



Review

Phosphorus Transport along the Cropland–Riparian–Stream Continuum in Cold Climate Agroecosystems: A Review

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Abstract: Phosphorus (P) loss from cropland to ground and surface waters is a global concern. In cold climates (CCs), freeze–thaw cycles, snowmelt runoff events, and seasonally wet soils increase P loss potential while limiting P removal effectiveness of riparian buffer zones (RBZs) and other practices. While RBZs can help reduce particulate P transfer to streams, attenuation of dissolved P forms is more challenging. Moreover, P transport studies often focus on either cropland or RBZs exclusively rather than spanning the natural cropland–RBZ–stream gradient, defined here as the cropland–RBZ–stream continuum. Watershed P transport models and agronomic P site indices are commonly used to identify critical source areas; however, RBZ effects on P transport are usually not included. In addition, the coarse resolution of watershed P models may not capture finer-scale soil factors affecting P mobilization. It is clear that site microtopography and hydrology are closely linked and important drivers of P release and transport in overland flow. Combining light detection and ranging (LiDAR) based digital elevation models with P site indices and process-based models show promise for mapping and modeling P transport risk in cropland–RBZ areas; however, a better mechanistic understanding of processes controlling mobile P species across regions is needed. Broader predictive approaches integrating soil hydro–biogeochemical processes with real-time hydroclimatic data and risk assessment tools also hold promise for improving P transport risk assessment in CCs.

Keywords: phosphorus; agriculture; biogeochemistry; riparian buffers; critical source areas; nutrient management; overland flow; hydrogeology; snowmelt; streamflow; tile drainage; water quality



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1. Introduction

Phosphorus (P) is an essential biosphere component and integral to cellular energy currency in the form of adenosine triphosphate. Phosphate molecules also form the backbone of deoxyribose nucleic acid and other important biological molecules. In addition to imposing important limits on both terrestrial plant and crop productivity, P availability is also the main factor affecting freshwater eutrophication risk [1]. Unlike carbon (C) and nitrogen (N), P does not undergo substantial atmospheric loss. Phosphine (PH₃) is the only known gaseous P form on Earth and its formation is not considered a substantial P loss mechanism from most soils or aquatic sediments [2]. In soil–water systems, pentavalent P forms appear to be most common (P⁵⁺); however, water-soluble reduced organic and inorganic P species have also been reported [3].

Once in solution, P acts as a weak Lewis acid with strong affinity for positively charged surface metal ligands, most notably aluminum (Al), iron (Fe), and manganese (Mn) hydroxides, often as organic matter–metal–P complexes [4,5]. Orthophosphate is bioavailable once in solution with maximum availability to (micro)organisms in soils and aquatic sediments near pH 7.0. Variably charged Al and Fe hydroxides are protonated at lower pH (and thus are highly soluble at lower pH), sorbing P from solution more efficiently [5]. As pH

increases above 7.0, Ca and Mg phosphate formation is thermodynamically favorable; however, a range of metal-P species occur over a wide pH range in soils and sediments [4–7]. The term legacy P refers to accumulation of P in soils/sediments over time accelerated by anthropogenic activities including P inputs from agriculture. Part of the challenge in sustainable water quality improvement is that legacy P stocks can function as a variable but continual source of P release, hampering the efficacy of remediation efforts.

Agricultural P sources are a leading cause of water quality impairment in US rivers and lakes [8]. Managing P for the dual purpose of profitable agriculture and water quality is a major challenge and is pivotal in the water–energy–food security nexus [8–11]. Once viewed as relatively immobile and subject to mainly erosional transport, carrier-facilitated P transport as particulate or colloidal P in addition to dissolved P forms are all vulnerable to transport in Dunne and Hortonian overland flow (a.k.a., overland flow or surface runoff), interflow, subsurface tile drainage, and shallow groundwater flow [4–6,10–20]. Soil physical properties impose important physical transport constraints on P fluxes from upland agricultural and forested landscapes to riparian buffer zones (RBZs) and streams [15,17–19]. While overland flow is an important P transport mechanism in many settings, P is also mobilized in shallow subsurface flows where it has the potential to contribute P to open waters including ditches, streams, rivers, lakes, wetlands, and RBZs.

Cold climates characterize a large number of agriculturally productive regions globally and can be qualitatively defined by areas where a snowpack and frozen soils substantially influence hydrology [19]. Managing P transport in CCs is uniquely challenged by the combination of short growing seasons, high snowmelt runoff, and seasonally wet and/or partially frozen soils [20]. Recent literature highlights gaps in our current understanding of P transport in CCs, suggesting new approaches are needed to more effectively mitigate P transport from cropland to streams and better understand RBZs effects on P speciation and fluxes [21–23].

Water quality is intimately connected to the landscapes through which streams flow. RBZs are widely recognized for their stream water quality benefits, however, their impacts on P transport are variable and site-specific. Traditionally, P transport research has tended to focus on cropland or RBZs exclusively, with relatively few studies evaluating P dynamics in both cropland and RBZs and/or along their natural hydrologic gradients. Since RBZs and cropland often have a close hydrologic connection with similar processes regulating P transport, in this review we focus on factors influencing P transport in surface and subsurface runoff flows along the continuum from cropland through RBZs to streamflow, defined here as the cropland–RBZ–stream continuum. We primarily draw on studies from the USA and Canada over the last two decades.

Sections 2 and 3 focus on the relationship among agronomic nutrient management, assessing agronomic P transport potential, and an overview of hydroclimatic and agricultural management factors influencing P transport. Sections 4 and 5 discuss the critical source area concept and the importance of soil properties for P transport modeling, mapping and risk assessment. The cropland–RBZ–stream hydrologic continuum concept is introduced in Section 6, followed by a review of RBZ impacts on P transport in overland and subsurface flow (interflow and shallow groundwater), including a Section 7 describing stream bank erosion effects on P loading to streams. Section 8 concludes with future research suggestions and some examples from the literature illustrating new approaches combining hydrologic modeling with geographic information system tools for mapping runoff flow pathways in cropland–RBZ–stream systems.

2. Agricultural Nutrient Management

2.1. Agronomic Phosphorus Site Indices

Agricultural nutrient management plans (NMPs) specify the form, method, rate, and timing of crop nutrient applications with the goal of increasing crop nutrient use efficiency while minimizing environmental losses and crop production risk. In the US, regulated livestock farms must follow nutrient management guidelines developed by

state Land Grant Universities and the USDA—Natural Resources Conservation Service (NRCS) (Figure 1). The amount of plant-available soil P (i.e., soil test P concentration) is a main driver of agronomic P recommendations. Unlike P, NMPs estimate plant-available N release from mineralization of soil organic matter, manure, and previous crops (using static rate estimates independent of in-season weather conditions). While NMPs account for total P inputs from manure applications, plant-available P release from mineralization of soil organic P is not considered. Similarly, while potentially ecologically important in some regions, atmospheric depositions of P (and N) are not considered.

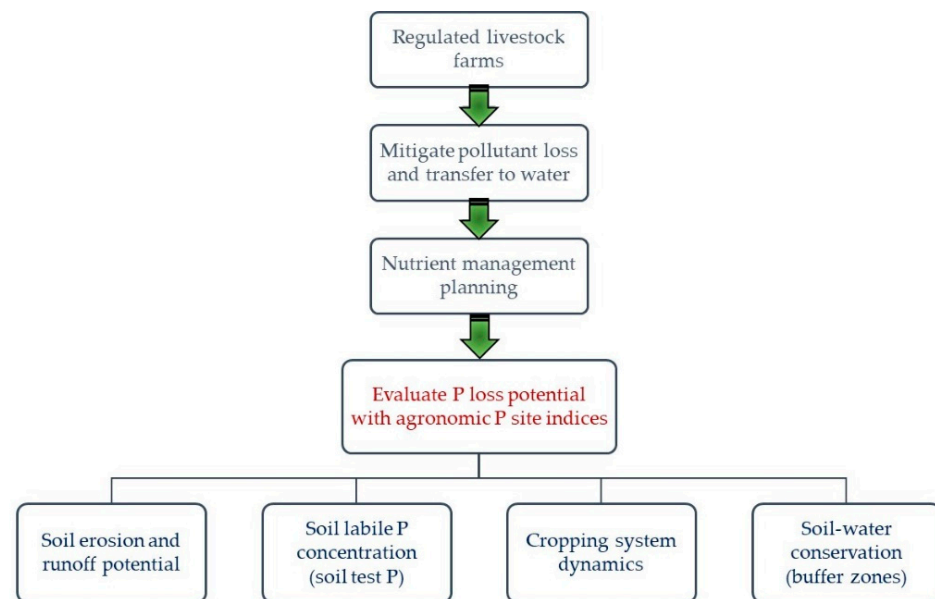


Figure 1. US livestock farms subject to federal Clean Water Act regulations or receiving grant monies must implement cropland nutrient management plans (NMPs) to reduce nonpoint source pollutant loss to open waters. Agronomic P site indices (PSIs) capture soil and management factors affecting annual P loss potential in overland flows and are used to rank P loss potential by fields.

Agronomic NMPs specify field-by-field crop nutrient needs and must include delineation of field characteristics related to erosion and nutrient loss potential, including modeled erosion estimates, presence of concentrated overland flow areas, and proximity to streams/ditches and other landscape features that affect water and nutrient movement (tile drains, karst topography, springs, swales, surface drain inlets). In general, these are also areas where manure and fertilizer P are not recommended during times of high runoff potential and, in some cases, are not to receive any further P applications. Watershed agencies may place further restrictions on land application of manure and fertilizer if farms are in priority watersheds with public drinking water supplies (i.e., New York City watershed, US Great Lakes, Lake Champlain).

Most NMPs in the US require a formal field site assessment of P loss potential using a research based, Land Grant University and NRCS-approved agronomic P site index (PSI). Agronomic PSIs include various rubrics for quantifying P source and transport factors to assign a P loss potential for individual fields based on soil and management factors [24] (Figure 1). Whereas some PSIs include more detailed runoff processes with calibration from edge-of-field runoff P data, many remain qualitative.

Recent US national guidance indicates that agronomic PSIs must establish threshold water quality risks to identify fields not to receive further P inputs. There is also a general consensus that, despite best efforts, P management practices are underperforming with respect to necessary water quality improvement and that there is a need to better account for site-specific hydrology, farm management, and biogeochemical processes influencing P fate and transport [10,11,19,22].

2.2. Precision Agriculture and Phosphorus Management

The ability to manage the timing and placement of crop nutrients in accordance with variable soil and weather conditions can help increase crop P uptake while minimizing losses in runoff. Precision agriculture takes advantage of known field spatial variability (from sampling) by using geographic information systems (GIS) to facilitate autonomous equipment navigation, real-time crop yield monitoring, and variable rate nutrient application. These tools also offer economic advantages for larger farms and are now fairly common [25]. Variable-rate fertilizer application technologies differentially apply P and other nutrients as soil and crop conditions vary across fields [26]. With variable rate application, auxiliary data important for P transport are also routinely collected including soil type boundaries, drainage features, erosion/runoff potential, and other spatially varying soil properties (soil test P, pH, organic matter content). These data can be used to refine P fertility for individual fields and used as inputs for PSIs and other P transport decision support tools aimed at better quantifying P transport potential.

3. Evaluating Cropland Phosphorus Transport Potential

3.1. Agricultural and Hydroclimatic Factors

Managing P inputs from manure and fertilizers for optimal crop production while protecting water quality is a challenge in CC agroecosystems. Livestock manure is an important source of C, N, and P for crops and has beneficial physicochemical effects on soil quality, however, P from manure can contribute to excessive soil P concentrations over time and can be readily transported by overland flow, particularly if not incorporated via tillage or injected beneath the soil surface [27–29]. Dairy manure contains relatively high P content with speciation and total P content dependent on animal species, age, diet, and other farm-specific factors [29]. However, once applied to soils, research indicates that much of the organic P transforms fairly rapidly to inorganic P [30,31] and subject to transport in runoff [10,18,20,22]. Recent research suggests that dairy manure application can be associated with larger and more variable overland flow P losses compared to fields receiving similar rates of fertilizer P [32].

It is clear that a range of P forms can be transported in both overland and shallow sub-surface flow in a variety of crop production systems receiving a mix of fertilizer and organic P mainly in the form of livestock manure [5,10,12–22,27–49]. While agricultural operations often account for a major nonpoint P source in the watershed via the combination of land disturbance and P applications, it is also important to recognize that streambank erosion and runoff from forested lands can contribute to loading to streams [50–53]. Irrespective of original source, landscape position, or form, P transfer risk to streams is greater during the non-growing season, when much of the annual runoff occurs in CC regions [15,18–22,34,35,45–47,52,54–60]. Biogeochemical reactions removing P from solution (sorption and plant and microbial assimilation) also diminish during the non-growing season, contributing to greater overall P mobility and the non-growing season is also a period of elevated overland flow potential. Frozen surface soil layers all but eliminate surface water infiltration and exacerbate overland flows during snow melting or mixed precipitation events. Additionally, decreased soil–water interaction in frozen or partially frozen soils contributes to lower P sorption and greater P mobility in overland flow compared to unfrozen soils. On the other hand, when soils are not frozen and infiltration is possible, greater soil–water interaction increases P removal from solution via sorption reactions and metabolic uptake prior to overland flow reaching streamflow.

Climate and the amount, form, and intensity of precipitation are important factors affecting overland flow, erosion, and P transport potential, and varies regionally in CCs. Hoffman et al. [35] monitored overland flow from five small agricultural watersheds (4 to 30 ha) over a 12-yr period in southwestern Wisconsin (WI) and showed that mixed precipitation events had greater mean dissolved reactive P (DRP; assumed to be mainly orthophosphate and bioavailable) concentrations (2.2 mg L^{-1}) than snow (1.9 mg L^{-1}) or rainfall events (1.2 mg L^{-1}). They also reported that snow (74%) and mixed (84%) events

had nearly two-fold greater proportions of DRP in overland flow compared to rainfall (39%), stressing the importance of field-specific interactions among precipitation types and soil physical conditions, temperature, and depth of frozen layers.

Vadas et al. [54] used 108 site years of edge-of-field overland flow data from WI and a calibrated P transport model (SurPhos) to evaluate P loss potential with differing soil hydrologic and P management. Unlike many current P transport models, SurPhos attempts to simulate snowmelt runoff dynamics and processes regulating DRP transfer from soil, fertilizer, and manure P sources using daily weather data. Their simulations indicated site hydrology was the overriding factor influencing P loss with winter application increasing P loss potential by 2.5 to 3.6 times relative to unfrozen soils. They reported that P loss potential was greatest in late January and early February (from melting events) and that P loss potential was reduced by a factor of 3.4 to 7.5-fold by applying manure to fields with a lower overland flow potential.

In a similar geographic region, Zopp et al. [60] used regression tree analysis to determine factors affecting flow-weighted mean total P (TP) and dissolved P concentrations/loads in the upper Midwest using a large regional edge-of-field overland flow and P export data set from WI and Minnesota with 26 fields, 123 site-yr of data, and >20 additional hydroclimatic and management variables. They reported that, when soils were frozen, the majority of overland flow TP was dissolved. Overall, labile soil P concentration at 0–5 cm was the most important predictor of flow weighted mean TP and DRP concentrations in frozen conditions. Soil labile P content is often highly correlated with overland runoff flow DRP concentrations [61] and a critical input for P transport models and PSIs. Additionally, recent edge-of-field runoff research suggests that surface soil P concentration is a main factor affecting DRP transfer to overland flows [62,63], emphasizing the need for NMP strategies to consider practices that slow down the rate of P accumulation in surface soils in addition to focusing on applying manure/fertilizer to fields under low P loss risk conditions (i.e., when soils are unfrozen).

3.2. Cropping System Impacts on Phosphorus Loss Potential

Soil erosion and total P loss in overland runoff flows are both generally greater under annually tilled crops compared to perennial forage crops or pasture due to mechanical disturbance of tillage operations and lack of continuous vegetative cover [55]. Despite this effect, dissolved P loss can still be substantial in overland flow from perennial forage and no-till systems due to P accumulation in surface soils [55,56]. On the other hand, in annually tilled systems, there is a wide range of impacts on erosion, overland flow, and P loss potential. Besides greater aeration and other potential agronomic benefits, tillage can decrease overland runoff flows compared to no-till by increasing surface roughness in finer-textured soils [57–59]. While there are well-known tradeoffs between greater erosion/particulate P loss with tillage versus lower erosion/particulate P loss with no-till, it is important to note that in some soils, tillage can decrease overland runoff potential, however, this effect is site-specific and depends on several other variables including the consistency and duration of no-till practices. Pasture land often comprises a substantial fraction of agricultural land and generally results in less erosion and particulate P transport compared to row crops; dissolved P forms can still be vulnerable to transport in overland flow (see Sections 4, 5 and 7 for more discussion). While beyond the scope of this review, it is important to recognize that pastured livestock with direct stream access can pose serious water quality challenges [55].

4. Critical Source Areas of Phosphorus

Source and Transport Factors

The critical source area concept assumes P transport potential is a function of hydrologic loss mechanisms interacting with P sources on the landscape at any given time [22,32]. Agricultural P sources subject to transfer in runoff pathways and streams along the cropland–RBZ–stream continuum include soil, manure, and fertilizer. From a watershed

biogeochemical perspective, RBZ sources must also be considered as potential P sources to streams in the form of overland and subsurface flows or via stream bank erosion [50–53]. Determining where and when P sources interact with hydrologic flow paths to physically transfer P to RBZs and streamflow is integral to critical source area and watershed “hotspot/hot moment” approaches and derives from distributed hydrologic modeling theory, now more commonly known as variable source area hydrology [64–67]. Variable source area hydrology posits that the amount and timing of overland flows are driven by topographic and soil moisture gradients [66–70]. Studies indicate that incorporating variable source area hydrology routines into watershed P transport models show promise for improving overland runoff flow P fluxes [15,22,32,66–70]. Overland flow sources to streamflow include cropland areas but also near-stream areas subject to variable soil moisture regimes and overland flow generation (i.e., RBZs, swales, springs/seeps, and other wetlands) [68,70,71]. Since topographic features are an important control on both overland flow generation and groundwater hydrology, accurate characterization of cropland–RBZ–stream topographic complexity is critical for developing realistic models and indices of P transport that can better account for RBZs impacts on P transport.

Both spring snowmelt and storm events are important times for P transfer from cropland to surface waters and from variable sources areas to streams [10,14,18,32,35]. Part of the difficulty of controlling CC cropland P transport resides in the seasonal asymmetry between greater non-growing season runoff potential and concomitant decreased P sorption potential and biological assimilation driven by lower soil temperatures, effectively increasing dissolved P availability to overland flow. Recognizing this asymmetry between elevated runoff potential and diminished P removal capacity is a critical aspect for NMPs to consider in CC regions to better manage cropland P loss risk and more effectively target P-specific best practices for mitigating P transport to streams.

5. Importance of Soil Properties for Evaluating Phosphorus Transport Potential

Modeling and Mapping

GIS tools and digital soil survey data are routinely used in agriculture to develop NMPs and to support other agronomic and environmental objectives. These tools can help identify and manage soil-related factors affecting crop yields while providing important input data for P transport risk assessment tools [72–74]. For example, digital elevation models (DEMs) are routinely used in P transport models and PSIs for estimating field slopes for erosion assessment. Agronomic PSIs and several P transport models [Agricultural Policy/Environmental eXtender Model (APEX); Environmental Policy Integrated Climate (EPIC) model; Soil and Water Assessment Tool (SWAT); Surface Runoff Phosphorus Model (SurPhos)] use soil survey data or measured properties as model inputs [22,32,54,59,69,70,75,76]. Riparian biogeochemical models including the Riparian Ecosystem Management Model (REMM) and RZ-TRADEOFF also use soil survey data [77–80].

While soil survey maps are useful for many applications, it is important to note that a number of them were performed in the 1960 and 1970’s. The maps were also done using different methods and mapping scales. Early mapping focused on agricultural areas with less emphasis on forested and stream areas in general. A soil survey conducted at 1:20,000 scale (a fairly representative soil survey scale) generally relates to a minimum mapping area (termed ‘mapping unit area’ by USDA-NRCS) of approximately 1.2 ha, implying variation <1.2 ha cannot be included. Thus, soil variation may or may not be reflected at a given map scale depending on a given objective. Moreover, US soil surveys operate on the general assumption that up to 15% of any soil series may be comprised of a taxonomically distinct series.

Modern soil survey mapping techniques can integrate traditional soil survey field data with a range of computational tools to predict soil associations (using classification, fuzzy logic, generalized linear modeling, geostatistics, neural networks, regression trees, machine learning/artificial intelligence algorithms and hybrid models) [81,82]. These approaches

are collectively aimed at improving digital soil mapping precision with the ability to integrate expert knowledge and prediction uncertainty [81,82]. Light detection and ranging (LiDAR) derived DEMs can provide detailed microtopographic information to help map soils and overland and subsurface hydrologic flow pathways. A few recent studies have used LiDAR-derived DEMs with hydrologic modeling to design variable-width RBZs based on landscape attributes to optimize agricultural land efficiency and stream water quality protection [71,82–85]. Given the strong association between soils, water movement and P biogeochemistry, characterization of soil hydrology and properties affecting P desorption potential (pH, redox, labile P status) is paramount for better understanding and predicting P fate and transport in CC cropland–RBZ–stream environments.

6. Cropland–Riparian–Stream Hydrologic Continuum

Hydrologic processes are important for understanding the relative contribution of different P sources to watersheds and the relative effectiveness of P transport mitigation practices such as RBZs [15–22,38–49,69,75,86–91]. Site hydrology is also critical for P transport from cropland to RBZs and from RBZs to streamflow. We define the cropland–RBZ–stream continuum as the contiguous land area between active cropland (including pastures) and the nearest perennial or intermittent stream capable of transporting P to downstream systems. Runoff pathways along the cropland–RBZ–stream continuum contributing to streamflow (Q_{sf}) include Hortonian and Dunne overland flow (Q_{of}), groundwater flow (Q_{gw}), and interflow (Q_{if}) (Figure 2). Subsurface tile drainage is a fairly common practice for farms in CCs with poorly drained soils to improve agronomic performance. Tile drain flows are a mix of shallow groundwater and vadose zone water fluxes. Since tile drainage represents a form of subsurface lateral flow, it is included with Q_{if} for simplicity. Stream flow (Q_{sf}) at any given time is thus the sum of individual flow components:

$$Q_{sf} = Q_{of} + Q_{if} + Q_{gw} \quad (1)$$

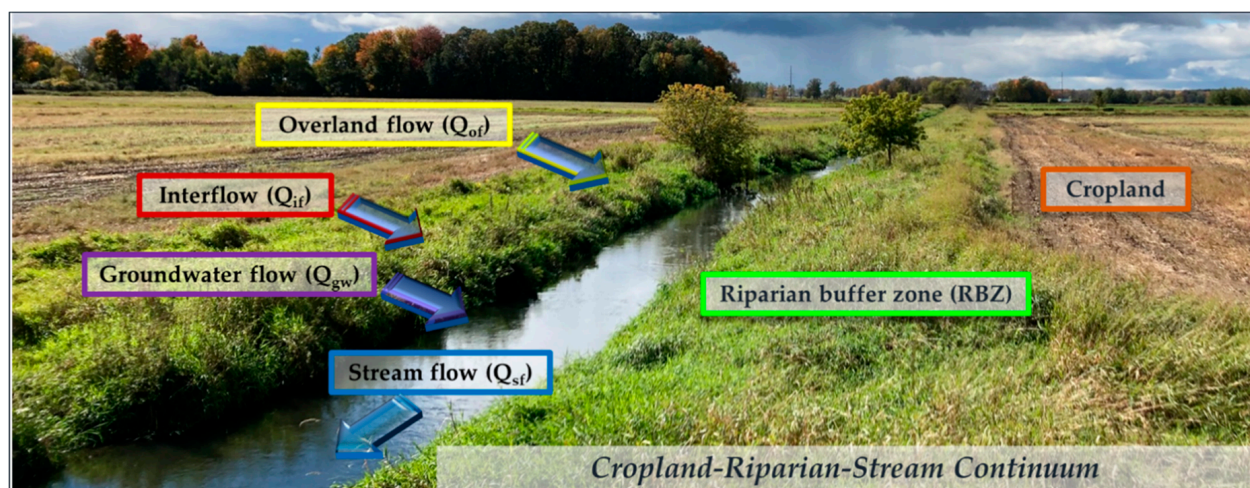


Figure 2. Hydrologic pathways contributing to streamflow along the cropland–riparian–stream continuum.

Note that groundwater flow components (Q_{gw}) are lumped for simplicity and likely include a mix of both shallow/younger and deeper/older flow paths. Stream baseflow is defined as those times when Q_{gw} is the main flow source contributing to Q_{sf} . Interflow (Q_{if}) includes infiltrated water subject to gravitationally driven lateral movement in the unsaturated zone often induced by the presence of a flow boundary. To reiterate, the uncultivated area between cropland edge-of-field areas and stream bank edges is defined as the RBZ (Figure 2).

RBZs include both semi-natural and unmanaged systems in addition to designed and well managed RBZs. The critical assumption is that RBZs must have permanent vegetation

maintained with no agricultural operations (i.e., no tillage or agrichemical applications) occurring. Riparian areas are largely owned and managed by farms in the US and exist in a wide range of field conditions. The grass buffer in Figure 2 is approximately 2 to 3 m wide, which is narrow relative to NRCS riparian forest buffer specifications (minimum width = 10.7 m). Maintaining minimum width RBZs is mandatory in some US states. For example, in Vermont, State Required Agricultural Practices mandate a 3 m permanent RBZ along drainage ditches and 7.6 m wide RBZ along perennial streams and lakes.

7. Riparian Buffer Zone Impacts on Phosphorus Transport

7.1. Phosphorus Transport in Surface Runoff (Q_{of})

Overland flow is an important P transport pathway in cropland as previously highlighted and also critical for P transport in RBZs, along with subsurface components (Figure 3). Properly maintained RBZs can contribute to improved stream water quality and other ecosystem benefits including fish habitat and biodiversity [73,92,93]. Research also indicates RBZs of varying width and composition can attenuate sediment and P fluxes in Q_{of} from upland agricultural areas [38,64,76,78,79,82,83,85,86,92]. In general, a curvilinear relationship is found between RBZ width and TP removal in Q_{of} ; however, RBZ width impacts on dissolved P fluxes are less clear. Research also indicates RBZ effects on dissolved P are more variable, with several studies noting dissolved P increases in RBZs [37,78,86,92,94–97]. Fixed width RBZs may not be the most efficient for mitigating P since landscape heterogeneity plays an important role in both cropland P loss and RBZ-P attenuation potential [82,86–90,94,97]. While RBZ width is an important consideration, other factors can have equal or greater importance on P transport from cropland to RBZs [75–79,86–92,94–100].

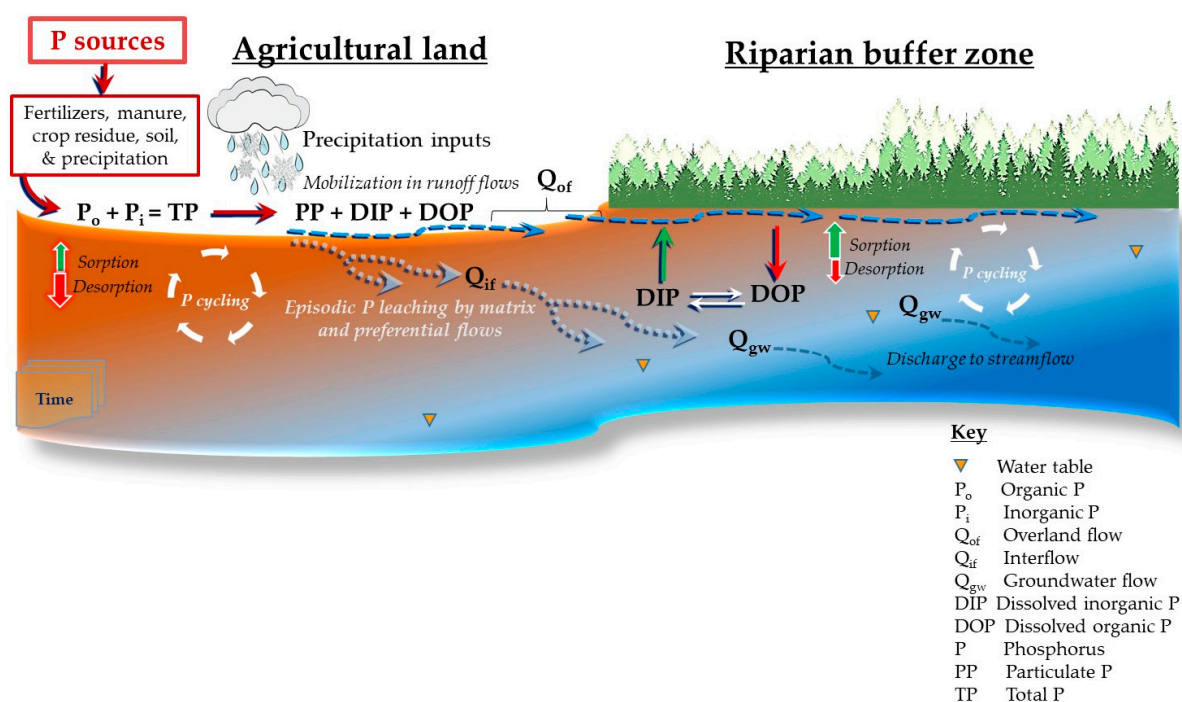


Figure 3. Conceptual diagram depicting hydro-biogeochemical and management factors driving phosphorus (P) fate and transport in cold climates (CCs). Dotted lines represent hydrologic flow pathways that transport P and other solutes. Red arrows represent P inputs into the system or P release via desorption reactions. Green arrows represent P removal via sorption reactions or metabolic uptake of dissolved inorganic P from solution. White arrows indicate biogeochemical processes affecting P bioavailability including pH fluctuations, redox reactions, organic matter cycling (mineralization), and hydrolysis of organic P that affect net P release and fluxes. Note presence of tile drains, stream bank erosion, and other aspects discussed in the text are omitted due to space limitations.

Adequately controlling dissolved and particle-bound P species in Q_{of} is a challenge in both agricultural fields and RBZs. Kieta et al. [94] reported wide variation in P removal efficiencies (from -36% to $+89\%$) for vegetated buffer strips and concluded that both soil P accumulation and freeze–thaw cycle effects on P release from vegetation were important variables related to P removal effectiveness in Q_{of} . They emphasized the difficulty in using vegetated buffers to control P transport in CC agroecosystems where frozen soils and snowmelt-runoff processes limit soluble P removal in Q_{of} , compared to warmer climates where plants and soils remain more biologically active in the non-growing season.

In a review of 41 field studies of crop biomass residue effects on P transport in cropland Q_{of} conducted in CC regions, Liu et al. [98] reported wide ranging biomass P concentrations with substantial P inputs in some cases (0.03 to 51.7 kg P ha $^{-1}$); however, 45 to $>99\%$ of P was retained by soil. Fields with lower erosion potential and biomass residue tended to increase DRP concentrations in Q_{of} compared to fields without residue, suggesting that biomass itself or the interaction of biomass residues with soils increased net P flux to Q_{of} . A similar process may operate in RBZ soils dominated by grass species, whereby a portion of organic P from vegetation and roots is recycled and contributes to the labile inorganic P pool. Labile soil P concentration modified crop residue effects on P transport; fields with lower soil test P and presumably greater sorption capacity tended to retain a greater fraction of P released compared to fields with higher soil P [98]. Beyond highlighting the importance of crop residue effects on P mobilization, these results support the idea that labile soil P concentration is a critical factor affecting P release to Q_{of} in both cropland and RBZs [100–105].

The combination of permanent vegetation and little disturbance in RBZs tends to result in net organic C and P accumulation [86–90,94,97]. Likewise, forest and long-term grassland soils often display organic C and P stratification with enriched surface layers. Dissolved inorganic P in O_{of} is important since it is immediately bioavailable; however, a substantial fraction of P in overland and subsurface flows can be organic in all of these systems [23,45,86,103–105]. Bol et al. [23] reviewed P fluxes in temperate forested ecosystems and reported total soil solution P concentrations of 1 to 400 $\mu\text{g P L}^{-1}$. Dissolved organic P was the main form, mainly composed of orthophosphate monoesters (phytic acid and its degradation products). Both labile and more strongly sorbed organic P forms can also be important in RBZ soils. Young et al. [104] reported that 78% of the mean water-extractable total P in surface RBZ soils was organic, nearly half of which was hydrolyzed to DRP after phosphatase enzyme addition, suggesting a substantial fraction of water-soluble organic P in Q_{of} could be bioavailable [104].

Strong linkages between soil C and P biogeochemical cycling have long been recognized by pedology and forest soils literature [106–110], however, as highlighted by Bol [23], little progress has been made on developing a quantitative framework to move static P measures. Dissolved and particle-bound organic P are covalently bound to C and partially account for correlations between soil C and P, however, organic C and other factors like pH and redox potential alters inorganic P solubility and orthophosphate sorption/desorption dynamics [104,111]. Several studies report significant correlations between labile soil inorganic P availability and soil organic C attributing the effect to dissolved organic C competing for P sorption sites [4,5,86–88,103,104,110]. It is well known that carboxylic acid (R-COOH; where R = an alkyl group) and other organic acids compete for P binding sites on soil surfaces after oxidation to carboxylate (COO $^{-}$), which is difficult to disentangle from inherent correlations between C and P. A certain fraction of organic P is also dynamically hydrolyzed to inorganic P, further confounding relations between C and P.

7.2. Streambank Erosion and P Loading to Streamflow

Streambank erosion is another potentially important P contributor to Q_{sf} with implications for legacy P transport in fluvial systems, aquatic P biogeochemistry and water quality [50–53,89,112]. Ishee et al. [51] combined GIS imagery and field sampling to track streambank erosion rates with field soil P analyses ($n = 76$ sites) to estimate P inputs from

streambank erosion over a 4-yr period. Approximately 6 to 30 % of the total P loading to Q_{sf} among sites was due to streambank erosion. The authors hypothesized that eroding streambanks could act as a sink for P since labile P concentrations were low compared to agricultural land uses. In the Mad River basin of Vermont (a subwatershed of Lake Champlain), Ross et al. [53] used aerial imagery and post-storm sampling to estimate P loading from Tropical Storm Irene in 2011. An area from six sites (0.87-km length of stream bank) contributed an estimated 17.6×10^3 Mg of sediment and 15.8 Mg of total P, similar to average annual watershed P export. Substantial streambank erosion and P loading has also been documented in the Midwestern US. Zaimes et al. [112] measured streambank erosion and associated P loads along forest RBZs, grass dominated buffers, pasture (stratified by continuous, rotational, and intensive rotational) and row-cropped fields for three distinct physiographic regions in Iowa where grazing is common. Forested RBZs had the lowest streambank erosion and P loss rates (2 to 6 kg P km⁻¹ year⁻¹), followed by grass RBZs (9 to 15 kg km⁻¹ year⁻¹). The greatest P loading rates were associated with pasture (range: 37 to 123 km⁻¹ year⁻¹) and row-cropped fields (108 kg km⁻¹ year⁻¹).

Collectively, results indicate that high P loading rates from streambank erosion can overwhelm TP loss inputs to Q_{sf} compared to other sources. Increased Q_{sf} from greater precipitation extremes related to climate change along with land use/cover effects (i.e., tile drainage/ditching cultivation of native prairie and wetlands) have also contributed to greater runoff flows to Q_{sf} and exacerbated nutrient loss [113–115]. For example, riverbank sediments were reported to be the major P source for the Lake Pepin sediment P pool before 1850, which then switched to both a source and carrier of anthropogenic P after European settlements in 1850 [50]. Similarly, sediment-bound P from streambank erosion and river sediment fluxes to coastal estuaries can be a net P source under steady state conditions with the extent of P desorption related to changes in pH and redox potential [48,49,52,116]. These and other studies indicate that streambank erosion itself can be an important P source to Q_{sf} compared to other sources, particularly if widespread throughout the watershed. However, whether or not these sediments ultimately act as a DRP source or sink is inherently dynamic and difficult to predict given the array of watershed scale land use management and variables influencing watershed P speciation and fluxes [10,11,19,22,23,38,40,42–44,66,69,75,86,94,115].

Using high frequency monitoring of Q_{sf} in two predominately forested watersheds of the Piedmont physiographic region in Maryland, USA, Inamdar et al. [52] showed winter storms after freeze–thaw cycles exported high loads of suspended sediment and particulate C and N, with peak suspended sediment and particulate N concentrations >5000 mg L⁻¹ and >15 mg L⁻¹. Based on their data and observations from other USGS monitoring stations, the authors speculated that much of the Q_{sf} sediment was derived from streambank erosion and fluvial sources. Inamdar et al. [116] sampled streambank legacy sediments in the Chesapeake Bay watershed, USA, along with upland soils, and evaluated P release potential using laboratory based measures with reducing and oxidizing conditions. Streambank legacy sediments had low average labile P concentrations and equilibrium P concentrations and might therefore act as a net P sink; however, sediments incubated under reducing conditions had nearly 5-fold greater DRP concentrations, suggesting legacy sediments could readily desorb P to Q_{sf} under conditions of low redox potential due to dissolution of Fe–P compounds. The authors highlighted the need for P transport models and indices to better account for spatially variable P legacy sediment impacts on aquatic ecosystems. In summary, while it is apparent that streambank erosion and fluvial transport of legacy sediments can contribute P to Q_{sf} , the relative water quality risk for downstream open waters depends on the amount, speciation and timing of P fluxes relative to other P sources, in addition to sediment characteristics (i.e., labile P content/speciation, P sorption capacity, pH, organic C) and biogeochemical changes in differing RBZ soil and Q_{sf} environments.

7.3. Riparian Zone Impacts on Subsurface Phosphorus Transport (Q_{if} and Q_{gw})

While there is considerable RBZ-P attenuation uncertainty surrounding Q_{of} , there is wider variation for shallow groundwater and vadose zone P attenuation [86,99]. Despite the fact that RBZs are commonly recommended for reducing P transport, information on RBZ effects on P speciation and fluxes is lacking, particularly in CC regions where hydro-biogeochemical processes and agricultural/riparian management interactions largely control nutrient fluxes [94,99]. Moreover, the hydrologic and soil processes driving P transport from upland agricultural areas to RBZs and Q_{sf} are themselves highly spatially and temporally variable, particularly during freeze–thaw cycles with diurnally fluctuating air temperatures and soil physical conditions (frozen/partially frozen) that complicate water infiltration, subsurface water movement, and therefore P transport [45–47,52,91,94,99,105,116]. An improved understanding of coupled soil hydro-biogeochemical processes driving P transport from RBZs to Q_{sf} in CC regions is needed, in addition to developing a broader set of predictive tools that can accommodate the multivariate and dynamic nature of subsurface P transport and subsequent movement and potential transfer to Q_{sf} .

Hydrology, soils and vegetation are intimately linked and their interactions largely control localized physicochemical environments and biogeochemical mechanisms regulating P availability to both matrix and macropore soil water flows [117,118] (Figure 3). This observation helps partially explain studies reporting mixed efficacy for RBZ subsurface P attenuation [13,37,78,86,95,96,117–124]. In shallow Q_{gw} of RBZs from eastern Canada, Carlyle and Hill [95] reported that RBZ shallow Q_{gw} with lower dissolved oxygen concentrations had higher ferrous iron (Fe^{2+}) and DRP concentrations, and suggested that Q_{gw} redox potential was a main factor affecting the likelihood of P release to Q_{gw} and discharging Q_{sf} . Young and Briggs [13] monitored P concentrations in soil solution (sampled via tension lysimeters, representing Q_{if}) and shallow Q_{gw} for 16 paired cropland-RBZ plots for >2-yr in Central New York. Mean DRP concentrations in Q_{gw} and Q_{if} were lower for RBZs compared to corn and hayfields; however, poorly drained RBZs had greater particulate reactive and dissolved unreactive P concentrations in Q_{gw} , suggesting poorly drained RBZs with elevated water tables and low to moderate labile P status were vulnerable to P release and transport in Q_{gw} compared to more oxidizing Q_{gw} zones. The importance of soil hydrology on P biogeochemistry was also supported by ammonium and nitrate-N patterns. Shallow Q_{gw} zones with lower dissolved oxygen concentrations had lower nitrate-N, higher ammonium-N, and significantly greater DRP concentrations, which suggests denitrification zones could be episodic P flux hotspots [13,125].

Gu et al. [126] combined Q_{gw} , Q_{if} , and Q_{of} measures in the Kervidy-Naizin catchment of Northwestern France over 4-yr with P concentrations and speciation to elucidate transport mechanisms in shallow subsurface flows ($Q_{if} + Q_{gw}$). The authors hypothesized that the main P transport mechanisms were related to soil hydrology via: (i) reductive dissolution of ferric (Fe^{3+}) phosphates during episodic saturation events (hot moment) and, (ii) P mobilization in soil water flows associated with rainfall events following dry periods (hot moment). The degree and duration of soil saturation is a critical factor affecting P release from RBZ soils since prolonged saturation can elicit both reductive dissolution of Fe-P and Mn-P compounds and encourages dissolution of Al-P, Ca-P, and other P complexes [86,87,111,127,128]. Changes in pH during saturation also affect release of dissolved organic P and other C-P complexes that may be more vulnerable to movement in Q_{if} and/or Q_{gw} due to lower affinity for P sorption sites compared to free orthophosphate [4,5,13,37,78,86,103,104,111,116–118,127,128]. Shallow Q_{gw} residence time is also an important factor influencing thermodynamic conditions and P release and retention in RBZs, particularly via the Fe-P redox cycle [86,111].

7.4. Artificial Subsurface Tile Drainage and Phosphorus Loss Potential

Installation of subsurface agricultural tile drainage systems (a.k.a., tile drains) is relatively common in CC agricultural regions with poorly drained soils [129]. Modern tile drainage systems consist of perforated plastic drainpipe (typically 10 cm ID for lateral

field lines) typically installed at a depth of 1.0 to 1.5 m deep with variable lateral spacing and designs. Hydrologically, the main objective is lowering the seasonally high ground water table elevation, which facilitates more rapid gravitational (macropore) soil water drainage compared to an undrained condition in a similar setting. Tile drains have long been recognized for their multiple agronomic benefits (e.g., greater yields, earlier planting/harvesting) and erosion mitigation potential [36,129]. Typically, tile-drained fields outlet to some type of surface ditch or directly to streams or open waters.

While accelerated nitrate-N loss via tile drainage flows has long been recognized, P leaching and transport in tile systems has gained more attention over the last two decades [12,16,36,45,63,105]. In a recent review, King et al. [36] discuss P transport dynamics in tile drained systems and the role of soil and nutrient management factors in controlling P concentrations and fluxes to tile drained soils (mainly the US and Canada). In addition to preventing soil P accumulation to high or excessive levels, the authors stressed the importance of soil type and the propensity for macropore flow in regulating P movement to tile drain flow. Unlike matrix soil water flow characterized by advection and dispersion mechanisms, macropore flow is much more rapid, decreasing the opportunity for P sorption reactions that might otherwise bind P and reduce transfer potential to tile flows [12,16,36,41,130].

While P leaching and transport to tile flow is a concern in some settings, it is also important to recognize that tile drains in general significantly reduce Q_{of} and as such can mitigate particulate and/or DRP transport in Q_{of} compared to undrained conditions in some settings [12,36,45,105]. From this standpoint, tile drains are part of the set of solutions to help mitigate P transport in Q_{of} using combinations of practices, while also potentially contributing to less P transfer to down-slope RBZs [131]. Therefore, while not considered environmentally beneficial with respect to N, tile drains may offer site-specific benefits for reducing erosion, Q_{of} , and P transport in Q_{of} . Early RBZ research with N suggested tile drains could lower the water table sufficiently to reduce interaction of cropland Q_{gw} with upper RBZ soil horizons, thus contributing to lower nitrate-N attenuation in the RBZ. However, the full scope of tile drain impacts in RBZ hydrology and P transport is far from clear since few studies have explicitly investigated the impacts of tile drainage designs on P loss compared to undrained conditions.

8. Future Research Considerations

Phosphorus Transport Modeling and Site Indices

Calibrated field and watershed-scale P transport models help in allocating P load estimates to different land uses and broad scale targeting of P transport mitigation practices. Incorporating variable source area hydrology algorithms into P models and agronomic PSIs show promise for improving P transport risk predictions [10,32,69,132]. However, watershed scale models are often designed to predict P transport over long time periods and over relatively large areas using historical weather and management data, potentially limiting their effectiveness as a dynamic P loss risk tool at the field scale without substantial modification. Additionally, model routines that can better capture snowmelt runoff processes and soil freeze–thaw dynamics in relation to water flow and P mobility are needed [35,59,99]. Given these potential limitations and the fact that large runoff events tend to dominate P losses from cropland to streams, developing tools that can better predict event based and real-time P fluxes and include RBZ hydro-biogeochemical impacts on P transport will be important, especially in high priority watersheds with chronic P pollution.

Combining LiDAR-based DEMs with hydrologic models and GIS tools show promise for enhancing agroecosystem services by creating opportunities to optimize agricultural land while maintaining RBZ water quality functions. For example, Shrivastav et al. [84] and Thomas et al. [71] combined LiDAR-DEMs and GIS tools to map and ground-truth Q_{of} pathways in cropland–riparian–stream settings (Figure 4a,b). These and other hydrologic studies have clearly demonstrated the tendency for Q_{of} heterogeneity in agricultural areas, highlighting the critical importance of targeting RBZs at known “delivery points” to

intercept dissolved and entrained P in Q_{of} prior to reaching Q_{sf} . Kuglerová et al. [82] used a high resolution LiDAR-DEM and a hydrologic model to establish variable width forest RBZs based on soil and landscape characteristics, whereby recharge areas more vulnerable to solute leaching had wider RBZs (Figure 4c,d).

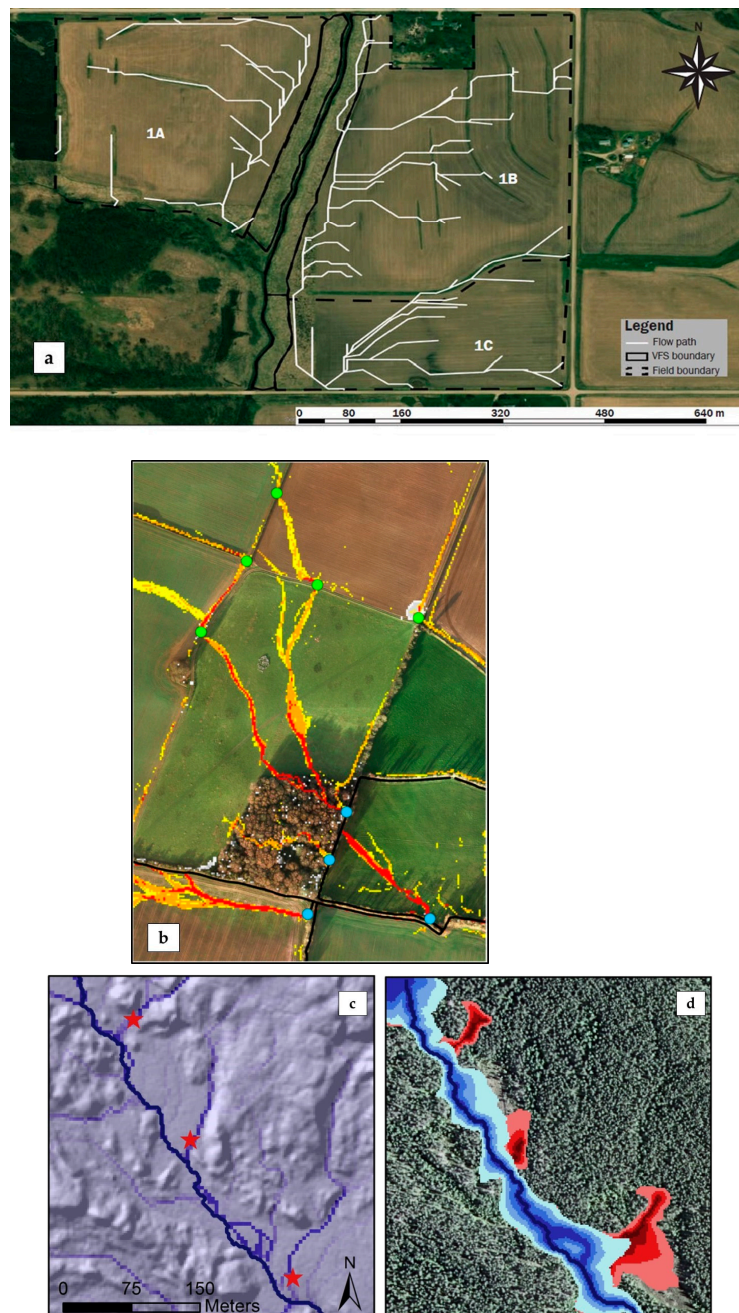


Figure 4. Model estimates of overland runoff flow (Q_{of}) pathways using light detection and ranging (LiDAR) based digital elevation models from Shrivastav et al. [84] (a) and Thomas et al. [71] (b) illustrating the tendency for non-uniform Q_{of} , and highlights the critical importance of targeting riparian buffers at known Q_{of} delivery points to intercept sediment and phosphorus prior to reaching streams. Yellow and red in 4b indicate Q_{of} areas and blue circles indicate Q_{of} delivery points. Variable width riparian forest buffer zones predicted by a LiDAR based groundwater hydrology model by Kuglerová et al. [82] (c,d). Panel 4c shows a sunlit LiDAR image of a stream section; blue lines are small streams and red stars are runoff collection points. In panel 4d, blue layers indicate model predicted groundwater discharge zones (darker blues indicate greater fluxes) and red areas are intermittent streams. All figures reproduced with permission.

While existing watershed P transport models and PSIs will remain important tools, simplified process-based models that can readily integrate LiDAR and other digital data will be important for simulating site-specific hydrologic and P transport processes. In a review of nutrient dynamics in CC agricultural catchments, Costa et al. [99] suggested that more parsimonious P transport models that simulate major soil and hydroclimatic processes governing runoff generation and P transport may be more advantageous than larger, more complex models. Several investigators have combined process-based model outputs with Bayesian networks, machine learning, and other artificial intelligence algorithms to develop predictive hydrologic and nutrient flux models along with uncertainty estimates [133–137].

In addition to innovative predictive tools that can account for more of the weather driven and seasonal dynamics of P transport, longer term management practices aimed at reducing P imbalances and soil P accumulation are needed. As previously indicated, current efforts are not sufficiently attenuating P transport or eutrophication risk in the US and other countries, and that new tools and practices are needed to further curb P transport from cropland to streams. While RBZs will remain an important practice, modifications may be needed to improve soluble P removal efficiencies. Not unlike cropland, RBZs must also be managed for optimal performance if P removal is a desired ecosystem service [138,139]. To this end, more widespread and routine soil P testing of RBZs is suggested (similar to P testing for NMPs). Routinely testing RBZs for soil P status as part of agronomic NMPs could be a simple and cost-effective way to provide a baseline indicator of labile P status. Additionally, soil P data could be combined with hydrologic data to further characterize P transport potential.

Given the strong relationship between pH and P availability in soils and legacy sediments [140,141], lowering or raising pH to decrease P availability (something commonly done on cropland to increase soil P availability) in RBZ soils offers a way to further decrease DRP transport from RBZs to Q_{sf} . However, altering soil pH has implications for plant communities, organic C cycling, and other ecological considerations. Careful research is necessary to evaluate potential tradeoffs between enhancing P sorption in RBZs via pH alterations and maintaining overall ecological integrity.

Riparian vegetation plays an important but poorly understood role in P transfer to Q_{sf} . More research to better understand RBZ soil-vegetation interactions and their impacts on P transport is another area of need [115]. Several studies suggest the periodic harvesting of RBZ vegetation to reduce labile soil P concentrations, remove P, and presumably reduce DRP release and transport potential [86,94,97,101,115,123,138,139]. While it is clear that RBZ vegetation can affect P biogeochemistry and physical transport, it is far from clear what the optimum soil-vegetation combinations are for maximizing P attenuation. More research dedicated to soil-vegetation interactions with the goal of maximizing DRP attenuation is needed (particularly for P sensitive watersheds) to enable prescriptive management combinations to mitigate P transport. Lastly, where appropriate, a broader set of predictive approaches should be considered (i.e., Bayesian neural networks, artificial intelligence, machine learning algorithms and various hybrid models) to P loss prediction and develop real-time, dynamic P transport prediction tools that can simultaneously quantify risk and uncertainty.

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