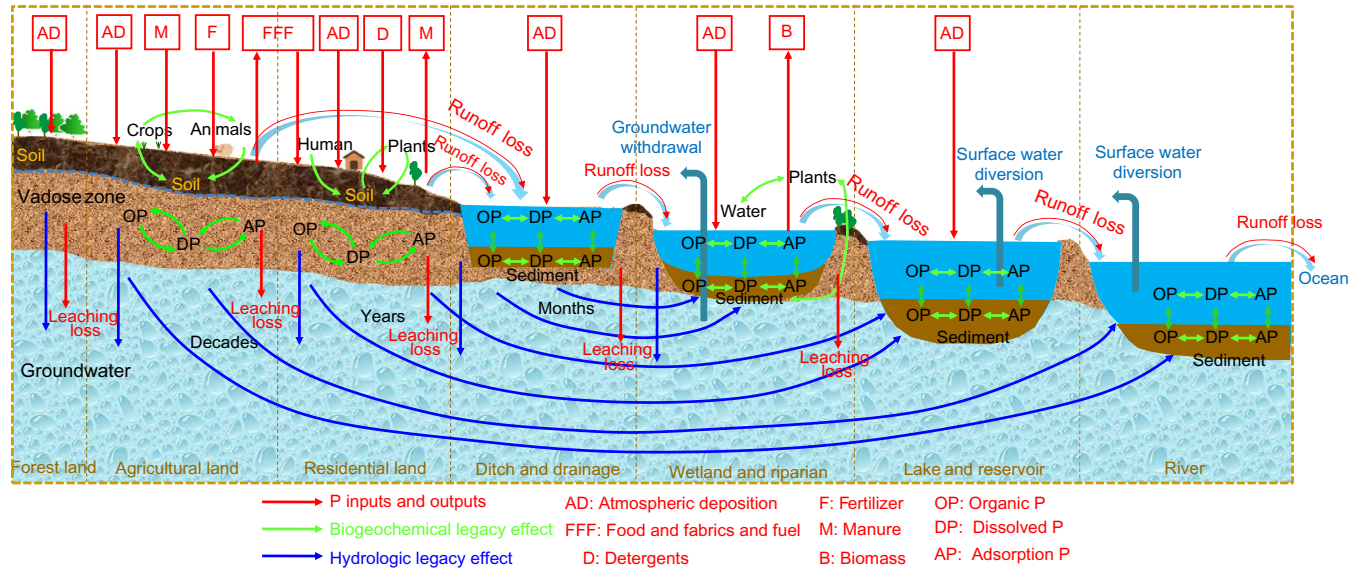


Fig. 2 Conceptual representation of anthropogenic factors, hydrologic and biogeochemical processes influencing legacy phosphorus dynamics in various landscapes at the watershed scale.

to excessive N inputs in many highly managed watersheds (Swaney et al., 2012; Tessier and Raynal, 2003). Therefore, many N balance studies conducted in many countries and regions (Chen et al., 2014a; Drury et al., 2011; Van Meter et al., 2016; Worrall et al., 2015) suggested a very large and ongoing storage of N in terrestrial ecosystem.

In terms of P, studies conducted for many watersheds across China, United States, and Europe (Chen et al., 2015b; Goyette et al., 2016; Han et al., 2012; Hong et al., 2012; Russell et al., 2008) indicated that synthetic fertilizer application and food and feed import are major sources for total anthropogenic P inputs over the past several years to decades. Due to lack of gaseous loss pathways, riverine export is the major conduits of surplus P transfer out of a given watershed to the downstream fresh and coastal waters. Although riverine export flux is increased dramatically with increasing anthropogenic inputs, riverine export fraction of anthropogenic P input usually shows relatively small. For example, a meta-analysis indicated that on average only 3.6% of net anthropogenic P input would be exported by riverine discharge for 158 watersheds in the world (Zhang et al., 2015). As a result, more than 90% of annual anthropogenic P input on average do not appear in riverine fluxes but rather must be potentially stored or retained in terrestrial and aquatic landscapes for building up as legacy P pools in many studied watersheds (Chen et al., 2015b, 2016c; Goyette et al., 2016; Han et al., 2012; Russell et al., 2008; Zhang et al., 2015).

2.1.2 Hydrologic Legacy Effect

Delivery of nutrient from sources (i.e., agricultural and residential systems) through different landscapes (e.g., ditch/drainage, wetland, and riparian zone) to receiving waters (i.e., lake/reservoir and river) is mainly stimulated by surface and subsurface hydrological pathways (Figs. 1 and 2). Nutrient cycling in various landscapes is also mediated by the hydrologic residence times in different landscape compartments (Hamilton, 2012; Sharpley et al., 2013). The hydrologic legacy effect can be recognized as the travel time required for nutrient delivery from the sources to the receiving waters along the hydrologic pathways (Chen et al., 2014b; Van Meter et al., 2016). It has been widely observed that hydrologic travel times throughout the watershed range from days to months for surface runoff and from months to years or decades for subsurface flow (Phillips et al., 2003; Tesoriero et al., 2013; Wang et al., 2012). The conveyance capacity of dissolved and particle nutrient delivery through landscapes is limited by the entrainment and transport capacity of the water flow, with reductions in flow

velocities in areas of water flow separation and divergence, increasing travel times and net nutrient retention.

Nutrient delivery via the fluvial system (e.g., rills, gullies, artificial drainage channels and tile lines, and river) has a relative low hydrologic travel time to downstream outlet bypassing the many sinks that exist. However, imported nutrient by direct wastewater discharge (i.e., point source pollution) as well as by surface runoff in fluvial systems would be partially deposited onto sediments due to water flow separation and hydraulic reduction (Chen et al., 2015c). The fluvial reaches having wide channel or bending or hydrophyte are favor of slowing flow and increasing nutrient depositions as well as uptake by biomass. The physical nutrient deposition in fluvial system is mainly occurring in the low-flow regime, while deposited nutrient would remobilize during high-flow regime (Jarvie et al., 2012). Fluvial storage of nutrient in surface bed sediment can be relatively short term, i.e., until the next high-flow event remobilizes them, with residence times of <1 year in many river systems (Collins and Walling, 2007a,b; Owens et al., 2001). However, flooding events would induce carried nutrient and sediment entering adjacent inundated floodplain or riparian, resulting long residence time (years to decades) for retained nutrient move through the fluvial system (Hamilton, 2012; Sharpley et al., 2013).

For lentic waters (i.e., wetland, riparian zone, lake, and reservoir) having long hydrologic residence times, the deposition of input nutrient can be critical for accumulating considerable sediment legacy nutrient pool. The lentic waters generally connect with fluvial systems and can trap sediments and associated nutrient quickly by decreasing hydraulic power and consequent increasing their depositions. For shallow lentic waters (i.e., wetlands, riparian buffers, and shallow lakes), detritus accumulation of vegetation material and sediment is usually the most important process for accumulating nutrient and plays relative higher contribution to accumulate nutrient pools in sediments of wetland than that of riparian buffers and shallow lakes (Fisher and Acreman, 2004; Hefting et al., 2005). For deep lentic waters (i.e., deep lakes and impoundments/reservoirs), physical deposition with particles onto sediment is a primary mechanisms for building up legacy nutrient pool. As the sediment is retained in deep bottom of standing waters that is hardly disturbed by the water movement on the top layers of lakes/reservoirs in general, it will cost much long times for nutrient to be released physically (Bloesch, 1995; Mei et al., 1997).

For nutrient delivery by surface runoff, the carrying capacity of nutrient through terrestrial-aquatic systems usually decreases with decreasing

topographic altitude, resulting in prolonging residence times and net deposition of particle nutrient in lowland soils and sediments. Due to distributed flat and expansively locations from uplands to lowlands along the surface runoff converging pathway, there is a dramatic increase in water and sediment retention times, promoting the accumulation of particulate nutrient or uptake of nutrient by biota. For example, locations where slope or channel geometry serves to lower water velocity (e.g., at the foot of hillslopes) and promotes sediment deposition are particular hot spots for particle nutrient accumulation (Sharpley et al., 2013). The episodic nature of surface runoff due to rainfall and thawing events induces carried nutrient experiencing transport–retention–remobilization alternant cycles before finally entering downstream waters, which prolongs sediment and nutrient travel time. The sediment and nutrient can accumulate rapidly (e.g., vertical accretion on floodplains) but which require much higher energy events or longer time frames to remove (e.g., through channel or bank erosion), referring to as “fast in–slow out” (Trimble and Fehr, 2010).

Dissolved nutrient (particular for nitrate) delivery via subsurface hydrologic pathway has a very long travel time through the watershed. Previous studies indicated that the residence time of shallow and deep groundwater can range from several months to years and from several years to decades in many regions, respectively (Lindsey et al., 2003; Tesoriero et al., 2013). Dissolved nutrient (with particular for P) infiltration along the soil profile is subjected to long travel time due to sorption and adsorption dynamics (Meals et al., 2010). For areas having thick unsaturated zones, water and solute movement through the unsaturated zone can also be protracted, resulting in long travel time between the land surface and underlying groundwater (McMahon and Böhlke, 2006). The movement of water through subsurface flow systems is better characterized by a distribution of transit times and is typically skewed with long tails, approximating a power-law distribution (Cardenas and Jiang, 2010; Godsey et al., 2010; Stewart et al., 2010). In other words, there is typically longer travel time of dissolved nutrient than that of the groundwater mean transit time. In fact, water and solute travel times in watersheds have been shown to follow an approximate power-law function, thus retaining a long chemical memory of past inputs (Kirchner et al., 2000, 2001).

2.1.3 Biogeochemical Legacy Effect

During nutrient delivery processes from sources to watershed outlet through various landscapes, nutrient is subjected to a range of biogeochemical

transformations of nutrient among different chemical forms and transports among soil/sediment, water, and biota in each landscape (Figs. 1 and 2). Biogeochemical nutrient legacy effect arises from the times elapsed due to biogeochemical nutrient cycling within or among soil/sediment, biota, and water before complete removals from a given landscape via gaseous emission, plant uptake, and water flow. Nutrient biogeochemical residence times vary in different systems, with surface soils ranging from <10 to ~70 years, aquatic sediments ranging from <10 years to ~100 years (Hamilton, 2012).

Common biogeochemical processes for N recycling in various ecosystems include: litter or plant root decomposition (Hättenschwiler et al., 2005; Knorr et al., 2005); soil organic matter ammonification (Möbius, 2013; Schimel and Bennett, 2004); nitrification (Di et al., 2009; Yan et al., 2009); denitrification, uptake by plants and soil microbial community (Jones et al., 2005; Seitzinger et al., 2006). Immobilization and mineralization dynamics are critical for accumulation legacy N in soils. Organic forms of N can be converted into simpler, soluble form that can be taken up by biota or denitrified by microorganism. Disturbance (e.g., cultivation) of the soils will break up aggregate structures that provide physical protection, results in increasing in oxidation and mineralization rates. After the initial balance of immobilization and mineralization, SON starts to accumulate in response to the continuing addition of root matter and other crop residues to soil (Van Meter et al., 2016). As a result, the turnover of N within plant–soil–microorganism system will cost a considerable time, resulting a long residence time of N for decades in croplands (Sebilo et al., 2013). The cycling of N legacy pool in sediments of wetlands and riparian systems as well as lakes/reservoirs also introduces residence times for years to decades (Jeppesen et al., 2005; Søndergaard et al., 2007). For sediments in lentic waters, deposited organic matters and detritus accumulation of aquatic organism are not easy for decomposition in water-logged sediments, which results in long residence time and formation of nutrient legacy pool (Avnimelech and McHenry, 1984; Zhu and Ehrenfeld, 2000).

Common P biogeochemical processes along the land–freshwater continuum include: mineral precipitation and dissolution (House, 2003; Pierzynski and McDowell, 2005); sorption and desorption (House et al., 1998; Reddy et al., 1999; Sharpley et al., 2012); organic P mineralization (Condrón et al., 2005; Jakobsen et al., 2005), uptake by biota and microorganisms (Jarvie et al., 2002), and molecular diffusion. These biogeochemical processes drive P cycles within and among soil/sediment, water, and biota,

resulting in long P turnover times that is favor of P accumulation. The unique function of P biogeochemistry is that its high sorption (particularly iron oxyhydroxides) or coprecipitation (particularly calcium carbonate) capacities with minerals as well as by clay particles. The sorption potential of P by most soils and sediments is at least several orders of magnitude greater than the corresponding concentration of P in solution (Frossard et al., 2000), which reduces P available for crops/plants uptake as well as loss via hydrological pathways. Consequently, P sinks or storages are ubiquitous in natural ecosystems, resulting in continuously accumulation of P in various landscapes before the P sorption saturation (when the release of sorbed P to solution occurs, Nair, 2014).

In the cropland and wetland/riparian zone, partial nutrient uptake by crops/plants can return to soil/sediment with litter withdraw or death, then available nutrients can be reutilized by crops/plants after degradation and mineralization. Such internal cycling would introduce long residence time for retaining nutrients in each landscape. For example, such residence time for nutrient can range from months to years in wetland depending on plant types (e.g., perennial and therophyte) (Hefting et al., 2005).

2.2 Distributions of Watershed Legacy Nutrient Pool

Overall, hydrological, biogeochemical, and anthropogenic factors exert interacting controls on the built-up of legacy nutrient pools across watershed landscapes. The variable hydrologic and biogeochemical residence times in different landscapes along the terrestrial–aquatic continuum give rise to distinct spatial and temporal patterns of legacy nutrient pools (Chen et al., 2014a; Sharpley et al., 2013). Legacy N hot spots always occur in large watersheds with longer time for groundwater updates and areas with longer time for N biogeochemical cycling (Worrall et al., 2015). The delivery of inorganic form N pool by hydrological pathway is mainly via slower flows, and the relatively long residence time will result in long-term N accumulation in vadose zone and groundwater (Costa et al., 2002; Scanlon et al., 2008). Low organic N transformation rates and low denitrification rates in watershed will promote N accumulation in soil, sediment, and groundwater. While the legacy P hot spots can occur where there is a dramatic change in water and sediment retention times, promoting the sedimentation and accumulation of P or uptake of P by biota (Hamilton, 2012; Sharpley et al., 2013). In large lentic water ecosystems, the positioning of hot spots can be dependent on a mosaic of physical disturbance and

biogeochemical processing mechanisms. Transitional landscapes (e.g., riparian or wetland) between terrestrial and aquatic environments also provide important areas of nutrient accumulation.

From the agronomic and environmental perspectives, soils, sediments, and vadose zone/groundwater across watershed landscapes are three major locations for accumulating legacy nutrient pools. We review the magnitudes of legacy nutrient pools in soil, sediment, and vadose zone/groundwater (Table 1) and examine the principles of these three hot spots of legacy nutrient dynamics in the following sections.

2.2.1 Legacy Nutrient Dynamics in Soils

Cropland soil that usually receives the majority of watershed anthropogenic nutrient inputs by fertilizer and manure applications is a major hot spot for building up legacy nutrient pool (Table 1). Excessive applications of fertilizer and manure have been persistent for decades in many regions across the world with relatively low use efficiencies of applied N (<50%) and P (<20%) in the first year (Bouwman et al., 2013; Fageria and Baligar, 2005). As a result, cropland soils used for agricultural row crops or livestock production often accumulate surplus nutrient in soils (Chen et al., 2014b; McLauchlan, 2006; Van Meter et al., 2016). The surplus N retained in agroecosystems for decades was also realized by the elevated upper layer soil total nitrogen or organic matter levels over the past decades (Van Meter et al., 2016; Yan et al., 2016). Several tracer studies with isotopically labeled fertilizer N suggested that 40%–60% of the applied fertilizer N is incorporated into the soil organic matter, which result in the formation of organic N pool (Jenkinson et al., 2004; Sebilo et al., 2013). Some urban and suburban areas also retained 25%–95% of N inputs in residential soils (Groffman et al., 2004; Whitall and Paerl, 2001). Comparing soils in forest and agricultural land, agricultural soil total P concentrations can range from 2- to 10-fold greater than that in forest, implying a legacy of historical P fertilization (Nash and Hannah, 2011; Vitousek et al., 2009).

SON has been recognized as the largest N legacy pool in soil across landscapes through immobilizing the residual N by soil microbes as soil organic matter (Galloway et al., 2003; Van Meter et al., 2016). The transformation efficiency of soil microbes is affected by various factors, such as the species distributions of microflora, available C content, vegetation, climate, soil characteristics, and land-use patterns (Billen et al., 2013; Chen et al., 2014c). Formation of organic N depends on activity and biomass of soil microflora and exoenzyme production (Zhu et al., 2013). The addition

Table 1 Summary of the Magnitudes of Legacy Nutrient Pools in Soil, Sediment, and Vadose Zone/Groundwater Study Area

Study Area	Legacy Pools	Nutrient	Studied Results		References
			Time	Magnitude	
Cultivated land in the Chaohu watershed, southeast China	Soils	P	1978–2012	0.0049–0.65 Tg	Jiang and Yuan (2015)
Uncultivated land in the Chaohu watershed, southeast China				0.0021–0.13 Tg	
Soil in the Illinois River in northeast Oklahoma and northwest Arkansas (4440 km ²)		P	1925–2015	0.15–0.23 Tg	Mittelstet and Storm (2016)
Soil in the Eucha-Spavinaw watersheds in northeast Oklahoma and northwest Arkansas (1100 km ²)				3.61×10^{-2} – 4.98×10^{-2} Tg	
Arable land in the UK (45,660 km ²)		P	1993	8.68×10^{-2} Tg	Withers and Bhadeshia (2001)
Managed grassland in the UK (67,690 km ²)				8.12×10^{-2} Tg	
Intensively farmed arable soils in China		P	1980–2007	Over 31 Tg	Li et al. (2011)
Global croplands		P	1965–2007	815 Tg	Sattari et al. (2012)
Agricultural–urban landscapes in the Yangtze Basin, China		P	1970–2010	31.74 Tg	Powers et al. (2016)
Surficial (0–10 cm depth) soil in the northeast (P-enriched) area in the Blue Cypress Marsh Conservation Area in Florida (80 km ²)		TP	2000	55.9 kg ha ⁻¹	Bostic et al. (2010)
Surficial (0–10 cm depth) soil in the northwest (unenriched) area in the Blue Cypress Marsh Conservation Area in Florida (80 km ²)				43.08 kg ha ⁻¹	
The northeast (P-enriched) area in the Blue Cypress Marsh Conservation Area in Florida (80 km ²)		TN	2000	1.97×10^3 kg ha ⁻¹	Bostic et al. (2010)
The northwest (unenriched) area in the Blue Cypress Marsh Conservation Area in Florida (80 km ²)				1.86×10^3 kg ha ⁻¹	

Croplands in the entire terrestrial land of China ($1.2 \times 10^6 \text{ km}^2$)	Organic N	1980–1990	$34 \pm 20 \text{ Tg}$	Gu et al. (2017)
Grasslands in the entire terrestrial land of China ($3.9 \times 10^6 \text{ km}^2$)		1980–2010	$21\text{--}12 \text{ Tg}$	
Cropland soil in the Mississippi River Basin ($2,981,076 \text{ km}^2$)	Organic N	1980–2010	142 Tg	Van Meter et al. (2016)
	N	1957–2010	$(2.01 \pm 0.95) \times 10^{-4} \text{ Tg}$	
Forested soils in European forests	N	1960–2000	188 kg ha^{-1}	De Vries et al. (2006)
The Thames basin (9948 km^2)	Organic N	1973–2008	3.13 Tg	Worrall et al. (2015)
Seine basin, Europe ($71,700 \text{ km}^2$)	N	2000	40.15 kg ha^{-1}	Billen et al. (2009)
Somme basin, Europe (5570 km^2)			46.30 kg ha^{-1}	
Scheldt basin, Europe ($19,860 \text{ km}^2$)			89.05 kg ha^{-1}	
The groundwater beneath the River Thames Drainage Basin in the UK (9948 km^2)	Groundwater Nitrate	2000–2004	$1571 \pm 608 \text{ Mg}$	Worrall et al. (2015)
Global deep groundwater	Nitrate	1900–2000	376 Tg	Bouwman et al. (2013)
The groundwater across the Mississippi River Basin ($2,981,076 \text{ km}^2$)	Nitrate	1800–1860	$0.36 \pm 0.18 \text{ Tg}$	Van Meter et al. (2017)
		1860–1920	$0.75 \pm 0.27 \text{ Tg}$	
Groundwater in a section of West Bear Creek, North Carolina, USA	Nitrate	2005–2006	$<0.98 \times 10^{-10}\text{--}0.25 \times 10^{-7} \text{ Mg}$	Kennedy et al. (2009)
Groundwater in the Chesterville Branch watershed, Atlantic coastal plain, Maryland	Nitrate	1990–1992	$2.70 \times 10^{-9}\text{--}8.60 \times 10^{-9} \text{ Mg}$	Böhlke and Denver (1995)
Groundwater in the Morgan Creek watershed, Atlantic coastal plain, Maryland			$<0.56 \times 10^{-10}\text{--}0.53 \times 10^{-8} \text{ Mg}$	
Groundwater in the Cohansey River Basin, New Jersey coastal plain	Nitrate	1995–1996	$0.56 \times 10^{-10}\text{--}0.16 \times 10^{-7} \text{ Mg}$	Modica et al. (1998)

Continued

Table 1 Summary of the Magnitudes of Legacy Nutrient Pools in Soil, Sediment, and Vadose Zone/Groundwater—cont'd

Study Area	Legacy Pools	Nutrient	Studied Results		References
			Time	Magnitude	
Ten Basins, China	Sediments	TP	2003–2004	Below detection limit— 5.327 g kg ⁻¹	Yang et al. (2017)
Han River, Korea		TP	1994–1998	0.580–1.450 g kg ⁻¹	Kim et al. (2004)
Tigris River, Turkey		TP	2009	0.988–2.053 g kg ⁻¹	Varol and Şen (2012)
Global river damming	TP		1970	0.68 Tg	Maavara et al. (2015)
			2000	1.30 Tg	
	RP		1970	0.28 Tg	
			2000	0.56 Tg	
Upper Chain of Lakes, Florida, USA	P	2007	0.59 × 10 ⁻² Tg	Belmont et al. (2009)	
Lake Istokpoga, Florida, USA			0.25 × 10 ⁻² Tg		
Lake Okeechobee in Northern Everglades Ecosystem	P	1998	3.64 × 10 ⁻² Tg	Fisher et al. (2001)	
East Taihu Lake, China	TN	1993	3.77 × 10 ⁻² Tg		
Dam-impounded Lake Kariba (Zambia/Zimbabwe)	TP	2007–2009	0.76 × 10 ⁻² – 3.40 × 10 ⁻² Tg	Kunz et al. (2011)	
	TN		0.022–0.12 Tg		

of organic matters can increase labile carbon and pH which stimulated microbial activity (Nelissen et al., 2015). By maintaining the pH in an optimal range, buffering the nutrient supply, adsorbing metabolites that are inhibitory to microbial growth, providing protection from desiccation and grazing through increased aggregation, clay minerals could promote microbial growth, which simulated inorganic N immobilization (Chen et al., 2014c). The immobilization of organic N is also affected by the C:N ratio, with a C:N ratio $>25:1$ simulate immobilization and $<25:1$ simulate mineralization (Chen et al., 2014c). A more recent study showed that depositional-position soil profiles contain up to three times more N than soil profiles in the eroding positions, which emphasizes the influence of soil erosion on N accumulation (Berhe and Torn, 2017). Lower levels of microbial biomass are always observed in arable compared to undisturbed forest and grassland soils, which is mainly due to the cultivation-induced losses of organic matter (Nsabimana et al., 2004). However, when the immobilization and mineralization are equalized, SON can accumulate in response to the continuing addition of root matter and other crop residues or manure to soil (Van Meter et al., 2016; Wang et al., 2001).

Depletion of soil legacy N pools is mainly dependent on gaseous and hydrological losses and uptake by plants. Since soil legacy N is mainly stored as organic N (Van Meter et al., 2016), SON mineralization is critical process controlling the depletion of soil legacy N pools. Mineralization of SON is affected separately and/or interactively by a wide range of factors, including soil organic C and total N contents, microbial biomass C and N contents, and the C/N ratio (Booth et al., 2005; Zhu et al., 2013). Both mineralization and immobilization are carried out by a wide array of microorganisms aerobes, anaerobes, fungi, and bacteria, and the ratio of available of C and N in the material (Chen et al., 2014c). Both drainage and tillage practices can influence the activity of soil organisms and decrease fungi-to-bacteria ratios through regulating soil aeration condition, resulting in lower N immobilization and higher mineralization of soil organic matter (Booth et al., 2005; Kopáček et al., 2013a,b; Myrold and Posavatz, 2007). In addition, artificial regulations such as soil liming and priming effects of synthetic N fertilizers can increase soil pH, decrease the fungi-to-bacteria ratio in soils, and further increase organic N mineralization (Högberg et al., 2007; Kopáček et al., 2013a,b), leading to the substantial SON mineralization. Followed by SON mineralization, nitrification will transform N into nitrate for further uptake by plants and denitrifying and leaching. Soil ammonia emission usually occurs in arid systems, whereas

more denitrification common happens in waterlogged soils where anaerobic conditions prevail, such as in paddy fields (Billen et al., 2013). A meta-analysis summarized that croplands with high N application rates and poor soil drainage lead to high denitrification rates, which could efficiently reduce soil N legacy pool (Hofstra and Bouwman, 2005).

Enormous built-up of legacy P in soils across various landscapes is mainly associated with the natural of high sorption capacity of phosphate on iron (Fe)- and aluminum (Al)-oxide and oxyhydroxide phases (Liu et al., 2014). Unlike the Al-oxides/oxyhydroxides, Fe-oxides/oxyhydroxides are subject to reductive dissolution under anoxic conditions, and thus redox conditions can play an important role in soil P bioavailability (e.g., Miller et al., 2001). Fe- and Al-complexes with organic matter also can be important sinks for phosphate, as can clays, but the latter are less efficient scavengers of phosphate than the oxyhydroxides. Mineralogy and morphology of oxyhydroxides also exert control on relative efficiency of P sorption; e.g., goethite is a more efficient substrate for P sorption than is hematite (Torrent et al., 1990). Dissolved organic phosphorus compounds can also be sorptively removed from soil solution by various solid-phase components, including clays, oxides, and oxyhydroxides. As a result, most legacy inorganic P compounds in soils fall into one of two groups: those containing calcium and those containing iron and aluminum. The availability of P in alkaline soils is determined largely by the solubility of the calcium compounds in which the P is associated. In acid soils, iron and aluminum minerals regulate the solubility of inorganic P. The relative proportion of each of the forms depends on soil types in the landscape (mineral vs organic) and source and forms of P added to the system.

Besides of excessive P application, other anthropogenic activities are also important to contribute to legacy P accumulation in soils. For example, soil conservation measures such as no-till and cover crops that aimed at reducing P loss via erosion would be beneficial for building up of legacy P pools (Sims and Kleinman, 2005). Legacy organic P would be increased with relative proportion of applied manure to fertilizer (Waldrip et al., 2015). Due to relative low availability of manure P for crop uptake, legacy P reserves in soils have also developed in regions where specialization and intensification of livestock production result in localized manure nutrient imbalances. For example, soil P concentrations on the Delmarva Peninsula have increased to levels that are nearly one order of magnitude greater than what is required for crop growth due to continuous application of poultry litter (Buda et al., 2010). Such accumulation would be more considerable in smallholder

cropping systems. Smallholder farmers in China as well as in other regions usually apply livestock manure only considering the N contained in the manure but without considering the P contained in the manure (Han et al., 2012; Yan et al., 2013), resulting in excessive P application when coupled with synthetic fertilizer P additions and P accumulation in cropland soils. As estimated previously, cropland soil legacy P pools could be 504–953 kg P ha⁻¹ in the China over the past three decades (Hou et al., 2013; Jiang and Yuan, 2015; Li et al., 2015). Increasing manure or organic waste application is also in favor of building up legacy organic P in cropland soils. For example, a long-term (>10 years) poultry litter application experiments (cultivated and grazed–ungrazed pasture) on a calcareous Texas Blackland Vertisol indicated that an average of 68% of total P was extractable with HCl, with organic P comprised the majority (95%) of HCl-extracted total P (Waldrip et al., 2015). The legacy nutrient associated with urban areas is mostly associated with the historic fertilization practices and sewage treatment systems, particular septic tanks. For example, previous estimates in many urban and suburban areas in China indicated that 19%–26% of anthropogenic P inputs were retained in residential soils (Li et al., 2010; Yuan et al., 2014), as evidenced that soils in urban greenbelts, roadways, parks, residential districts, and campuses have been enriched in N and P compared to agricultural soil (Yuan et al., 2014).

Depletion of soil legacy P pools is mainly dependent on loss to waters and uptake by plants. Soil legacy P is potentially released to solution, and it effectively buffers soluble P concentrations. Effective reduction of elevated soil test P levels and runoff P concentrations from such soils by ceasing P applications appears to involve lag times on the order of a decade or more, depending on the degree of soil P accumulation (Dodd et al., 2012). Soil legacy P depletion dynamics can be usually described as a first-order chemical reaction with a rate constant proportional to the initial soil P content following cessation of P fertilization. For example, Schulte et al. (2010) modeled that there were 7–15 years lag times for soil test P decline from 14.3 and 8.3 mg kg⁻¹ Morgan's soil P (excessive: >8 mg kg⁻¹) to 7.5 and 4.7 mg kg⁻¹ (optimum: 5.1–8 mg kg⁻¹), respectively, for eight long-term cropland experiments in Ireland since 1996. Similarly, in plot studies of P fertilization and soil P depletion under continuous corn (*Zea mays* L.), Zhang et al. (2004) reported a Mehlich-3 soil test P decline of 3.96 mg P kg⁻¹ year⁻¹ following cessation of P fertilization, and it would require about 28 years to deplete the 110 mg P kg⁻¹ of soil P built-up during 6 years of high-rate P fertilizer addition to baseline levels. Changes in land

use that exacerbate erosion can dramatically increase soil legacy P loss to waters. For instance, [Duan et al. \(2012\)](#) observed significantly higher particulate P loads in watershed effluent following residential development of agricultural land. Other human activities, such as liming application and conversion of dry land to paddy field, also can enhance release from legacy mineral-P associations by changing conditions including increased pH or decreased redox potential (i.e., following depletion of dissolved oxygen) ([Haygarth et al., 2006](#); [Ulén and Jakobsson, 2005](#)). Although legacy P generally accumulated in soil upper layers, under conditions of long-term loading that leads to P saturation of surface soils, P can move downward to the deeper layers along the soil profile. Many field experiments indicated that long-term manure application increased dissolved reactive P concentrations in leachate as a result of a decreased adsorption potential caused by preferential sorption of manure organic P to soil-binding sites ([Hansen et al., 2004](#); [Tarkalson and Leytem, 2009](#)).

2.2.2 Legacy Nutrient Dynamics in Sediments

In fluvial systems (i.e., ditches/drainages and streams/rivers), built-up of sediment legacy P pools results from the deposition of particulate P as fluvial bed sediments ([Ballantine et al., 2009](#)), sorption of dissolved P onto riverbed sediments ([Haggard et al., 2005, 2007](#); [Stutter et al., 2010](#)) or onto suspended sediments that are subsequently deposited on the riverbed ([Owens and Walling, 2002](#)). Net N retention in sediment is mainly associated with the deposition of organic N, physical sorption, and biogeochemical interception (formation of organic N) by sediments in fluvial bed ([Brunet and Astin, 1997](#); [Noe and Hupp, 2005](#)). In general, deposition of eroded particulate nutrients from croplands is a major cause for legacy nutrient accumulation in agricultural ditches and rivers, while the sorption of both particle and dissolved nutrients derived from sewage or septic effluent or erosion from impervious surfaces onto riverbed sediments or onto suspended sediments might be particularly important for in residential drainages and rivers ([Neal et al., 2010](#); [Withers et al., 2009](#)). Built-up of legacy nutrient within the fluvial systems is associated with the incorporation of water-column nutrient into plant or microbial biomass on the riverbed sediments ([Drake et al., 2012](#); [Schade et al., 2011](#)). Higher biological nutrient retention has been reported in headwater environments, where shallow water, light penetration to the benthic interface, and lower water volume to the benthic surface area provide greater potential for biological nutrient exchange processes ([Bukaveckas, 2007](#)). The balance between biotic and abiotic

nutrient retention tends to shift along the river continuum, with abiotic nutrient retention often increasing in significance downstream, linked to higher ambient dissolved nutrient concentrations (Drake et al., 2012).

Fluvial sediment legacy P accumulation and depletion dynamics is highly dependent on hydrological conditions. From the channel/stream reach scale, physically or biologically deposited P in/on sediments may also be temporary, subject to resuspension in future high-flow events or as channels migrate laterally or as benthic botany died. As a result, the residence time of legacy P within a given reach is usually as short as <1 year due to the seasonal hydrological and botany growth cycles. In terms of sediment texture, the finer fraction (silt and clay), which tends to be more mobile and sensitive to hydraulic conditions, usually carries a greater P load per unit mass than the bulk sediment (Naden, 2010). Such deposited P in fine surface bed sediment also has short residence time of <1 year in many fluvial systems (Collins and Walling, 2007a,b; Owens et al., 2001). For the entire drainage–stream/river system, however, sediment and its attached P can take years to move downstream due to repeatedly deposited–resuspended–redeposited dynamics along the hydrological pathways by episodic high-flow events. This process may delay P transport (when P adsorbed to sediment particles constitutes a large fraction of the P load) from headwaters to downstream outlet by years or even decades at the watershed scale. Denitrification is considered the primary pathway for permanent N removal in fluvial networks, with other processes (e.g., organic matter burial in sediment, sediment sorption, and plant and microbial uptake) acting as temporary N storages (Seitzinger, 1988). For example, a study conducted in the Lake Taihu region with the N₂/Ar technique suggested that the N removed by denitrification accounted for about 43% of the total aquatic N load input to the river system (Zhao et al., 2015). Therefore, it seems that legacy N store in fluvial sediments is limited in magnitude with short residence times compared to those of P.

In lentic waters (wetlands/riparian buffers, lakes, and impoundments/reservoirs), built-up of legacy nutrient in sediments is more efficient due to long hydrological and biogeochemical residence times. These lentic waters generally connect with fluvial systems and can trap nutrient quickly by decreasing hydraulic power and consequent increasing deposition. The major processes for legacy N accumulations in the lentic waters are organic matter deposition on sediments and dissolved N uptake by plant (Gälman et al., 2008). For example, a review of organic matter in lacustrine sediments demonstrated that organic matter that is primarily derived from the

particular detritus constitutes an important fraction of lake sediments (Meyers and Ishiwatari, 1993). The principle processes for legacy P accumulations in the lentic waters are settling of sediments, plant uptake and related detritus deposition, and sorption/desorption interactions with bottom sediments or parent materials (Maavara et al., 2015). In many lentic waters, nutrients taken up by plants remain in the system only temporarily and may be gradually released by mineralization of plants detritus later, which increases the residence time of nutrients considerably by reducing their mobility (Fisher and Acreman, 2004; Hefting et al., 2005). For wetlands/riparian buffers, legacy nutrient pool dynamics is regulated by hydraulic loading, residence time, season and temperature, vegetation, mineral and organic matter contents of soil/sediment, pH, microbial activity, and age of waters (Fisher and Acreman, 2004; Groffman et al., 1992; Mayer et al., 2007). Low hydraulic loading and longer residence time provide a greater probability for organic N and particulate bound P of settling out of the water column on sediments and for dissolved nutrient uptake or sorption by biogeochemical processes (Groh et al., 2015). Sediments having high Al, Fe, and organic matter contents are favor of accumulating legacy P pools since flooding promotes the P adsorption by created noncrystalline forms of Fe, Al, and organic matter (Ardón et al., 2010). In terms of geographical location, standing waters that located closer to the source (e.g., croplands and wastewater discharge) can more substantially retain nutrients (Kynkäänniemi et al., 2013). In shallow and productive waters, P accumulation rate can be enhanced by increasing of dissolved oxygen at the sediment surface in response to fluctuating water levels and vegetation growth cycles (e.g., summer) or by receiving Fe and Al loads from entered runoff (Reddy and DeLaune, 2008). Due to rich organic matter and low oxygen in many wetland and riparian zone sediments, denitrification is usually very active for reducing inflowing N loading (30%–70%, Gälman et al., 2008; Teranes and Bernasconi, 2000). However, denitrification cannot fully account for fates of reduced N loads through wetland or riparian zone, implying considerable N storages in sediment and biomass. For example, a synthetic study demonstrated that denitrification rates were 25–33 and 2–33 g N m⁻² year⁻¹ in European herbaceous and forested buffer sites, with net N retention rates in sediments of 2–6 and 4–16 g N m⁻² year⁻¹, respectively (Hefting et al., 2005). In deeper lentic waters, where prolonged periods of thermal and dissolved oxygen stratification may occur, accumulated legacy nutrient (mainly in organic form) is mainly contained within anaerobic bottom sediments, and therefore, they may be slowly flushed out through surface water outflows with low export rates.

Depletion of legacy N pool in sediments is mainly related to denitrification and discharge to downstream water. However, most of the sediment legacy N in lentic systems is present in the organic form, with a small percentage in inorganic forms such as NH_4 and NO_3 , largely limiting the legacy N removal by denitrification. Therefore, denitrification of legacy N in sediments is mainly dependent on oxic condition that leads to organic N mineralization and nitrification of mineralized ammonia into nitrate. For wetlands or riparian zones, enhanced organic matter decomposition following water-level drawdown due to natural and artificial regulations can increase inorganic N (NH_4 , NO_3), and consequently they will partially move downward into the anaerobic layer, resulting N removal via denitrification. The way of N in sediment losses to waters is similar to P, which is the only pathway for P depletion in sediment. Depending on rainfall (particular for storm events) and water movement, legacy nutrient in sediments can be transported with water flow from wetlands or riparian zones, which acts as a considerable source for downstream.

2.2.3 Legacy Nutrient Dynamics in Vadose Zone/Groundwater

Due to the high solubility and mobility as well as long residence times, dissolved N (particular for nitrate) accumulating in the vadose zone/groundwater is liable to build up as a legacy N pool derived from soil surplus N. Legacy N pool in vadose zone/groundwater is usually occurring in many highly managed lands where the recharge zone receives excessive anthropogenic N inputs (i.e., croplands and residential lands, [Costa et al., 2002](#); [Scanlon et al., 2008](#); [Walvoord et al., 2003](#); [Zhou et al., 2016](#)). The N accumulation in vadose zone and groundwater is mainly facilitated by rapid infiltration and percolation ([Hamilton, 2012](#)). Therefore, legacy nitrate magnitudes in vadose zone and groundwater would be enhanced by high N application rate, high rainfall and frequent storm events, coarse soil texture, and intensive tillage and irrigation ([McMahon and Böhlke, 2006](#); [Zhou et al., 2016](#)). A long-term (1998–2012) field experiment in the North China Plain indicated nitrate accumulations in vadose zone increased by ~ 40 -fold when applied N fertilizer rates increased from 0 to $600 \text{ kgN ha}^{-1} \text{ year}^{-1}$ ([Zhou et al., 2016](#)). [Costa et al. \(2002\)](#) also emphasized that intensive irrigations could lead to increasing N accumulations in cropland vadose zones. Accumulation of N in vadose zone is commonly observed in arid or semiarid region with high N surplus due to low carbon content, strong mineralization and nitrification abilities, and weak immobilization and denitrification abilities ([Scanlon et al., 2008](#); [Walvoord et al., 2003](#); [Zhou et al., 2016](#)). In many humid regions, nitrate would further

gradually move downward to the groundwater from the upward vadose zone. Groundwater reservoir comprising about 99% of available fresh water in a global scale (Puckett et al., 2011) receives N from various sources by hydrological pathways (leaching from vadose zones of different systems), showing a high potential of accumulating N (Table 1). Over the past decades, groundwater nitrate concentrations have been significantly elevated as observed in the United States (increased from 2 to 15 mgL⁻¹ during 1940–2003 period) (Puckett et al., 2011; Qi et al., 2011), Europe (39% of monitoring stations exceeded 25 mgL⁻¹) (Angelopoulos et al., 2009; Worrall et al., 2015), India (average concentration exceeded 50 mgL⁻¹ in northern India) (Suthar et al., 2009), and China (28% exceeded 10 mgL⁻¹) (Gu et al., 2013; Ju et al., 2004). Although ammonia leaching is usually limited along the soil profile, increasing evidences indicated that leaching from landfills and septic tanks or other sewage disposal plants has resulted in a considerable ammonia accumulation in groundwater, presenting a high potential for storing ammonia in residential groundwater (Umezawa et al., 2009).

Depletion of legacy N pools stored in the vadose zone/groundwater is mainly related to denitrification and discharge to surface water. Denitrification requires anoxic conditions and an electron donor (such as organic carbon, sulfide, or Fe²⁺, Slomp and Van Cappellen, 2004; Starr and Gillham, 1993; Tesoriero et al., 2000). Due to the oxic environment and lack of carbon sources, denitrification is usually limited in vadose zones, with particular in semiarid regions (Zhou et al., 2016). Although groundwater DO concentrations usually decrease with groundwater age (Daughney et al., 2010), denitrification is likely limited by the lack of a microbially labile organic carbon source in many regions (Pabich et al., 2001). In shallow, well-oxygenated groundwater, denitrification is limited by the presence of oxygen although dissolved organic carbon or pyrite is usually available (Sanford and Pope, 2013). However, denitrification would be active when groundwater passes through the riparian buffers and hyporheic zones with rich organic carbon and low DO, which can reduce carried legacy N in groundwater before finally entering the receiving water (Billen et al., 2013; Boano et al., 2014). Tesoriero et al. (2000) suggested that the presence of shallow confining layer restricts groundwater to a local flow system where the subsurface flowpaths are likely to intercept riparian sediments with rich electron donors that may facilitate denitrification. Because of the often very long residence time in vadose zone/groundwater, the N concentration may not yet be in

equilibrium with the N concentration in the inflowing water, as is frequently observed (Billen et al., 2013). Therefore, until equilibrium is reached, the vadose zone/groundwater acts as net N store and releases less N than it receives.

Under conditions of long-term high loading that leads to P saturation of surface soils, P can move downward into the vadose zone and underlying groundwater for accumulating legacy P pool (Sharpley et al., 2013). An increasing number of studies have highlighted the elevated P concentrations in shallow groundwater in many areas across the world (Domagalski and Johnson, 2011; Holman et al., 2008). For example, Holman et al. (2008, 2010) have documented the extent of groundwater P contamination across the United Kingdom and Ireland and shown many instances where groundwater P concentrations are elevated enough to contribute to the eutrophication of surface waters due to saturation of the soil P retention capacity. Areas with shallow groundwater tables, coarse soils, intensive manure addition, and leakages of wastewater (i.e., residential area) are usually most at risk for accumulating legacy P pool in groundwater. Vadas et al. (2007) proposed that in the shallow (<3 m) groundwater on an intensely ditch-drained poultry farm located on Maryland's Lower the highest dissolved P concentrations near the soil surface reached 0.65 mgP L^{-1} . High groundwater P concentrations (above 4 mgL^{-1}) were also found in a residential area in the Lake Arendsee watershed reached associated leakages from on-site septic tank systems, the municipal sewage system, and house connection sewers (Meinikmann et al., 2015). Leached wastewater and manure solution usually create anoxic conditions and have high organic matter, which are favor of inhibiting phosphate adsorption onto mineral surfaces, e.g., Al, Mn- and Fe-containing oxides and hydroxides, and calcite (Ptacek, 1998; Spiteri et al., 2007; Zanini et al., 1998) or onto solid organic carbon (Harman et al., 1996). Superimposed on these conditions is a long-lasting continuous supply of P, resulting in considerable P load transport to the vadose zone and consequent the groundwater for accumulating legacy P pools. However, these mechanisms would be overwhelmed for areas where artificial wastewater discharge into the vadose zone and groundwater was considered as a reduction measure of point source pollution, inducing large legacy nutrient pools in many residential areas (McCobb et al., 2003; Robertson, 2008). Discharge to surface water is the only process for depleting the accumulated legacy P in vadose zone/groundwater, which is dependent on contributed water quantities to surface waterbodies and the dissolved P concentrations.

As we mentioned earlier, there are usually long transmission pathways from uplands and long transit times for legacy nutrients delivery to receiving waters via subsurface runoff and groundwater discharge (years to decades) at the watershed scale. Such long transmission pathways and long transit times provide desired settings continuously receiving dissolved nutrient load from various soils with intensive anthropogenic activities over long-term period, favoring of accumulating legacy nutrient in groundwater. Therefore, once legacy nutrient pool formed in vadose zone/groundwater, it would slowly deplete and be persistent for long time period in nutrient level contributing to surface waters.



3. MODELING LEGACY NUTRIENT DYNAMICS AT THE WATERSHED SCALE

3.1 Limitations of Current Watershed Models for Addressing Legacy Nutrient Dynamics

Quantitative understanding the legacy nutrient dynamics at the watershed scale is critical for developing efficient nutrient management measures. Due to great spatial and temporal heterogeneities, it is almost impossible to achieve that by direct monitoring efforts. Mathematical models are major and useful tools to quantify watershed nutrient inputs to receiving waters and to predict the effects of climate and land-use changes. Some good review works have well summarized the currently prevailing watershed numerical models and figured out their structures, procedures, functions, applicability, and suggestions for future improvements (Borah and Bera, 2004; Moriasi et al., 2007; Wellen et al., 2015). Available numerical models range from lumped or statistical models, such as the export coefficient model, GWLF, SPARROW, GlobalNEWS, and PolFlow, to mechanistic models, such as INCA, HBV, ANSWERS, AGNPS, HSPF, and SWAT. These models have been widely applied worldwide and improved our quantitative understanding of watershed nutrient dynamics for supporting the development of relevant management measures and policies.

However, currently prevailing watershed models are generally lack of an explicit mechanism to describe the legacy nutrient dynamics and delivery lags (Kleinman et al., 2015; Meals et al., 2010). Lumped or statistical watershed models such as the export coefficient model, GlobalNEWS, GWLF, PolFlow, and SPARROW generally assume that the nutrient cycle to be at a steady state, either on a yearly basis or over a multiyear period (e.g., 5-year average, Alam and Goodall, 2012; De Wit, 2001; Swaney et al., 2012;

Wellen et al., 2012). However, a major challenge remains in determining the appropriate length of the multiyear period that should be used to consider nutrient source inputs into models to satisfy the steady-state assumption (Chen et al., 2014b). For example, the lag times between watershed anthropogenic N inputs and riverine export associated with biological and hydrological processes can be 10 and 24.5 years as indicated in the Yongan watershed in eastern China and the Southern Ontario watershed in the United States, respectively (Chen et al., 2014a; Van Meter and Basu, 2017), which is significantly longer than 5 years used in some lumped and statistical models.

Legacy effect is also not well addressed and formulated in most current watershed mechanistic models (Bouraoui and Grizzetti, 2014; Meals et al., 2010; Sanford and Pope, 2013) due to the limited quantitative knowledge concerning residence times and biogeochemical mechanisms for nutrient loss (Hamilton, 2012; Sebilo et al., 2013; Van Meter and Basu, 2015). For example, in some mechanistic models (e.g., AGNPS, SWAT, and HSPF) groundwater dynamics is simulated usually by using a water balance method or by just taking a certain parameter to describe the groundwater delay time (Douglas et al., 1992). This is hard to catch the realistic long delivery times of groundwater (several years to decades) as estimated by chemical analysis methods in many watersheds (McDonnell et al., 2010; McGuire and McDonnell, 2006). Although the mechanistic models simulate all the major components of the hydrological cycle (e.g., evapotranspiration, groundwater flow, overland flow, and return flow), they are usually calibrated only to streamflow in practice, implying that we do not know how realistically these models reproduce the hydrological cycle (Wellen et al., 2015). Artificial water conservancy facilities (e.g., damming and flow diversion) and natural bank collapses can greatly influence sediment legacy nutrient dynamics (Maavara et al., 2015), which is also not well handled in many current models (Glibert et al., 2008). Furthermore, most current models have lacked an ability to accurately represent wash-off (incidental transfer) processes for P (Vadas et al., 2007) and in-stream stores and sinks of P (Haggard et al., 2007).

The biogeochemical residence times within and among different nutrient pools (i.e., soil, groundwater, sediment, and biomass) can also range from several years to decades (Hamilton, 2012). However, many mechanistic models usually ignore the impacts of historical nutrient inputs and land-use management measures on nutrient and hydrological residence times (Martin et al., 2017). The measured riverine nutrient concentration is a

mixture of nutrient having different ages, and very often the residence time of nutrient in landscapes is much longer than the temporal extent of the calibration data available (Howden et al., 2011; Meals et al., 2010). Due to the lack of capacity for addressing hydrological and biogeochemical legacy effects in many current watershed models, their predictions for water quality improvement after the implementation of relevant nutrient management measures rarely come true (Kleinman et al., 2015).

3.2 Advance in Modeling Watershed Legacy Nutrients Dynamics

3.2.1 Statistical Models

Based on literature review, 19 studies are currently available for modeling watershed legacy nutrient dynamics with 14 works for N and 5 works for P (Table 2). Compared with process-based models, statistical models are predominant for addressing watershed legacy nutrient dynamics. Based on long-term (>30 years) observations, statistical models between annual riverine nitrate flux and previous several years' average net anthropogenic nitrogen inputs (NANI) were developed to address N leaching lag effect in the Mississippi River watershed (previous 2–5 and 6–9 years' average NANI) in 1960–1998 (McIsaac et al., 2001) and the Yongan watershed (previous 0–6 years' average NANI) in eastern China in 1980–2009 (Chen et al., 2014b). Other several statistical models were directly established between annual riverine nutrient flux and current year's NANI or NAPI, hydroclimatic, and land-use variables in the Yongan watershed and Yangtze watershed in China (Chen et al., 2015b, 2016c). Using these statistical models, contribution of watershed legacy nutrient sources to riverine nutrient flux was estimated as predicted riverine nutrient fluxes when setting current year's nutrient inputs as zero through adjusting by natural background sources. Considering the difference of accumulated legacy nutrient pools across landscapes, Chen et al. (2016a,b) further developed statistical models for linking net anthropogenic N or P inputs to agricultural/forest and residential systems with riverine TN or TP flux and then identified contributions of agricultural and residential legacy nutrient sources in Yongan watershed in eastern China in 1980–2010. In these statistical models, relationships between riverine nutrient flux and anthropogenic nutrient inputs were usually expressed as an exponential function, which may be a consequence of anthropogenic nutrient inputs exceeding the capacity of terrestrial and/or aquatic systems to assimilate or retain excessive nutrient (Chen et al., 2015b; McIsaac et al., 2001; Sharpley et al., 2013).

Table 2 Summary of Currently Available Models for Addressing Watershed Legacy Nutrient Dynamics

Types	Model Descriptions	Model Efficiency	Study Area	References
Statistical	$N = 0.66 \times W^{0.93} \times \exp(0.132 \text{NANI}_{2-5} + 0.062 \text{NANI}_{6-9})$ where N is the annual nitrate flux ($\text{kgN ha}^{-1} \text{year}^{-1}$), NANI_{2-5} is the average annual net anthropogenic nitrogen input during the previous 2–5 years ($\text{kgN ha}^{-1} \text{year}^{-1}$), NANI_{6-9} is the average annual NANI during the previous 6–9 years ($\text{kgN ha}^{-1} \text{year}^{-1}$), and W is the annual water yield (m year^{-1})	$R^2 = 0.95$ ($n = 39$)	Mississippi River Basin, 1960–1998	McIsaac et al. (2001)
Statistical	$C_N = 0.41 \times (0.84 + 0.094 \times \text{NANI} + 0.261 \times D\%)$ where C_N is the annual average TN concentration (mgN L^{-1}), NANI is the net anthropogenic nitrogen input ($\text{kgN km}^{-2} \text{year}^{-1}$), and $D\%$ is the drained agricultural area	$R^2 = 0.77$ ($n = 52$)	Upper Vltava River watershed, 1900–2010	Kopáček et al. (2013b)
Statistical	$\text{TN} = 0.08 \times Q^{0.89} \times \exp(8.7 \times 10^{-3} \times \text{NANI}_{0-6} + 0.147 T_{0-4} D\%_{0-3})$ where TN is the annual riverine TN flux ($\text{kgN ha}^{-1} \text{year}^{-1}$), Q is the annual average discharge ($\text{m}^3 \text{s}^{-1}$), NANI_{0-6} is the average annual NANI during the previous 0–6 years ($\text{kgN ha}^{-1} \text{year}^{-1}$), T_{0-4} is the average air temperature during the previous 0–4 years ($^{\circ}\text{C}$), and $D\%$ is the drained agricultural area percentage during the previous 0–3 years	$R^2 = 0.96$ ($n = 30$)	Yongan River watershed, eastern China, 1980–2009	Chen et al. (2014b)
Statistical	$\text{DIN} = 0.002 \times Q^{2.72} \times \exp(1.4 \times 10^{-4} \times \text{NANI})$ where DIN is the annual riverine dissolved inorganic nitrogen flux ($\text{kgN km}^{-2} \text{year}^{-1}$), Q is the annual average discharge ($\text{m}^3 \text{s}^{-1}$), and NANI is the net anthropogenic nitrogen input ($\text{kgN km}^{-2} \text{year}^{-1}$)	$R^2 = 0.90$ ($n = 33$)	Yangtze River Basin, 1980–2012	Chen et al. (2016c)
Statistical	$\text{TN} = \alpha \times Q^{\beta_1} \times [\text{AD}\%^{\beta_2} \times \exp(\beta_3 \times \text{NANI}_{AF}) + D\%^{\beta_4} \times \exp(\beta_5 \times \text{NANI}_R)]$ where TN is the annual riverine TN flux ($\text{kgN ha}^{-1} \text{year}^{-1}$), NANI_{AF} and NANI_R are net anthropogenic nitrogen inputs to forest/agricultural and residential systems ($\text{kgN ha}^{-1} \text{year}^{-1}$), respectively, Q is the annual average river discharge ($\text{m}^3 \text{s}^{-1}$), $D\%$ is the developed land area percentage, $\text{AD}\%$ is the agricultural lands with improved drainage percentage, and α , β_1 , β_2 , β_3 , β_4 , and β_5 are fitting parameters	$R^2 = 0.93\text{--}0.97$, $\text{NS} = 0.92\text{--}0.97$ $(n = 31)$	Three catchments in the Yongan River watershed, eastern China	Chen et al. (2016b)

Continued

Table 2 Summary of Currently Available Models for Addressing Watershed Legacy Nutrient Dynamics—cont'd

Types	Model Descriptions	Model Efficiency	Study Area	References
Processes	A catchment-scale numerical method that integrated the nitrate time bomb model, GIS Groundwater, and the nitrate transport model in the saturated zone together was developed to investigate the nitrate lag time in the groundwater system in the Eden Valley, UK	$R^2 = 0.92$ ($n = 36$) for long-term steady-state groundwater levels	Eden Valley, UK, 1991–2004	Wang et al. (2012)
Processes	$C_s = (1 - D_s)(1 - D_r) \sum_{i=1}^{N_{yr}} \left[\left(\frac{Q_{ag}}{Q_r} \right) C_{iag} + \left(\frac{Q_{na}}{Q_r} \right) C_{na} - D_g t_i \right]$ $C_{iag} = [L_{ij}(1 - E_j) + L_{im}(1 - E_m)] / (R_w A_w)$ <p>where C_s is the mean nitrate concentration for a stream for a given year (mgN L^{-1}), D_s and D_r are soil and riparian denitrification factors (dimensionless), respectively, N_{yr} is the number of yearly base-flow-age bins ($=200$), (Q_i/Q_r) is the fraction of baseflow of that age within the stream's total baseflow (dimensionless), C_{iag} and C_{na} are concentrations of nitrate in agricultural and nonagricultural land recharge (mgN L^{-1}), respectively, D_g is a groundwater denitrification factor ($\text{mgN L}^{-1} \text{ year}^{-1}$), t_i is the base-flow age (year), L_i is an annual nitrogen application (load) at the land surface (mgN year^{-1}), E is an uptake efficiency (dimensionless), R_w is the mean annual recharge for a watershed ($\text{m}^3 \text{ year}^{-1}$), A_w is the area of a watershed (m^2), and the subscripts r, ag, na, f, and m correspond to recharge, agricultural, nonagricultural, inorganic fertilizer, and poultry manure, respectively</p>	$R^2 = 0.77$ – 0.96 ($n = 25$)	Delmarva Peninsula area of Chesapeake Bay watershed	Sanford and Pope (2013)
Processes	$\text{TN}_t = [1 - \exp(-\beta_t \Delta t)] \times \text{NANI}_t + [1 - \exp(-\beta_t \Delta t)]$ $\times (N_{t-1} - B_{t-1}) \times \frac{\exp(-\beta_{t-1} \Delta t - \theta_{t-1} \Delta t)}{[1 - \exp(-\beta_{t-1} \Delta t)]} + B_t$ <p>where TN_t is the annual riverine TN flux ($\text{kgN ha}^{-1} \text{ year}^{-1}$), subscript t is the tth year, β and θ denote the first-order rate coefficients for export by river and loss by denitrification, nonharvested biomass uptake, and wood product export (year^{-1}), respectively, B denotes riverine N flux derived from natural background sources ($\text{kgN ha}^{-1} \text{ year}^{-1}$)</p>	$R^2 = 0.91$, $\text{NS} = 0.90$ ($n = 31$)	Yongan River watershed, eastern China, 1980–2010	Chen et al. (2014a)

Table 2 Summary of Currently Available Models for Addressing Watershed Legacy Nutrient Dynamics—cont'd

Types	Model Descriptions	Model Efficiency	Study Area	References
Processes	$\ln(\text{TN}_t) = \ln(a) + \sum_{j=1}^m [b_j \ln(\theta_{t,j})] + \beta_0 \text{NANI}_t + \lambda \prod_{k=1}^n R_{t-1,k}$ $[\ln(\text{TN}_{t-1}) - \ln(a)] - \sum_{j=1}^m [b_j \ln(\theta_{t-1,j})]$ <p>where TN is the annual riverine TN flux ($\text{kgN ha}^{-1} \text{ year}^{-1}$), subscript t denotes the tth year, NANI_{t-i} denotes NANI in the previous ith year, and $\theta_{t,j}$ denotes the normalized value of the jth explanatory variable that influences fractional export of NANI to rivers in the ith year. Unknown parameters a and b_j denote the response magnitude of N export efficiency to changes in explanatory variables (e.g., meteorology, hydrology, and land use). Unknown parameter β_0 represents the export fraction coefficient for the current year's NANI_t and historical (legacy) NANI_{t-i} to the river, which is independent of watershed temporal attributes and reflects the influence of inherent watershed geological and geomorphologic characteristics; λ is the decay coefficient for historical NANI_{t-i} and denotes the response magnitude of decay to changes in explanatory variables, $R_{t-i,k}$ denotes the normalized value of the kth explanatory variable that influences N removal through riverine export, denitrification, and forest biomass uptake/storage/export</p>	$R^2 = 0.90$, $\text{NS} = 0.90$ ($n = 31$)	Yongan River watershed, eastern China, 1980–2010	Chen et al. (2015a)
Processes	<p>The outlet concentration is assumed as a function of both the hydrologic and biogeochemical legacy, and the patterns of land-use change:</p> $C(t) = \int_0^\infty C_s(t - \tau) f(\tau) \exp(-k\tau) d\tau$ <p>where $C(t)$ is the N concentration at catchment outlet, $C_s(t - \tau)$ is the contaminant input function or “source function” from the unsaturated zone (i.e., biogeochemical legacy), $f(\tau)$ is a specific groundwater travel time distribution (i.e., hydrologic legacy), and $k [T^{-1}]$ is the first-order rate constant that describes removal processes in the aquifer</p>	NA	The Walnut Creek Watershed, Iowa, USA	Van Meter and Basu (2015)

Continued

Table 2 Summary of Currently Available Models for Addressing Watershed Legacy Nutrient Dynamics—cont'd

Types	Model Descriptions	Model Efficiency	Study Area	References
Processes	$M(t) = M_{prot} + \left[\frac{\lambda}{k(t-1)} + \frac{a_0}{k} \right] + \left(M_{act0} + \frac{k - a_0}{k} \right) \exp(-kt)$ <p>where $M(t)$ is the mass of soil organic N (SON) pool (kgN ha^{-1}), M_{act_0} and M_{prot} are the initial masses of the active and protected SON pool (kgN ha^{-1}), respectively, a_0 is the initial net N input, λ (kgN ha^{-1}) is the rate of increase in the net N inputs, and k is the mineralization rate constant (year^{-1}). Net N inputs are the difference between TN inputs (fertilizer N, atmospheric N deposition, biological N fixation) and N outputs via crop uptake</p>	NA	Mississippi River Basin	Van Meter et al. (2016)
Processes	A modeling approach that coupled the Nitrate Time Bomb model, a NEAP-N and a simplified hydrogeological conceptual model was developed to simulate the impacts of historical nitrate loading from agricultural land on the evolution of groundwater nitrate concentrations at the regional or national scale	NS = 0.55–0.67 (18–24)	England and Wales, 1925–2150	Wang et al. (2016)
Processes	<p>The ELEMeNT modeling approach (Exploration of Long-tErM Nutrient Trajectories) couples a source function of the accumulation and depletion of soil organic N (SON) within the root zone with a travel time-based approach that accounts for transport and transformations along hydrologic pathways to determine N loading trajectories at the catchment outlet $M_{out}(t)$:</p> $M_{out}(t) = \int_0^\infty Js(t - \tau)f(\tau) \exp(-\gamma\tau) d\tau + (1 - k_h)W(t)$ <p>where $M_{out}(t)$ is the riverine nitrate–N mass flux (kgN year^{-1}), $Js(t - \tau)$ is the contaminant input function or “source function” that describes the mass flux of nitrate from the unsaturated zone to the groundwater, $f(\tau)$ is the distribution of travel times to the catchment outlet, γ is the first-order rate constant that describes N removal via denitrification along hydrologic pathways (year^{-1}), $W(t)$ is the human N consumption, and k_h is the denitrification rate constant for human waste</p>	NA	Mississippi River Basin (MRB) and Susquehanna River Basin (SRB), 1800–2014	Van Meter et al. (2017)
Processes	A modeling framework was developed by coupled Hydrus 1D model with meteorological and soil physical data, and boundary conditions to evaluate catchment lag time for nutrient or solute transport through unsaturated zone	NA	A grassland and an arable catchment ($\sim 10 \text{ km}^2$) in Ireland	Vero et al. (2017)

Table 2 Summary of Currently Available Models for Addressing Watershed Legacy Nutrient Dynamics—cont'd

Types	Model Descriptions	Model Efficiency	Study Area	References
Statistical	$P = 0.379 \times R^{1.779} \times DA\%^{1.404} \times D\%^{0.109} \times \exp(0.245 \times NAPI)$ where P is the annual riverine TP flux ($\text{kgP ha}^{-1} \text{ year}^{-1}$), R is the annual precipitation (m year^{-1}), $D\%$ is the developed land area percentage, $DA\%$ is the drained agricultural land area percentage, and $NAPI$ is the net anthropogenic P inputs ($\text{kgP ha}^{-1} \text{ year}^{-1}$)	$R^2 = 0.94$, $NS = 0.92$ $(n = 186)$	Six catchments in Yongan River watershed, eastern China, 1980–2010	Chen et al. (2015b)
Statistical	$P = 0.66 \times R^{1.30} \times [DA\%^{2.67} \times \exp(0.54 \times NAPI_{AF}) + D\%^{2.08} \times \exp(1.42 \times NAPI_R)]$ where P is the annual riverine TP flux ($\text{kgP ha}^{-1} \text{ year}^{-1}$), R is the annual precipitation (m year^{-1}), $NAPI_{AF}$ and $NAPI_R$ are net anthropogenic phosphorus inputs to agricultural/forest and residential systems ($\text{kgN ha}^{-1} \text{ year}^{-1}$), respectively, $D\%$ is the developed land area percentage, and $DA\%$ is the drained agricultural land area percentage	$R^2 = 0.96$ ($n = 32$)	Yongan River watershed, eastern China, 1980–2011	Chen et al. (2016b)
Statistical	$L_i = P_i + N_i = AQ_i^B + CQ_i^D$ $T_D = \frac{TP_O}{Cl_O} Cl_L - TP_L$ where L_i is the riverine TP load (kgP d^{-1}), P_i and N_i are point source and nonpoint source TP load (kgP d^{-1}), respectively, subscript i is the i th day, A , B , C , and D are model parameters, Q_i is the daily average river discharge ($\text{m}^3 \text{ s}^{-1}$), T_D is the daily deposited effluent P load (kgP d^{-1}) during the low-flow regime, TP_O is the original point source input load (kgP d^{-1}), Cl_L and TP_L are measured average daily Cl^- (kgd^{-1}) and TP (kgP d^{-1}) loads during the low-flow regime, respectively	NA $R^2 > 0.41$; $NS > 0.37$ for TP concentration; $R^2 > 0.91$; $NS > 0.87$ for TP load ($n = 33\text{--}44$)	Illinois River watershed, 1997–2007 Yongan River watershed, eastern China, 1980–2010	Jarvie et al. (2012) Chen et al. (2015c)
Processes	A generic model was developed by comprising two sub models: a catchment model and a lake model. The catchment model is a soil column model that accounts for the heterogeneity of soils in the catchment and the surface runoff process. The lake model describes the dynamics of total P in the lake water and sediment as a result of in and outflow processes, water sediment interactions, and the presence of macrophytes	NA	Average Dutch catchment shallow lake system	Schippers et al. (2006)
Processes	A watershed modeling framework was developed by combining the modified Agro-IBIS, a terrestrial ecosystem model (THMB), a hydrologic and nutrient routing model, and the Yahara Water Quality Model to predict water quality outcomes under alternative scenarios of P storage in watershed soils and stream sediments	$R^2 = 0.24$ and 0.29 (calibration, $n = 120$), $R^2 = 0.16$ and 0.43 (validation, $n = 120$)	Yahara lake watershed, Midwestern in USA, 1986–2013	Motew et al. (2017)

As an exception, a linear function was found to be the best for the Upper Vltava River watershed where riverine N flux was more related to mineralization of SON pools than to NANI (Kopáček et al., 2013b). To address in-stream sediment legacy effect, two works combined the river load apportionment modeling and wastewater conservative tracer (chloride) mass balance analysis methods to quantify the contribution of stored and remobilized point source input P within sediments to annual riverine TP fluxes in the Illinois River in 1997–2007 (Jarvie et al., 2012) and the Yongan River in 1980–2010 (Chen et al., 2015c).

The statistical models generally presented a considerable accuracy (Table 2) and provide simple but efficient tools for predicting annual riverine nutrient export due to legacy effects. In developing these statistical models, selected independent variables (e.g., anthropogenic nutrient inputs, hydroclimate, and land-use management variables) and function types for expressing quantitative relationships between riverine nutrient export and each of independent variables are usually determined by individual regression analyses for a specific watershed. Such approach might be unreasonable when more than two independent variables are combined together due to their interaction effects and self-correlations, which may imply a considerable uncertainty in the model structure. Most important, statistical models do not explicitly express hydrological and biogeochemical legacy effects; thus, it is unable to figure out how realistically they reproduce the legacy nutrient dynamics and what cause uncertainty associated with their modeled results.

3.2.2 Processes-Based Models

As far as processes-based models, only eight attempts are available for modeling watershed legacy N dynamics and two works for P (Table 2). To investigate the nitrate residence times in the groundwater system, a catchment-scale numerical method that integrated the nitrate time bomb model, GIS Groundwater model, and the nitrate transport model in the saturated zone together was developed and calibrated by long-term average steady-state groundwater levels in 39 boreholes ($R^2=0.92$) and annual average nitrate concentration in 1 borehole in the Eden Valley, United Kingdom (Wang et al., 2012). In 2016, a national modeling approach that coupled the nitrate time bomb model, a NEAP-N, and a simplified hydrogeological conceptual model was further developed and calibrated by the annual nitrate concentrations for the 28 selected aquifer zones to simulate the impacts of historical agricultural nitrate loading from the evolution

of groundwater nitrate concentrations from 1925 to 2150 in England and Wales (Wang et al., 2016). To quantify role of groundwater legacy N in delaying improvements to Chesapeake Bay water quality, Sanford and Pope (2013) developed a new N mass balance regression model that coupled the distribution of groundwater return times obtained from a regional groundwater flow model, the history of N application rates over the last century, and denitrification parameters. The calibrated model presented a considerable accuracy and was used to predict N loads of seven watersheds in the Delmarva Peninsula to the Chesapeake Bay under scenarios of different N load reductions to the groundwater table. Another recent attempt is applying Hydrus 1D model with meteorological and soil physical data, and boundary conditions to evaluate catchment lag time for nutrient or solute transport through unsaturated zone in a grassland catchment and an arable catchment ($\sim 10 \text{ km}^2$) in Ireland (Vero et al., 2017).

By adopting simple mass balance and equivalent substitution rules, Chen et al. (2014a, 2015a) developed two new dynamic models to express the watershed legacy N mass and the indefinite number of lag terms from previous years' NANI by functions of the previous 1 year's riverine N flux. The two models were well calibrated by 31 years recodes in the Yongan watershed eastern China and yield close results concerning the legacy N source contributed riverine N fluxes (i.e., 72%–85% vs 64%–81%) and N leaching lag time lengths (i.e., 12 years vs 11 years). These two models also allow partitioning of the complete long-term mass balance for the fate (e.g., transient storage, riverine export, and loss/retention by denitrification, biomass uptake, and wood product export) of annual NANI (Chen et al., 2014a) and to estimate dynamic export of annual NANI by river over years (Chen et al., 2015a). Based on these efforts, Van Meter and Basu (2015) coupled the MODFLOW/MODPATH approach and a simple SON decomposition function to address hydrologic (nitrate in groundwater) and biogeochemical (sorbed organic N within the root zone) N legacies. Using available parameters and data, the model was applied to predict the N concentration dynamics in both shallow groundwater beneath sites as well as riverine N concentrations in response to different spatial patterns of land-use conversion in the Walnut Creek watershed. Successively, Van Meter et al. (2016) modified the above SON decomposition function through dividing SON pool into active and protected pools to model decadal agricultural SON depletion and accumulation dynamics under intensive agriculture. The modified model was calibrated by available parameters and data in Rooks County (Kansas) and then was applied to address

biogeochemical lag time of accumulated agricultural SON in the Mississippi River Basin in recent 30 years. In recent, [Van Meter et al. \(2017\)](#) further coupled an ELEMeNT modeling approach and a source zone dynamic function that expresses the accumulation and depletion of agricultural SON within the root zone with an exponential travel time distributions-based approach to determine N loading trajectories at the catchment outlet. The model was calibrated by both current levels of agricultural SON and riverine N loading at the catchment outlets for the Mississippi and Susquehanna River Basins for the years 1979–2013 and then was used to explore the travel times of N from its entry into the terrestrial system to its exit at the catchment outlet, as well as the sources of annual N outputs of two basins in 1800–2014. Compared with modeling works conducted by [Chen et al. \(2014a, 2015a\)](#), the modeling works conducted by [Van Meter and Basu \(2015\)](#) and [Van Meter et al. \(2017\)](#) further partitioned legacy N stored in shallow soil and groundwater reservoirs. In terms of legacy P, the first attempt developed a catchment lake-coupled model, which considers soil P dynamics and surface runoff process as well as the dynamics of total P in the lake water and sediment, to predict the response time delays of lake water P levels to changes in soil P surplus levels for the average Dutch catchment shallow lake system ([Schippers et al., 2006](#)). A recent study combined the modified Agro-IBIS, a terrestrial ecosystem model, a hydrologic and nutrient routing model, and the Yahara Water Quality Model for predicting water quality outcomes under alternative scenarios of legacy P storage in watershed soils and stream sediments in the Yahara Watershed of southern Wisconsin ([Motew et al., 2017](#)).

These processes-based modeling efforts provide important tools to address watershed legacy nutrient dynamics and to predict lag time of response of water quality to land-use management measures. Due to lack of efficient knowledge concerning watershed legacy nutrient accumulation, release/removal and export processes over time and space, however, currently available processes-based models still have several considerable drawbacks: (i) they generally simplify legacy nutrient accumulation, release/removal, and export processes with several lumped parameters and were only calibrated to riverine nutrient exports or cropland soil nutrient storage, which may mask compensation of positive and negative errors of these processes; (ii) majority of their modeled results is lack of efficient validations by comparing to field observations (e.g., long-term changes of soil, groundwater and sediment nutrient, denitrification, and water ages); and (iii) each

model is usually developed based on available data, parameters, and knowledge for a specific watershed, limiting their applicability in other watersheds.

Although legacy effect is progressively concern, current modeling efforts are still inefficient to address legacy nutrient dynamics for guiding development of efficient management measures. Since our understanding of legacy nutrient sources and delivery lags is still developing, most currently prevailing watershed models do not adequately represent these processes. An urgent requirement is to explore principles of watershed legacy nutrient accumulation, rerelease/removal, and export processes across different landscapes (e.g., soils, vadose zone/groundwater, and sediments) over times and their controls. Then, biogeochemical and hydrological modules in many current watershed mechanism models should be modified and improved to fully express residence times for nutrient passing through watersheds before removing by riverine export or gaseous loss. For available processes-based models that considered legacy effect, they should be further improved in structures and refined in parameters to well express watershed legacy nutrient dynamics. In terms of the statistical modeling approach, they are required more rigorous statistical and mechanism tests when they are developing and applying for a specific watershed. Overall, more efforts should be spent on improving our capacity for modeling watershed legacy nutrient issue to provide more realistic predictions concerning response of water quality to changes in climate, land use, and land management and the timescales over which they act, which are critical for developing sustainable nutrient management measures.



4. AGRONOMIC AND ENVIRONMENTAL IMPLICATIONS OF LEGACY NUTRIENTS

4.1 Agronomic Implication of Legacy Nutrients

Legacy nutrients in soils appear to be largely available for supporting crop production, suggesting that they are a potentially accessible nutrient resource. Some long-term field, watershed, and regional studies demonstrated crop recover of legacy nutrients from historical overapplication of fertilizer or manure with no reduction in crop yields for several years to decades after cessation of fertilization (Table 3). These studies show that: (i) soil legacy nutrients can solely or partially support adequate crop yields on many soils for several years to decades with P having a longer persistence than N; (ii) the maintenance period for supporting crop production is dependent on legacy nutrient magnitude, available nutrient form, soil

Table 3 Studies Examining Recovery of Soil Legacy Nutrients by Crop Uptake

Study Area	Nutrient	Study Results			References
		Lag Time	Soil Nutrient Changed	Legacy Nutrient Uptake	
19 Cropland field studies in US, Canada, and Ireland	Olsen P, Mehlich P, and Bray P	4–27 years	$\downarrow 0.4\text{--}30 \text{ mgP kg}^{-1} \text{ year}^{-1}$	NA	Sharpley et al. (2013)
Semiarid Prairie Agricultural Research Centre, Canada, 1995–2010	Olsen P and Mehlich-3 P	>15 years	$\downarrow 1.0 \text{ mgP kg}^{-1} \text{ year}^{-1}$ for Olsen P; $\downarrow 1.5 \text{ mgP kg}^{-1} \text{ year}^{-1}$ for Mehlich-3 P	NA	Liu et al. (2014)
Croplands in Yongan watershed, China, 1980–2010	Olsen P and TP	NA	$\uparrow 0.81\text{--}2.37 \text{ mgP kg}^{-1} \text{ year}^{-1}$ for Olsen P; $\uparrow 9.01\text{--}19.63 \text{ mgP kg}^{-1} \text{ year}^{-1}$ for TP	$0.47\text{--}3.45 \text{ kgP ha}^{-1} \text{ year}^{-1}$	Chen et al. (2017)
Grassland soils on a hillslope site in Northern Ireland, 2005–2011	Olsen P	11 years	$\downarrow 0.71\text{--}3.14 \text{ mgP kg}^{-1} \text{ year}^{-1}$	$0.11\text{--}0.37 \text{ kgP ha}^{-1} \text{ year}^{-1}$	Cassidy et al. (2017)
Four long-term pasture fertilizer trials across New Zealand, 1985–1988	Olsen P and water-extractable P (WEP)	0–7 years for Olsen P 23–44 years for WEP	$\downarrow 0\text{--}3.71 \text{ mgP kg}^{-1} \text{ year}^{-1}$ for Olsen P $\downarrow 0.001\text{--}0.005 \text{ mgP kg}^{-1} \text{ year}^{-1}$ for WEP	NA	Dodd et al. (2012)
Croplands with wheat near Swift Current, Saskatchewan, Canada, 1994–2005	Olsen P	12 years	$\downarrow 0.50\text{--}1.17 \text{ kgP ha}^{-1} \text{ year}^{-1}$	$5.67\text{--}8.83 \text{ kgP ha}^{-1} \text{ year}^{-1}$	Selles et al. (2011)
An agricultural field (33.8 ha) in southern Sweden, 1973–2011	TP	>10 years	NA	$\sim 10 \text{ kgP ha}^{-1} \text{ year}^{-1}$	Ulén et al. (2015)

Eight long-term cropland experiments in Ireland since 1996	Morgan's P	5–12 years	$\downarrow 0.2\text{--}1.2 \text{ mgP kg}^{-1} \text{ year}^{-1}$	$7\text{--}30 \text{ kgP ha}^{-1} \text{ year}^{-1}$	Schulte et al. (2010)
Northeast Iowa Research Farm near Nashua, Iowa, USA, 1979–2002	Bray P	6–9 years	$\downarrow 0.67 \text{ mgP kg}^{-1} \text{ year}^{-1}$	NA	Dodd and Mallarino (2005)
Cropland with continuous corn near Monmouth, Illinois, USA, 1994–1996	Soil N	<1 year	NA	$2.2\text{--}7.8 \text{ kgN ha}^{-1} \text{ year}^{-1}$	Stevens et al. (2005)
National croplands of China, 1980–2010	Soil N	NA	$\uparrow 1.43 \text{ mgN kg}^{-1} \text{ year}^{-1}$	$8.0\text{--}46.4 \text{ kgN ha}^{-1} \text{ year}^{-1}$	Yan et al. (2014)
Cropland with continuous corn in river valley in Colorado, USA, 2000–2003	Nitrate and organic nitrogen	4 years	$\downarrow 42.8 \text{ kgN ha}^{-1} \text{ year}^{-1}$	$108 \text{ kgN ha}^{-1} \text{ year}^{-1}$	Halvorson et al. (2005)
Cropland lysimeters for wheat and sugar beets, Châlons en Champagne, France, 1982–2009	Soil N	27 years	NA	$0.22\text{--}0.33 \text{ kgN ha}^{-1} \text{ year}^{-1}$	Sebilo et al. (2013)
Croplands with a winter oilseed rape—winter wheat—winter barley rotation near Kiel, Germany, 2000–2002	$\text{NO}_3^- + \text{NH}_4^+$	>3 years	NA	$14.6\text{--}24.0 \text{ kgN ha}^{-1} \text{ year}^{-1}$	Sieling et al. (2006)

properties, crop types, and management patterns; (iii) conversion of P from moderately labile forms (e.g., NaOH-extractable P) to labile inorganic P occurs actively and is pH dependent, while transformation of P from non-labile P to labile P forms occurs when labile P is exhausted; and (iv) crop recovery of legacy soil N mainly occurs from surface layers and depends on SON mineralization process that is regulated by pH, moisture, and crop rooting depth.

Legacy P may not all be readily available for crop uptake due to its immobilization by sorption onto soil mineral (clay, Fe, Al, and Ca) surfaces and/or occlusion within soil minerals and retention within the soil organic matter pool (Frossard et al., 2000; Sattari et al., 2012; Shen et al., 2011). The availability of P in alkaline soils is determined largely by the solubility of the calcium compounds, while iron and aluminum minerals regulate the solubility of inorganic P in acid soils (Reddy et al., 2011). The relative proportions of labile and nonlabile forms vary depending on soil type (parent material and degree of pedogenesis), soil pH, soil moisture conditions, and soil biological activity (MacDonald et al., 2012; Negassa and Leinweber, 2009). Previous studies using sequential soil P fractionation schemes and spectroscopic analysis concluded that, in general, legacy soil P has accumulated as labile and moderately labile inorganic P forms in temperate soils, and as moderately labile and nonlabile inorganic P forms in tropical soils (Bai et al., 2013; Beauchemin et al., 2003; McDowell et al., 2005; Negassa and Leinweber, 2009). In theory, the length of time that soil legacy P can support crop production without a significant yield loss could be estimated from linear or exponentially decline patterns of legacy soil P levels in response to the observed or projected crop P uptake rates and agronomic critical levels (i.e., 8–28 mg P kg⁻¹ for Olsen P; 5.1–8.0 mg P kg⁻¹ for Morgan's P; 16–20 mg P kg⁻¹ for Bray-P; Bai et al., 2013; Dodd and Mallarino, 2005; Johnston et al., 2014; Li et al., 2011). However, in some studies crops have not shown a yield decline when P fertilizer is withheld until soil P falls below the critical agronomic level, since soils can supply adequate labile P in solution even when soil labile P levels are low. This is because nonlabile P pools can be converted to labile P forms at low labile P levels through physical diffusion processes and/or rhizosphere mobilization processes regulated by crop root extracts that release legacy P into the soil solution. Current methods for measuring concentrations and forms of soil P are inefficient in fully capture the role of rhizosphere processes in soil P acquisition. Additional studies of P recovery efficiency from soil legacy pools by crop production are required from long-term monitoring

of soil P levels and crop P uptake dynamics after cessation or reduction of fertilizer and manure application.

Legacy N storage in cropland soils occurs in both mineral (primarily as ammonium and nitrate) and organic (SON) forms, with SON usually dominant. The mass of SON is generally considered to consist of two pools, an active pool subject to mineralization or immobilization, and a protected pool that persists in a steady state with no appreciable net mineralization or immobilization (Van Meter et al., 2016). Due to relatively shallow root depth of many crops (<30 cm), recovery of legacy soil N by crop uptake is mainly controlled by the magnitude of the mineral N pools and mineralization rate of active SON in the surface soil layers. Crops can utilize legacy soil mineral N in the rooting zone quickly following cessation of N inputs. Several field experiments indicate that the recovery percentage of legacy mineral N in the 0–30 cm soil layer by crops could vary from 1% to 30% after 1 year to several decades (Fromme et al., 2017; Mayer et al., 2003; Sebiló et al., 2013; Zhang et al., 2017a).

Mineralization of SON is largely a microbial process, mostly dependent on soil aeration, temperature, and moisture, and is, consequently, affected by factors like soil type and structure, climate, tilling, drainage, water table management, and microbial composition (e.g., fungi to bacteria ratios, Kopáček et al., 2013a). Therefore, N availability is generally greater in the upper compared with lower soil layers due to more favorable conditions for N mineralization in the upper soil profile (higher organic matter content, higher O₂ diffusion). Nitrogen additions can boost microorganism activity and decomposition of organic matter, especially in soils with high C/N ratios. Liming temporarily increases mineralization of SON, increases soil pH, and decreases fungi to bacterial ratios, which promote nitrification and increase the soil inorganic N pool. Drainage and tillage can also increase soil aeration and N mineralization (Chen et al., 2014b). However, not all the residual or microbially generated mineral N in soil is used by plants, since it is subject to chemical and biological transformations that lead to gaseous N losses, assimilation by microorganisms, and leaching losses (primarily as nitrate) from the rooting zone.

Rooting depth varies greatly between species and crop growth stages and thus determines the ability of a crop to intercept and uptake mineral N from the soil profile. SON or immobilized N can also be introduced to the soil solution through crop root exudates. A ¹⁵N-labeled, in situ experiment indicated that 70% of the residue soil N in 0–20 cm layer was recovered in the microbial biomass during the flowering stage and decreased to about 50% at

maturity, while the recovery in wheat and rape increased from 30% at flowering to 50% at maturity (Mayer et al., 2003). Therefore, the soil legacy N pool recovered by crop uptake can be enhanced by root development during crop growth.

Considering the large legacy nutrient pools accumulated in croplands soils due to historical excessive nutrient additions in many regions (Table 1), improving recovery of legacy nutrients from cropland soils by crop productions is critical for reducing nutrient loss to waters (e.g., runoff/erosion and leaching) and the atmosphere, as well as decreasing the expense of nutrient amendments (Rowe et al., 2016; Sattari et al., 2012; Van Meter et al., 2016). Therefore, great agronomic and environmental benefits could be realized from use of legacy nutrients in croplands resulting in appreciable reductions of new nutrient additions. Some practical measures are available for improving use of soil legacy nutrient resources. For example, breeding more P efficient plants will lower P demand and allow legacy soil nutrient resources to be utilized over a longer period. Therefore, plant breeding for more extensive rooting systems and greater rhizosphere mobilization/acquisition efficiency (e.g., enzyme release, mycorrhizae associations) are important component of agroengineering and sustainable farming systems. Changes in farm management, such as precision agricultural practices and inclusion of manure legume crops, could also enhance utilization of available inorganic and organic nutrients in soil (Haygarth et al., 2013). In some acidic soil regions, conversion of upland to paddy field management can improve bioavailability of legacy soil P as a result of flooding events (iron reduction and oxidation cycles, Chen et al., 2017). In many alkaline soil regions, decreasing soil pH through ammonium application can facilitate mobilization of P from calcium phosphates, leading to enhanced N and P uptake at early critical growth stages (Jing et al., 2010). Several commercial bioinoculant products containing single fungal and bacterial species, or mixtures of species, are now available that purport to stimulate rooting and solubilize strongly bound soil inorganic P through acidification and ligand exchange at P sorption sites (Khan et al., 2007; Owen et al., 2015; Rashid et al., 2012). Phosphorus-solubilizing microorganisms can also contribute to increased biological N fixation resulting in a 30%–40% increase in crop yield and/or reduce inputs of inorganic P fertilizer by 50% without affecting crop yield (Khan and Joergensen, 2009).

In terms of legacy soil N resources, the soil legacy reactive N in the root zone is likely to be available for crop uptake, and thus appropriate soil

nutrient testing could inform appropriate N fertilizer application rates (Castellano and David, 2014). On the other hand, crop residue decomposition and legacy SON mineralization also can provide a large quantity of available N during the crop growing season, suggesting further potential to reduce N fertilizer application rates (Halvorson et al., 2005). Measures that favor SON mineralization (e.g., efficient soil water, pH, and fertilizer managements) are critical to consider for supplementing available N to the crops when the nutrient demands of plants are higher. To retain legacy N in the rooting zone, deficit irrigation or water-saving management is a potentially effective practice for maintaining nutrients in the rooting zone for crop uptake (Zhang et al., 2017b). Similarly, field retention of crop residues combined with inorganic N fertilizer could increase SON mineralization and soil N uptake by crops (Herai et al., 2006; Malhi et al., 2011). While SON mining may contribute to agronomic production for several crop rotations (Reis et al., 2016), it is not sustainable in the long term; however, reducing reactive N has large environmental benefits as N losses to the atmosphere and surface and groundwaters will be substantially reduced. We still lack the detailed knowledge concerning how long legacy soil N can support crop production in an economically viable manner. Thus, greater efforts should be focused on improving SON mineralization and recovery by crops, especially for matching seasonal crop N demand dynamics, and to minimize N losses to the atmosphere and surface and groundwaters.

4.2 Environmental Implication of Legacy Nutrients

From an environmental perspective, many long-term field, watershed, and regional studies have indicated that legacy nutrients in soils, sediments, and groundwater have a considerable impact on water quality of receiving waters (Table 4). These studies show that: (i) legacy sources contributed appreciable nutrient fluxes that in some cases were the dominant source of nutrients in receiving waters; (ii) legacy nutrient sources contributed nutrient fluxes to receiving waters persisted for several years to decades (i.e., lag time) in response to reduction of anthropogenic nutrient inputs or implementation of other beneficial management practices (BMPs); (iii) legacy P loss forms and pathways vary over landscapes, i.e., particle P via surface runoff/erosion and dissolved P via subsurface soil drainage, particle P remobilization for river/stream sediments, dissolved P release for lentic system sediments (i.e., lake, reservoir, and wetlands), and dissolved P loss for groundwater; (iv) nitrate derived from mineralization of SON and storage in the vadose

Table 4 Studies of Lag Time Response to Nutrient Level in Receiving Waters From Reductions in Source Nutrient Inputs or Implements of Management Measures

Study Area	Legacy Pools	Nutrient	Studied Results		References
			Lag Time	Legacy Nutrient Flux	
Upper Vltava River watershed, Czech Republic, 1900–2010	Soils	TN	NA	On average >11.5 kg N ha ⁻¹ year ⁻¹	Kopáček et al. (2013b)
Mississippi River Basin, USA		Organic N	35 years	NA	Van Meter et al. (2016)
A grassland and an arable catchment (~10 km ²) in Ireland		Dissolved nutrients	>11 years (grassland) >6 years (arable land)	NA	Vero et al. (2017)
Maumee River watershed, Ohio, USA, 1981–2010		TP and DRP	30–40 years	NA	Muenich et al. (2016)
Cropland lysimeters for wheat and sugar beets, Châlons en Champagne, France, 1982–2009		Nitrate	~100 years	9.6–19.6 kg N ha ⁻¹ year ⁻¹	Sebilo et al. (2013)
Agricultural catchment in southern Sweden, 1973–2011		TP and TN	>18 years	0.29 kg P ha ⁻¹ year ⁻¹ 25 kg N ha ⁻¹ year ⁻¹	Ulén et al. (2015)
Lake Okeechobee Basin (LOB) and Everglades Agricultural Area (EAA), Florida, USA, 1981–2009		TP	22–55 years for LOB 47–118 years for EAA	500 Mt. P year ⁻¹ for LOB 170 Mt. P year ⁻¹ for EAA	Reddy et al. (2011)
Dairygold Research Farm, Teagasc, Animal and Grassland Research and Innovation Centre, Moorepark, Fermoy, Co. Cork, Ireland, 2009–2012		Nitrate	9 years	8.5 kg N ha ⁻¹ year ⁻¹	Fenton et al. (2017)
Yongan River watershed, eastern China, 1980–2009		TN	NA	3.6 kg N ha ⁻¹ year ⁻¹ (35%)	Chen et al. (2014b)

Delmarva Peninsula area of Chesapeake Bay watershed, USA	Groundwater	Nitrate	20–40 years	NA	Sanford and Pope (2013)
Walnut Creek Watershed, Iowa, USA		Nitrate	19 years	NA	Van Meter and Basu (2015)
Seven USA streams by USGS, 1995–2004		Nitrate	18–32 years	3.6–8.0 mg N L ⁻¹	Tesoriero et al. (2013)
Savoy Experimental Watershed (Karst), USA		SRP and TP	>10 years	NA	Jarvie et al. (2014)
Eden Valley, UK		Nitrate	12 years (0–61 years)	NA	Wang et al. (2012)
Seven watersheds of different sizes, USA		Nitrate	4–>50 years	NA	Meals et al. (2010)
Twenty-eight aquifer zones in England and Wales		Nitrate	>10 years	NA	Wang et al. (2016)
110 world lakes, 1970–2014		PO ₄ -P and nitrate	Decades	0.74–2900 mg P m ⁻² year ⁻¹ 0.001–640 g N m ⁻² year ⁻¹	Lewandowski et al. (2015)
Illinois River watershed, USA, 1997–2007	Sediments	TP	NA	1%–32% at Siloam site and 4%–68% at Tahlequah site	Jarvie et al. (2012)
Yongan River watershed, eastern China, 1980–2010		TP	NA	0.8–35.5 Mg P year ⁻¹ (2%–29%)	Chen et al. (2015c)
35 Lakes in USA and Europe		TP	10–15 years	NA	Jeppesen et al. (2005)
		TN	<5 years	NA	
Lake Søbygård, Denmark		TP	20 years	NA	Søndergaard et al. (2007)
Seven lakes in USA and Europe		TP or dissolved P	5–30 years	NA	Sharpley et al. (2013)

Continued

Table 4 Studies of Lag Time Response to Nutrient Level in Receiving Waters From Reductions in Source Nutrient Inputs or Implements of Management Measures—cont'd

Study Area	Legacy Pools	Nutrient	Studied Results		References
			Lag Time	Legacy Nutrient Flux	
Mississippi River Basin, USA, 1960–1998	Entire watershed	Nitrate	9 years	NA	McIsaac et al. (2001)
Yongan River watershed, eastern China, 1980–2009		TN	7 years	On average 3.6 kgN ha ⁻¹ year ⁻¹ (35%)	Chen et al. (2014b)
Yangtze River Basin, 1980–2012		DIN	NA	2.33–5.10 kgN ha ⁻¹ year ⁻¹ (29%–51%)	Chen et al. (2016c)
Yongan River watershed, eastern China, 1980–2010		TN	NA	0.2–3.8 kgN ha ⁻¹ year ⁻¹ (10%–28%)	Chen et al. (2016a)
Yongan River watershed, eastern China, 1980–2010		TN	>12 years	4.0–19.1 kgN ha ⁻¹ year ⁻¹ (72%–85%)	Chen et al. (2014a)
Yongan River watershed, eastern China, 1980–2010		TN	11 years	3.68–16.1 kgN ha ⁻¹ year ⁻¹ (64%–81%)	Chen et al. (2015a)
Mississippi River Basin (MRB) and Susquehanna River Basin (SRB), USA, 1960–2014		Nitrate	>10 years	85% for MRB and 47% for SRB	Van Meter et al. (2017)
Average Dutch catchment shallow lake system	TP	5–50 years for surface runoff P level; 69 years for sediment P level; 150–1700 years for soil layer percolation P level	NA	Schippers et al. (2006)	

Yahara Lake watershed, Midwestern USA, 1986–2013	TP	NA	0.61–1.43 kgP ha ⁻¹ year ⁻¹	Motew et al. (2017)
Yongan River watershed, eastern China, 1980–2010	TP	NA	0.023–0.098 kgP ha ⁻¹ year ⁻¹ (8%–58%)	Chen et al. (2015b)
Yongan River watershed, eastern China, 1980–2010	TP	NA	0.01–0.18 kgP ha ⁻¹ year ⁻¹ (8%–27%) in agricultural and forest landscapes; 0.002–0.14 kgP ha ⁻¹ year ⁻¹ (3%–6%) in residential landscapes	Chen et al. (2016b)

zone and groundwater is the major N loss form, and subsurface flow and groundwater recharge are the major loss pathways for legacy N loss; and (v) anthropogenic (e.g., land use, dam/reservoir development or removal, and cropland management measures) and natural (e.g., precipitation, storm events, and climate change) disturbances can enhance legacy nutrient release and loss by influencing hydrological and biogeochemical processes.

4.2.1 Legacy Nutrients in Cropland Soils

Transport of legacy P from soils to drainage/stream systems occurs primarily in particulate form due to surface runoff/erosion (Haygarth et al., 2006; Withers et al., 2009) but can also occur in dissolved forms via subsurface flow in artificial-drained systems. The magnitude of soil legacy P loss is usually dependent on the degree of soil P accumulation, rainfall/runoff dynamics and soil management (e.g., tillage, cover crops, buffers, grass waterways, and drainage patterns). Storm events typically generate the majority of particle-transported legacy P from surface soils via surface runoff/erosion. Eroded sediments are typically enriched with P relative to the bulk soil (up to fivefold) due to the preferential removal of fine soil particles with greater P content. Therefore, even where overall soil P levels may be low, legacy P sources can contribute significantly to runoff/erosion, especially in hydrologically active and erodible landscapes (Gburek and Sharpley, 1998).

In general, critical source areas contributing to P pollution loads within a watershed are attributed to high hydrological connectivity and high soil P concentrations due to long-term overfertilization (Kleinman et al., 2007). Several field experiments demonstrated that transport of dissolved forms of soil legacy P via tile drainage or macropores were the major pathways for croplands, especially when manure was applied and erosion potential was low. Downward movement of legacy P into the unsaturated zone and underlying groundwater can be particularly problematic in regions where soil P sorption capacity has been exceeded (Vadas et al., 2007), and areas with intensive manure additions, shallow groundwater and coarse-textured soils (Holman et al., 2008, 2010). Legacy P mobility and leaching in cropland soils is enhanced when soil P levels exceed the threshold P saturation ratio (a molar ratio of Mehlich extractable P to [Fe + Al], Nair, 2014). Moreover, conservation tillage measures (e.g., reduced tillage and no-till) could significantly reduce particle P transport, but in turn could exacerbate dissolved P leaching. Reduced tillage increases organic matter in surface soils leading to increased mineralization and release of dissolved P for potential transport by surface and subsurface runoff as well as

groundwater (Daloglu et al., 2012). In general, mean dissolved P concentrations in shallow groundwater closely mirror P concentration trends in the soil, with the highest dissolved P concentrations near the soil surface and progressively lower concentrations with increasing soil depth. Due to chemical and biological transformations, adsorption/desorption, dissolution/precipitation dynamics of legacy soil P, reducing P enrichment, especially in surface soils, will lower the potential for P losses by runoff/erosion and leaching; however, the response to reduced P additions may take several years to decades (Dodd et al., 2012).

Legacy soil N loss from croplands to drainage/stream systems is associated with surface runoff/erosion of both particulate and dissolved N forms and with subsurface flow of dissolved N forms, primarily nitrate. Legacy soil N transport to drainage/stream systems is influenced by factors such as precipitation, soil texture, hydrologic flowpaths, N inputs, crop type and rotation, tillage, and land drainage. Accumulated particulate N (including exchangeable NH_4^+ and organic N bound to clay particles) as well as mineral N in surface soils is susceptible to loss through surface runoff/erosion. Due to the high mobility of NO_3^- in most soils and the transient stability of NH_4^+ and organic N (due to conversion by mineralization and nitrification) in surface soil layers, loss of them via surface runoff to drainage/stream systems is usually considerable (Berhe and Torn, 2017). Although loamy and clayey soils usually have more N loss via surface runoff and less N loss via subsurface flows compared to sandy soils, subsurface loss of legacy dissolved and particle N is more rapid and direct through preferential flowpaths (i.e., tile drainage and macropores) to stream systems and groundwater. Carter et al. (2003) reported that particulate-associated N represented up to 27% of the total N transported in tile drain outflow.

The majority of legacy N in cropland is stored in SON (Kopáček et al., 2013a; Van Meter et al., 2016); thus, nitrate leaching derived from mineralization of SON is an important pathway for legacy N loss to drainage/stream systems. Factors that enhance SON mineralization (e.g., increasing pH, improving soil drainage, increased soil disturbance, and organic matter) can increase legacy N losses via subsurface flow. For example, mineralization of SON pools due to improved drainage and lime application contributed to an increased riverine N flux of $>11.5 \text{ kg N ha year}^{-1}$, which dominated riverine N inputs to the Upper Vltava watershed over the 1959–2010 period (Kopáček et al., 2013b). In terms of intraannual variation, loss of legacy SON is enhanced by wetting and drying cycles that cause soil macroaggregates to break apart, exposing physically protected organic matter to erosion,

degradation, and mineralization (Lundquist et al., 1999). As a result, it is widely observed in both field and watershed studies that soil N is usually stored during “dry” years or seasons and flushed from watersheds during “wet” years or seasons (Howarth et al., 2012). Dependent on SON magnitude and hydraulic conductivity and connectivity, it usually requires several years to decades for N levels in groundwater to respond to changing N fertilization levels. For example, Owens et al. (2008) reported that due to mineralization of residual SON nitrate levels in groundwater took several years to observe in a small (<2 ha) pasture watershed following cessation of N fertilization. Modeling results from the Mississippi River Basin indicated that depletion of legacy SON from croplands would require ~35 years as N is lost to groundwater, streams, atmosphere, and biomass removal (Van Meter et al., 2016). In the United Kingdom, N concentrations are still increasing in some lowland aquifer regions due to fertilizer N inputs from over 50 years ago (Howden et al., 2011). Thus, the lag time associated with removal of transiently stored N from soils typically requires several decades making groundwater nitrate remediation a long-term problem.

Although there are limited studies concerning soil legacy N on N₂O emissions, several long-term experiments indicated that cropland soil legacy N derived from historical fertilizer and manure additions could contribute considerable N₂O emissions (Adviento-Borbe et al., 2010; Drury et al., 2014). For example, a 10-d incubation experiment indicated soils with a 20-year N fertilization history could increase N₂O emissions by roughly one order of magnitude on average relative to historically unfertilized control plots, which mainly related to differences in soil legacy available and readily mineralizable N (LaHue et al., 2016). These results suggest that ignoring soil legacy N would potentially underestimate the fertilizer and manure contributed N₂O emissions from cropland soils.

4.2.2 Legacy Nutrients in Sediments

Legacy P stored in sediments of drainage/stream and lentic systems may have a considerable contribution to the overlying water column as well as downstream waterbodies. Due to the short hydrological residence time of fluvial systems, legacy P is usually stored in the surface sediment layer and has short-term effect resulting from physical deposition and remobilization processes (Sharpley et al., 2013). Fluvial P deposition in sediments mainly occurs during the low-flow regime, and subsequently the retained P can be being remobilized via erosion of fine bed sediments, advective release of dissolved P from pore waters, and scouring of biologically incorporated P from

benthic sources during high-flow regimes (e.g., storm events). Therefore, the lag time of such P sediment dynamics (deposition/remobilization) within fluvial channels is generally on the order of months. However, such short-term legacy effects may cause a considerable underestimation of point source P inputs and provide an important ecological connection to algal requirements for bioavailable P, especially during the spring and summer. For example, legacy P in riverine sediments accounted for 1%–32% of annual riverine P load at the Siloam site and 4%–68% at the Tablequah site in the Illinois River watershed in 1997–2007. Similarly, legacy P accounted for 2%–29% of annual riverine P load in the Yongan watershed of eastern China (1980–2010) where summer (i.e., May to September) rainfall results in high nutrient inputs, temperatures, and sunlight that fuels algal nutrient uptake (Chen et al., 2015c; Jarvie et al., 2012). Under these circumstances, the point source P pollution load would be underestimated by a large amount if riverine legacy P from sediment dynamics was not considered. Converging with nonpoint source P loading, such remobilized legacy P would enhance P pollution and aggravate alga blooms. Stream/river sediments can also contribute a considerable P flux due to sediment PO_4 desorption or organic matter mineralization. A literature review by Fitzgerald et al. (2015) showed that high groundwater PO_4 is often linked with desorption from sediments or organic matter mineralization. In terms of an entire drainage/river system, sediment-bound P can take years to move downstream as particles are repeatedly deposited, resuspended, and redeposited within the drainage network by episodic high-flow events. This process can delay particulate P transport from upstream channels to the downstream outlet by years or even decades.

Due to long hydrological residence times, legacy P accumulated in sediments behind river impoundments or dams (reservoirs), lake, and wetlands can become an important source of P and a potential risk for downstream water quality. Release of legacy P from sediments in lentic systems (standing waters) is influenced by biotic and abiotic regulation, such as external P loadings, dissolved oxygen, carbon and sulfur inputs, pH, and anthropogenic disturbances. For example, Jeppesen et al. (2005) examined the recovery of 35 lakes after external nutrient load reduction and found that internal P loading from legacy sources delayed ecological recovery of these lakes by 10–15 years. Compared to shallow lakes or reservoirs, deep lakes and reservoirs experiencing seasonal stratification demonstrated that legacy sediment P loading remained an important driver of eutrophication for longer time periods (20–70 years) following P input reductions (Carpenter, 2005;

Schippers et al., 2006). Net release of nutrients is regulated by microbial nutrient requirement and C/P and N/P ratios of the substrate undergoing decomposition in wetlands. A high sediment organic C content promotes migration of the redox boundary to, or above, the sediment–water interface resulting in reductive dissolution of the PO_4 sorbing Fe-oxyhydroxides in the surface sediments. For example, sediments in the northern Gulf of Mexico released $0.02\text{--}4.4\text{ mg kg}^{-1}\text{ d}^{-1}$ of bioavailable-P under anoxic sediment conditions, indicating the role of hypoxia events in releasing available-P to the water column (Adhikari et al., 2015). Mechanical disturbance of the “oxidized cap” of surface sediment can also enhance release of P-rich pore waters from anoxic sediments into the overlying water column. Net P release is initiated by flooding previously dry soil/sediment, such as following reservoir creation or wetland restoration. For example, in the 2 years following hydrologic reconnection of a restored wetland in the North Carolina coastal plain, a P mass balance documented release of $0.6\text{ kg P ha}^{-1}\text{ year}^{-1}$ (Ardón et al., 2010). In terms of seasonal dynamics, spring and summer base-flow periods have the highest eutrophication risk and are therefore times when legacy P export from wetlands can contribute most significantly to primary production and degradation of downstream water quality and aquatic ecosystems (Edwards and Withers, 2007).

Although release of legacy N from sediments is not as pervasive and widely reported as P due in part to sediment denitrification, legacy N in sediments occurs in many aquatic systems. Particulate N mineralization in anoxic sediments generates NH_4^+ , which will not undergo denitrification until nitrification converts the NH_4^+ to NO_3^- (requires aerobic conditions). Thus, high levels of NH_4^+ and PO_4^{3-} accumulate in the pore waters of anoxic sediments where they can diffuse upward into the water column (Zamora et al., 2013). Although wetlands and riparian buffers usually serve as a sink for nutrients, some studies indicate that wetlands and riparian buffers may eventually increase nutrient loadings by collecting and transforming particulate N into soluble N loadings. This results in a progressive biological saturation of N with aging and the ultimate release of legacy N to downstream waterways where eutrophication may be stimulated (Fisher and Acreman, 2004). For aged wetlands, N as well as P storage in aboveground macrophyte biomass is usually short lived with most nutrients released by decomposition in months to years for potential downstream transport. For example, up to 30% of the nutrients contained in wetland plant biomass are lost by leaching during the first few days of decay (Vymazal, 2007); leaching and decay are enhanced by higher temperature (Beutel et al., 2014). In lakes, studies of

sediment cores indicate that sediments released 30%–70% of their N to the water column within 5 years with additional N release in the following decade (Gälman et al., 2008). Enhanced N as well as P release from anoxic sediments is an important positive feedback mechanism that reinforces the eutrophication process and could delay the response to reduced nutrient loadings. Kemp et al. (2005) discussed the lag in response to changes in nutrient loading to Chesapeake Bay estuary in terms of a nonlinear feedback mechanism.

For river impoundments, natural collapse, or purposeful removal of dams for ecosystem restorations (e.g., recovery salmon migration), a considerable release of legacy nutrients from newly aerobic sediments was shown with nutrient export to downstream waterbodies (Walter and Merritts, 2008). For example, after dam removal at Murphy Creek, California, N leaching from reservoir sediments was largely a seasonal process and resulted in TN and $\text{NO}_3\text{-N}$ concentrations on average twofold greater than before dam removal (Ahearn and Dahlgren, 2005). Stream bank and reservoir shoreline erosion contribute legacy sediments as well as particulate N and P that are recognized as a potential source of sediments and nutrients to surface waters (Merritts et al., 2010; Walter et al., 2007). A field observation of four streams after historical mill dam removal or collapse in the Chesapeake Bay watershed demonstrated N and P release from legacy bank sediments of 264–1782 kg N $\text{ha}^{-1} \text{year}^{-1}$ and 224–629 kg P $\text{ha}^{-1} \text{year}^{-1}$, respectively, which were 32–223 and 43–121 times higher than reference stream levels (Shuman and Shuman, 2011). Overall, release of legacy sediment N in stream systems is mainly regulated by physical disturbance (e.g., dam removal or collapse), while in lentic waters it is mainly influenced by the biological N saturation status.

4.2.3 Legacy Nutrients in Groundwater

In spite of its relatively low mobility through many soils, legacy P can contribute to elevated levels of P in groundwater. Areas with high fertilizer/manure inputs that exceed the soil P sorption capacity (Vadas et al., 2007), shallow groundwater, and coarse-textured or weakly weathered soils (Holman et al., 2008, 2010; Schippers et al., 2006) are particularly susceptible to groundwater P contamination. Subsequently, groundwater discharge of P to surface waters can contribute to eutrophication if there is good connectivity between groundwater and surface waters, intensive land use occurs on soils prone to leaching, and groundwater P is not attenuated during transport through the aquifer. High contributions of groundwater

P to surface waters are usually linked to old groundwater age, intensive land use (i.e., dairy and urban), and a high base-flow index (BFI) (Ballantine et al., 2009; Morgenstern and Daughney, 2012). The relationship between dissolved reactive P and groundwater age is purported to exist because older groundwater is more likely to be reduced (anoxic) (Daughney et al., 2010) resulting in favorable conditions for iron oxide dissolution and release of associated P (Carlyle and Hill, 2001). Groundwater contribution of dissolved P is also dependent on the redox condition of the stream hyporheic zone, where oxic conditions at the streambed interface may allow SRP sorption or mineralization coupled with iron reduction reactions (Carlyle and Hill, 2001; Ptacek, 1998; Van der Grift et al., 2014). In many sites where the majority of streamflow is groundwater derived and baseflow occurs predominantly in summer–autumn when the potential for periphyton growth is greatest (e.g., New Zealand, United Kingdom, California, and Ireland), periphyton growth is strongly regulated by dissolved P inputs from groundwater (Biggs and Smith, 2002; Brennan et al., 2017; Holman et al., 2008, 2010). For example, the mean dissolved P concentration for the sites under a dairy in New Zealand was 0.33 mg L^{-1} in groundwater and $\sim 0.05 \text{ mg L}^{-1}$ in surface water, which were in excess of P concentrations considered likely to cause nuisance periphyton growth in streams and rivers (McDowell et al., 2005). Phosphorus-rich groundwater in urban areas may also be hot spots contributing high P concentrations to surface waters (Holman et al., 2010). For example, the study of a 28-m urban stream reach found that groundwater contributed $\sim 9 \text{ g P d}^{-1}$ of soluble reactive P to the stream, which compares to background baseflows loads of $20\text{--}1100 \text{ g P d}^{-1}$ (Fitzgerald et al., 2015). In some specific sites, such as karst landscapes, legacy P is retained by reaction with clays and coprecipitation with CaCO_3 . However, in epikarst, and within the fractures and conduits along the groundwater flowpath, there is considerable potential for remobilization and release of the retained P resulting in a long-term source of slowly released legacy P to surface waters (Jarvie et al., 2014).

Due to the high mobility of nitrate through soils, groundwater has been widely recognized as a hot spot for contributing legacy N to surface waters (Hamilton, 2012; Tomich et al., 2016). The contribution of groundwater legacy N to surface waters is dependent on N concentrations in groundwater (mainly associated with human activities), the baseflow index (BFI), and riparian and hyporheic zone function. Across agricultural and urban landscapes, legacy N in groundwater has been observed to discharge a considerable N load to surface waters across wide range of watershed

characteristics. Due to groundwater legacy N contributions, Owens et al. (2008) reported that stream water quality response to changes in N fertilization rate took several years, even in a very small (<2 ha) agricultural catchment. Groundwater can supply a significant amount of water and N to streams as exemplified by about half of the N load in streams of the Chesapeake Bay watershed originating from groundwater with a median groundwater age of 10 years (Phillips et al., 2003). A study of six urban sub-watersheds in St. Paul, Minnesota showed that baseflow, which was dominated by groundwater inputs, contributed to 31%–68% of the warm season total N loads and 7%–32% of the warm season total P loads to receiving surface waters (Janke et al., 2014). Groundwater legacy N contributions are believed responsible for why many agricultural and urban rivers in the United Kingdom still carry elevated nitrate loads in spite of considerable reductions in watershed N inputs (Burt et al., 2011; Howden and Burt, 2009). The BFI has been recognized as a good first approximation of the expected groundwater contribution to surface water nitrate loads. For example, nitrate concentrations were usually high in upland groundwater and in streambed pore waters in seven agricultural watersheds with high BFIs in the United States (Tesoriero et al., 2013). The groundwater legacy nitrate contribution will elevate nitrate concentrations in these stream for decades even if N applications within the watershed are considerably reduced. Large groundwater–surface water legacy effects are widely expected to occur in many agricultural regions of the United States with BFI >0.4 (Tesoriero et al., 2013).

Denitrification, the anaerobic microbial respiratory pathway in which nitrate is converted to reduced N gases (e.g., N_2 , N_2O), is a predominant removal process for attenuating legacy N loads in groundwater and subsequently to surface waters. Net groundwater contributed N load can be further attenuated by denitrification occurring in the stream riparian zone and hyporheic zone. For example, Galavotti (2004) and Gu et al. (2007) found that most of the groundwater nitrate was denitrified during transport through a 30-cm thick organic-rich layer located directly beneath the sediment surface. For shallow groundwater, a number of studies have highlighted the denitrification potential and nitrate removal occurring during transport through the subsurface riparian zone (Fisher and Acreman, 2004; Flewelling et al., 2012; Hinshaw and Dahlgren, 2016). Stable isotopic (^{18}O), radioisotopic (3H), and dissolved gas (e.g., dissolved chlorofluorocarbon gases) analyses to determine groundwater transit times to surface water indicate a wide range of transit times from several years to decades

(McDonnell et al., 2010; McGuire and McDonnell, 2006). Therefore, high legacy N or P levels contributed by groundwater will be persistence in receiving surface waters having appreciable groundwater inputs.

Legacy nutrient accumulation in various landscapes within watersheds has been recognized as a primary cause for the failure of water quality improvement after implementing nutrient source controls (i.e., reduction of anthropogenic nutrient inputs) and BMPs for several years to decades. It is necessary to integrate the concept of transient legacy nutrients and nutrient leaching lag times into sustainable nutrient management strategies for future food, bioenergy, and water security (Rowe et al., 2016). In addition to agronomic benefits, adopting relevant measures to improve the utilization of legacy soil nutrients will reduce future nutrient application needs for crop production and simultaneously yield important environmental benefits through a gradual attenuation of nutrient to groundwater and aquatic systems (Jarvie et al., 2013; Sharpley et al., 2013).

BMPs usually include placing limits on the amount, timing, and methods of nutrient application to land, intercepting nutrients during transport and remediation of receiving waters. Relevant field BMPs should be encouraged to decrease losses of legacy soil N and P via runoff/erosion from fields to downstream landscapes (e.g., drainage, wetlands, riparian buffers, and streams/rivers). Although interception measures (such as wetlands, bio-retention fields/basins, riparian buffers, and vegetated filter strips) are able to retain nutrient within the landscape, they require considerable management to avoid biological N and physical P saturations which leads to the remobilization of the retained nutrients. Current control measures for attenuating legacy nutrient loss to surface water are limited by: (1) inefficiency in reducing dissolved nutrient losses from terrestrial legacy nutrient pools to groundwater and surface waters due to the fact that most BMPs are focused on reducing erosion and surface runoff or placement of fertilizer nutrients below the surface (Dodd and Sharpley, 2016); (2) inefficiency in mitigating the groundwater legacy nutrient export source due to the fact that most BMPs are focused on terrestrial surface transport processes (Penn et al., 2014); (3) inefficiency in avoiding or controlling nutrient release derived from legacy nutrients in sediment from wetlands, streams, and lakes/reservoirs; and (4) the appreciable time required for measures to produced their desired effects considering the significant amount of legacy nutrients that must be removed over long time periods (Meals et al., 2010).

For waters experiencing appreciable legacy nutrient pool contributions, it is necessary to adopt and develop other measures to decrease nutrient loads

derived from legacy pools in groundwater and sediments, as well as to improve the efficiency for reducing dissolved nutrient losses from the soil zone. For example, in situ P removal structures contain P sorbing materials (such as steel slag and fly ash) and denitrification beds/barriers (such as wood chip and straw) can be placed in a location to intercept subsurface runoff with high dissolved nutrient concentrations (Penn et al., 2014). For regions having high legacy nutrient levels in groundwater, permeable reactive barriers containing reactive materials for removal of N and P along the groundwater flowpath should be effective in mitigating groundwater legacy nutrient loads to surface waters in ecologically critical zones. It may also be efficient to reduce legacy nutrient loads from set BMPs (e.g., wetlands and buffers) by regulating their hydrological linkages to the receiving waters. In terms of eutrophication, it may be possible to adopt relevant measures to change the timing of legacy nutrient remobilization from sediments (e.g., reservoir release strategies) for avoiding reactive nutrient release and discharge during ecologically critical times (Edwards and Withers, 2007). We highlight the need to incorporate legacy nutrient issues into a comprehensive watershed nutrient management framework, particularly for regions experiencing historical and/or current periods of excessive anthropogenic nutrient inputs.



5. FUTURE RESEARCH NEEDS CONCERNING LEGACY NUTRIENTS

Past human activities have led to the buildup of considerable legacy nutrient pools across various landscapes within watersheds (Table 1), which result in significant agronomic and environmental impacts (Tables 3 and 4). As indicated in many case studies worldwide, several years to decades will be required to drawdown the legacy N and P stores in soils, sediments, vadose zone, and groundwater via crop uptake, hydrological loss, and gaseous removal, even if new anthropogenic N and P inputs were totally eliminated (Chen et al., 2014a, 2016b; Howden et al., 2011; Sharpley et al., 2013; Van Meter et al., 2016; Withers and Bhadeshia, 2001). Previous studies suggest that legacy nutrients from past anthropogenic inputs present a large and potentially long-term source of nutrients to receiving waters, as well as a potentially important nutrient source for future crop production that could reduce reliance on inorganic fertilizers. Considering increasing global population, possible future rock phosphate shortages, denitrification contributions to greenhouse gas emissions (N_2O), and water pollution, it is

strongly warranted to integrate legacy nutrients into sustainable watershed nutrient management plans for future food, bioenergy, and water security. These plans require strategies to maximize use of legacy nutrients and minimizing their loss to the atmosphere and surface waters. Achieving these critical goals requires qualitative and quantitative knowledge concerning the distribution and magnitude of legacy nutrients, measures for enhancing recovery via crop production and mitigating losses to the atmosphere and surface waters. Due to the paucity of sufficient research on legacy nutrients and the lag time associated with their transport, there is currently a lack of comprehensive knowledge to efficiently address plausible BMPs. From agronomic and environmental perspectives, we review four major knowledge gaps that are critical for improving our understanding and management of watershed legacy nutrient pools.

(i) How to determine legacy nutrient accumulation and losses at the watershed scale?

Information on the magnitude, distribution, forms, and transformations of legacy nutrients across various watershed landscapes is critical for evaluating potential agronomic and environmental impacts. Due to lack of historical records in many regions, it is difficult to directly determine net nutrient accumulations in soil, sediments, and groundwater and in what forms these legacy nutrients have accumulated at the watershed scale. Estimated results from mass balance studies are usually subject to considerable uncertainty associated with site-specific parameters sourced from local reports or extrapolated from other regions. Thus, it is very difficult to develop historical watershed nutrient input–output balances due to lack of available information for individual nutrient input and output pathways. A critical example is the inherent difficulties in measuring denitrification given the considerable uncertainty that exists regarding denitrification rates across different watershed landscapes (Hofstra and Bouwman, 2005; Seitzinger et al., 2006; Van Meter et al., 2016). Given the presumed importance of denitrification at the watershed scale (30%–50% of NANI, Chen et al., 2014a, 2015a), it is critical to constrain denitrification losses. A promising approach for constraining denitrification fluxes in the use of groundwater $N_2:Ar$ dissolved gas ratios to provide a direct measure of denitrification within a given groundwater flowpath (Bourbonnais et al., 2015; Hinshaw and Dahlgren, 2016; Singleton et al., 2007). The high spatial and temporal variability in natural and anthropogenic processes, nutrient inputs, transport, transformations, and outputs at the watershed scale greatly increases the difficulty for characterizing where and when nutrients accumulate in. To effectively determine

legacy nutrient pools, this study highlights the need for long-term monitoring efforts to determine changes in nutrient dynamics in soil, sediments, groundwater, and surface waters along with their responses to human activities and climate changes. It is also necessary to improve time- and site-specific estimates of nutrient fate and transport at the watershed scale.

(ii) How to efficiently balance soil legacy nutrient and new nutrient sources for sustainable crop production?

Cropland soil is the dominant landscape component for accumulating legacy nutrient pools from historical fertilizer and manure applications (Table 1), which provides a great potential nutrient source for crops. The availability (i.e., nutrient form and soil depth distribution relative to crop rooting zone) of soil legacy nutrients for crop utilization is dependent on soil type, pH, organic matter, microbiological communities, tillage, drainage, crop rooting depth, and land-use history (MacDonald et al., 2012; Negassa and Leinweber, 2009; Powers et al., 2016). Cropland soil legacy N is mainly stored in SON, while legacy P primarily accumulates in labile and moderately labile inorganic P forms in temperate soils, and as moderately labile and nonlabile inorganic P forms in tropical soils. Therefore, measures aimed at improving legacy nutrient utilization by crops are necessary to reduce reliance on new fertilizer inputs. A range of measures from crop breeding, tillage, moisture regulation, cultivation, intercropping, and adopting artificial bioinoculant products are available for enhancing utilization of soil legacy nutrients by crops. Individual measures might be applicable for specific sites, but it is difficult to match heterogeneous settings with different soil legacy nutrient forms and soil profile distributions in different farming systems. Multidisciplinary research integrating soil, plant, and microbial disciplines are clearly required to develop efficient measures for enhancing legacy nutrient recovery in different farming systems. To avoid decreasing crop yields, knowledge concerning contributions of soil legacy nutrient and their depletion rates relative to applied fertilizer/manure to crop uptake is required. Based on these efforts, an integrated framework that includes new precision farming technologies, plant breeding, and microbial engineering should be developed to optimize exploitation of legacy soil nutrient sources.

(iii) How to determine the contribution of legacy nutrients to nutrient pollution loads and their effective integration into watershed models?

It is clear that we must implement efficient measures that not only reduce nutrient losses from current fertilizer and manure nutrient inputs but also address the mobilization and delivery of legacy nutrients in leachate, runoff,

and erosion. Quantitative information concerning the contribution of legacy nutrient sources to nutrient pollution loads and the lag time associated with legacy nutrient transport are critical components required to optimize pollution control expenditures, strategies, and schedules, as well as to set appropriate expectations for the public (Bouraoui and Grizzetti, 2014; Sanford and Pope, 2013; Sharpley et al., 2013). What remains unclear is the extent to which today's eutrophication results from current anthropogenic activities vs legacy nutrients from past anthropogenic activities. This issue is of fundamental importance for policy development and setting realistic expectations regarding the impact of current nutrient reduction strategies on nutrient loads. Legacy nutrient stores and their impact on waterbody recovery trajectories therefore need to be better quantified to inform nutrient load reduction strategies. Watershed source apportionment of the nutrient pollution loads to receiving water usually relies on simulation models. However, most current watershed models do not effectively incorporate legacy nutrients, while recently developed models (Table 2) are simplistic in their treatment of legacy nutrients resulting in great uncertainty in their projections related to legacy nutrients. Therefore, significant improvements are needed to watershed models for representing soil, sediment, vadose zone, and groundwater legacy nutrient dynamic processes to provide more realistic nutrient source apportionment results and predictions of changes in water quality.

(iv) How to mitigate legacy nutrient losses with beneficial management measures?

Although a range of BMPs are available for reducing nutrient pollution, they are often not equally effective in attenuating legacy nutrient losses as opposed to current nutrient losses to surface waters. Due to the time required for BMPs to produce a desired effect, there is usually a considerable lag time (ranging from several years to decades) between implementation of BMPs and their measureable response in water quality at the watershed scale (Meals et al., 2010). Many BMPs, such as conservative tillage, buffer zones (e.g., grass and vegetative filter strips), and managed riparian zones, which are mainly aimed at trapping particulate nutrients on the landscape, are subsequently becoming legacy sources for dissolved nutrients once they reach nutrient saturation with respect to biological demands (Dodd and Sharpley, 2016; Meals et al., 2010). Due to the high bioavailability of dissolved nutrients derived from legacy sources, these nutrient inputs enhance the risk of eutrophication and harmful algae blooms in downstream surface waters. Therefore, consideration should be given to modifying and improving current BMPs to reduce the potential for biological nutrient saturation that

contributes to sustained nutrient loss and a considerable lag time for nutrient losses. Further research investigating new technologies (e.g., in situ removal structures, groundwater permeable reactive barriers, denitrification barriers, etc.) is warranted to remediate legacy nutrient contributions from groundwater and sediments. Based on a realistic understanding of watershed nutrient delivery processes, a specific and systematic remediation framework can be developed to implement appropriate selection, setting, and monitoring of BMPs for a given watershed.



6. CONCLUSION

This review documents that historical nutrient management practices have led to the accumulation of considerable legacy nutrient pools in the soil, sediment, vadose zone, and groundwater of many watersheds worldwide. The location, magnitude, and chemical forms of legacy nutrients accumulated in watersheds are subject to complex interactions among hydraulics, hydrology, geomorphology, biogeochemistry, and land management. Most current watershed models fail to effectively incorporate legacy nutrient dynamics associated with biogeochemical and hydrological processes. Models that consider legacy nutrient dynamics are still rare available and are subject to great uncertainties associated with oversimplification of related processes and the lack of comprehensive data for parameterization and validation. In many highly managed watersheds, it will take many years or decades to attenuate legacy nutrient pools via crop uptake, atmospheric emissions, and hydrological losses, implying that legacy nutrients will continue to contribute to long-term water quality degradation for years to come. However, there is great potential, especially for P, to utilize a large fraction of the legacy nutrient pool stored in the soil zone for crop production thereby reducing reliance on future inputs of inorganic fertilizers. This study highlights the importance of integrating legacy nutrient considerations into sustainable watershed nutrient management strategies for future food, bioenergy, and water security through implementation of strategies for crop utilization of legacy nutrients that will in turn attenuate their loss to surface and groundwaters. Future research needs to work toward a better understanding of quantifying legacy nutrient pools across watershed landscapes, enhancing soil legacy nutrient recovery by crops under different farming systems, partitioning current surface water nutrient loads between legacy and current nutrient sources, and modifying and developing new strategies (BMPs) for mitigating legacy nutrient losses.

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