Seasonal watershed-scale influences on nitrogen concentrations across the Upper Mississippi River basin

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ABSTRACT
In the Upper Mississippi River basin, after spring fertilizer application, total nitrogen concentration [TN] in streams drops by ~73% from June to September, consistent with effects of seasonal nutrient loading. We hypothesized that this seasonal variability might be affected by land cover (e.g., wetland, cultivated area extent). To test this hypothesis, we adopted a linear mixed-effects modeling approach including periodic functions. However, inclusion of wetland area was not indicated, suggesting that increased model complexity associated with inclusion of contemporary wetland extent was unjustified. While consideration of cultivated extent in relation to mean annual [TN] was shown to improve performance, no evidence was observed that cultivated extent could enhance explanation of intra-annual [TN]. Improved understanding of cause and effect will require improved spatiotemporal data on nitrogen sources and additional critical field experimentation, which in turn is expected to set the stage for advancement in physically- or process-based modeling of nutrient concentrations.

1 Introduction
Numerous rivers (Meybeck and Helmer 1989), lentic inland waters (Brooks et al. 2016), and receiving coastal waters (Diaz and Rosenberg 2008) are impacted by increasing rates of anthropogenic nutrient loading since the 1850s (Vitousek et al. 1997) to sustain Earth’s human population of ~7.9 billion. With projections of continued population growth (Gerland et al. 2014) requiring expansion or further intensification of agriculture, in the absence of dramatic measures, already realized environmental degradation will persist or increase in extent or severity (Liu et al. 2012). Excess nutrient loads can lead to deterioration of ecosystems, harmful algal blooms (Brooks et al. 2016), and hazards to human health (Perrin et al. 2014). Integrating the economic consequences of excess nitrogen (N) impacts yields a staggering economic burden on the order of hundreds of billions USD per year (Sutton et al. 2011, Sobota et al. 2015, Houlton et al. 2019), a cost that might be partially offset through wetland restoration (Rankinen et al. 2014, Houlton et al. 2019).

At the global scale, 64% of inorganic nitrogen export originates from anthropogenic sources, and 54% occurs as a consequence of diffuse agricultural inputs (Seitzinger et al. 2005), though urban contributions are important as well (Chen et al. 2016). At regional scales as much as 78% of N loading can be a consequence of agricultural fertilization (Compton et al. 2019). Riverine export rates have been observed ranging from 5% (David et al. 2010) to 38% (Compton et al. 2019) of N inputs. While some have attributed observed nitrogen loading in part to legacy effects (Basu et al. 2010, Van Meter et al. 2018), others have attempted to distinguish between legacy versus contemporary loading hypotheses and have found stronger evidence for the role of on-going large-scale fertilization (Ballard et al. 2019, Stackpoole et al. 2019). However, in the absence of large-scale critical experimentation (Platt 1964), the relative importance of possible legacy effects across different systems remains uncertain.

Nitrogen, along with phosphorus, is a key limiting nutrient that, in excess, contributes to observed widespread eutrophication in coastal (Ryther and Dunstan 1971), riverine (Dodds and Smith 2016), and lacustrine (Conley et al. 2009) environments. Nitrogen-laden leachate and surface runoff that flows downstream toward rivers, lakes, and oceans may first intersect connecting floodplain (Sanchez-Perez et al. 2003) and/or non-floodplain wetlands (Lane et al. 2018). In the anaerobic sediments underlying these wetlands, nitrogen in the form of nitrate (NO₃⁻) may be converted to nitrogen gas (N₂) by the denitrification process (Sanchez-Perez et al. 2003). Evidence has therefore emerged that wetlands may substantially reduce nitrogen loading of surface waters at the watershed scale (Fisher and Acreman 2004, Hansen et al. 2018, Golden et al. 2019). The efficacy of wetlands in reducing nitrogen loading has been observed across a range of flow conditions and seasons (e.g. Uuemaa et al. 2018).

Investigations of fertilizer inputs and wetland impacts on nitrogen loading are commonly conducted at an annual time scale (Basu et al. 2010, Thompson et al. 2011, Van Meter et al. 2016, 2018, 2019, Golden et al. 2019). Yet temporal variability is critically important, not least because it influences the timing
and frequency of events in which nutrient concentrations exceed levels safe for human consumption (e.g. 10 mg L\(^{-1}\) in the US; 4.4 mg L\(^{-1}\) in Germany). Despite recent advances in understanding the role of wetlands in influencing solute concentrations across spatial scales, improved understanding of temporal variability remains a priority (Bloschl et al. 2019).

In this paper, we explore the seasonal role that nitrogen inputs and wetlands play in influencing downstream solute concentration at the watershed scale. We capitalize on recently developed databases of watershed metrics, in addition to distributed measurements of streamflow and total nitrogen concentration [TN](Mengistu et al. 2020). We apply a linear mixed-effects model to assess the seasonal variability of [TN] in watersheds across the Upper Mississippi River basin (UMRB) in the Midwestern US.

2 Methods

2.1 Study area

The Mississippi originates at Lake Itasca, Minnesota. The study area is the UMRB (492,000 km\(^2\); Fig. 1), an important contributor of residual nitrogen to the Mississippi River basin (Burkart and James 1999, Qi et al. 2020). The UMRB consists principally of the Great Plains, northern forests, and eastern temperate forests ecosystems (Omernik and Griffith 2014). The surficial geology of the UMRB is dominated by thick silty glacial till sediments interspersed with thinner units (Soller and Reheis 2004). Additionally, thick coarse-grained proglacial sediments are present, typically toward the basin’s northern extent. Precipitation averages 920 mm year\(^{-1}\), two thirds of which falls in spring and summer. Precipitation varies spatially from a low of 600 mm year\(^{-1}\) in the northwest to a high of 1200 mm year\(^{-1}\) in the southeast (Daly et al. 2008). Potential evaporation increases from a low in January to a peak in July. Elevation, which serves as a hydraulic driver in topographically driven flow regimes, ranges from 520 m in the northeast to 140 m in the southeast.

Overlaid on climate dynamics and natural physiography, human alterations in the form of conversion of perennial vegetation to seasonal crops (Zhang and Schilling 2006) and artificial drainage have pervasively amplified the hydrological cycle by increasing stream discharge (Blann et al. 2009, Belmont et al. 2011, Schottler et al. 2014). The Upper Mississippi River is also influenced by the presence of numerous locks (Gramann et al. 1984) and dams. Integrating the natural environmental conditions with human alterations yields a hydrological regime in which specific discharge (the quotient of streamflow volume and contributing area) increases throughout the winter to a peak in the spring (May), decreases through the summer, and remains low in the fall.

The UMRB drains some of the continent’s most fertile arable land, which is predominantly under either corn or soybean production. Because of these and other land uses, a variety of nutrients and contaminants have been observed in the waters of the Mississippi River. The majority of fertilizer is applied in the spring prior to or after planting, though dry fall fertilizer applications range from 0 to 25% of the total annual amount (Cao et al. 2018). However, sub-annual nutrient source timing and magnitude is not well known at the watershed scale. Nutrient loading has been exacerbated by land management practices, such as artificial drainage, that enhance discharge in the Upper Mississippi River (Schilling et al. 2010). River sediment cores have revealed an increase by a order of magnitude of sediment deposition since the 1830s (Engstrom et al. 2009). In the UMRB the mean N fertilizer use rate in 2015 was 49 (maximum = 173) kg N ha\(^{-1}\) year\(^{-1}\), corresponding to 2.4 \(\times 10^6\) t N year\(^{-1}\) (Cao et al. 2018). The use rate within the UMRB exceeds NO\(_3\)-N loads discharged from the Mississippi River into the Gulf of Mexico as reported by Van Meter et al. (2018). Excess nutrients, including a tripling of NO\(_3\)-N input to the Gulf of Mexico (Goolsby et al. 2001, McIsaac et al. 2002), are credited with causing the hypoxic zone in the Gulf of Mexico, which has been measured at 20 700 km\(^2\) in extent (Rabotyagov et al. 2010) and has raised questions about the current approaches to reducing nutrient loads in the Mississippi River (McLellan et al. 2015).

2.2 [TN] data

We obtained quality controlled stream [TN] (unfiltered total nitrogen as N) data (1995–2007) from Mengistu et al. (2020), which was originally compiled by the SPARROW (Spatially Referenced Regression on Watershed Attributes) water quality modeling group, from federal, state, and local government monitoring (Saad et al. 2011). Sites (Fig. 1) included at least 25 stream [TN] measurements per site (over the course of the 13-year sampling window) distributed throughout the year to ensure representation of all seasons (see Supplementary material, Table S1). We subset this dataset to include only those sites with less than 10% impervious area. We also excluded sites 05331580, 05465500, and 05592900 due to a discrepancy between watershed area as reported by Mengistu et al. (2020) relative to United States Geological Survey (USGS) records. This resulted in a total of 6204 [TN] measurements divided amongst 76 sites, all of which included corresponding discharge measurements. [TN] values in this dataset range from 0.1 to 25.1 mg L\(^{-1}\) (median = 3.4). These measurements are taken from streams draining watersheds of median area 2694 km\(^2\) (mean = 6890), ranging from small catchments (163 km\(^2\)) to large watersheds (50 100 km\(^2\)).

2.3 Derivation of variables

To describe the variation in our response variable [TN], we used static (i.e. time-invariant) watershed-scale predictor variables developed by Mengistu et al. (2020) that aimed at quantifying watershed characteristics. The variables (see Supplementary material, Table S2) reflect potentially important elements of watershed-scale nutrient cycling, including sources (e.g. nutrient loading via cultivated areas) and sinks (e.g. denitrification via wetland areas). The derivation and a detailed list of these variables are given in Mengistu et al. (2020).

The static variables are supplemented by time-varying values developed in this study: daily discharge (from USGS gauges; see Supplementary material, Table S1), monthly
wetness index (the quotient of spatially averaged precipitation and potential evaporation) derived from Precipitation-elevation Regressions on Independent Slopes Model (PRISM) climate data (Daly et al. 2008), year of [TN] sampling, and day of year of [TN] sampling. Potential evaporation (PET) was estimated following Hargreaves (1994), where
daily minimum and maximum temperatures were extracted from PRISM for each watershed. Areal extent calculations were performed in the Albers Equal Area projection for the conterminous US. All geospatial analyses were conducted in ArcGIS 10.7 and R.

2.4 Modeling approach

To investigate the potential watershed-scale wetland and landscape drivers of seasonal [TN] variability we applied a linear statistical model with seasonal harmonics (i.e. periodic functions). Based on our understanding of important drivers of seasonal [TN] variability and previous exploratory work (Wine et al. 2020b), we selected a sparse set of candidate variables to develop linear mixed-effects (LME) models that capture and reproduce the cyclical seasonal nature of [TN] (see the next section).

2.5 Mixed-effects modeling

Mixed-effects modeling is an extension of simple linear modeling and is widely used in investigating complex water resource problems (Ahearn et al. 2005, Araujo et al. 2012, Hurley and Mazumder 2013, Bart 2016, Wine et al. 2018, Bywater-Reyes et al. 2018). This is particularly true for those situations in which part of the natural variability is associated with measured phenomena (i.e. fixed effects) and part of the natural variability results from complex phenomena (i.e. random effects) such as site-specific characteristics. LME also offers tools to overcome heteroscedasticity. In this way, LME relaxes certain assumptions commonly associated with the application of simpler methods (Zuur 2009). A key assumption of LME models is correct model specification, which requires that all relevant terms and interactions are included along with appropriate treatment of model residuals’ variance.

We anticipated seasonally cyclic behavior in [TN] across the UMRB, particularly because seasonal nutrient loading from agricultural fertilization, as well as from other diffuse nutrient sources and point discharges, is prominent across the UMRB. Helsel et al. (2020) suggest representing this cyclic behavior with periodic functions or harmonics (i.e. sine and cosine) and identifying and addressing cases where cycles shorter than one year may occur. We used this approach for our intra-annual [TN] LME models. However, we did not anticipate that all 76 watersheds would exhibit identical periodic behavior (i.e. amplitude and timing of peak). Hence, we included these periodic functions as random effects, which allows the parameters defining each harmonic to vary by watershed. Though harmonics offer the potential to reproduce secular variability in [TN], this approach alone cannot explain what may be causing observed variability.

To explore what hydrological processes may be driving [TN], we sequentially added variables informed by previously reported random forest results (Wine et al. 2020b), ensuring that variables representing key concepts from the advection diffusion reaction equation (ADRE, Equation 1) were represented. Such key concepts include nitrogen sources, fluid advection, and reactions (i.e. denitrification). While we did not intend to solve the transient ADRE (Oldham et al. 2013) here, we nonetheless considered it briefly as a lens into the physical processes underlying the temporal dynamics of non-conservative solute concentrations (c):

\[
\frac{\partial c}{\partial t} = -\nabla \cdot (cu) + \nabla \cdot (D \nabla c) - \frac{\partial q}{\partial t} + S, \tag{1}
\]

which are controlled by velocity (u), the diffusion coefficient (D), concentration change due to reactions (q), and sources and sinks (S). These dynamics are transient in time (t) and distributed across space. This transient equation allows for seasonal variations in [TN] as a consequence of advective \((\nabla \cdot (cu))\), diffusive \((\nabla \cdot (D \nabla c))\), reactive \((\frac{\partial q}{\partial t})\), or additive \(S\) processes. With respect to the source term, the timing of fertilization is expected to yield a key seasonal source, whereas crop growth serves as a sink. In UMRB it is reasonable to expect that [TN] is influenced by coupled surface and subsurface flow and transport dynamics. Though a physically based approach to understanding seasonal nitrogen dynamics is beyond the scope of this work, this approach nonetheless remains reference.

To build our LME models, we considered first-order interactions for those variables perceived as having an interactive influence on [TN], i.e. in cases where a predictor’s influence on [TN] was expected to depend on the value of another predictor. Following successive Bayesian information criterion (BIC) improvements, model development was ceased when the aforementioned key concepts and interactions had been represented. Note that BIC is given as:

\[
BIC = -2 \log(L) + k \log(n),
\]

where L is the likelihood function, k is the number of parameters, and n is the length of the response variable (Neath and Cavanaugh 2011).

To ensure that modeling assumptions were met, we examined the model residuals of each watershed for heteroscedasticity at the completion of the modeling analyses and dealt with heteroscedasticity among watersheds by assigning a fixed variance structure.

3 Results

3.1 Seasonal variability of [TN] across UMRB

Among all sites and across the 13-year study period, [TN] varies strongly in the UMRB – by a factor of 250. Concentrations range from 0.1 to 25.1 mg L\(^{-1}\). In 12% of the measurements, [TN] exceeds 10 mg L\(^{-1}\), the maximum permitted contaminant level for nitrate as N in the US, and in 41% of the measurements [TN] exceeds 4.4 mg L\(^{-1}\), the drinking water standard in Germany (as an example of more stringent global water quality standards). Considering all watersheds, [TN] is lowest in September, increases during the fall when fertilizer is sometimes applied, remains steady through the winter, and increases further in the spring when fertilizer is commonly applied (Fig. 2). Between June and September, median [TN] drops by 73% (Fig. 2). In addition to this pattern
Most commonly, higher [TN] was observed at a higher stream stage, though the strength of this relationship was variable. It is also important to note that spring fertilization occurs coincident with spring rains, which thereby reflects a high source availability during a high-flow period. This combination is anticipated to enhance solute transport. The largest BIC decrease is realized when discharge is added as a random effect. A smaller BIC decrease is observed when the first and second harmonics are added as random effects (Table 1). Attempts at inclusion of additional random effects increased time to model convergence and the possibility of instability. Overall, the largest BIC decreases occurred during fitting of the random effects components of the model.

Two fixed-effect terms were added to the model: cultivated area and monthly wetness index. Wetland area was considered for inclusion in the model but was ultimately excluded because it caused a BIC increase. This implies that what wetland area remains today after the large majority has been lost in UMRB (Fig. 6) does not explain enough marginal [TN] variance in our dataset to justify the added model complexity associated with inclusion of a wetland term. (Note that in this dataset wetland area constitutes no more than 15% (mean = 3%) of watershed area, which apparently is insufficient to bring about a substantial effect size.) To explain the observed seasonality of [TN], an interaction term between monthly wetness index

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**Figure 2.** Stream total nitrogen (TN) concentrations peak in June following spring fertilizer loading. By September concentrations have decreased by 73%, consistent with contemporary nutrient loading as the primary cause of observed [TN] increases. Data are from 76 watersheds in the Upper Mississippi River basin (1995–2007). Recommended timings for fertilizer application (i.e. spring and fall) are shaded gray. (The gray dashed lines refer to the highest and lowest monthly median [TN], respectively.)

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3.2 Linear mixed effects: sequential results

Our linear mixed-effects modeling aimed initially to reproduce the cyclical variability in [TN] and then to link [TN] to watershed characteristics. The resulting idealized model (Table 1, Equation (5)) represents cyclical trends in [TN]. To determine the final model, we fit five sequential, increasingly complex models.

In the first four models (Table 1), our goal was to reproduce site-specific behavior in [TN] seen across the study area (e.g. see Figs 2 and 3, and also large watersheds, as seen in Fig. 4) but represented inadequately via the fixed-effects model terms. The first model consists of a wetness index and a random effect describing the intercept associated with each watershed (Table 1, Equation (1)). We next included discharge as a random effect (Table 1, Equation (2)), noting the potential importance of concentration–discharge relationships and that such relationships may be direct, inverse, or weak (Fig. 5). (Fitting discharge as a random effect allows LME to assign positive or negative coefficients of appropriate magnitudes.)
and cultivated area was fitted. However, this interaction increased the BIC and was therefore discarded. The final model form (Table 1, Equation (5)) explained the greatest amount of the observed variability in [TN] (Fig. 7).

We accounted for observed heteroscedasticity in model residuals by quantifying the variance of model residuals by watershed in an initial model run (of Equation (5) in Table 1) and assigning these variances in a fixed variance structure for the final model.

Circling back to the model fit, we then observe, as anticipated, the weakest fit at gauge 05379500 (Trempealeau River at Dodge, WI; 1665 km²), where both seasonality and the concentration–discharge relationship are weak. In contrast, at 05317000 (Cottonwood River near Ulm, MN), a station exhibiting marked seasonality and a readily discernable concentration–discharge relationship, the strongest fit is observed. Moving east and north – to areas with greater abundance of relatively natural land cover – model residuals tended to decrease, suggesting that detailed spatiotemporal data on cultivation practices and N loading would be valuable.

4 Discussion

4.1 Seasonality of TN

In the presence of recurrent anthropogenic nitrogen loading from fertilizer across the UMRB, which coincides in time with peak discharges (Fig. 2), flowpaths were likely activated proximal to the nitrogen source at the land surface, resulting in dominant dynamics in the form of relatively high [TN] during high discharge periods (Domagalski et al. 2008). Lower flows tended to occur from July through February in the UMRB, out of phase with spring fertilizer application. However, certain watersheds with smaller proportions of cultivated area exhibited
Figure 4. Four examples of larger watersheds in the UMRB (>27 000 km²) showing that total nitrogen (TN) concentration dynamics are variable. In watersheds with less cultivated land (18%, top right; 27%, bottom left), dilutional dynamics prevail with relatively low [TN] and decreasing concentrations as flows increase. In watersheds with greater cultivated area (83%, top left; 67%, bottom right) [TN] tends to peak in June and reach a trough in September or October. (The gray dashed line references 1 mg L⁻¹.)

Table 1. Total nitrogen models of increasing complexity, where $y_j$ refers to log₁₀[TN] from the jth day of year measured at the jth watershed. Predictors include wetness index during the preceding month ($x_{j,0}$), discharge ($x_j$), and cultivated area ($x_j$). The mixed-effects model involves both fixed effects, which involve fitting scalar coefficients ($\beta$), and random effects, which fit vectors ($u$).

| Model | Model form | New term | Akaike Information Criterion (AIC) | Bayesian Information Criterion (BIC) |
|-------|------------|----------|-----------------------------------|-------------------------------------|
| 1     | $y_j = \beta_0 + u_{0j} + \beta_1 \cdot x_{0j} + e_j$ | Discharge: random effect | 10 988 | 11 015 |
| 2     | $y_j = \beta_0 + u_{0j} + \beta_1 \cdot x_{0j} + u_{1j} \cdot x_{1j} + e_j$ | | 7174 | 7214 |
| 3     | $y_j = \beta_0 + u_{0j} + \beta_1 \cdot x_{0j} + u_{1j} \cdot x_{1j} + u_{2j} \cdot \sin \left(\frac{2\pi \cdot t}{365}\right) + u_{3j} \cdot \cos \left(\frac{2\pi \cdot t}{365}\right) + e_j$ | First harmonic: random effect | 6493 | 6580 |
| 4     | $y_j = \beta_0 + u_{0j} + \beta_1 \cdot x_{0j} + u_{1j} \cdot x_{1j} + u_{2j} \cdot \sin \left(\frac{2\pi \cdot t}{365}\right) + u_{3j} \cdot \cos \left(\frac{2\pi \cdot t}{365}\right) + e_j$ | Second harmonic: random effect | 5818 | 5980 |
| 5     | $y_j = \beta_0 + u_{0j} + \beta_1 \cdot x_{0j} + u_{1j} \cdot x_{1j} + u_{2j} \cdot \sin \left(\frac{2\pi \cdot t}{365}\right) + u_{3j} \cdot \cos \left(\frac{2\pi \cdot t}{365}\right) + \beta_2 \cdot x_{2j} + e_j$ | Cultivated area: fixed effect | 5764 | 5933 |

Dilutional dynamics (Fig. 4) in which peak spring flows brought lower [TN]. Nonetheless, one difficulty in determining the cause of [TN] seasonality is the absence of information on N sources at the watershed spatial scale and at a sub-annual temporal resolution. Artificial tile drainage decreases the residence time of water in the vadose zone (Danesh-Yazdi et al. 2016) in many of the watersheds throughout the UMRB, thereby facilitating rapid transport of recurrently applied N and reducing the
potential for denitrification. However, elucidating the role of artificial drainage in influencing \([\text{TN}]\) seasonality remains a topic for future research.

Our results regarding the seasonality of \([\text{TN}]\) may be read in the context of past assertions that Gulf of Mexico water quality goals may not be achieved because of legacy nitrogen (e.g., Van Meter et al. 2018). Our observations of a 73% drop in \([\text{TN}]\) between June and September and \([\text{TN}]\) increases that tend to occur coincident with fertilization – during the spring and fall – may instead be indicative of the importance of contemporary basin-scale nitrogen loading (Van Meter et al. 2020). Our findings may agree with retrospective analyses observing rapid recovery of groundwater nitrate concentrations from initial values exceeding 10 mg L\(^{-1}\) to values below this threshold at the time scale of months with cropland to grassland conversion (Van Meter and Basu 2015). Based on empirical observations (Fig. 2), if excess fertilizer applications ceased, we speculate that a large portion of the observed water quality impairment would resolve on a time scale of months. However, improved understanding of cause and effect will require improved spatiotemporal data on nitrogen sources and additional critical field experimentation, which in turn is expected to set the stage for advancement in physically- or process-based modeling of nutrient concentrations.

### 4.2 Wetlands and [TN]

Previous work has suggested that lower [TN] is observed in the presence of wetlands (Lane et al. 2018), including in the UMRB (Mengistu et al. 2020) and the Minnesota River basin (Hansen et al. 2018). Our finding of no BIC improvement if wetland extent is included contrasts with those prior findings. Relative to Hansen et al. (2018), where wetland extent exceeded 25% of watershed area in certain sampling sites, our dataset wherein wetland extent is less than 15% of watershed area at all sites
Figure 6. Proportion of wetlands within each of the 76 study watersheds in the Upper Mississippi River. Historic distribution of wetlands from the (a) Global Lakes and Wetlands Database (Lehner and Doll 2004) and (b) Horvath et al. (2017). (c) Contemporary distribution of wetlands from the National Wetland Inventory.

presents an important contrast. Taking the results of Hansen et al. (2018) together with our own might suggest that a threshold for detection of wetland effects may lie in the 15–20% range, which is analogous to a similar threshold described by Stednick (1996) and Bosch and Hewlett (1982). However, there are two caveats. The first is that even though BIC increases if wetland area is added as a predictor, Akaike Information Criterion (AIC) decreases. This can be taken to imply that wetland area may marginally improve model predictions, subject to the following additional caveat. Since land-cover fractions in a watershed are complementary, retrospective statistical methods cannot distinguish the effects of one land cover fraction (e.g. wetland area) relative to those of another (e.g. cultivated area). This latter consideration may be dealt with through future work that adopts a physically- or process-based approach that can suggest whether results are physically plausible. Also, the wetland effect may be more nuanced than simply an additive term as in our model.

4.3 Uncertainty

A critical reading of the literature on drivers of nitrogen concentrations in streams and related issues readily reveals the uncertainty of the science, with certain studies of a single region yielding contrasting results (Table 2). Acknowledging this uncertainty is key to reliable predictions (Juston et al. 2013). Some have argued that certain classes of models describing complex systems cannot be validated (e.g. Konikow and Bredehoeft 1992) due to issues of non-uniqueness or equifinality. In this study one of the key uncertainties is structural – is the statistical model specified correctly? In mixed-effects modeling, when random effects explain substantial variance, the importance of such terms must be viewed not only as controlling for site-specific characteristics, but also as an indicator of the uncertainty inherent in the modeling approach. For example, fitting the concentration–discharge relationship as a random effect “explains” correlated variance, but it provides no information about what is causing such relationships to vary. (Application of
process-based models that represent hypotheses regarding hydrological processes presents an alternate path, though one with its own uncertainties.) Decreasing BIC values notwithstanding, the problem of understanding reactive solute transport at the basin scale constitutes one such instance, wherein models are likely to be equifinal. In this case we can still aspire to quantifying the full range of uncertainty. In streams with elevated [TN] in UMRB, the possibility that substantial recovery could occur on the time scale of months should not be discounted. However, this possibility, as in results derived by modeling other systems affected by equifinality, requires confirmation by critical experimentation.

4.4 Study implications

We find ourselves at a point in which the measures humans take to secure our well-being simultaneously threaten our health and the security of water resources. For example, as we observed here, widespread nitrogen loading and the increase in agricultural land at the expense of wetlands is expected to improve agricultural productivity, though it simultaneously has increased [TN]. Future research quantifying direct human impacts on solute concentrations and other state variables in hydrology has the potential to address associated knowledge gaps.
Recently, greater emphasis has been placed on approaching complex water resource challenges from an interdisciplinary or transdisciplinary approach that considers perspectives from all relevant disciplines (Melsen et al. 2018, Quinn et al. 2018). In this case the challenge involves securing freshwater in the face of powerful interests together with an unprecedented human population. Indeed, there is growing acknowledgement within the water resource community of the role of water resource securitization in influencing hydrological process understanding (Brooks and Trotter 2010, Yu et al. 2015, Farnum 2018, Grech-Madin et al. 2018, Schmeier and Shubber 2018, Wine 2019, 2020a, Wine and Laronne 2020, Koutsoyiannis and Mamassis 2021). This involves the characterization of an issue as an existential threat requiring the implementation of extraordinary measures. Consequently, “much of the scientific literature, perhaps half, may simply be untrue” (Horton 2015, Koutsoyiannis et al. 2016). With respect to [TN] in the UMRB, there is a need to examine the role played by water resource securitization in hydrological processes and our understanding of them, including how it influences the relative importance of many foci such as legacy effects or the uncertainty associated with nonpoint-source pollution origin or best management practice siting.

5 Conclusion

Principally as a consequence of on-going seasonal nitrogen loading in agriculture, [TN] in the UMRB is elevated to the extent that it regularly exceeds the US federal maximum contaminant level for nitrate-nitrogen, with exceedance most likely in June. Expansion of agriculture into former wetland areas together with widespread contemporary nitrogen fertilization (in excess of crop uptake) are primary drivers of the observed degraded conditions. However, [TN] in UMRB streams is not static in time, but rather highly dynamic. Our results suggest that this dynamism is poorly explained by interactions between cultivated extent and climate variability as represented by monthly wetness index. Though magnitude and timing of nitrogen sources are not well known at the sub-annual temporal scale or the watershed spatial scale, improved quantification of such sources could facilitate future efforts to model [TN] intra-annual variability. However, the results of this statistical investigation require confirmation or refinement by critical (field-based) experimentation and physically or processed-based modeling approaches.

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Author contribution

Conceptualization, MLW and OM; data curation, MLW; formal analysis, MLW; investigation, MLW; methodology, MLW and OM; software, MLW and OM; supervision, OM; writing – original draft, MLW; writing – review and editing, MLW and OM.

Disclosure statement

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Data availability

Precipitation and temperature data were obtained from the PRISM Climate Group (https://prism.oregonstate.edu/). Solute concentration data are available from the SPARROW (Spatially Referenced Regression on Watershed Attributes) Group.

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