Seasonally dynamic nutrient modeling quantifies storage lags and time-varying reactivity across large river basins

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Abstract

Nutrients that have gradually accumulated in soils, groundwaters, and river sediments in the United States over the past century can remobilize and increase current downstream loading, obscuring effects of conservation practices aimed at protecting water resources. Drivers of storage accumulation and release of nutrients are poorly understood at the spatial scale of basins to watersheds. Predicting water quality outcomes in large river basins demands modeling storage lags and time varying reactivity that models of mean conditions typically cannot elucidate. We developed a seasonally dynamic approach to large-scale nutrient modeling based on a multiscale framework and nutrient storage lags were quantified for the nearly 190,000 small catchments that feed the rivers across the northeastern United States where catchment mean transit times were found to be around 4.7 (2–10) years for nitrogen and 1.3 (0.7–2) years for phosphorus. Nutrient loads carried in river flow in the current season contained a significant—and sometimes dominant—portion of mass lagged in its release from catchment storage repositories. Our approach of integrating storage releases with seasonally dynamic hydroclimatic drivers sets the stage to assess the accumulated effects of nutrient storage and lagged releases to the river interacting with seasonally varying nutrient reactivity and societal management actions throughout large river basins.

1. Introduction

Challenges in meeting water quality targets in many watersheds have been linked, in part, to the lagged downstream delivery of nutrients that have accumulated over the past century in soils and groundwaters of intensively farmed and urbanized areas in the United States (Van Meter et al 2018, Stackpoole et al 2019). Legacy storage of nutrients also might occur in ponds, reservoirs, and river channels, beyond the immediate control of edge-of-field best management practices, releasing at later times (Posch et al 2012, Hall et al 2013). Changing land use and climate have altered water runoff (Hammed et al 2019, Reitz and Sanford 2019), influencing the mobilization of nutrients from legacy storage areas in farm soils (Raymond et al 2008). However, drivers of storage accumulation and release, as well as the extent of accumulation and lag timescales, although reasonably understood in small, well-studied watersheds (Ilampooranan et al 2019), are poorly understood and not well represented in models of large river basins.

Estimating nutrient sources and their delivery to sensitive downstream waters can benefit from modeling that connects hydroclimatic drivers with terrestrial and in-stream processes of many watersheds to identify dominant controls of nutrient fate in large river basins to inform priorities for management (Garcia et al 2016, Hoos and Roland 2019, Robertson and Saad 2019). Dynamic drivers of storage accumulation and release are currently poorly specified in contemporary large-scale nutrient models—for
example, nutrient estimates of major river basins are typically aggregated annually (Preston et al 2011), but estimates in well-studied, smaller watersheds also often focus on drivers operating on timescales greater than a decade (Ilampooranan et al 2019)—which limits a model’s value in addressing many water-resource challenges influenced by storage legacies, including reducing excess nutrient deliveries to receiving waters that exacerbate hypoxia and harmful algal blooms (e.g. northern Gulf of Mexico and Chesapeake Bay are prominent examples; U.S. EPA 2008, Keisman et al 2018).

Improving the capabilities of large-scale nutrient models requires more focus on representing storage processes. For example, phosphorus (P) released from legacy storage zones may be greater in agricultural areas where P has accumulated in soils over time (Kleinman et al 2011, Stackpoole et al 2019) while nitrogen (N) released from legacy storage may increase from areas where N has built up over time in soils and groundwaters (Tesoriero et al 2015, Hansen et al 2017). Recent breakthroughs have used empirical approaches to examine decadal trends and quantify P legacies (Stackpoole et al 2019) and additions of simple transport physics to quantify decadal trends in N legacies and release (Van Meter et al 2018); these approaches have revealed the extensive scope of nutrient legacies, but they lack dynamic process attribution to climatic drivers that influence storage accumulation and release (Raffensperger et al 2017) and are therefore limited as forecasting tools. Dynamic river corridor processes also need greater representation in large-scale nutrient models because, for example, N and P uptake in rivers is driven by seasonal changes in streamflow and temperature (McDowell et al 2017) that typically cause less removal of nutrients by reactions and by biological uptake in rivers in fall and winter compared to spring and summer (Miller et al 2016).

Nutrient modeling in selected watersheds is usually performed using detailed process-based models (Ilampooranan et al 2019). Modeling in large river basins, however, generally follows the philosophy of parsimonious model structures to represent heterogeneous behaviors (Beven 2002, Kirchner 2006). Most basin-scale nutrient models are time-averaged representations based on several years of measurements, which provide estimates of long-term controls (Preston et al 2011, Ilampooranan et al 2019). To make hydrologic models more dynamic, some suggest aggregating watershed-level information to represent the time-varying behavior of storage and runoff behavior in large river basins (Kirchner 2006).

Here we develop a parsimonious model of the seasonal dynamics of watershed nutrient sources, transport, and reactivity in major river basins. Dynamics are assessed by modeling the mean seasonal behavior of N and P loads in the northeastern US. The model predictions are constrained with seasonally averaged observations at numerous river monitoring sites, which provides a basis for hypothesis testing and uncertainty analysis of the predictions in the many unmonitored watersheds. We tested hypotheses through statistical regression of many different types of terrestrial and aquatic explanatory data aimed at answering the following questions using the northeastern US as a test case: (a) What are the dominant controls on the accumulation and release of stored nutrients, and resulting lag times in a large river basin? (b) What fraction of downstream load in a season originates from the release of nutrients that had been stored in previous seasons? (c) How do storage dynamics vary spatially and temporally across a river basin? (d) During what season and where in the river basin are the most productive nutrient sinks?

2. Methods

Dynamic modeling of the transport and fate of constituents in large river basins has the potential to account for both short- and long-term nutrient storage processes (Smith 2012, Smith et al 2014). The SPARROW (spatially referenced regression on watershed attributes) model (Schwarz et al 2006) was developed to track nutrient sources and accumulated river corridor processing at large (basin to continental) spatial scales but is traditionally steady-state and driven by streamflow and nutrient datasets aggregated annually rather than seasonally and, therefore, cannot elucidate newly generated nutrient sources that enter the river in the current season versus nutrients that have accumulated in storage repositories such as soils, groundwaters, and riparian and other vegetation in previous seasons, years or decades and have been lagged in their delivery to rivers until the current season, which we refer to as a storage lag.

SPARROW is updated here from a long-term mean annual model to a long-term mean seasonal model that statistically estimates mass source, sink, and transport processes of river reaches and associated catchments of the National Hydrography Dataset (NHDPlusV2; U.S. Geological Survey 2016), which provides the common framework for spatial referencing at the spatial scale of small watersheds and source tracking from headwaters to large rivers. The dynamic statistical regression approach is framed within SPARROW’s physically based transport equation that includes an enhanced representation of both terrestrial and river features to allow for hypothesis testing to discover which explanatory data (e.g. precipitation, runoff, temperature, soil type, etc) significantly explain the partitioning between new sources of nutrients entering rivers within the current season versus nutrients released from storage repositories in the current season. Our
updated model also estimates seasonally varying nutrient reactivity in rivers that was not possible with the mean annual approach, which we refer as dynamicSPARROW-MS:

\[
L_{out,i} = \sum_{n=1}^{N} \alpha_n I_{n,i} f_i I_{n,i} + \alpha_2 L_{i-1}, f S_{S,i} \times \exp \left( -\frac{\tau f_i}{d_i} \right)
\]

where \( L_{out} \) [M T\(^{-1}\)] is the incremental river load delivered to the outlet of each NHDPlusV2 catchment \( i \) across the river basin; \( L_t \) [M T\(^{-1}\)] is the load delivered from the catchment to the river (i.e. edge-of-stream flux); \( I \) [M T\(^{-1}\)] is the mass of new within-season source input to the catchment (e.g. crop fertilizer and manure); \( t \) is the time period (i.e. season); \( \alpha_n \) are positive source input coefficients that estimate the mean fraction of source input \( n \) that is delivered to the river; \( N \) is the number of source inputs including human and natural; \( \alpha_2 \) is a positive coefficient that represents the average fraction of \( L \) that is delivered from the storage repository; \( f_i \) and \( f_2 \) are the land-to-water delivery functions that include the explanatory data; \( \tau \) [T] is the travel time through the river reach for mean seasonal streamflow; \( d \) [L] is the depth for mean seasonal streamflow; and \( \nu_f \) is the uptake velocity [L T\(^{-1}\)], which estimates the net rate of biogeochemical reactions in the river that remove and replenish instream N or P. The key update to the modeling approach is that we partition the total load delivered to the river in the current season, \( L_i \) [M T\(^{-1}\)], into new inputs generated and delivered from the catchment to the river within the current season, \( L_{i,t,n,i} = \sum_{n=1}^{N} \alpha_n I_{n,i} f_i I_{n,i} \) [M T\(^{-1}\)], and release from storage repositories in the catchment and delivered to the river, \( L_{S,i} = \alpha S L_{i-1}, f S_{S,i} \) [M T\(^{-1}\)]. The rate of release from each catchment’s storage repositories for each period is estimated by \( \alpha S f S_{S,i} \), and its inverse provides an approximate mean transit time mass is lagged. See supplementary material for details (available online at stacks.iop.org/ERL/16/095004/mmedia).

Below we lay out the conceptual model for predicting large river-basin fluxes of N and P and the variable sources derived from ‘new’ within-season catchment inputs and from storage repositories. These dynamic measures of nutrient transport and fate are constrained by time-varying versions of publicly available climatic data and water quality observations.

2.1. Conceptual model for quantifying seasonally dynamic nutrient delivery across river basins

The mean seasonal approach presented here has four timesteps to allow for incorporating more explanatory data than the traditional mean annual approach, which permits new inferences into dominant seasonally varying processes, as well as long-term drivers such as land use, on nutrient sources, storages, and storage release.

To develop a constituent model structure that can be aggregated and calibrated across a river basin, we start with the discrete form of the mass balance of the catchment storage repository, assuming all mass passes through the repository (Smith 2012, Smith et al 2014) (figure 1):

\[
\Delta S_{i,j} = I_{i,j} - R_{i,j} - L_{i,j}
\]

where \( S \) [M T\(^{-1}\)] is the accumulated mass in the storage repository and \( R \) [M T\(^{-1}\)] is the mass permanently removed during transport. For simplicity, let \( r_i \) represent the rate of release from the repository for the current season:

\[
L_{i,i} = r_i (I_{i,i} + S_{i-1,i})
\]

where \( L_{i,i} = r_i I_{i,i} \) [M T\(^{-1}\)], \( L_{S,i,i} = r_i S_{i-1,i} \) [M T\(^{-1}\)], and \( i \) and \( i-1 \) designate the current and previous season, respectively. Although it accounts for storage timescales longer than one season, equation (3) is referred to as a one-period lag specification. The storage process continuously operates across all periods—looking back one-period provides a first-order approximation to \( L_S \), meaning \( S \) is a lumped representation of all unused mass that has accumulated at any time previous to the current period \( t \). Therefore, a one-period lag specification accounts for \( S \) operating at timescales longer than a season but shorter than the period of record of observations for the mean seasonal model, usually a decade or more. However, the actual amount of mass accumulated in storage, \( S \), is an unknown quantity and not directly estimated—we instead estimate the flux of mass released from the storage repository, \( L_S \), and infer the average time that mass is lagged in the storage repository. Quantification of \( L_S \) is based on current season conditions while quantification of \( L_S \) is based on both previous season conditions and a change in conditions between consecutive seasons.

For efficiency, the mean seasonal approach uses a feedback loop between the last and first seasons because each period represents long-term mean conditions. In this feedback loop, the output of the last season provides the input of the first season, which is a computationally efficient dynamic analysis of storage because the model has only four periods and does not require initial conditions to allow for efficient application at large spatial scales (figure 1).

The change in storage release (\( \Delta L_S \)) from one season to the next is approximated as:

\[
\Delta L_{S,i,i} = L_{S,i,i} - L_{S,i-1,i}
\]

A positive \( \Delta L_S \) indicates an increase in storage release (i.e. mass in storage repositories decreasing) while a negative \( \Delta L_S \) indicates a decrease in storage release.
Figure 1. Diagram of conceptual model of the mean seasonal catchment mass balance. Load delivered to the river from each catchment is assumed to contain new mass originating from inputs within the current season and delivery of older mass that had accumulated in the storage repository. For applications at large spatial scales, each period represents long-term mean seasonal conditions where a feedback loop between the last and first seasons is applied. This diagram is of a single catchment but applied and aggregated to explain seasonal nitrogen and phosphorus load across the northeastern United States of over 190,000 NHDPlusV2 river reaches and associated catchments from headwaters to large rivers.

(i.e. mass in storage repositories increasing). This approximation allows for identification of areas that accumulate or release nutrients each season, which is useful for understanding the balance between seasonal inputs and storage release.

2.2. Mean seasonal total N and P models of the northeastern United States

We accounted for seasonality of chemical transformations in the river and catchment storage by solving our modified SPARROW code in over 190,000 NHDPlusV2 river reaches and associated catchments from headwaters to large rivers across the northeastern US. Total N and P models were each calibrated to long-term (period-of-record 1994–2004) mean seasonal observations (total N observed at 363 stations and total P observed at 455 stations) through nonlinear least squares regression to estimate and evaluate the statistical significance of coefficients mediating the source, sink, and transport processes. These mean seasonal models are parsimonious and thus minimally parameterized to allow for testing hypotheses as necessary for dominant process attribution and predictions at basin to watershed scales.

The new within-season N source inputs include delivery from point sources from treated wastewater, fertilizer for crop production, crop fixation, manure from livestock production, urban coverage, and atmospheric deposition. The new within-season P source inputs also include delivery from point sources, crop fertilizer, manure, and urban coverage, with additional sources from geological background material and small headwater streams due to their erosive power.

The fertilizer and manure data applied to each catchment are available on an annual timescale; generally, fertilizer is assumed to be applied just before planting and manure is assumed to be applied before planting and after harvest. Seasonal fertilizer applications were specified as 0% winter, 60% spring, 30% summer, and 10% fall, and seasonal manure applications were 0% winter, 50% spring, 10% summer, and 40% fall following general guidance provided by Cao et al. (2018) and typical crop planting and harvest (U.S. Department of Agriculture 2010). However, to assess the uncertainty caused by the lack of seasonal application data, we used the calibrated models in simulation mode to estimate the range in L₁ and L₂ based on other plausible seasonal fertilizer and manure applications. For fertilizer application, seasonal bounds were assumed of 0%–25% (winter), 25%–100% (spring), 0%–50% (summer), and 0%–50% (fall). For manure application, seasonal bounds were assumed of 0%–25% (winter), 25%–75% (spring), 0%–25% (summer), and 25%–75% (fall).

Land use was assumed constant over the period of record but seasonal explanatory variables that modify input and storage delivery include precipitation, runoff, quick-flow runoff, and vegetation indices that represent photosynthetic activity or growth. Other variables include overland flow distance, carbonate geology, soil characteristics, small ponds (<1 ha) (Schmadel et al. 2019, Schmadel and Harvey 2020), temperature, and streamflow. These variables, when adjusted by model coefficients, act as surrogates to processes such as crop uptake and harvest, biogeochemical reactions, and erosion. Negative coefficients, for example, suggest losses or removal processes, which include biogeochemical reactions in soils and groundwaters that remove or replenish nitrogen including biotic assimilation.
and crop harvest, burial, remineralization, and denitrification.

We further extended the capabilities of the mean seasonal models to account for seasonally varying river corridor processes. Streamflow variability should introduce seasonality in nutrient removal in the models, but temperature is likely to be an even larger driver of nutrient uptake in river corridors (Miller et al. 2016, McDowell et al. 2017). We tested how N and P uptake velocities in rivers vary nonlinearly with seasonal streamflow and temperature of small headwaters to large rivers of the northeastern US. We applied a flexible statistical optimization approach to test for a significant temperature effect on the rates of N and P removal that are not first order, are spatially explicit, and vary seasonally. We also estimated the nutrient uptake velocities of lakes and reservoirs and high-resolution small impoundments (Schmadel and Harvey 2020) based on their seasonal residence timescales.

See supplementary material for details regarding the data sources (figures S1–S5 and table S1), model specifications, and calibrations (figures S6–S9 and tables S2 and S3). All data inputs and model outputs are also provided in a data release (Schmadel et al. 2021).

3. Results

3.1. Seasonal N and P storage delivery patterns across the northeastern United States

Significant coefficients in the model calibrations indicate that seasonal changes in runoff, precipitation, and photosynthetic vegetation influence where and when nutrients are accumulating or being released from storage (figure 2). Release of stored N is associated with an increase in runoff from the previous to current season (table S2, figure S4). Release of stored P is associated with an increase in precipitation from the previous to current season (table S3, figure S4), which provides evidence that the release of stored P responds more quickly to a change in climatic conditions compared to stored N. Conversely, an increase in the amount of actively photosynthesizing vegetation from the previous to current season indicates accumulation of storage, whereas a decrease in photosynthesizing vegetation indicates release of storage, for both N and P, which is a signal of the decay and release of fixed nutrients (tables S2 and S3, figure S4). Taken together, these and other geological and soil property predictors guide the model calibrations toward results that identify where nutrients from fertilizer and manure applications are
Figure 3. Seasonal proportions of nutrient sources and sinks arising from new (within-season) source inputs transported to the river versus lagged deliveries from storage, expressed as percentages of the total (a) nitrogen and (b) phosphorus load delivered throughout the river network, excluding point sources. The proportions of mass sinks and sources of load are relative to the total mean annual load delivered to rivers, providing the relative amounts that are permanently removed, delivered from new within-season inputs, or delivered from storage per season (plausible ranges due to uncertain timing of fertilizer and manure applications are provided in brackets; figure S15). Proportions per stream order are incremental through the river basin to locate the largest sinks and sources of load in the river basin. Therefore, the sum of each line indicates the total contribution to the entire river basin mass balance per year. The grey shaded region is the seasonal difference between load delivered to the river and load removed in the river (i.e. sinks), which equates to the amount of net export per season. The current period load delivered is comprised of load generated from the new seasonal inputs (e.g. fraction of fertilizer and manure applied that season that is delivered to the river network) and load released from the storage repository.

3.2. Seasonal N and P sources and sinks throughout the river basin

A breakdown by seasonal source and sink components of nutrient load throughout the river basin further reveals how the interactions between land use and time-varying source inputs, climate, channel flow, and other aquatic features affect the delivery of N and P from headwaters to receiving waters (figures 3, S13, S14, and S15). The largest within-season inputs of N and P enter the river network from the headwater system (i.e. stream order 1; figure 3). The contributions from mass lagged in storage repositories are also largest from headwater catchments for both N and P, indicating that the unused source inputs have accumulated over time, but the seasonal magnitudes and timing of storage lag differ between N and P.

The relative contribution of mass released from storage is generally lower for N than for P. The amount of N released from storage was largest in winter (45% of load delivered) and summer (35% of load delivered) due to changes in precipitation and photosynthetic vegetation (figure 3(b)). Lacking specific data for application timing of fertilizer and manure, however, contributes around 10% uncertainty to the storage lag estimate (but potentially up to 60% underestimated during high release periods) (figure S15). Our results therefore indicate that the contribution from storage is significant and sensitive to seasonal controls that affect whether nutrient applications in fertilizer and manure are used by crops, enter a soil or shallow groundwater flow stored on the landscape and later released to the river, prolonging the period of high in-stream concentrations (figures S10–S12).

Generally, N and P accumulate in storage during the growing seasons and are released from storage during the colder and wetter seasons in the northeastern US (figure 2). However, the timing of N and P storage accumulation and release varied geographically, raising important implications for managing nutrient loads in rivers. The pattern of nutrient storage differed between the New England basin (NE) and the Chesapeake Bay basin (CB) as well as between mountainous areas and coastal lowlands. Notably, the release of stored N and P increased in the NE but decreased in the CB during the winter-spring transition compared to the fall-winter transition (figures 2 and S5). During the transition from spring to summer, the release of stored N continued to decrease in agricultural areas of the CB yet extended farther into the NE. In contrast, from spring to summer, the release of stored P increased across the coastal plain from Virginia to New Jersey. The largest increases in N and P storage release occurred during winter in urban and agricultural centers located mostly in valleys and coastal lowlands due to increased precipitation and runoff and decreased vegetative growth as compared to fall conditions (figures 2 and S3–S5).
Temperature has a significant effect on reaction kinetics in the river corridor. The reaction rate is above first order at temperatures above the mean and below first order for temperatures below the mean, as indicated by positive coefficients for temperature (tables S2 and S3). As a result, the warmer temperatures in spring and summer drove proportionally higher N and P removal in the river corridor compared to fall and winter, drastically reducing the amount of N and P exported downstream (‘Net export’ in figure 3). Lower summer streamflow and higher residence times in the river corridor boosted removal further (‘Sinks’ in figure 3). Counter to previous mean annual studies that did not account for seasonal uptake of nutrients in the river corridor (Schmadel et al 2019), our results suggest that larger rivers lower in the basin removed more N and P than the entire headwater system when summed across seasons (figure 3). Likewise, previous studies have estimated that the net removal of P in rivers is zero by averaging over seasonal drivers (Moore et al 2011), whereas our results suggest that P removal occurs in larger rivers and increases with higher temperatures.

Storage lag times varied by over an order-of-magnitude for both N and P because precipitation, runoff, soil characteristics, vegetative growth, and land use vary widely across the river basin. Our results infer that catchment mean transit times for N are generally longer compared to those for P (figure 4), further indicating that the two models are sensitive to the different storage processes affecting N and P. The resulting transit time distributions of stored N and P inferred by our models generally agree with the typical range of water transit times inferred from water tracers (e.g. using a Gamma distribution to represent water storage; Kirchner 2016; figure S16). We found that the distribution of mean storage lag times for NHDPlusV2 catchments across the northeastern US is wide for N, with a regional mean of 4.7 years, but the highest density around 2 years (figure 4(a)). For P, the highest frequency mean transit time is around 1.3 years (figure 4(b)). Our results confirm that a delay in the downstream response to management practices should be expected and this modeling approach could be updated to forecast and quantify those management effects if appropriate datasets existed. As a first-order approximation to the storage process, excess phosphorus will lag approximately a few seasons to 2 years whereas nitrogen will lag approximately from 2 to 10 years.

4. Discussion

4.1. Importance of storage for water quality management plans

Nutrients that have gradually accumulated in soils and groundwaters of intensively farmed and urbanized areas of the US since early European settlement mobilize and serve as a continual nutrient source on the timescale of years to decades, thus masking conservation efforts (Van Meter et al 2018). However, dynamic drivers of storage accumulation and release, as well as the extent of storage accumulation,
are poorly understood at the spatial scale of basins to watersheds. Our results demonstrate how seasonal fluctuations in N and P loading to streams and rivers relate to release of stored N and P from soils, groundwaters, and other storage repositories (figure 2). The contribution of storage to downstream N and P loads across the northeastern US was significant, averaging 20% of a given season’s river load being derived from release of previously stored nutrients, indicating that N and P are driven in part by climatic conditions and management actions of previous seasons or flow conditions (figure 3). Our results agree with empirical baseflow separation studies that observed increases in baseflow contributions of nutrients to total river load during periods of higher precipitation and runoff (Raffensperger et al 2017), yet also confirm that N and P are influenced by different storage processes. Runoff that reflects the natural water balance is a significant explanatory variable for N storage while surface proxies of precipitation and soil properties are significant variables for P storage (figure S4 and tables S2 and S3), which agrees with findings that agricultural N can store and lag in groundwater flow paths (Hansen et al 2017) while P tends to store and lag in soils (Kleinman et al 2011).

Identifying why and how source inputs of nutrients are stored in basins and delivered to rivers provides valuable information regarding catchment processes and farming practices including whether applied fertilizers are efficiently used by crops or readily transported into rivers, thus bypassing management controls and delivered downstream where harm may occur to aquatic systems. Our model predictions are sensitive to any uncertainty in the timing and amount of fertilizer and manure applied. Whereas the total estimate of storage contribution was not sensitive to the timing of fertilizer applications, our predictions of the magnitude of seasonal releases from storage was sensitive. Based on this sensitivity, however, we can, for example, examine how distributing fertilizer applications more evenly from spring through fall might increase the amount of winter storage release and undesirable loss or leaching of fertilizer to downstream waters. The estimated timing of fertilizer and manure application can readily be refined in the model with appropriate datasets to reduce the potential error in the storage lag process, but to our knowledge, those datasets are difficult to obtain or would take a substantial amount of effort and resources to produce.

Our approach is a first-order approximation to storage processes but provides a fundamental step towards quantifying seasonal fluctuations in N and P load delivered across entire river basins. The relatively short decadal period used to compute mean seasonal loads likely causes the analysis to be insensitive to long-term shocks to storage associated with extreme events. The model is flexible and therefore can be modified or extended to further improve process representation. Integration with a groundwater flow model, for example, could better parse age distributions and constrain timescales longer than a decade (Zell et al 2018). Integrating our model with a groundwater flow model may improve the representation of N storage and lag, and certainly would be useful for estimating N storage and depletion at longer decadal timescales, but would likely not improve the estimates of P storage and lag times because P is more dominantly tied to soils and sediments (Stackpoole et al 2019).

4.2. Seasonality of the river corridor

We observed that seasonally varying streamflow and temperature were key drivers of N and P uptake in river corridors. Our mean seasonal models estimated net removal capacities for N and P that vary seasonally in accordance with expected influences of varying streamflow and temperature (figure S9). Consistent with our modeling, empirical studies have shown that river uptake of nutrients scales positively with temperature and negatively with streamflow (McDowell et al 2017), accounting for a lower rate constant for nutrient uptake in colder waters of fall and winter but proportionally higher removal of nutrients during spring and summer (Miller et al 2016). However, N and P removal may be temporary, especially in spring and summer associated with uptake by algae and aquatic vegetation. Those nutrients may be released at later times due to scour during higher flow and vegetation senescence (Hall et al 2013). P in rivers also has been observed to undergo seasonal oscillations by uptake or storage in one season followed by release from storage in another season (Doyle et al 2003). For example, particulate P is often stored seasonally or longer in reservoirs, especially after dam construction, which at later times becomes susceptible to releases with increased sediment infill or following summer stratification (Hall et al 2013). P in rivers also has been observed to undergo seasonal oscillations by uptake or storage in one season followed by release from storage in another season (Doyle et al 2003). For example, particulate P is often stored seasonally or longer in reservoirs, especially after dam construction, which at later times becomes susceptible to releases with increased sediment infill or following summer stratification (Hall et al 2013). P in rivers also has been observed to undergo seasonal oscillations by uptake or storage in one season followed by release from storage in another season (Doyle et al 2003). For example, particulate P is often stored seasonally or longer in reservoirs, especially after dam construction, which at later times becomes susceptible to releases with increased sediment infill or following summer stratification (Hall et al 2013).
is significant storage occurring in river corridors, it is currently reflected in the calibrated value of a single lumped storage term that incorporates all the detected storage. Our model formulation could be updated to accommodate an additional river corridor storage term separate from terrestrial storage; however, it is not yet clear whether current data inputs can simultaneously constrain both terrestrial and river corridor storage terms. Other researchers hypothesize that river corridor storage and release of nutrients are small compared to storage in terrestrial soils and groundwaters (Stackpoole et al 2019), although definitive mass balance measurements of nutrient storage and release are lacking in rivers. Further conceptualization and improvements to our seasonal models should help improve the estimation of seasonal storage and release of nutrients in river corridors.

Data availability

The data that support the findings of this study are openly available at the following URL/DOI: https://doi.org/10.5066/P9NRFWOV.

Acknowledgments

N M S was primarily supported by a US Geological Survey (USGS) Water Mission Area Mendenhall Postdoctoral Fellowship with additional support from USGS Water Quality Processes Proxies and Integrated Water Availability Assessments Water Reuse Influence projects. J W H and G E S received support from the USGS Water Availability and Use Science Program and Integrated Water Availability Assessments Water Reuse Influence projects. The authors thank Richard Smith and Richard Alexander for sharing their insights and providing helpful feedback regarding dynamic and storage representations. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the US Government. The authors declare no conflicts of interests.

Author contributions

G E S, N M S, and J W H conceived the study, N M S, J W H, and G E S compiled the data and conducted the modeling, and N M S and J W H wrote the paper with contributions from G E S. All authors interpreted results.

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