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Biogeochemical and climate drivers of wetland phosphorus and nitrogen release: Implications for nutrient legacies and eutrophication risk

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Abstract

The dynamics and processes of nutrient cycling and release were examined for a lowland wetland-pond system, draining woodland in southern England. Hydrochemical and meteorological data were analyzed from 1997 to 2017, along with high-resolution in situ sensor measurements from 2016 to 2017. The results showed that even a relatively pristine wetland can become a source of highly bioavailable phosphorus (P), nitrogen (N), and silicon (Si) during low-flow periods of high ecological sensitivity. The drivers of nutrient release were primary production and accumulation of biomass, which provided a carbon (C) source for microbial respiration and, via mineralization, a source of bioavailable nutrients for P and N co-limited microorganisms. During high-intensity nutrient release events, the dominant N-cycling process switched from denitrification to nitrate ammonification, and a positive feedback cycle of P and N release was sustained over several months during summer and fall. Temperature controls on microbial activity were the primary drivers of short-term (day-to-day) variability in P release, with subdaily (diurnal) fluctuations in P concentrations driven by water body metabolism. Interannual relationships between nutrient release and climate variables indicated "memory" effects of antecedent climate drivers through accumulated legacy organic matter from the previous year's biomass production. Natural flood management initiatives promote the use of wetlands as "nature-based solutions" in climate change adaptation, flood management, and soil and water conservation. This study highlights potential water

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Abbreviations: DIN, dissolved inorganic nitrogen; DO, dissolved oxygen; ECN, Environmental Change Network; ER_{av}, daily average ecosystem respiration; GPP_{av}, daily average gross primary production; SRP, soluble reactive phosphorus; TDN, total dissolved nitrogen; TFe, total iron; TP, total phosphorus.

quality trade-offs and shows how the convergence of climate and biogeochemical drivers of wetland nutrient release can amplify background nutrient signals by mobilizing legacy nutrients, causing water quality impairment and accelerating eutrophication risk.

1 | INTRODUCTION

Eutrophication arising from excessive phosphorus (P) and nitrogen (N) inputs to surface freshwaters accelerates growth of nuisance and harmful algae and can profoundly impair water quality and aquatic ecosystems (Dodds & Smith, 2016; Smith, 2003). Changing climate patterns are intensifying the hydrological cycle and modifying the biogeochemical cycling and delivery of N and P along the land–water continuum (Jarvie, Jickells, Skeffington, & Withers, 2012; Moss, 2012; Ockenden et al., 2016, 2017; Whitehead, Wilby, Battarbee, Kernan, & Wade, 2009). Wetlands can provide important hotspots for biogeochemical cycling of nutrients at the interface between terrestrial and aquatic systems (Cheng & Basu, 2017; Land, Tonderski, & Verhoeven, 2019) and are a focus of accumulation of legacy nutrients within watersheds (Chen et al., 2018; Sharpley et al., 2013). These functions are also vulnerable to climate change impacts, including changing precipitation patterns, temperatures, and water levels (Macrae, Devito, Strack, & Waddington, 2013; Winter, 2000).

There is considerable interest in restoring, protecting, and constructing wetlands (including on-farm ponds) as "nature-based solutions" for flood management and for soil and water conservation based on the capacity of these landscape features to retain water, sediments, and particulate P; to denitrify N inputs; and to improve habitat complexity (Dadson et al., 2017; Erwin, 2009; Hansson, Bronmark, Nilsson, & Abjornsson, 2005; Lane, 2017). However, wetlands are also known to transition between sinks and sources of nutrients (Audet, Zak, Bidstrup, & Hoffmann, 2020; Fisher & Reddy, 2001).

This paper explores climatic and biogeochemical drivers of N and P release in a relatively pristine wetland setting with no anthropogenic nutrient inputs from agriculture or wastewater. Long-term water chemistry data collected for two decades were combined with detailed hydrochemical monitoring and high-resolution in situ sensor measurements and meteorological data to explore the dynamics and drivers of wetland N and P cycling. The influence of climate, water-body metabolism, and biogeochemical processes were examined in relation to patterns of P and N release across a hierarchy of temporal scales from decadal and seasonal to subdaily.

2 | MATERIALS AND METHODS

2.1 | Site description

This study was undertaken at the Radbrook wetland-pond system at Wytham Woods in Oxfordshire, United Kingdom (Supplemental Figure S1), which drains nationally scarce valley-side fen and reed swamp that is dominated by *Phragmites australis* (reed), *Equisetum telmatela* (great horsetail), and *Carex acutiformis* and *C. riparia* (sedges) (Savill, Perrins, Kirby, & Fisher, 2011). Radbrook pond (surface area, 1,022 m^2) was created in 1898 by damming the outflow from the wetlands. The wetland-pond discharges into a headwater stream that is part of the River Thames watershed. Although there are areas of ancient woodland (predominantly beech trees, ∼200 yr old), the majority of the catchment area draining into the wetland-pond system (193,360 m^2) is composed of secondary woodland. The site is managed by the University of Oxford and is part of the Environmental Change Network (ECN), the United Kingdom's long-term, integrated monitoring and research program, which began in 1992 (Morecroft et al., 2009; Savill et al., 2011; Sier & Monteith, 2016). Aerial photographs since 1946 show that catchment land use changed from rough grazing common land to woodland, which was planted by the University of Oxford Forestry Department from the 1950s onward (Savill et al., 2011). There have been no dwellings or septic tanks within the wetland catchment area. Therefore, the Wytham wetlands provide a relatively pristine wetland habitat within the intensively farmed and densely populated rural landscape of southern England. A site description is available at data.ecn.ac.uk/sites/ecnsites.asp?site=T08. The Wytham Woods site is encompassed by a loop of the River Thames, 5 km northwest of Oxford (Supplemental Figure S1). The altitude ranges from 60 m on the river flood plain to 165 m at the top of Wytham Hill. The geology is Oxford Clay with large areas of deep, heavy soils, which are often waterlogged during winter. Close to the hilltop there is a thin band of sandstone, with sandy soil in places. The hilltop is composed of coral rag limestone covered by thin, well-drained soils. Nutrient sources to the wetland are background sources recycled from mineralization of leaf litter and other organic matter, atmospheric deposition, and soil erosion from the woodland catchment. There are also potential "legacy" nutrient sources

derived from soil erosion during the woodland planting and from rough grazing more than 65 yr ago.

2.2 | Water quality sampling

2.2.1 | Environmental change network

Weekly ECN water chemistry sampling was undertaken at the wetland-pond outflow from January 1995 until June 2017 (Supplemental Figure S2) (Rennie et al., 2017). A suite of standard parameters was measured, including total P (TP), soluble reactive P (SRP), total dissolved N (TDN), ammonium (NH_4–N), nitrate (NO_3–N), and total iron (TFe) (Rennie et al., 2020).

2.2.2 | Hydrochemical sampling campaign 2016–2017

Additional detailed hydrochemical monitoring was undertaken at the wetland-pond outflow from July 2016 through December 2017, including during a high-intensity nutrient release event (release of both P and N) that occurred from August through October 2016. Measurements included TP, SRP, TDN, NH_4–N, NO_3–N, chloride (Cl^-), sulfate (SO_4–S), and dissolved reactive silicon (Si). Surface grab water samples were taken immediately adjacent to the ECN sampling from a dedicated sampling platform constructed at the wetland-pond outflow (Supplemental Figure S1). Samples were taken up to twice daily during the initial phase of nutrient release in August 2016. Water samples were analyzed according to detailed protocols (Bowes et al., 2018) outlined in the Supplemental Information.

In situ high-resolution SRP monitoring was undertaken at hourly intervals from August through November 2016 using a Cycle-PO_4 analyzer, which was submerged via a plastic tube attached to the sampling platform (Supplemental Figure S1). The sample inlet for the Cycle-PO_4 analyzer was located approximately 10–15 cm from the bed. The Cycle-PO_4 analyzer used molybdate-based colorimetry to quantify the reactive P concentration of filtered (10 μm) water samples (Seabird Scientific). The instrument analyzed an onboard calibration solution once per day to ensure data quality. Further information about the comparability of grab sampled and laboratory-measured SRP with the Cycle-PO_4 SRP measurements is provided in the Supplemental Information.

Dissolved oxygen (DO), pH, specific conductance, water temperature, and water levels were measured at 15-min intervals from August through November 2016 using an YSI EXO2 multiparameter water-quality sonde (Xylem Inc.). The EXO2 sonde was also submerged via a plastic tube attached to the sampling platform (Supplemental Figure S1). The EXO2

Core Ideas

- This study combines 20-yr nutrient monitoring and use of high-resolution in situ sensors.
- Concurrent releases of soluble P, NH_4–N, and Si were observed during summer and fall.
- Nutrient release was linked to climate drivers of biomass accumulation and turnover.
- High-intensity nutrient release events reflected legacies of previous years' biomass.
- This research highlights water-quality tradeoffs of wetlands for soil and water conservation.

sonde and the Cycle-PO_4 analyzer were cleaned and calibrated, and data were downloaded during weekly site visits.

2.3 | Laboratory analysis of water samples

Information on chemical analysis of water samples is provided in the Supplemental Information.

2.4 | Hydrological and meteorological measurements

A V-notch weir was used to measure flow from the wetland into the headwater stream. Hourly ECN meteorological data were collected at the Wytham ECN site automatic weather station (Supplemental Figure S1) and included solar radiation, air temperature (dry bulb), wind speed, and rainfall totals (see Supplemental Information).

2.5 | Data analysis

2.5.1 | Stream metabolism

Daily average gross primary production (GPP_{av}) and daily average ecosystem respiration (ER_{av}) were calculated from the series of diurnal DO curves using the Delta method (Chapra & Di Toro, 1991; Jarvie, Sharpley et al., 2018; Williams, White, Harrow, & Neal, 2000; details provided in the Supplemental Information). Daily P and N removal through primary production (assimilation) and release by microbial respiration (mineralization of organic matter) were then calculated from GPP_{av} and ER_{av} using the Redfield molar ratio for organic matter of 138O:1P and 16N:1P (Palmer-Felgate, Mortimer, Krom, & Jarvie, 2010; Palmer-Felgate, Mortimer, et al., 2011).

2.5.2 | Nutrient thresholds

Nutrient concentrations measured at the wetland-pond outflow were compared with threshold concentrations of 0.05 mg P L^{-1} and 0.4 mg N L^{-1}, below which P and N would likely become limiting (Jarvie, Smith, et al., 2018; Mainstone & Parr, 2002). These thresholds are supported by experimental studies: SRP concentrations of approximately 0.05 mg P L^{-1} have also been identified as a "breakpoint" for P limitation using flume experiments (Bowes et al., 2012; McCall, Hale, Smith, Read, & Bowes, 2017; McCall et al., 2014), and the N breakpoint was estimated to be around 10 times higher than the P breakpoint (Keck & Lepori, 2012).

Summary statistics (mean, standard deviations, medians) and interdeterminant regression analyses were performed using R (R Core Team, 2019). Owing to data gaps during the first 2 yr, the analysis focused on the 20-yr dataset, from 1997 to 2017.

3 | RESULTS AND DISCUSSION

3.1 | Decadal and seasonal patterns in wetland nutrient release

The dominant features of the 22-yr nutrient concentration timeseries from the wetland-pond outflow (Supplemental Figure S2) were the sustained elevated concentrations of TP and TDN during low-flow summer–fall periods (July/August through October/November) in certain years. These periods of sustained nutrient release typically lasted for 3–5 mo and were distinct from the periodic and short-lived spikes in nutrient concentrations linked to rainfall/runoff events, which typically lasted for no more than 1 or 2 wk. Figure 1 shows the annual mean and standard deviation in P and N concentrations for the critical summer–fall period of nutrient release (1 July to 31 October) from 1997 to 2017. During these periods of summer–fall nutrient release, SRP was the dominant P fraction and NH$_4$–N the dominant N fraction.

Seven of these 20 monitoring years showed summer–fall nutrient release (Figure 1), and there were two distinct types of low-flow nutrient release events: (a) high-intensity nutrient release events (summer–fall of 2004, 2005, and 2016), which were characterized by higher SRP release (exceeding 0.1 mg P L^{-1} and up to a maximum of 0.288 mg P L^{-1}) accompanied by low-flow NH$_4$–N release (up to 5.72 mg N L^{-1}), and (b) moderate-intensity SRP release (summer–fall of 1997, 1998, 2006, and 2007), with SRP release exceeding 0.05 mg P L^{-1} (and up to a maximum of 0.124 mg P L^{-1}) but with no corresponding prolonged low-flow N release.

During the low-flow high-intensity nutrient release events, there was a strong positive correlation between TP and TDN ($r^2 = .577$; $P < .001$; $n = 145$) and between SRP and NH$_4$–
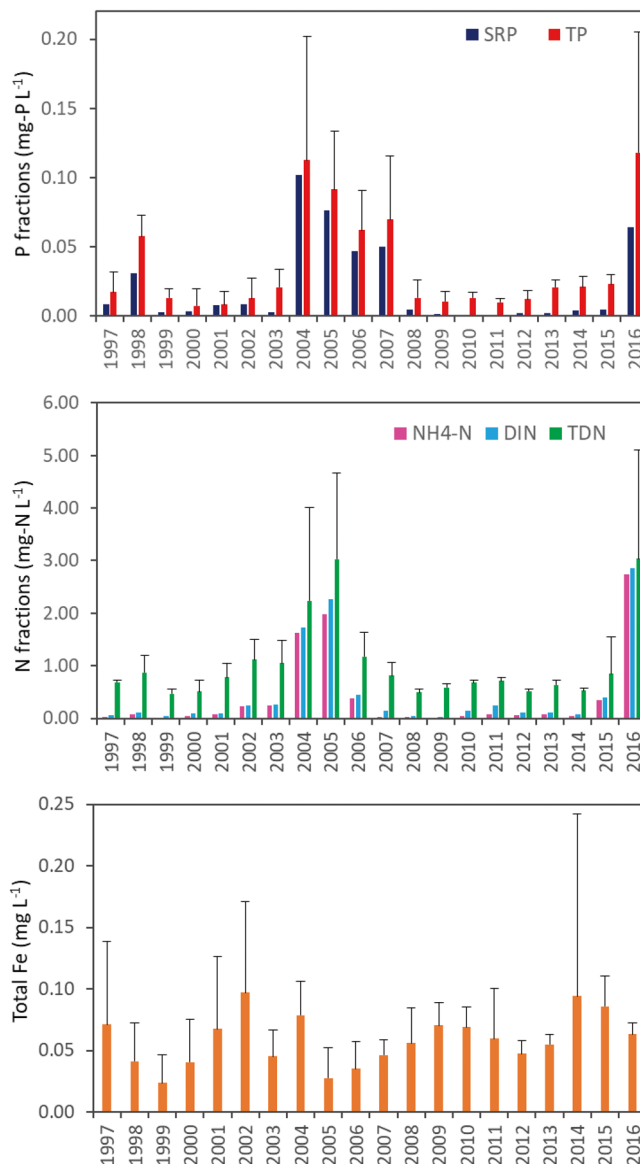

FIGURE 1 Mean annual P (soluble reactive P [SRP] and total P [TP]), N (NH$_4$–N, dissolved inorganic N [DIN], and total dissolved N [TDN]), and total Fe (TFe) concentrations, during summer and fall (1 July–31 October), showing SDs in TP, TDN, and TFe concentrations.

N ($r^2 = .484$; $P < .001$; $n = 150$) (Supplemental Table S1). However, during the moderate-intensity nutrient release events, there were no correspondingly significant correlations between P and N fractions.

Outside of the low-flow summer-fall periods of nutrient release, SRP and dissolved inorganic N (DIN: NH$_4$–N + NO$_3$–N) concentrations remained very low: SRP was typically below analytical detection limits of 0.005 mg P L^{-1}, and median NH$_4$–N, NO$_3$–N, and DIN concentrations were 0.04, 0.05, and 0.12 mg N L^{-1}, respectively. Thus, during these baseline conditions, P and N concentrations were below the thresholds of 0.05 mg P L^{-1} and 0.4 mg N L^{-1}, indicating
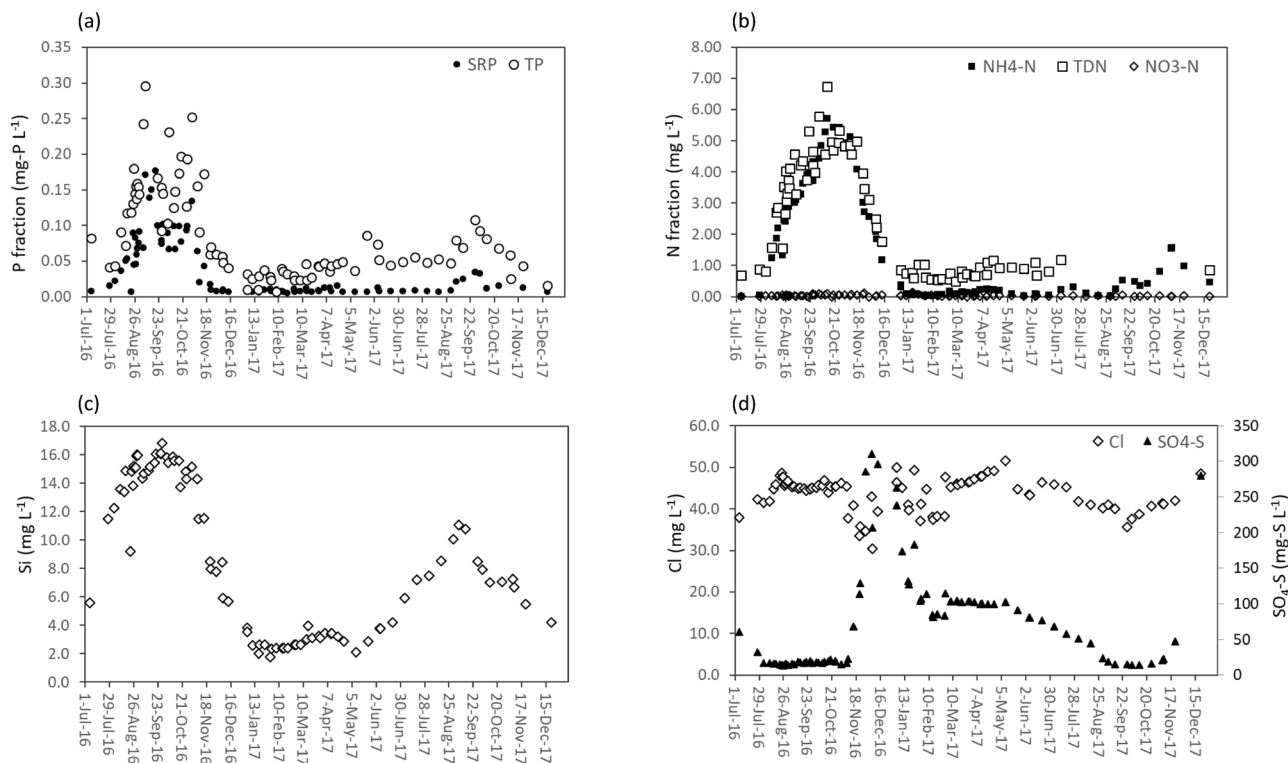
FIGURE 2 Detailed hydrochemical monitoring of (a) P (total [TP] and soluble reactive P [SRP]), (b) N (NO$_3$–N, NH$_4$–N, and total dissolved N [TDN]), (c) dissolved reactive Si, and (d) Cl$^-$ and SO$_4$–S concentrations, from July 2016 to December 2017.

that both P and N could potentially co-limit primary production (Jarvie, Smith, et al., 2018).

The detailed hydrochemical monitoring of a high-intensity nutrient release event (August through November 2016; Figure 2) revealed large-scale concurrent release of SRP (up to 0.18 mg P L^{-1}), NH$_4$–N (up to 5.7 mg N L^{-1}), and Si, a vital nutrient for diatom growth (Struyf & Conley, 2009) (up to 17 mg Si L^{-1}). Chloride was used here as a conservative marker of hydrological dilution and evapo-concentration to confirm that the observed changes in SRP, NH$_4$–N, and Si concentrations were not simply a function of hydrological concentration or dilution effects (Jarvie, Sharpley, et al., 2012). Between early July and late August, Cl$^-$ concentrations increased by a factor of 1.3, but there were much larger increases in Si, SRP, and NH$_4$–N concentrations (by a factor of 2.4, 11.3, and 123, respectively). Therefore, these increases in Si, SRP, and NH$_4$–N concentrations could not be accounted for by hydrological concentration effects alone but instead reflected biogeochemical nutrient cycling and release processes. During the subsequent termination of the high-intensity nutrient release event in November through December 2016, Cl$^-$ concentrations decreased by a factor of 1.5 as a result of hydrological dilution from rainfall and runoff. In contrast, NH$_4$–N and Si concentrations decreased by a factor of 2.6, and SRP decreased by a factor of 13.4, indicating that other processes were removing SRP, NH$_4$–N, and Si from the water column in addition to the diluting effects of runoff.

3.2 | Using high-resolution in situ monitoring to characterize the dynamics of wetland P release

High-resolution in situ monitoring (Figure 3) captured the dynamics of P release from August 2016 and through the termination of P release in early November 2016. The P dynamics were explored in relation to water levels, meteorological conditions (air temperature, rainfall, wind speed, and solar radiation), water temperature, and dissolved oxygen (Figure 3), which were used to calculate GPP$_{av}$ and ER$_{av}$ (see Supplemental Information).

During the first phase of P release, SRP concentrations increased from 0.03 mg P L^{-1} on 22 Aug. 2016 to 0.09 mg P L^{-1} on 28 Aug. 2016, after which SRP concentrations remained above the ecological threshold of 0.05 mg P L^{-1} until the P release was terminated in November 2016 (Figure 3a). Grab samples were used to ground-truth the in situ SRP measurements from the Cycle-PO$_4$ analyzer; 29 of the 33 grab sample SRP measurements were in close agreement with the Cycle-PO$_4$ SRP measurements, but four grab sample measurements showed markedly higher concentrations (Figure 3a; see Supplemental Information and Section 3.5 for explanation).

Although there was a declining trend in water temperature over the monitoring period, day-to-day increases in SRP concentration tracked the periodic increases in water temperature,
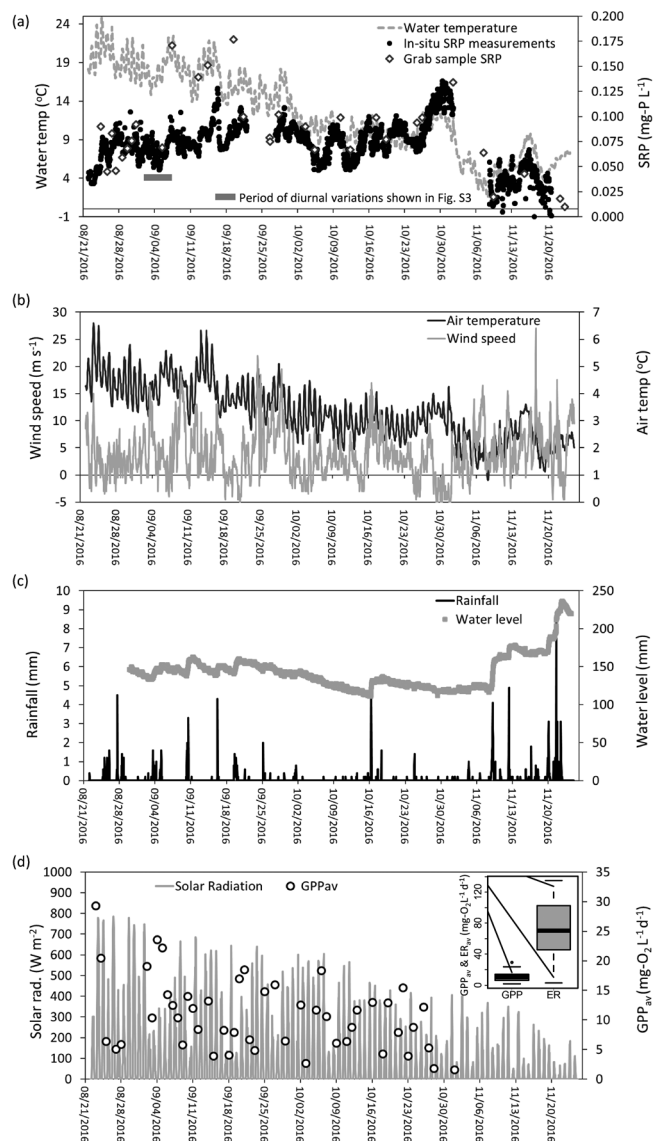
FIGURE 3 High-resolution monitoring of the high-intensity P release event from August through November 2016, showing (a) in situ hourly monitoring of soluble reactive P (SRP) concentrations and water temperature, with SRP concentrations for ground-truth laboratory-measured grab samples; (b) hourly monitoring of air temperature and wind speed; (c) hourly rainfall and water levels; and (d) hourly solar radiation and daily average gross primary production (GPP$_{av}$) estimated from in situ 15-min dissolved oxygen concentrations. Boxplots are shown as an inset to (d) for comparison of GPP$_{av}$ and daily average ecosystem respiration (ER$_{av}$).

which were superimposed upon this declining temperature trend, especially during the final large-scale P release event in late October 2016 (Figure 3a). The SRP release from late August until late October corresponded with a general decline in solar radiation and GPP$_{av}$ (Figure 3d). During this time, ER$_{av}$ did not show a corresponding decline (not shown), but ER$_{av}$ consistently exceeded GPP$_{av}$ (see inset boxplots in Figure 3d). The final and greatest period of SRP release in

late October (with SRP concentrations rising from 0.066 mg P L^{-1} on 25 Oct. 2016 to a peak of 0.134 mg P L^{-1} on 31 Oct. 2016) corresponded with a 5 °C increase in water temperature (from 8 to 13 °C) (Figure 3a). Peak SRP concentrations also corresponded with a period of very low wind speed (Figure 3b) and a marked reduction in GPP$_{av}$ (Figure 3d). The termination of the P release event commenced on 1 November with a dramatic reduction in SRP concentration to 0.02 mg P L^{-1} by 6 Nov. 2016 and corresponded with a rapid reduction in water temperature (from 13 °C on 31 Oct. 2016 to 4.5 °C on 6 Nov. 2016) and with an increase in wind speeds.

The accelerated SRP release in late October and the subsequent dramatic reduction in SRP concentrations occurred during a period of stable water levels (Figure 3c). During late August through October 2016, rainfall events had relatively little impact on water levels. The first major increase in water levels occurred on 9 Nov. 2016 in response to the first major rainfall event occurring after leaf-fall (i.e., reduced canopy rainfall interception). This increase in water levels occurred more than a week after the termination of the SRP release event, further confirming that the increases and decreases in SRP concentrations were driven by temperature and biogeochemical processes and not by hydrological effects.

3.3 | Biogeochemical drivers of nutrient release

3.3.1 | Iron redox controls on SRP release

Summer–fall release of TFe was observed each year, reflecting a regular yearly cycle of reductive dissolution of bed-sediment Fe oxyhydroxides, resulting in relatively little year-to-year variability in summer–fall TFe concentrations (Figure 1; Supplemental Figure S2). Seasonal release of soluble P in freshwaters, including ponds and wetlands, is typically attributed to the reductive dissolution of Fe oxyhydroxides in bed sediments during anoxic conditions, releasing PO$_4^{3-}$, when flow velocities decrease, water and sediment temperatures increase, and oxygen becomes depleted as a result of higher rates of microbial activity (Dupas, Tittel, Jordan, Musolff, & Rode, 2018; Gu et al., 2017, 2019; Palmer-Felgate et al., 2010; Palmer-Felgate, Bowes, Stratford, Neal, & MacKenzie, 2011). The prolonged periods of TFe release observed during the summer and fall each year indicate that the chemistry of the wetland outflow at these times was dominated by anaerobic processes occurring within the pond and the marginal wetlands, which are submerged all year. The consistently low NO$_3$–N concentrations throughout the 22-yr time series (median NO$_3$–N, 0.042 mg N L^{-1}) may also have been important in promoting reductive dissolution of Fe and release of SRP. Nitrate acts as an important redox buffer for Fe dissolution and SRP release, and redox-mediated SRP

release requires $NO_3–N$ to be depleted for P to be released to the aqueous phase (Dupas et al., 2017, 2018; Parsons, Rezanezhad, O'Connel, & Van Cappellen, 2017).

However, the interannual patterns in seasonal SRP release in the Wytham wetland did not correspond with interannual patterns in seasonal Fe cycling across all 22 yr (Figure 1), indicating that the release of SRP was decoupled from the seasonal cycles of reductive dissolution of Fe oxyhydroxides. There was a stronger correlation between SRP and TFe for the moderate-intensity nutrient release events ($r^2 = .137$; $P < .001$; $n = 196$; Supplemental Table S1) compared with the high-intensity nutrient release events ($r^2 = .079$; $P = .001$; $n = 150$). This indicates a greater role of redox-related SRP and Fe release during these moderate-intensity events (where there was no corresponding $NH_4–N$ release) and that other processes contributed to SRP release during the high-intensity nutrient release events when $NH_4–N$ was also released. For the other years, no SRP release occurred despite the annual summer–fall TFe release. This suggests that, during the non-nutrient release years, SRP released by reductive dissolution of Fe oxyhydroxides may be immediately subject to uptake and removal by other biogeochemical processes at, or close to, the sediment–water interface (Jarvie et al., 2008). Given the observed state of nutrient limitation under normal baseline conditions, the sudden availability of SRP as a result of dissolution of Fe oxyhydroxides may have stimulated enhanced rates of biological P assimilation, thus removing released SRP before it was able to diffuse into the overlying water column.

3.3.2 | Biological controls on P and N uptake and release

The release of P, but with no equivalent N release, during moderate SRP release events (Figure 1; Supplemental Figure S2) suggested that either (a) the major source of P during these moderate-intensity SRP release events was not mineralization of organic matter but may have resulted from reductive dissolution of Fe oxyhydroxides, advective P release from the sediments, and/or recycling of polyphosphate from bacteria and/or algae or (b) N released by organic matter mineralization was removed through denitrification. In contrast, the concurrent release of both SRP and $NH_4–N$ during the high-intensity nutrient release events (Figures 1 and 2; Supplemental Figure S2) indicated that microbial respiration and the resultant mineralization of organic matter was likely to be a dominant nutrient source during these prolonged high-intensity P- and N-release events.

To explore the biological controls on P and N uptake and release during the high-intensity nutrient release event of late summer–fall 2016, we calculated the P and N removed from the water column by assimilation from primary production and the P and N supplied by respiration of organic mat-

ter (mineralization) using GPP_{av} and ER_{av} (Palmer-Felgate et al., 2010; Palmer-Felgate, Mortimer, et al., 2011) (Table 1). Daily net P and N release rates were calculated by subtracting the P and N assimilated from the P and N supplied. Two periods were compared (Table 1; Figure 3): (1) toward the start of the nutrient release event in early September 2016, when GPP_{av} was highest; and (2) in late October 2016, when GPP_{av} had declined, and nutrient release was at a maximum, just before the nutrient release event was terminated in early November 2016. In early September 2016, the estimated net P and N release rates were 0.016 mmol P L^{-1} d^{-1} and 0.255 mmol N L^{-1} d^{-1}, rising to 0.020 mmol P L^{-1} d^{-1} and 0.320 mmol N L^{-1} d^{-1} in late October 2016. However, the molar ratios of N/P in the water column during this high-intensity nutrient release event were markedly higher than the expected (Redfield) N/P ratio of 16 for mineralization of plant/algal biomass. The average molar N/P ratio increased from 86 in early September to 100 in late October before the nutrient release event was terminated. This indicates that there were other biogeochemical processes removing P at a higher rate than N. These selective P uptake processes potentially include enhanced rates of P assimilation into microbial biomass (including luxury P uptake for polyphosphate storage; Hupfer, Gloess, & Grossart, 2007) or P sorption by non–redox-sensitive minerals, such as Al oxides, or co-precipitation with $CaCO_3$ (House, 2003)

The overwhelming dominance of $NH_4–N$ and the extremely low $NO_3–N$ indicated that nitrate ammonification was the dominant N-cycling process during these high-intensity nutrient release events. Indeed, dissimilatory $NO_3–N$ reduction to $NH_4–N$ by heterotrophs tends to be favored over denitrification where there are abundant sources of labile carbon (C) (Falcao & Vale, 1998). Microbial respiration and mineralization of organic matter may also have been further stimulated by the increase in P and N availability (White & Reddy, 2000) because the normal baseline water chemistry (outside of the nutrient release events) indicated P and N co-limitation. This has potential to accelerate both SRP and $NH_4–N$ release within a positive feedback cycle, sustained by abundant availability of organic C sources, because heterotrophic microbial activity in surface sediments is often limited by the availability of electron donors that fresh organic matter supplies (Orihel et al., 2017).

Interannual variability in the abundance and availability of organic matter therefore likely drove the difference between the moderate SRP release events (with no corresponding $NH_4–N$ release) and the intensive release of both SRP and $NH_4–N$ (White & Reddy, 2000). During moderate-release events, SRP was released from reductive dissolution of Fe oxyhydroxides (e.g., House, 2003), with any release of P and N from microbial mineralization at least partially compensated for by assimilation and denitrification (e.g., Jarvie, Sharpley, et al., 2018).

TABLE 1 Mean daily gross average primary production (GPP$_{av}$), average ecosystem respiration (ER$_{av}$), P and N assimilation and release, and net P release for two periods within the high-intensity nutrient release event of 2016

Parameters	Start of high-intensity nutrient release (7–12 Sept. 2016)	Max. nutrient release (before termination) (19–27 Oct. 2016)
Mean GPP$_{av}$	0.36 mmol O$_2$ L^{-1} d^{-1}	0.30 mmol O$_2$ L^{-1} d^{-1}
P assimilation (from GPP$_{av}$)	0.003 mmol P L^{-1} d^{-1}	0.002 mmol P L^{-1} d^{-1}
N assimilation (from GPP$_{av}$)	0.042 mmol N L^{-1} d^{-1}	0.034 mmol N L^{-1} d^{-1}
Mean ER$_{av}$	2.56 mmol O$_2$ L^{-1} d^{-1}	3.06 mmol O$_2$ L^{-1} d^{-1}
P supply (from ER$_{av}$)	0.019 mmol P L^{-1} d^{-1}	0.022 mmol P L^{-1} d^{-1}
N supply (from ER$_{av}$)	0.297 mmol N L^{-1} d^{-1}	0.354 mmol N L^{-1} d^{-1}
Net P release	0.016 mmol P L^{-1} d^{-1}	0.020 mmol P L^{-1} d^{-1}
Net N release	0.255 mmol N L^{-1} d^{-1}	0.320 mmol N L^{-1} d^{-1}

3.4 | Links between SRP and NH$_4$–N release and biogeochemical cycling of S and Si

Other redox processes may also have been responsible for the observed decoupling of Fe and SRP release (Figure 1; Supplemental Figure SI2), such as redox-mediated S cycling (Caraco, Cole, & Likens, 1989; Roden & Edmonds, 1997). The termination of the high-intensity nutrient release event in 2016 was marked by a dramatic increase in SO$_4$–S concentrations (Figure 2), which is indicative of a sudden reversal of anoxia and a rapid transition to more oxidizing conditions within the water column and surface sediments, releasing SO$_4$–S (Warren, Waddington, Bourbonniere, & Day, 2001). The depletion of SO$_4$–S during the period of SRP and NH$_4$–N release reflects the reduction of SO$_4$–S to aqueous bisulfides during oxidation of organic C (Orihel et al., 2017). Aqueous bisulfides react with FeII to form FeS, removing FeII from solution and inhibiting the precipitation of vivianite within the sediments, which can be an important permanent sink for P (Rothe, Frederichs, Eder, Kleeberg, & Hupfer, 2014). This formation of FeS effectively increases the availability of SRP relative to Fe (Roden & Edmonds, 1997), with SRP then subject to retention by microbial assimilation or by sediment sorption.

Silicon cycling may have also contributed to the observed P dynamics during the 2016 nutrient release event and its subsequent termination in November 2016. High concentrations of Si (up to 17 mg Si L^{-1}) were observed during the period of SRP and NH$_4$–N release, compared with concentrations of <4 mg Si L^{-1} during non–nutrient release baseflow periods (Figure 2). Release of Si can also be driven by high availability of labile C sources. Prolonged periods of anoxia, where microbial activity is uninhibited by C source availability, can result in accelerated dissolution of mineral and biogenic Si, including siliceous diatom frustules and the silica-rich emergent wetland plant *Phragmites australis*, which is abundant along the pond margins (Siipola, Lehtimaki, & Tallberg, 2016; Struyf & Conley, 2009; Tallberg, Heiskanen, Niemisto, Hall, & Lehtoranta, 2017; Villnas, Norkko, Lukkari, Hewitt,

& Norkko, 2012). Silicate anions released during prolonged periods of anoxia can compete with PO$_4^{3-}$ for sorption sites (e.g., on Al oxides), thus increasing SRP availability (Hartikainen, Pitkanen, Kairesalo, & Tuominen, 1996). However, in this case, the high concentrations of Si at the time of termination of the nutrient release event may have helped to accelerate subsequent SRP removal by inhibiting formation of crystalline Fe oxides and promoting the production of amorphous Fe oxides, which have a higher surface area and high P sorption capacity (Siipola et al., 2016). Indeed, the formation of Fe-Si colloids and the aggregation and sedimentation of Fe-Si particulates provides a plausible mechanism to explain the observed removal of Si during the nutrient release termination phase.

3.5 | Colloid and particulate interactions

The formation of colloids and their aggregation into larger particulates, as well as the presence of P in suspended phytoplankton cells, may help to explain the differences observed between TP and SRP concentrations in grab samples (as seen during the detailed hydrochemical sampling of the 2016 nutrient release event; Figure 2). Algae, particulate, and colloid interactions may also explain the apparent discrepancies between in situ high-resolution SRP monitoring and SRP in grab samples during the 2016 nutrient release event (Figure 3a). Grab sampling closer to the surface of the water column may have unintentionally captured higher concentrations of phytoplankton (which migrate to the surface to increase light capture), leading to higher TP relative to SRP (Figure 2a). Grab sampling closer to the surface may also capture higher concentrations of colloidal P, owing to precipitation of P-enriched Fe oxide colloids in the more oxic surface waters compared with subsurface water layers sampled by the in situ monitoring equipment (the inlet to the Cycle-PO$_4$ analyzer was located approximately 10–15 cm above the bed). This may account for the higher SRP concentrations in
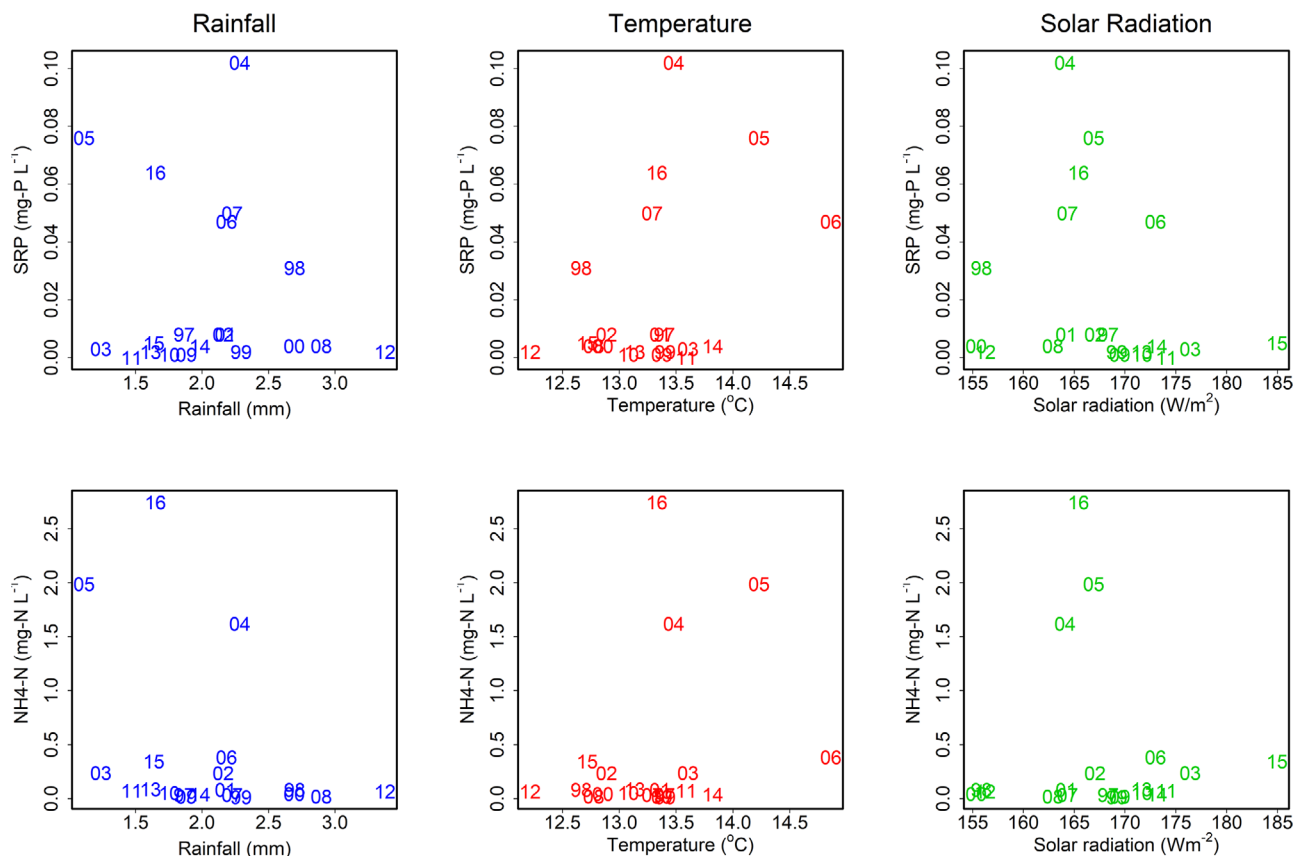
FIGURE 4 Relationships between mean summer-fall soluble reactive P (SRP) and NH_4–N concentrations (1 July–31 October) and spring–fall climate indices (mean rainfall, mean temperature, and mean solar radiation, 1 April–31 October). Individual years (1997–2016) are denoted as two-digit numbers.

the four grab samples collected between 7 and 19 Sept. 2016, compared with measurements by the Cycle-PO_4 analyzer (Figure 3a).

3.6 | Climatic drivers of wetland nutrient release

Climate-related controls on wetland biogeochemistry and nutrient release were explored across a hierarchy of temporal scales, from interannual and seasonal to subdaily.

3.6.1 | Interannual climate drivers

The interannual variability in summer–fall (from 1 July to 31 October) SRP concentrations was most closely linked with spring–fall rainfall amounts (from 1 April to 31 October), with lower rainfall linked to higher SRP release (Figure 4). The years showing marked summer–fall SRP release exhibited a negative relationship between mean SRP concentration and mean daily spring–fall rainfall, with higher concentrations of SRP in the lower rainfall years. The 3 yr when high-intensity

nutrient release of both SRP and NH_4–N (2004, 2005, and 2016) occurred were characterized by relatively low mean spring–fall rainfall (mean, 1.68 mm d^{-1}) relative to years with no nutrient release (mean, 2.09 mm d^{-1}). A combination of lower water levels and higher temperatures is generally conducive to higher rates of microbial activity. However, the years with no nutrient release span a wide range of rainfall, temperature, and solar values (Supplemental Table S2), and it was difficult to discern any further clear relationships between SRP and NH_4–N concentrations and rainfall, air temperature, and solar radiation statistics.

For two of the three high-intensity nutrient release years with the highest SRP release (2004 and 2016), the preceding years (2003 and 2015) showed the highest solar radiation (Figure 4; Supplemental Table SI2). High solar radiation is expected to promote higher rates of primary production, biomass accumulation, and P and N assimilation and may result in some year-to-year "carry-over" of legacy organic matter and nutrients from the previous year's standing crop. This carry-over may result in a larger pool of organic matter for decomposition and nutrient release during the subsequent summer–fall period.

High levels of solar radiation and photosynthesis also confer opposing or antagonistic effects on net nutrient release by increasing primary production and biomass accumulation but also by limiting the development of anoxia through daytime O_2 production and by assimilating SRP and NH_4–N released (Halliday et al., 2015). However, these opposing effects of oxygen and biomass production operate on different timescales: oxygen production responds rapidly to changing ambient light levels, and O_2 has a short residence time (minutes to hours), being rapidly removed from the water column uptake via respiration and degassing (Williams et al., 2000). In contrast, biomass accumulation (aquatic macrophytes, algae, and terrestrial leaf litter) has potential for longer-term interannual "carry-over" or legacy effects of organic matter, with much longer residence times (months to years). This study indicates that high rates of solar radiation and the accumulation of biomass during the 2003 and 2015 growing seasons may have carried over into 2004 and 2016, providing a larger pool of organic matter for microbial respiration and SRP and NH_4–N release during these two high-intensity nutrient release years. Thus, interannual legacies of organic matter production may, to some extent, have superseded the climate effects of any given year in driving microbial nutrient release.

3.6.2 | Seasonal climate drivers

There was clear seasonality in wetland nutrient release, starting typically in July/August and ending in October/November (Figures 2 and 3; Supplemental Figure SI2). The period of maximum P release corresponded with declining rates of photosynthesis relative to respiration, driven primarily by the seasonal reductions in solar insolation (Figure 3d). By the late summer and fall, despite declining temperatures, there were high rates of respiration and organic matter mineralization, relative to photosynthesis. These high rates of respiration were likely driven by the seasonal accumulation of organic matter, arising from higher rates of primary production earlier in the growing season. Indeed, the relative availability of labile C, either from the current year's growing season (and/or the "legacy" of biomass production in previous growing seasons) likely determined the scale and nature of seasonal patterns in nutrient release (i.e., whether [a] nutrient release occurred at all, [b] nutrient release was moderate and just SRP was released, or [c] there was a high-intensity nutrient release event, where both SRP and NH_4–N were released, as a result of an abundance of organic matter mineralization and a switch in N cycling from denitrification to nitrate ammonification). Thus, the seasonal climate drivers of solar radiation and air temperature, through their control of rates of respiration relative to photosynthesis, appear to have played an important role in both the timing and scale of nutrient release.

3.6.3 | Short-term (day-to-day and diurnal) climate drivers

The high-resolution monitoring (Figure 3) showed that water temperature was a major driver of day-to-day variations in SRP release. Despite a progressive decline in baseline water temperature during the main phase of nutrient release, day-to-day variability in SRP release was closely linked to day-to-day variability in water temperature, particularly in late September through November ($r^2 = .517$; $n = 4{,}451$; $p = <.001$). Water temperature variations mirrored the day-to-day patterns in air temperature (Figure 3a,b), indicating that the major driver of changing rates of SRP release were primarily linked to weather/climate factors and not the heat flux generated by the microbes within the sediment.

Diurnal variability in SRP (i.e., the range in concentrations within a 24-h period) was relatively small scale compared with the day-to-day SRP variations (i.e., the range in concentrations between consecutive days), and marked diurnal variability occurred only during the early phase of this high-resolution monitoring period (August through early September 2016; Supplemental Figure S3). In early September, the amplitude of diurnal SRP variability was ~0.03 mg P L^{-1}, and, although the day-to-day increases in SRP release tracked day-to-day increases in water temperature, the diurnal SRP maxima corresponded with diurnal water temperature minima (Supplemental Figure S3). Diurnal SRP maxima occurred just as DO concentrations started to rise in the morning, with SRP minima occurring just after the peak in dissolved oxygen. Therefore, although temperature controls on microbial activity are the primary drivers of day-to-day variability in SRP release, at the subdaily scale, diurnal fluctuations in SRP concentrations appeared to be driven by daily patterns in water-body metabolism. This reflected the balance between P assimilation by photosynthesizing plants during daylight hours and P release linked to microbial respiration (Palmer-Felgate, Mortimer, et al., 2011).

3.7 | Ecological implications of wetland nutrient release

The results of this study show that, under low flows during summer and fall and with sufficient labile C availability, the wetland was capable of converting background organic matter inputs from a pristine woodland environment into highly bioavailable nutrient fractions at concentrations that can potentially cause ecological impairment. During the high-intensity nutrient release events, SRP and NH_4–N increased from baseline values, which were close to detection limits, to concentrations capable of causing nuisance excessive plant growth in downstream streams and rivers (>0.05 mg P L^{-1} and >0.4 mg N L^{-1}) (Jarvie, Smith, et al., 2018). During the

high-intensity nutrient release event of late-summer and fall 2016, SRP and TP concentrations reached 0.18 and 0.30 mg P L^{-1}, respectively, and NH$_4$–N and TDN concentrations reached 5.7 and 6.8 mg N L^{-1}, respectively. These N and P concentrations are characteristic of water bodies impaired by agricultural and/or wastewater sources (Jarvie, Neal, & Withers, 2006; Withers et al., 2009). Indeed, the magnitude and timing of nutrient release from this pristine wetland-pond system, which had no effluent or agricultural nutrient sources, mimic typical "point-source" signals: elevated concentrations under low flows due to low baseflow dilution (Jarvie et al., 2006). In this study, the release of N, P, and Si occurred during the fall diatom bloom period, which is a period of high ecological sensitivity. Headwater streams are aquatic ecosystems of particular vulnerability to eutrophication (Riley et al., 2018). Depending on the spatial extent of wetlands within the catchment and their hydrological connectivity with the stream network, the cumulative effects of wetland nutrient release have potential to impair downstream water quality under late summer/fall baseflow periods of eutrophication risk, exceeding criteria for good ecological status (Poikane et al., 2019).

3.8 | Wider land-use management implications: Climate change adaptation and nutrient legacies

Climate change predictions for the next century indicate that the United Kingdom will be subject to increasing air temperatures, particularly during summer; increases in winter rainfall amounts and intensity with decreases in summer rainfall; and increases in evapotranspiration and summer soil moisture deficits, resulting in hotter and drier summers and wetter winters (Watts et al., 2015). The 2017 U.K. Committee for Climate Change report specifically identified exposure to higher summer temperatures, heat waves, and droughts, along with increasing winter flood risk, as the greatest direct climate-related threats to the United Kingdom, with wetlands expected to be particularly vulnerable to reduced summer water availability (UKCCC, 2017). These scenarios align with the conditions we observed to be conducive for increases in biomass production, microbial respiration, and organic matter mineralization, potentially increasing the likelihood of high-intensity SRP, NH$_4$–N, and Si release events. Moreover, wetter winters and increased runoff may also increase delivery of terrestrial biomass, such as woodland leaf litter, into the wetland, potentially increasing the organic matter pool for microbial mineralization and further accumulating the stores of legacy organic matter and nutrients from previous years' biomass production.

There is increasing interest in the protection, re-establishment, and construction of wetlands, including on-farm ponds, to address flood risk and to assist in buffering against rainfall and flow extremes as part of "Natural Flood Management" initiatives. These aim to reduce flood risk by slowing the flow of water by increasing water storage (Dadson et al., 2017; Kay, Old, Bell, Davies, & Trill, 2019; Lane, 2017). They also offer potential ecosystem service co-benefits, such as augmenting baseflows during times of water scarcity, water purification (through denitrification and sedimentation of P-rich particulates), and improving biodiversity through increases in habitat complexity and C sequestration and storage (Dadson et al., 2017; Hansson et al., 2005; Lane, 2017). However, numerous existing studies demonstrate wider tradeoffs and conflicting effects between N retention, P retention, biodiversity, and water management in wetlands receiving agricultural runoff and wastewater (e.g., Colloff et al., 2016; Hansson et al., 2005). This study highlights potential trade-offs in water quality, through accelerated P and N release, even in relatively pristine wetland settings.

Wetlands receiving agricultural runoff and wastewater can accumulate large nutrient legacies (Jarvie et al., 2013; Sharpley et al., 2013). In this study, the accumulated nutrient legacy was derived from background organic matter and soil erosion inputs from a woodland headwater watershed as well as from potential longer-term legacies from more than 65 yr ago linked to woodland planting and earlier rough grazing activities. The importance of wetlands as sources of legacy nutrients is also governed by the interactions between nutrient processing rates, water residence times, and the hydrologic connectivity between the legacy P source and the stream network (Palmer-Felgate, Bowes, et al., 2011; Palmer-Felgate, Mortimer, et al., 2011; Reddy, Newman, Osborne, White, & Fitz, 2011; Sharpley et al., 2013). If wetlands discharge directly to headwater stream networks as in this study, or are hydrologically connected with the stream via shallow groundwater, riparian, or hyporheic water pathways, the legacy nutrient contributions can provide a source of highly bioavailable nutrients at baseflow and help maintain headwater streams in a sustained eutrophic state.

4 | CONCLUSIONS

By combining long-term water quality monitoring over more than two decades, with detailed event-based hydrochemical and high-resolution in situ sensor measurements, this study shows how the convergence of climate and biogeochemical drivers of nutrient release in wetlands can amplify background nutrient input signals and mobilize legacy nutrients, causing water quality impairment and accelerating eutrophication risk. There was clear synchrony between day-to-day variability in air and water temperature and nutrient release. However, the observed complexities in relationships between inter-annual nutrient release and climate variables also potentially reflect the "memory" effects of antecedent climate drivers

from previous years through the influence of accumulated legacy organic matter from previous years' biomass production.

Climate change scenarios predict hotter drier summers and wetter winters in the United Kingdom, which are likely to increase terrestrial biomass delivery into water bodies and accelerate aquatic biomass production and turnover, potentially increasing the magnitude and frequency of nutrient release events. Natural flood management initiatives are currently promoting the use of wetlands as "nature-based solutions" in climate change adaptation. Our study highlights the potential trade-offs in water quality, through accelerated release of highly bioavailable P and N fractions, even in relatively pristine wetland settings. Accordingly, careful consideration will be needed in balancing the benefits and potential wider trade-offs of wetlands as a beneficial management tool in climate change adaptation, flood management, and soil and water conservation.

CONFLICT OF INTEREST

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.