Received: 16 August 2021 | Accepted: 5 January 2023

DOI: 10.1111/1752-1688.13107

RESEARCH ARTICLE

AMERICAN WATER RESOURCES ASSOCIATION
JAWRA
JOURNAL OF THE AMERICAN WATER RESOURCES ASSOCIATION

Instream sensor results suggest soil–plant processes produce three distinct seasonal patterns of nitrate concentrations in the Ohio River Basin

Morgan Gerlitz[1] | Jimmy Fox[1] | William Ford[2] | Admin Husic[3] | Tyler Mahoney[4] | Mindy Armstead[5] | Susan Hendricks[6] | Angela Crain[7] | Jason Backus[8] | Erik Pollock[9] | Wei Ren[10] | Bo Tao[10] | Brenden Riddle[1] | David White[6]

[1]Department of Civil Engineering, University of Kentucky, Lexington, Kentucky, USA

[2]Department of Biosystems and Agricultural Engineering, University of Kentucky, Lexington, Kentucky, USA

[3]Civil, Environmental and Architectural Engineering, University of Kansas, Lawrence, Kansas, USA

[4]Civil and Environmental Engineering, University of Louisville, Louisville, Kentucky, USA

[5]Natural Resources Department, Marshall University, Huntington, West Virginia, USA

[6]Hancock Biological Station, Murray State University, Murray, Kentucky, USA

[7]Ohio-Kentucky-Indiana Water Science Center, United States Geological Survey, Louisville, Kentucky, USA

[8]Kentucky Geological Survey, University of Kentucky, Lexington, Kentucky, USA

[9]Stable Isotopes Laboratory, University of Arkansas, Fayetteville, Arkansas, USA

[10]Department of Natural Resources and the Environment, University of Connecticut, Storrs, Connecticut, USA

Correspondence
Jimmy Fox, Department of Civil Engineering, University of Kentucky, Lexington, KY, USA.
Email: james.fox@uky.edu

Funding information
Kentucky Senate Bill 271B Water Quality Program; National Science Foundation United States, Grant/Award Number: 1632888 and 1933779

Abstract

The Ohio River Basin (ORB) is responsible for 35% of total nitrate loading to the Gulf of Mexico yet controls on nitrate timing require investigation. We used a set of submersible ultraviolet nitrate analyzers located at 13 stations across the ORB to examine nitrate loading and seasonality. Observed nitrate concentrations ranged from 0.3 to 2.8 mg L^{-1} N in the Ohio River's mainstem. The Ohio River experiences a greater than fivefold increase in annual nitrate load from the upper basin to the river's junction with the Mississippi River (74–415 Gg $year^{-1}$). The nitrate load increase corresponds with the greater drainage area, a 50% increase in average annual nitrate concentration, and a shift in land cover across the drainage area from 5% cropland in the upper basin to 19% cropland at the Ohio River's junction with the Mississippi River. Time-series decomposition of nitrate concentration and nitrate load showed peaks centered in January and June for 85% of subbasin-year combinations and nitrate lows in summer and fall. Seasonal patterns of the terrestrial system, including winter dormancy, spring planting, and summer and fall growing-harvest seasons, are suggested to control nitrate timing in the Ohio River as opposed to controls by river discharge and internal cycling. The dormant season from December to March carries 51% of the ORB's nitrate load, and nitrate delivery is high across all subbasins analyzed, regardless of land cover. This season is characterized by soil nitrate leaching likely from mineralization of soil organic matter and release of legacy nitrogen. Nitrate experiences fast transit to the river owing to the ORB's mature karst geology in the south and tile drainage in the northwest. The planting season from April to June carries 26% of the ORB's nitrate and is a period of fertilizer delivery from upland corn and soybean agriculture to streams. The harvest season from July to November carries 22% of the ORB's nitrate and is a time of nitrate retention on the landscape. We discuss nutrient management in the ORB including fertilizer efficiency, cover crops, and nitrate retention using constructed measures.

KEYWORDS
nitrate, sensor, Ohio River, karst, tile drainage

Paper No. JAWR-21-0131-P of the *Journal of the American Water Resources Association* (JAWR).

Discussions are open until six months from publication.

Research Impact Statement

Time-series analyses of a nitrate sensor network show that the majority of nitrate leaving the Ohio River Basin occurs during a winter dormant period when nitrate delivery is high across all subbasins analyzed, regardless of land cover.

1 | INTRODUCTION

The Mississippi River in the central United States is one example of a major world river where nitrate reductions are needed, in this case to reduce the area of a hypoxic zone in the Gulf of Mexico. However, like many world rivers, nitrate (measured as NO_3-N + NO_2-N) concentration remains high in the Mississippi River. Since 1980, flow-normalized nitrate concentrations and loads have either increased or remain unchanged for many of the water quality data stations on the Mississippi River and its tributaries (Murphy & Hirsch, 2013; Sprague et al., 2011). Agricultural management, such as enrollment of vulnerable lands in the Conservation Reserve Program, has been credited as reducing sediment and phosphorus loads to the Gulf of Mexico (Kreiling & Houser, 2016); however, nitrate concentration and load have not decreased during the past four decades. A 45% nitrogen load reduction in the Gulf of Mexico calls for aggressive nitrogen-removal practices, including wetland and stream channel restorations, drainage-ditch enhancements, and flood-plain reconnection (McLellan et al., 2015). However, implementing nitrogen-removal strategies is expensive. Current knowledge gaps exist in how hydrologic and biogeochemical processes control nitrate export in the Mississippi River vary seasonally throughout the year and may be mitigated through restoration activities.

The ambiguity of nitrate patterns in the Mississippi River requires investigation of major tributaries that generate disproportionate discharge or nitrate loads to the mainstem (Zimmer et al., 2019). In this paper, we focus on temporal nitrate patterns in the Ohio River Basin (ORB). The ORB and the Upper Mississippi River Basin are the two major contributors of water, phosphorus, sediment, and nitrate to the Mississippi River; by itself, the ORB contributes 40% of the water and 35% of the nitrate load to the Mississippi River (White et al., 2005; White & Hendricks, 2022). The ORB's 35% nitrate load contribution to the Mississippi River is higher than might be expected given that the ORB is just 15% of the Mississippi River's drainage area and the ORB's land use is only 19% corn and soybean cropland. Like the Mississippi River, nitrate concentrations in the ORB exhibit chemostatic behavior (i.e., lack of dependence on river water discharge) in all seasons of the year despite the contention that extreme discharges may control nitrogen loading (Royer et al., 2006; Zimmer et al., 2019). Nitrate concentrations at the ORB's confluence with the Mississippi have been shown to have near-constant levels for most of the year casting questions on controls, albeit some data show slightly increased levels in the winter and again in late spring (Duan et al., 2014). Some authors have suggested that nitrate peaks in large rivers in January and June reflect the seasonal application of ammonium nitrate fertilizers (e.g., Duan et al., 2014; Sprague et al., 2011). Few, if any, studies have examined the seasonal relationships of nitrate loads with terrestrial or aquatic processes in the ORB.

Observations with submersible ultraviolet nitrate analyzer (SUNA) networks allow investigations and hypothesis testing for terrestrial and aquatic controls on nitrate delivery in large basins such as the ORB. SUNA nitrate sensors enable near-continuous (i.e., 15 min) readings for multi-year periods to examine nitrate loading and seasonality (Pellerin et al., 2013). The nesting of the sensors throughout a basin and across scales enables inference of nitrate source and delivery mechanisms, as well as linkages to processes. Time-series decomposition including seasonal trend analyses and empirical mode decomposition (EMD) methods allow quantitative statistical evaluation of the timing and seasonality of nitrate measurements in a basin (Ford et al., 2015, 2018, 2019). Terrestrial controls on nitrate reflect soil–plant processes that are distributed across the landscape, such as the seasonality of crops and other plants including fertilization, growth, harvest, and senescence or dormancy. Soil–plant processes associated with a terrestrial control also reflect soil nitrate leaching during wet periods of the year and during periods when plant demands are low. Aquatic controls on nitrate reflect assimilatory demand by autotrophs and cyanobacteria during spring green algae blooms and late summer blue-green algae (cyanobacteria) blooms.

Our objective was to investigate terrestrial and aquatic controls on potential seasonality of nitrate concentration and loads in the ORB and specifically to (1) investigate nitrate concentration and nitrate load from an ORB network of SUNA nitrate sensors managed by the United States Geological Survey (USGS) and university researchers; (2) perform time-series decomposition including seasonal trend analyses and EMD of nitrate measurements to quantify the timing and seasonality of nitrate measurements; (3) use ancillary biogeochemical and physical data and interviews with land owners to infer terrestrial and aquatic controls on nitrate timing in the ORB; and (4) discuss potentially managing Ohio River nitrate timing and loading in the Mississippi River.

2 | METHODS

2.1 | Study site

The ORB has a continental temperate climate. Mean annual precipitation is 104 cm, mean annual temperature is 12°C, and mean annual water temperature is 14°C. The Ohio River accounts for 40% of the water entering the Mississippi River with a mean discharge of 8733 $m^3 s^{-1}$ (White et al., 2005; White & Hendricks, 2022). The Ohio River (Figure 1) is a ninth-order river that drains 529,000 km^2 of the east-central US. It is the only major river with river kilometers measured from its origin to its mouth. The Ohio River proper (river km 0) begins at the confluence of the Allegheny and Monongahela rivers at Pittsburgh, Pennsylvania, and then flows in a westerly direction to its mouth at the Mississippi River

FIGURE 1 Nitrate sensing stations and land cover for the Ohio River Basin (ORB). The Ohio River flows from east to west. The ORB increases in cropland cover (corn and soybean) from east to west. Ironton, OH is the upper nitrate sensor site on the main stem, Cannelton, IN is a mid-river site, and Olmsted, IL is the station just upstream of the junction with the Mississippi River. Nitrate sensors used in this study and their sub-basins are indicated throughout.

(river km 1575). The basin lies in the Eastern Temperate Forests and Northern Forests Level I ecoregions. The Ohio River headwater tributaries originate in the Appalachian and Allegheny mountains. Tributaries entering from the north lie primarily in the Central Lowland physiographic province while most entering from the south lie in the nutrient-poor Appalachian and Interior Low Plateaus physiographic provinces (White et al., 2005; White & Hendricks, 2022).

Alfisols dominate soil order across most of the basin due to the humid temperate climate and predominance of deciduous forests during the Holocene (Huang et al., 2021). The northern half of the basin is near the glacial margin during the Late Pleistocene. The eastern region is dominated by deciduous forest, the northern and western regions have a high concentration of cropland, and the central and southern region have a high concentration of pasture. Overall land use in the basin is 53% forest, 19% cropland, 15% pasture, 9% urban, and 4% other. Corn and soybeans dominate and account for 98% of croplands (Huang et al., 2021). Corn and soybeans are used in rotation and show approximately equal coverage for the entire basin at Olmsted, Illinois and across individual watersheds (Table 1). There are also small amounts of other crops, such as fruits and vegetables that comprise 1% or 2% of the basin's land area (Table 1). The cropland density (i.e., corn and soybean) increases as you move east to west across the basin to the Mississippi River (Figure 1). Northern croplands are characterized by poorly drained soil conditions with slopes often <5%, and tile drainage is used throughout the northern croplands (Huang et al., 2021). Cropland soils are well-drained in the south across various slope conditions (~57% well-drained, Schilling et al., 2015), and topography in the south is underlain with high concentrations of karst bedrock. Cattle production dominates land used for pasture in the ORB, and cattle inventory is greatest in the central and southern ORB. Kentucky and Tennessee have the greatest inventory of cattle totaling 2 million head and 1.8 million head, respectively, in 2021 (NASS, 2021). A common practice is to assign 0.8 ha for each grazing animal.

2.2 | Nitrate sensor network and ORB subbasins

This study used data from 13 nitrate sensor sites distributed throughout the lower ORB (Table 1; Figure 1). The USGS collects and maintains water discharge estimates at all sites. Three sites were on the Ohio River main stem including Ironton, Ohio (Ohio River km 528) at the most upstream site (157,513 km^2, USGS03216070); Cannelton, Indiana (Ohio River km 1160) at approximately the middle of the basin (251,229 km^2, USGS03303280); and Olmsted, Illinois (Ohio River km 1552) at the most downstream site (525,869 km^2, USGS03612600) located just upstream of the confluence with the Mississippi River. The other 10 sites were divided into "large" and "small" watersheds. The large watersheds range in drainage areas from 75,716 to 9306 km^2 (Table 1) and include the Wabash River (USGS03378500), White River (USGS03374100), Green River (USGS03321500), Kentucky River (USGS03290500), and Licking River (USGS03254520). The small watersheds range in drainage areas from 275 to 12 km^2 and include Eagle Creek (USGS03353200), Cane Run at Royal Spring (USGS03288110), School Branch (USGS03353420), Sugar Creek (USGS03361650), and South Elkhorn Creek (USGS03289000). Nitrate sensor data were collected by the University of Kentucky at the Cane Run and South Elkhorn Creek sites, and nitrate sensor data were collected by the USGS at the other sites. The USGS monitors discharge

TABLE 1 Land area and land use percentages for all nitrate concentration sites in the ORB via the cropland data layer 2018.

Location	Area (km^2)	Forest	Urban	Pasture	Corn	Soybeans	Misc crops	Total crop	Misc land	Water
Ohio River										
Olmsted, Illinois	525,869	53	9	15	8	10	1	19	2	2
Cannelton, Indiana	251,229	61	10	15	5	6	1	12	1	1
Ironton, Ohio	157,513	70	9	12	2	2	1	5	2	1
Large Watersheds										
Wabash River, Indiana	75,716	22	10	8	26	30	2	58	1	1
White River, Indiana	29,280	33	12	10	19	24	2	44	0	0
Green River, Kentucky	23,779	49	6	25	7	10	2	20	0	1
Kentucky River, Kentucky	16,006	63	9	25	1	1	1	2	0	1
Licking River, Kentucky	9,306	53	6	35	1	2	1	4	1	1
Small Watersheds										
Eagle Creek, Indiana	275	8	14	17	20	37	1	59	1	0
Sugar Creek Indiana	240	7	8	10	31	41	1	74	0	0
Cane Run, Kentucky	118	2	34	57	3	3	1	6	1	0
South Elkhorn, Kentucky	62	14	48	34	2	2	0	4	0	0
School Branch, Indiana	12	3	9	20	20	41	6	67	0	0

at all sites. Sensor datasets were supplemented with National Water-Quality Assessment nitrate grab samples at Cannelton, Wabash River, and Sugar Creek. Additional information for the tributary sites is included in Table S1.

Subbasins were delineated in ESRI ArcGIS 10.4.1 using the sampling site locations with a 1.5 m digital elevation model and stream network map. The land use map was built from the USDA Cropland Data Layer (CDL). The CDL provides multi-year land use and land cover maps across the conterminous U.S. at a spatial resolution of 30 m, with an emphasis on the crop-specific distribution (Boryan et al., 2011; Johnson & Mueller, 2010). The map is based on a range of satellite imageries including Advanced Wide Field Sensor (AWiFS), Landsat TM/ETM, the Indian Remote Sensing RESOURCESAT-1 (IRS-P6), MODIS, etc. (Reitsma et al., 2015). The earliest available CDL data for our study area was 2008. We compared the land use percentage for each subbasin for 2008, 2013, and 2018 and determined there were no large changes in land use over that time period except for some year-to-year changes in the ratio of corn to soybeans spatially across the basin, which was indicative of crop rotation (Table 1; Figure 1, data from 2018 CDL).

2.3 | Nitrate sensor measurements

Continuous nitrate data were collected using Satlantic SUNA sensors with a 5-mm optical path length by researchers at the USGS and the University of Kentucky (UK). The nitrate data were collected at the sampling locations in Figure 1 from 2011 to 2020. Data were not available at all sites for all years as the sensor program was developed and expanded over the past decade. Measurement intervals were set to every 15 min. USGS data were transmitted hourly by the Geostationary Operational Environmental Satellite for archival in the publicly available USGS National Water Information System (U.S. Geological Survey, 2016). UK data were monitored by UK personnel using an SDI-12 connection to a Campbell Scientific CR-1000 Datalogger powered by a 12-volt rechargeable battery that was changed out bi-weekly when data were downloaded. Intermittent gaps in nitrate reflected periods when the sensors underwent calibration.

To ensure the sensor data quality, USGS field crews routinely conducted site inspections at intervals ranging between 2 and 6 weeks depending on field conditions, and UK crews inspected stations every 2 weeks. Field sensor checks during site inspections ensured sensor integrity by quantifying sensor drift due to biofouling and verifying the accuracy of the sensor using deionized water and known nitrate standard concentrations (Pellerin et al., 2013). Site inspections of the nitrate sensors and data processing followed methods described in Pellerin et al. (2013). Discrete water samples were collected at the sensor location and served as systematic bias checks on the sensors and documented any changes in the environmental conditions between site inspections. Cross-sectional discrete water samples were also collected and served to determine the degree of mixing of the river and to verify that the data measured at the sensor location represented the hydrographic flow conditions across the entire site. All USGS discrete water samples were collected following USGS sampling protocols (USGS, 2020) and analyzed for concentrations of NO_3-N + NO_2-N as nitrogen by the USGS National Water Quality Laboratory (Patton & Kryskalla, 2011). All UK discrete water samples followed established protocols (EPA-240-B-01-003 2001; EPA-240-B-06-001 2006; KDOW 2005) and were analyzed at the Kentucky Geological Survey laboratory at the University of Kentucky.

2.4 | Time-series decomposition

Time-series decomposition was carried out using seasonal trend analysis and EMD. The seasonal trend was decomposed from each nitrate concentration dataset and nitrate load continuous estimate using centered moving averaging. Seasonal analyses of peaks were carried out for each nitrate concentration dataset and nitrate load time series using all available subbasin-year combinations. Seasonal peaks were quantified in the detrended results as the occurrence of a nitrate concentration data peak (±30 day) analyzed for each subbasin-year combination when data were available; and the process was repeated for detrended nitrate load results. The mean values for periods quantified as nitrate lows were analyzed against the mean of the seasonal periods falling immediately before and after to quantify the result as a nitrate low.

Empirical mode decomposition was used to quantify the statistical significance of nitrate concentration and loading peaks given recent successes of the methodology for hydrologic and water quality time series throughout the ORB (Ford et al., 2015, 2018, 2019; Nazari et al., 2020). EMD is an adaptive time-series analysis method that decomposes data into a set of Intrinsic Mode Functions (IMFs), which are a finite series of amplitude and frequency modulated, oscillatory functions. The lowest frequency IMF is identified as the base (residual) trend and the highest frequency trend is considered noise for well-sampled datasets (Wu et al., 2007). EMD was performed using MATLAB version R2019b. A statistical significance test was performed on EMD results based on the method explained in Wu et al. (2007) to determine whether IMFs were significantly different from white noise IMFs. Statistically significant frequencies between 2 and 18 months were included in our analysis since we were interested in intra-seasonal and seasonal timing of peaks, effectively removing event-based and longer-term (e.g., crop rotation) trends. EMD was applied to two of the tributary sites including Eagle Creek (a small tributary watershed) and Green River (a large tributary watershed).

2.5 | Supplemental data and interviews

Additional water quality and soil data and information from interviews were assimilated to assist with the interpretation of nitrate temporal patterns in the Ohio River and its subbasins. A number of these datasets were already published, partially published, or part of ongoing water quality efforts throughout the basin made by the co-authors herein. This information is described in the Supplemental Online Information file.

3 | RESULTS

3.1 | Nitrate concentration and load in the Ohio River

Nitrate concentration and load increased longitudinally in the Ohio River from Ironton, Ohio (Ohio River km 528), in the upper portion of the basin to Cannelton (Ohio River km 1160) and to Olmsted, Illinois (Ohio River km 1552), near the Ohio River mouth (Figure 2). Sensor data showed that nitrate concentration increased by 50% across the 1024 km study length of the Ohio River from an annual average of 0.80–1.44 mg L^{-1} NO_3-N + NO_2-N at Ironton and Olmsted, respectively. The increase in nitrate concentration corresponded with a land use shift from forest cover to crop cover (corn and soybean) (Table 1). The upper basin at Ironton is 70% forest and 5% cropland while the entire ORB at

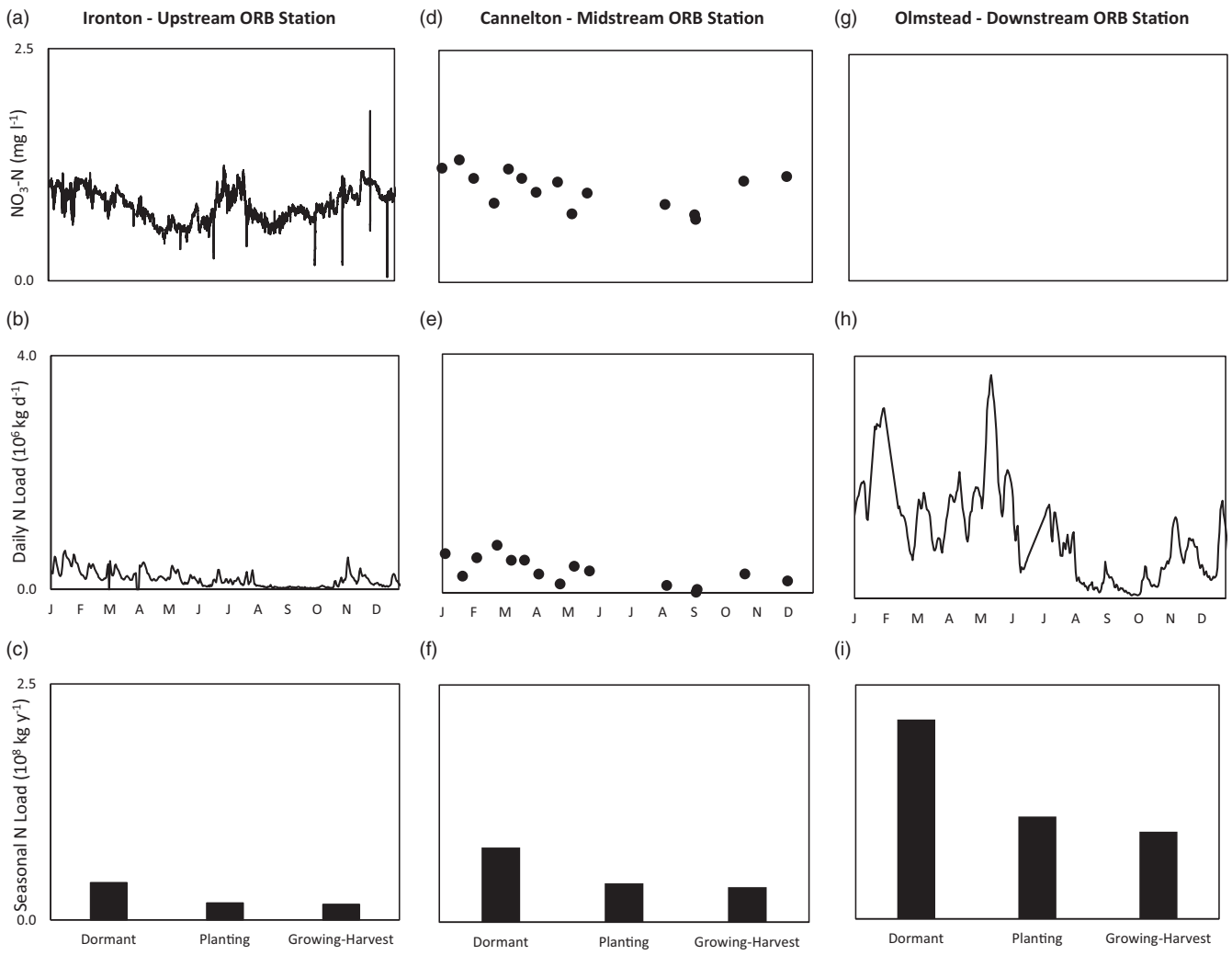

FIGURE 2 The increase in nitrate concentration and nitrate load per year from the Upper ORB to the junction with the Mississippi River, and the three seasons of nitrate for the mainstem of the Ohio River. Plots show nitrate concentration, nitrate load per day, and net seasonal nitrate load at Ironton, Ohio (a–c), Cannelton, Indiana (d–f), and Olmsted, Illinois (g–i). A twofold increase in nitrate concentration and a fivefold increase in N load are observed across the mainstem of the Ohio. This information has been added to the paper. NO_3-N and daily N load plots are presented for 1 year to illustrate the time variability. The seasonal N load plots were calculated using all years for which data were available.

Olmsted is 53% forest and 19% cropland. Longitudinally, annual water load increased by 340% between Ironton and Olmsted, coinciding with the percent increase in drainage area. The Ohio River experiences a greater than fivefold increase in annual nitrate load from the upper basin to the river's junction with the Mississippi River (74–415 Gg year^{-1}).

The influence of cropland on the annual nitrate load can also observed in the second half of the basin's drainage area, as the annual nitrate load increases by 270% from the Ohio River site at Cannelton to the Ohio River site at Olmsted (156–415 Gg year^{-1}). Drainage area increases by 210% and so the water load more than doubles and accounts for much of the increase. In addition, the increase in cropland likely contributes. The land area drained between the Cannelton and Olmsted Ohio River sites is 25% cropland as compared to 12% cropland for the drainage area upstream of Cannelton. Much of the cropland is concentrated in the northwestern portion of the ORB, for example, see the Wabash subbasin in Figure 1, and it is likely that the increased load along this stretch of river is attributed to cropland influence. This is further evidenced in this stretch of the Ohio River by the higher annual nitrate load entering the river via the Wabash River subbasin to the north (1213 kg km^{-2} year^{-1} and 58% cropland) relative to the Green River subbasin to the south (761 kg km^{-2} year^{-1} and 58% cropland).

3.2 | Seasonal patterns of nitrate for the ORB

Nitrate load rates at Olmsted showed observable peaks in winter (January and February) and again in late spring/early summer (May and June) (Figure 2h). Nitrate concentrations at Olmsted remained consistently high from winter through spring (Figure 2g). Late summer and fall months showed reduced nitrate concentrations and load. Nitrate concentrations at Ironton (Figure 2b) showed winter and late spring/early summer highs, and nitrate load at Ironton showed an average decline from winter to the late summer/fall. Nitrate point measurements at Cannelton (Figure 2d) tended to fall between Ironton and Olmsted. The winter nitrate peaks, late spring nitrate peaks, and fall nitrate lows along the mainstem of the Ohio River prompted additional analysis of nitrate seasonal patterns at the tributaries across the ORB.

Three distinct seasonal nitrate concentration and load patterns were identifiable from the nitrate sensor observations located across the river network of the ORB. The seasonal patterns included nitrate concentration and load exhibiting broad winter highs with peaks centered in January; a well-defined nitrate peak centered in June; and then nitrate lows through summer and the fall months. The seasonal patterns were shown for most subbasins, albeit subbasins without extensive corn and soybean cropland cover did not show as pronounced spring/early summer nitrate highs. We show nitrate concentration results for 10 subbasins in Figure 3 and divided the sites into small watersheds (10–300 km^2 drainage area) and large watersheds (9000–80,000 km^2 drainage area). Similar trends were observed in both small and large subbasins where basins with the highest percentage of cropland (over 20%) had both a pronounced winter and spring peak, while the basins with less than 10% cropland not showing as pronounced spring peaks. The spring peak was strongest in the two smaller watersheds, Sugar Creek (240 km^2) and School Branch (12 km^2), with the highest percentage of crops (>60%). The June seasonal peak nitrate concentration became less distinct or disappeared as the percent of cropland decreased (Figure 3). A considerable decrease in nitrate concentration was observed comparing small with large watersheds. For example, South Elkhorn Creek (62 km^2) and the Licking River (9306 km^2) had identical cropland cover, but the South Elkhorn had three to five times the nitrate concentration, depending on the month.

Time-series decomposition was used to quantify nitrate concentration and load peaks in January and June, and lows in the summer/fall. The regularity of the seasonal patterns was evident in the decomposition results for nitrate concentration (Figure 4 left pane, Table 2) as well as for nitrate load (Figure 4 right pane, Table 3). For nitrate concentration analyses, 36 out of 42 subbasin-year combinations (86%) showed the occurrence of January peaks, and 36 out of 38 (95%) showed June peaks. All sites with available data showed a consistent late summer/early fall low period, with the exception of the Ironton, Ohio site. Nitrate concentration measurements at the Ironton site showed less temporal variability overall (Figure 4h) and potentially reflect the forest land cover dominance of the Ironton drainage, relative to the other stations (Table 1). The percentage of cropland within a subbasin did not dictate the presence of nitrate concentration peaks in January and June (Figure 3). For nitrate load results, 98% of subbasin-year combinations showed January peaks while just 60% of subbasin-year combinations showed peaks in June. These results were divided across subbasins with higher versus lower percentage of cropland. In all, 20 out of 25 subbasin-year combinations showed June peaks for nitrate load for subbasins with greater than or equal to 20% cropland while just 1 out of 10 subbasin-year combinations showed June peaks for nitrate load with less than 10% cropland. All subbasin-year combinations showed a nitrate load low period from June to January.

EMD results highlighted that seasonal peaks and low periods observed in the aforementioned time-series decomposition were statistically significant (Figure S1). For both the Green River and Eagle Creek sites, statistically significant IMFs were observed at time scales ranging from less than 1 month to greater than 2 years for both nitrate loading and concentration (Figure S1; right panel). Significant IMFs ranging in frequency from 2 to 18 months were summed and plotted to highlight seasonal and within season processes (Figure S1; left panel). Peaks for the statistically significant IMFs consistently occurred in winter and late-spring, with low periods in late summer–fall. Loadings also showed the pronounced winter peak and June to January minima, with periodic secondary peaks in June (e.g., 2015 and 2017 for Eagle Creek).

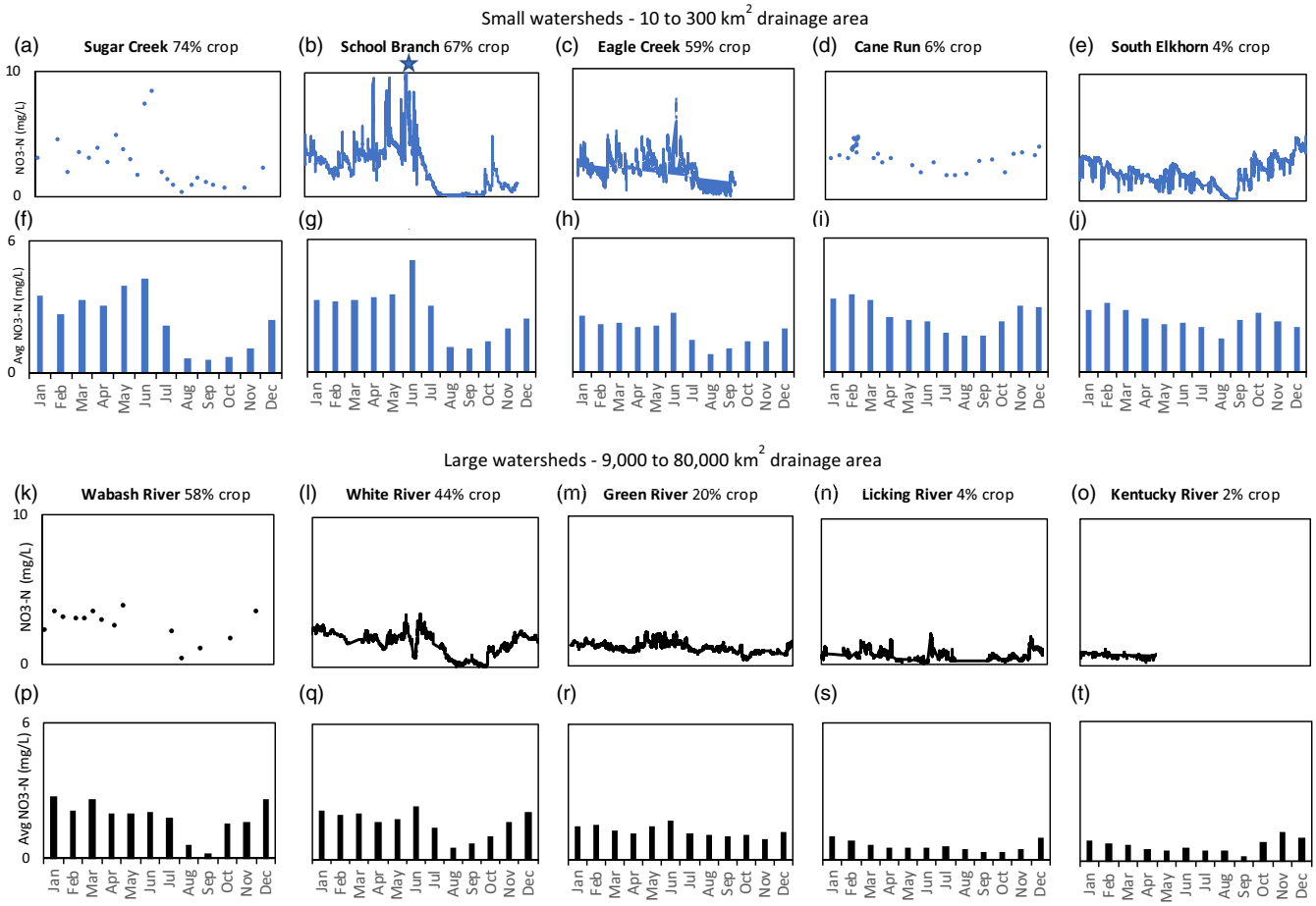

FIGURE 3 Nitrate sensor measurements including instantaneous data and monthly averages for the small (a–j) and large (k–t) subbasins in this ORB study. The planting season peak nitrate concentration becomes less observed or disappears as percent of cropland decreases. A considerable decrease in nitrate concentration is observed comparing small to large subbasins, attributed to internal cycling. Note the star in plot B reflects a peak nitrate concentration in water of 17.2 mg/L NO_3-N measured on June 23, 2017.

4 | DISCUSSION

4.1 | Seasonal nitrate patterns are controlled by soil–plant processes

The results indicate seasonal patterns of nitrate concentration and load across the ORB are controlled by soil–plant processes across the landscape, as opposed to river discharge and/or internal cycling. The timing of the results supports nitrate seasonal variation that reflects soil–plant processes across a dormant winter season when corn and soybeans are not planted and other plants are fairly inactive in terms of nitrogen uptake, and therefore the nitrate leaches through soils resulting in winter nitrate highs in the river. A spring planting season when crops are fertilized with N fertilizers that can runoff or follow quickflow groundwater pathways producing the June nitrate highs. A growing-harvest season when the soil–plant system retains water and nitrate result in a lower nitrate period in the ORB's main stem and tributaries. As one example, the Green River had especially observable January and June peaks for nitrate concentration and nitrate loads as well as the summer/fall seasonal lows (Figure 5). In Figure 5, vertical lines separating dormant, planting and growing-harvest seasons allow clear observation of nitrate highs for both nitrate concentration and nitrate load during the dormant season, peaks again in the spring, and nitrate lows through the growing-harvest season. The dates of these seasons and the nitrate seasonal patterns coincide, and are attributed to the cycle of trees, grasses and shrubs (non-crops) across the landscape, the cycle of corn and soybean (crops), and soil water levels throughout the year, as are further evidenced below using independent datasets.

The dormant season occurred from approximately December 1 to April 1 in the ORB and showed the highest nitrate concentrations and loads across the ORB river network. The season corresponds with dormant plants in this temperate region that has four distinguishable seasons, including this winter period when deciduous plants lose their leaves and herbaceous plants undergo senescence. By winter, corn

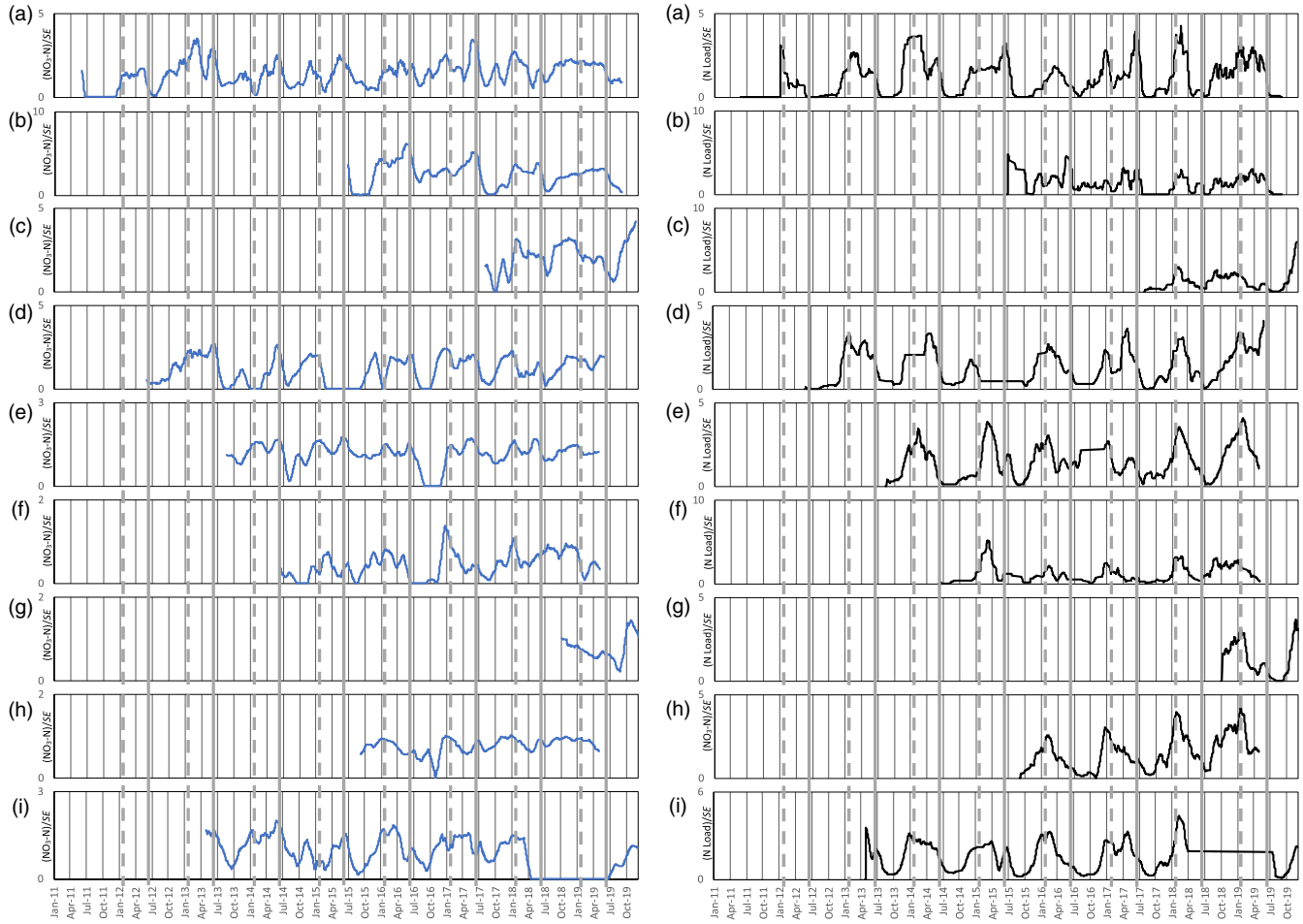

FIGURE 4 Time-series decomposition of nitrate concentration in the left pane (blue lines) and nitrate load in the right pane (black lines) to analyze seasonal patterns for 2011–2019 for (a) Eagle Creek, (b) School Branch, (c) South Elkhorn Creek, (d) White River, (e) Green River, (f) Licking River, (g) Kentucky River, (h) Ohio River at Ironton, Ohio, and (i) Ohio River at Olmsted, Illinois. Vertical axes are normalized nitrate concentration (left pane) and normalized nitrate load (right pane) calculated as the nitrate concentration measurement or calculated nitrate load divided by the standard error for each individual dataset. Vertical dashed gray and solid gray lines indicate January-centered and June-centered timestamps, respectively.

TABLE 2 Seasonal results from the decomposition of ORB nitrate concentration measurements. N/A reflects that a low period was not highly evident, so neither yes nor no was selected for the result.

Nitrate station and subbasin	Percent of years with peaks in January	Percent of years with peaks in June	Results show late summer/ fall low period
Eagle Creek	75	100	Yes
School Branch	100	100	Yes
South Elkhorn	100	100	N/A
White River	71	100	Yes
Green River	100	100	Yes
Licking River	100	100	Yes
Kentucky	0	100	N/A
Ironton, O. R.	100	100	No
Olmsted, O. R.	80	60	Yes

and soybeans in the ORB have been harvested and are no longer growing, and adoption of cover crops is low for this region (see figure 2 in Wallander et al., 2021). Therefore, plant demand for water and nitrate is low during this period (Ueda et al., 2010). The lack of plant growth and cooler temperatures with lower evapotranspiration leads to N buildup in soils and subsequent leaching.

TABLE 3 Seasonal results from the decomposition of ORB nitrate load.

Nitrate station and subbasin	Percent of years with peaks in January	Percent of years with peaks in June	Results show late summer/ fall low period
Eagle Creek	88	63	Yes
School Branch	100	100	Yes
South Elkhorn	100	0	Yes
White River	100	100	Yes
Green River	100	60	Yes
Licking River	100	0	Yes
Kentucky	100	100	Yes
Ironton, O. R.	100	0	Yes
Olmsted, O. R.	100	60	Yes

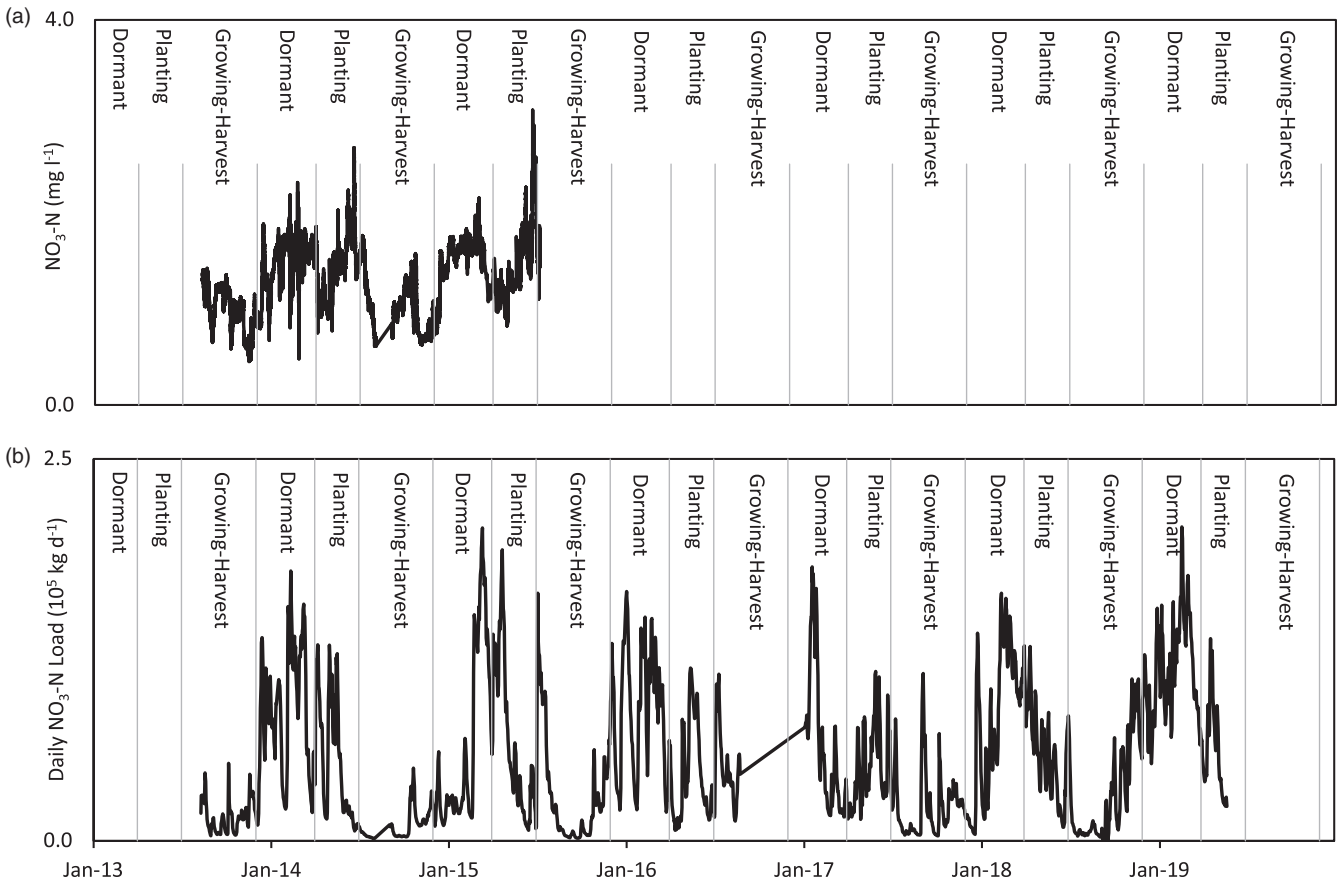

FIGURE 5 The three seasons of nitrate identified with sensor data for the Green River sub-basin of the ORB using (a) nitrate concentration measurements and (b) nitrate load estimates. The Green River has an order of magnitude smaller drainage area than the ORB at Olmsted but nearly identical land use/cover distribution.

This nitrogen assimilated and released from soils is suggested to exhibit control on the winter seasonal peaks, as opposed to transport of N fertilizers. Winter fertilizer applications by farmers are very uncommon in the ORB. Recommendations support fall and spring applications with side-dressing in late spring and early summer for row crops (e.g., Williams et al., 2016). Based on our team's work with Ohio, Indiana and Kentucky farmers, we have not seen producers applying N fertilizers in winter. N release and transport of assimilated N from buildup in soils is rather the likely source of nitrate in winter periods. N release in the winter is likely the result of assimilation, mineralization, and then leaching during saturated conditions (Di & Cameron, 2002). Crop residue, soil organic matter, and livestock waste are mineralized continuously, likely fairly evenly in deeper soils where temperature is buffered. Crop residue left on the fields after harvest or leaf litter from abscission in forests provides organic matter available for oxidation, N mineralization, and buildup (Cameron, 2012; Savard et al., 2010). On pasturelands, urea from livestock can add to the N soil buildup because urea is hydrolyzed by the urease enzyme to ammonia and then reacts with water on wet

soils to produce ammonium. Grazed pasture will have higher levels of nitrate leaching because while grasses are efficient at utilizing N during growth, 60%–90% of the nitrogen ingested is then excreted as manure and urine; with urine-N loading usually exceeding the needs of the pasture grasses for cattle. As with urea, manure contributes much more nitrate in wet and freely draining soils (Cameron, 2012), which is more typical in winter periods, particularly in basins such as the Kentucky and Licking rivers. Cattle production is common in the ORB, especially in the southwestern portion of the basin (e.g., Kentucky and Tennessee). In-depth analysis of winter N derived from livestock was not carried out in this study; however, livestock sourced N that was assimilated to soil and then released in the winter is likely.

During winter in the ORB, results are attributed to saturated conditions that allow release of legacy soil nitrogen. Deeper soils are saturated and perched water tables are prominent such that surface waters may become more connected to these deeper profiles due to matrix–macropore interaction during saturation excess conditions. We suggest these processes as occurring in both tile-drained systems of the northern ORB and karst regions in the south. This accumulated legacy store of mineralized N is then released during high connectivity. This is supported by the work of Woo and Kumar (2019), who show that the age of soil water below tile lines increases after drainage is implemented because there is less mixing of newer inorganic nitrogen at depth.

The winter leaching and transport of the soil nitrogen to the river network is relatively fast in the tile drainage and karst bedrocks systems of the ORB. Soil nitrate leaching is the fluid transport of nitrate from the soil column to groundwater or surface water stores that occurs when there is high amount of nitrate available in the soil profile followed by high drainage volume of water through to soil system (e.g., Di & Cameron, 2002). In the ORB, precipitation rates are relatively constant throughout the year, on average, but soil moisture is highest in the dormant season due to lack of plant uptake and low evapotranspiration (Figure S2). These high moisture levels lead to exceedance of field capacity and leaching of water and accumulated nitrate through soils. Based on published studies, leached nitrate in the ORB is quickly transported to the stream network on the order of days to weeks (Ford et al., 2018; Husic et al., 2019). This short residence time of leached nitrate in the ORB has been reported in Ford et al. (2018) and Husic et al. (2019) and is due to the widespread use of tile drainage in the northern basin and extensive karstic bedrock systems in the central and southern basin. The northern ORB drains central Ohio, central Indiana and western Illinois, and these regions contain some of the highest density of tile drainage usage in the United States (figure 3 in Valayamkunnath et al., 2020). The central and southern ORB drains southern Indiana, Kentucky, Tennessee, western Virginia, and southern West Virginia, and these regions contain one of the most highly developed, mature karst regions in the United States (USGS, 2020). These tile drainage and karst systems likely lead to low residence times and quick delivery of leached nitrate to the Ohio River.

Prior studies support high soil nitrate loading from watersheds in the ORB in the winter regardless of land cover. For example, nitrate data collected from our animal research farm in central Kentucky showed high connectivity to deeper portions of the soil profile that results in peak nitrate concentrations during the winter (Ford et al., 2019). Similarly, our watershed research sites with corn and soybean dominance showed peak nitrogen loading in late winter and early spring with upland soil controlling baseflow and stormflow nitrate levels (Ford et al., 2018).

The importance of nitrate leaching for soils in the ORB is further corroborated by stable isotope results from two of our small subbasins that suggests the source of nitrate in the dormant season is from soils (Figure S3). The stable oxygen and nitrogen isotope values of nitrate in water leaving South Elkhorn Creek subbasin and Cane Run subbasin collected from December to March suggest soil leaching origin based on the isotope source differentiation method of Kendall (1998). In all, 52 out of 54 (96%) nitrate stable isotope values suggest nitrate originates in the soil and undergoes denitrification. The isotope datasets were limited to the South Elkhorn and Cane Run subbasins, because this was the extent of our data availability. However, monthly mean nitrate concentrations for all of the small subbasins and the large subbasins show nearly identical distributions during the winter months (Figure 3, plots F through J and P through T). Nitrate isotope results in other seasons may be potentially impacted by fertilizer inputs and instream processes, which will cause deviation from the results here. While we do not have results for these conditions, some discussion is possible. For example, δ^{18}O from fertilizers with nitrate are ^{15}N enriched (Figure S3; Halder et al., 2022) and would be reflected in nitrate isotope results from tributaries. In summer months, the likelihood of sensitivity to instream processes is also higher, and for example low flows promoting turnover of benthic algae and dentification will be expected to increase δ^{15}N values during summer and early fall months (Ford et al., 2015). Future research is suggested to carry out sampling and analyses of the nitrate isotope distributions for streams with varying conditions in the ORB, such as those in this study.

Taken together, these results further support the plausibility of soil N leaching importance in the dormant season. The region receives sufficient rainfall in the winter to promote soil leaching, and the region is dominated by the tile drainage and karst subsurface networks that can quickly transport nitrate leached from soils to the river network. In this manner, the soil N leaching is responsible for causing the January peaks in nitrate concentration and nitrate load observed in results at the river and subbasin scales (Figures 2–4).

The nitrate concentration and load peaks in the late spring and early summer (Figure 5) are attributed to origin from N fertilization during the planting season. The planting season is suggested to impact nitrate peaks from April 1 to June 30, as this time period coincides with seasonal peaks in Figures 4 and 5. This time period reflects a time of N fertilization of crops and then relatively fast transit of water and nitrate in the river network. For example, corn is typically planted between April 1 and May 25 in the ORB, dependent on soil reaching a temperature above 10°C for several days. Nitrogen fertilizers are applied at the time of planting and/or fertilizer is "side dressed" or applied between the rows of growing corn (i.e., see Interviews in Supplemental Information). The hydrology of the ORB produces conditions to quickly mobilize N fertilizers during the spring and early summer that, in turn, produces the June nitrate concentration and nitrate load peaks. The ORB receives

high rainfall during this time (9, 10.5, and 9 cm average rainfall in April, May, and June, respectively; White et al., 2005). The rainfall is suggested to mobilize nitrogen fertilizers to cause peaks at the sampling stations because of fast transit. The ORB is indicative of karst geology in the south and tile drainage in the north, where the dual permeability of the system causes short circuiting of the nitrate from the soil column to the watershed outlets (Woo & Kumar, 2019). For example, our results from this region show the pulse of fertilizer N in rainfall immediately after application (see Figure S4; see also Ford et al., 2018, 2019 cited in the original and revised paper). These event-based data support the lack of retention for a substantial enough fertilizer N to the river system. This is further supported by mapping of the extensive tile and karst network for this region (USGS, 2020; Valayamkunnath et al., 2020).

Nitrogen fertilizers producing peak concentrations and loads during the planting season is corroborated by recent data (Ford et al., 2018). They showed edge-of-field results for tile drain flow and dissolved N following N fertilization in Mercer County, Ohio. Planting in May, fertilization in June, and then a rainfall event 2 weeks later shows dissolved N reaching 73 mg-N L^{-1} for water leaving tile drains (Figure S4). Precipitation and tile drain flow produce five zones including (1) pre-event, (2) matrix re-wetting, (3) saturated conditions with peak flow, (4) receding limb, and (5) post-event. Saturated conditions with peak flow resulted in maximum N concentration from tile drains. In another study, Ford et al. (2019) recently showed that nitrogen fertilizers applied to corn fields in central Indiana in early June produced nitrogen peaks at the catchment outlet from rainfall 1 week later due to tile drainage. In another similar study by Ford et al. (2019) for similar corn system, nitrogen peaks were always found in late May or June on fertilized corn systems with tile drainage. Husic et al. (2019) recently showed a hydrologic response of a watershed system underlain by karst bedrock produced nitrate peaks 3–4 days after rainfall, and peaks were attributed to nitrogen mobilized from agricultural soils. Taken together, it is reasonable that the spring/early summer planting season at least partially corresponds with nitrate peaks from N fertilization.

The growing-harvest season of low nitrate load from late summer/fall from July 1 to November 30 corresponds with a time period of high soil evaporation, plant growth, crop growth, and harvesting with less water and nitrate mobilization from the landscape to the river network. Plant demand for soil water and soil nitrate is high during this warm temperature period. Precipitation depth in the ORB does experience pronounced seasonality; however, soil moisture is lowest in the late summer/fall season (Figure S2) due to high evapotranspiration demand. In turn, transport of water and nitrate to the river is relatively low. For example, analyses of average monthly data for the ORB published by White et al. (2005) show 42% of annual precipitation falls during the 5-month period from July to November which agrees exactly with the amount of the year by time (5 months/12 months = 42%); however, only 21% of the ORB's annual runoff is produced during this time period. Results also reflect the lower nitrate concentrations, lower river discharge, and low nitrate load during this time period of high evapotranspiration demand.

The Green River results and the prominence of the January and June nitrate concentration and load peaks across the 6 years of data (Figure 5) provide some interesting comparison with the ORB export to the Mississippi River at the Olmsted, Illinois site. Nitrate concentration and nitrate load at the Olmsted site show January and June peaks in most years (Figure 4i left and right panes), although a prolonged high nitrate period can exist from January to June or intermittent peaks between January and June. The Green River subbasin has nearly equal percent forest cover and crop cover (corn and soybean cover) as the ORB at Olmsted (Table 1); however, the Green River subbasin has one-twentieth the drainage area of the ORB. Differences between the basins reflect the high transit time of water through the Green River subbasin and the dilution of nitrate and assimilation of many subbasins' contributions at the Olmsted station. Until it flows through the west Kentucky Coal Fields, the Green River basin lies almost entirely in the Pennyrile portion of the Interior Low Plateau, which is characterized by extensive karst aquifers that form underground "rivers" and empty to the Green River in its middle and lower reaches (White & Hendricks, 2022). Water flowing through a karst aquifer travels much faster than through a traditional aquifer. The importance of quickflow and intermediate flow groundwater potentially contributes to the seasonal nitrate signals seen at the other subbasins because karst bedrock in the southern basins and tile drainage in the northern basins can cause relatively fast subsurface water and nutrient transport in the ORB (Ford et al., 2018, 2019; Husic et al. 2017, 2019). The prominent nitrate peaks of the subbasins can be dampened at Olmsted due to dilution and assimilation. Kentucky Lake and Lake Barkley (i.e., Tennessee River and Cumberland River, respectively) join the Ohio River upstream of Olmsted and comprise 29% the of the Ohio River drainage basin at Olmsted. Both the Tennessee and Cumberland basins have average nitrogen concentrations of 0.1–0.2 mg L^{-1}, an order of magnitude lower than the Ohio River (White et al., 2005). On average, nitrate concentrations at Olmsted are reduced by 24% due to dilution from these tributaries, which, in turn, dampens the nitrate peaks observed at Olmsted (Figure S5).

4.2 | Alternative hypotheses

The alternative hypotheses that nitrate seasonal patterns are an artifact of river discharge or internal cycling are marginalized based on data analyses. Ohio River nitrate concentrations show chemostatic behavior, that is, lack of dependence on river discharge (Figure S6). This result agrees more broadly with Mississippi River Basin results showing chemostatic behavior (Zimmer et al., 2019). At the small subbasin scale, low-order streams of the ORB show event response of nitrate and dependence on discharge (e.g., Ford et al., 2018; Husic et al., 2019). However, at the Olmsted site, we attribute chemostatic behavior to loss of imprint of individual events associated with the nearly uniform distribution

of mean monthly precipitation in the ORB throughout the year (Figure S2)—primarily as rainfall coupled with substantial quickflow component for rainfall, mixing of tributary junctions longitudinally and regulation of flow in the river longitudinally.

Internal cycling is also marginalized as the reason for the seasonal patterns of nitrate in the ORB, although internal cycling likely decreases nitrate concentration, dampening peaks and further decreasing N levels during the late summer and fall. Internal cycling of nitrogen includes direct denitrification in the river and autotrophic (i.e., phytoplankton and benthic algae) and microbial assimilation that leads to organic matter growth, turnover and denitrification of at least some portion of regenerated nitrogen (e.g., Peterson et al., 2001). The overall importance of internal cycling on nitrate concentration in the basin is evidenced by the scale dependence of results, where nitrate concentration shows an overall decrease for each season from small watersheds to large watersheds to the Ohio River stations (Figure 2; Figure S7). Also, the order of magnitude lower nitrate concentration of Kentucky Lake and Lake Barkley waters is the result of the internal cycling in the lakes and is the reason for the aforementioned dilution effect at the Olmsted site. Nevertheless, surrogates of autotrophic behavior do not suggest the existence of January and June nitrate peaks are an artifact of internal cycling during other time periods. Algal densities indicated by chlorophyll concentration in the Ohio River suggest fairly stable behavior of chlorophyll equal to $2\,\mu g\,L^{-1}$ at upstream sites (Greenup Pool) increasing to $8\,\mu g\,L^{-1}$ at downstream sites (Brookport, IL) (Figure S8). Peaks of chlorophyll at upstream sites above $6\,\mu g\,L^{-1}$ occur in April, June, and September and average summer chlorophyll concentration reach $15\,\mu g\,L^{-1}$ at downstream sites. Reasons for the peaks are warmer waters, N fertilizer runoff blooms of green algae in April and June, and slow-moving waters centered around September triggering blooms of cyanobacteria. The primary production peaks likely cause internal decreases of spring and summer nitrate concentration and load peaks observed at Olmsted (Figure 2), and thus some relative increase in internal mitigation of nitrate loads to the Mississippi River may occur in the planting season relative to the other seasons. Regardless, Ohio River data suggest primary productivity is typically stable and small relative to nitrate loads because although N is not limiting throughout the year ($N > 0.25\,mg\,L^{-1}$). Taken together, the data results suggest internal cycling does create a distinct seasonality of Ohio River nitrate concentrations that would overprint the nitrate seasonal variation results attributed to soil–plant processes across the landscape.

4.3 | Ohio River nitrate timing across seasons

We quantified ORB nitrate timing and loading across the dormant, planting, and growing-harvest seasons defined previously (e.g., Figure 5) for the main stem Ohio River sites and the subbasins. Nitrate load during each season increases longitudinally in the Ohio River main stem to its junction with the Mississippi River (Figure 2c,f,i). Based on our differentiation of seasons, 51% of the nitrate exported from the Ohio River at Olmsted corresponded to the dormant season, 26% from the planting season, and 22% from the growing-harvest season. The dominance of the dormant season nitrate yield was also found for the subbasins (Figure 6), with 8 out of 10 subbasins showing the dormant season as the season with the greatest nitrate yield. The two exceptions were the two small subbasins with dominant cropland (i.e., Sugar Creek with 74% cropland, School Branch with 67% cropland), which both showed the planting season as the season with the greatest nitrate yield. The nitrate yield during the planting season is similar to the dormant season for crop dominated subbasins, and nitrate yield decreases in the planting season as the percent of cropland cover decreases. Comparing the small watersheds to the large watersheds (columns one and two in Figure 6) shows an overall decrease of nitrate yield per drainage area in every season, which is attributed to internal stream cycling of nitrate and potentially differences in land cover (e.g., the land cover distributions of the side-by-side plots in Figure 6 do not match exactly).

4.4 | Managing Ohio River nitrate loading to the Mississippi River Basin

Reducing nitrate loading from the Mississippi River to the Gulf of Mexico remains an important goal for basin managers and scientists. Nitrate concentrations and nitrate loads have either increased or remain unchanged for much of the Mississippi River since 1980 (Murphy & Hirsch, 2013; Sprague et al., 2011). The Ohio River and Upper Mississippi River are the two major tributaries that deliver nutrients to Mississippi River (Duan et al., 2014). The timing of the dominant nitrate loading from these tributaries is different and might be considered in management. The Ohio River results show dual peaks in nitrate load to the Mississippi River centered in January and June (Figures 2h and 4i), and the winter dormant season is responsible for two times as much nitrate loading as the spring planting season (51% vs. 26% of the nitrate load, respectively). Results from the Upper Mississippi River show a single nitrate loading peak in June, and nitrate loading in June is four times greater than nitrate loading in the winter months (Figure S10). If nitrate is to be reduced in the Mississippi River, managing ORB nitrate will be an important part of the solution given that 35% of the Mississippi River nitrate load is contributed from the Ohio River (White et al., 2005; White & Hendricks, 2022).

Regarding nutrient management, the observations from the nitrate sensor network coupled with the land cover and geology in the ORB provided noteworthy results as follows. (i) Nitrate increases substantially from Ironton to Olmsted as the drainage area transitions from 5% to 19% cropland. (ii) The dormant season dominates nitrate loading (51%) from the ORB to the Mississippi River. (iii) All watersheds with varying

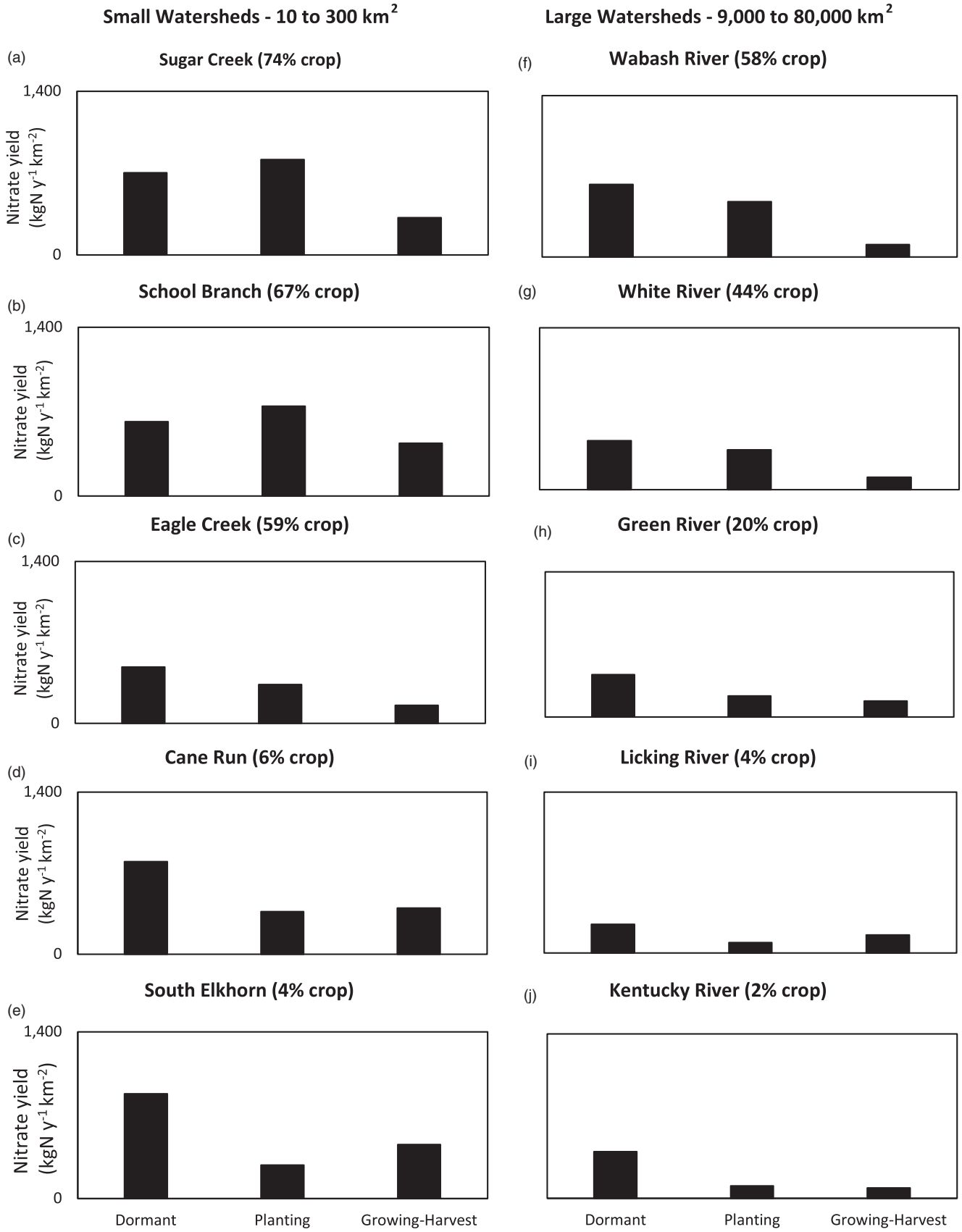

FIGURE 6 Nitrate yield in each season for small (a–e) and large (f–j) ORB watersheds in this study. Observation shows the overall importance of high nitrate yield during the winter dormant season. The nitrate yield in the planting season decreases as the percent of cropland cover decreases. The overall decrease in nitrate yield in every season comparing small to large watersheds is attributed to internal cycling and differences in land cover.

land uses contribute high nitrate during the winter dormant season. (iv) Much of the ORB is underlain by mature karst geology or tile drainage that can cause fast transit of water and nitrate to the river and in turn short circuit the more traditional pathways where shallow groundwater storage can help to self-mitigate soil derived nitrate.

Results highlight the potential for reducing a nitrate pulse during the planting season by applying methods to reduce fertilizer inputs and reduce nitrogen fertilizer runoff. Reducing nitrate levels in the Ohio River might be most easily performed through reduction of nitrogen fertilization when possible and use of nitrogen inhibitors to improve efficiency. Nitrate yield from crop dominated watersheds is two to three times greater than low crop-cover basins (Figure 6) suggesting potential to reduce nitrate yield during the planting season.

However, N fertilizer reductions are not enough, and many more management practices are needed to reduce the annual nitrate load. For example, given the 19% cropland cover in the ORB and the fact that approximately 26% of nitrate loading is associated with the planting season, an ambitious threefold reduction in nitrate export from croplands in the ORB only reduces the total nitrate loading per year to the Mississippi River by 7%. We qualify that more efficient fertilizer use may also lead to reduction of aged fertilizer nitrate that is stored in the soil (Woo & Kumar, 2016, 2017) and released during other seasons from the cropland soils to the water systems. However, the scenario points out that focusing only on cropland fertilizers produces only a 7% reduction in the planting season when a 45% reduction of annual nitrate load has been recommended (McLellan et al., 2015), and practices are needed beyond merely best management of fertilizers.

Reducing soil nitrate leaching during the winter dormant period is recommended for all the land uses across the ORB, since this is the season of greatest nitrate yield for the Ohio River and most subbasins studied (Figures 2 and 6). Management strategies for reducing nitrate yield from cropland, pastureland, and urban land uses might all be considered. For lands with corn and soybeans, winter cover crops such as rye and winter wheat can keep nutrients in the soil. A modeling scenario carried out by Kladivko et al. (2014) showed that cover crops have the potential to reduce nitrate loads to the Mississippi River by approximately 20% for the tile drained portion of the corn–soybean and continuous corn cropping systems in Ohio, Indiana, Illinois, Iowa, and Minnesota. Cover crop adoption rates remain low in the ORB with less than 10% of the harvested cropland being planted with winter cover crops for the overwhelming majority of counties in the ORB and adoption rarely exceeding 15% of harvested cropland (Wallander et al., 2021). The potential of cover crops in the ORB is promising however if adopted at a high land cover density.

Reducing winter nitrate loading from pastureland is more difficult and its potential importance is highlighted by the fact that the highest dormant season nitrate yield came from subbasins with relatively high amounts of pasture (i.e., South Elkhorn and Cane Run in Figure 6 and land-use data in Table 1). Removing livestock from stream corridors cuts down on direct manure inputs and should be promoted, although much of the soil nitrate leaching is likely related to manure inputs already assimilated to the soil, that is, legacy nitrogen, which travels through the subsurface. The control of N fertilizers and transport on urban and suburban lands is also potentially helpful for reduction. 9% of the ORB is urban/suburban (see Olmsted site in Table 1), and future research could investigate if widespread use of best fertilization practices will substantially reduce ORB nitrate levels.

Across all land uses, water retention and nutrient recycling are a potential, albeit expensive, solution. Also, care is needed in installation of these methods because mature karst geology and tile drainage networks can cause fast transit of water and nitrate to the steam systems. Increasing wetland and stream channel restorations, drainage-ditch enhancements, flood-plain reconnection, drainage water recycling to reduce tile drain flow, and impoundments will certainly retain water and reduce nitrate through autochthonous assimilation and denitrification. The efficacy of such reductions has been shown with modeling (McLellan et al., 2015). Water retention and increases in nutrient spiraling rates are well evident in the lakes systems such as the order of magnitude lower nitrate levels leaving Kentucky Lake (Figure S5). Such approaches appear essential at some level, although the number of artificial retention methods would need to be massive given the extent of land surface of the ORB. One partial solution is the reestablishment of larger wetland–riparian zones as part of new stream and watershed restoration projects (Hester et al., 2016; Welsh et al., 2017). For example, these restorative methods are gaining popularity in some local levels of the ORB and promoting the approach for basin-wide initiatives might further promote implementation.

Assessing nitrate reductions from management methods may take many years to decades, and nitrate sensing networks show the potential to help with these assessments. The dormant season nitrate loading is suggested to be linked with soil nitrate leaching, and therefore legacy nitrogen already stored in the landscape may continue to leach to the river network even if surface nitrogen inputs were reduced. This concept suggests promoting basin-wide stewardship to reduce nitrogen inputs and expansion of nitrogen retention infrastructure, but at the same time some degree of patience will be needed to assess effectiveness. To this end, the sensor network of SUNAs across the ORB serves as a promising resource for assessing effectiveness across subbasins with different scales. For example, the number of USGS "Super gage" sites that monitor nitrate has nearly doubled across the ORB in the last 2 years, and university-led projects continue to add nitrate monitoring stations. Organization of these resources across the ORB provides a method to consider intra-annual variability of nitrate transport controlled by soil–plant processes from season-to-season.

AUTHOR CONTRIBUTIONS

Morgan Gerlitz: Formal analysis; writing – original draft. **Jimmy Fox:** Conceptualization; data curation; formal analysis; funding acquisition; investigation; methodology; project administration; resources; supervision; visualization; writing – original draft; writing – review and editing.

William Ford: Data curation; formal analysis; funding acquisition; investigation; methodology; writing – review and editing. **Admin Husic:** Data curation; investigation; methodology; resources; writing – review and editing. **Tyler Mahoney:** Data curation; investigation; methodology; resources; software; validation; writing – review and editing. **Mindy Armstead:** Data curation; investigation; resources; writing – review and editing. **Susan Hendricks:** Data curation; funding acquisition; investigation; methodology; writing – review and editing. **Angela Crain:** Data curation; validation; writing – review and editing. **Jason Backus:** Data curation; methodology; validation; writing – review and editing. **Erik Pollock:** Data curation; methodology; resources; validation; writing – review and editing. **Wei Ren:** Data curation; resources; software; writing – review and editing. **Bo Tao:** Data curation; resources; software; writing – review and editing. **Brenden Riddle:** Investigation; validation; writing – review and editing. **David White:** Conceptualization; funding acquisition; investigation; project administration; resources; writing – review and editing.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support of this research from the Kentucky Senate Bill 271B Water Quality program and National Science Foundation Awards #1632888 and #1933779. Special thanks to U.S. Geological Survey field personnel in the Louisville, KY and Murray, KY Offices for their exceptional efforts in operating and maintaining the continuous nitrate sensors on the large rivers in the lower ORB. We thank the undergraduate students who assisted with data collection and processing.

CONFLICT OF INTEREST STATEMENT

The author declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ORCID

William Ford https://orcid.org/0000-0001-7940-9826

REFERENCES

Boryan, C., Z. Yang, R. Mueller, and M. Craig. 2011. "Monitoring US Agriculture: The US Department of Agriculture, National Agricultural Statistics Service, Cropland Data Layer Program." *Geocarto International* 26: 341–58. https://doi.org/10.1080/10106049.2011.562309.

Di, H., and K. Cameron. 2002. "Nitrate Leaching in Temperate Agroecosystems: Sources, Factors and Mitigating Strategies." *Nutrient Cycling in Agroecosystems* 64: 237–56 10.1023/A:1021471531188.

Duan, S., R.T. Powell, and T.S. Bianchi. 2014. "High Frequency Measurement of Nitrate Concentration in the Lower Mississippi River, USA." *Journal of Hydrology* 519: 376–86. https://doi.org/10.1016/j.jhydrol.2014.07.030.

Ford, W.I., J.F. Fox, E. Pollock, H. Rowe, and S. Chakraborty. 2015. "Testing Assumptions for Nitrogen Transformation in a Low-Gradient Agricultural Stream." *Journal of Hydrology* 527: 908–22. https://doi.org/10.1016/j.hydrol.2015.05.062.

Ford, W.I., A. Husic, A. Fogle, and J. Taraba. 2019. "Long-Term Assessment of Nutrient Flow Pathway Dynamics and In-Stream Fate in a Temperate Karst Agroecosystem Watershed." *Hydrological Processes* 33: 1610–28. https://doi.org/10.1002/hyp.13427.

Ford, W.I., K. King, and M.R. Williams. 2018. "Upland and In-Stream Controls on Baseflow Nutrient Dynamics in Tile-Drained Agroecosystem Watersheds." *Journal of Hydrology* 556: 800–12. https://doi.org/10.1016/j.jhydrol.2017.12.009.

Halder, J., Y. Vystavna, and L.I. Wassenaar. 2022. "Nitrate Sources and Mixing in the Danube Watershed: Implications for Transboundary River Basin Monitoring and Management." *Scientific Reports* 12: 2150. https://doi.org/10.1038/s41598-022-06224-5.

Hester, E.T., B. Hammond, and D.T. Scott. 2016. "Effects of Inset Floodplains and Hyporheic Exchange Induced by In-Stream Structures on Nitrate Removal in a Headwater Stream." *Ecological Engineering* 97: 452–64.

Huang, Yawen, Bo Tao, Zhu Xiaochen, Yanjun Yang, Liang Liang, Lixin Wang, Pierre-Andre Jacinthe, Hanqin Tian, and Wei Ren. 2021. "Conservation Tillage Increases Corn and Soybean Water Productivity across the Ohio River Basin, Agricultural Water Management." 254: 106962. https://doi.org/10.1016/j.agwat.2021.106962.

Husic, A., J. Fox, E. Adams, J. Backus, E. Pollock, W. Ford, and C. Agouridis. 2019. "Inland Impacts of Atmospheric River and Tropical Cyclone Extremes on Nitrate Transport and Stable Isotope Measurements." *Environmental Earth Sciences* 78: 36. https://doi.org/10.1007/s12665-018-8018-x.

Husic, A., J. Fox, C. Agouridis, J. Currens, W. Ford, and C. Taylor. 2017. "Sediment Carbon Source, Fate, and Transport in a Fluviokarst Watershed (Part 1): Conceptual Model Development." *Journal of Hydrology* 549: 179–193. https://doi.org/10.1016/j.jhydrol.2017.03.052.

Johnson, D.M., and R. Mueller. 2010. "The 2009 Cropland Data Layer." *Photogrammetric Engineering and Remote Sensing* 76: 1201–05.

Kendall, C. 1998. "Tracing Nitrogen Sources and Cycling in Catchments." In *Isotope Tracers in Catchment Hydrology*, edited by Carol K. and Jeffrey J. McDonnell, 519–76. Elsevier. https://doi.org/10.1016/B978-0-444-81546-0.50023-9 .

Kladivko, E.J., T.C. Kaspar, D.B. Jaynes, R.W. Malone, J. Singer, X.K. Morin, and T. Searchinger. 2014. "Cover Crops in the Upper Midwestern United States: Potential Adoption and Reduction of Nitrate Leaching in the Mississippi River Basin." *Journal of Soil and Water Conservation* 69(4): 279–91. https://doi.org/10.2489/jswc.69.4.279.

Kreiling, R.M., and J.N. Houser. 2016. "Long-Term Decreases in Phosphorus and Suspended Solids, but Not Nitrogen, in Six Upper Mississippi River Tributaries, 1991–2014." *Environmental Monitoring and Assessment* 188: 454. https://doi.org/10.1007/s10661-016-5464-3.

McLellan, E., D. Robertson, K. Schilling, M. Tomer, J. Kostel, D. Smith, and K. King. 2015. "Reducing Nitrogen Export from the Corn Belt to the Gulf of Mexico: Agricultural Strategies for Remediating Hypoxia." *Journal of the American Water Resources Association* 51: 263–89. https://doi.org/10.1111/jawr.12246.

Murphy, Jennifer C., and Robert M. Hirsch. 2013. "Nitrate in the Mississippi River and Its Tributaries, 1980–2010: An Update (Scientific Investigations Report No. 2013–5169)." US Department of the Interior, USGS.

NASS. 2021. National Agricultural Statistics Service, United States Department of Agriculture. Census of Agriculture. https://www.nass.usda.gov/index.php.

Nazari, S., W.I. Ford, and K.W. King. 2020. "Impacts of Preferential Flow and Agroecosystem Management on Subsurface Particulate Phosphorus Loadings in Tile-Drained Landscapes." *Journal of Environmental Quality* 49(5): 1370–83.

Patton, C.J., and J.R. Kryskalla. 2011. "Colorimetric Determination of Nitrate Plus Nitrite in Water by Enzymatic Reduction, Automated Discrete Analyzer Methods." U.S. Geological Survey Techniques and Methods, Book 5, Chap. B8, 34 pp.

Pellerin, B.A., B.A. Bergamaschi, B.D. Downing, J.F. Saraceno, J.A. Garrett, and L.D. Olsen. 2013. "Optical Techniques for the Determination of Nitrate in Environmental Waters—Guidelines for Instrument Selection, Operation, Deployment, Maintenance, Quality Assurance, and Data Reporting." U.S. Geological Survey Techniques and Methods, Book 1, Chap. D5, 37 pp. https://doi.org/10.3133/tm1D5.

Peterson, B.J., W.M. Wollheim, P.J. Mulholland, J.R. Webster, J.L. Meyer, J.L. Tank, E. Martí, et al. 2001. "Control of Nitrogen Export from Watersheds by Headwater Streams." *Science* 292(5514): 86–90.

Reitsma, K.D., B.H. Dunn, U. Mishra, S.A. Clay, T. DeSutter, and D.E. Clay. 2015. "Land-Use Change Impact on Soil Sustainability in a Climate and Vegetation Transition Zone." *Agronomy Journal* 107(6): 2363–72.

Royer, T.V., M.B. David, and L.E. Gentry. 2006. "Timing of Riverine Export of Nitrate and Phosphorus from Agricultural Watersheds in Illinois: Implications for Reducing Nutrient Loading to the Mississippi River." *Environmental Science & Technology* 40: 4126–31. https://doi.org/10.1021/es052573n.

Savard, M.M., G. Somers, A. Smirnoff, D. Paradis, E. Van Bochove, and S. Liao. 2010. "Nitrate Isotopes Unveil Distinct Seasonal N-Sources and the Critical Role of Crop Residues in Groundwater Contamination." *Journal of Hydrology* 381: 134–41. https://doi.org/10.1016/j.jhydrol.2009.11.033.

Schilling, K.E., C.F. Wolter, and E. McLellan. 2015. "Agro-Hydrologic Landscapes in the Upper Mississippi and Ohio River Basins." *Environmental Management* 55(3): 646–56.

Sprague, L.A., R.M. Hirsch, and B.T. Aulenbach. 2011. "Nitrate in the Mississippi River and Its Tributaries, 1980 to 2008: Are We Making Progress?" *Environmental Science & Technology* 45: 7209–16. https://doi.org/10.1021/es201221s.

U.S. Geological Survey. 2016. "USGS Water Data for the Nation." U.S. Geological Survey National Water Information System Database. https://doi.org/10.5066/F7P55KJN.

U.S. Geological Survey. 2020. "National Field Manual for the Collection of Water-Quality Data." U.S. Geological Survey Techniques of Water-Resources Investigations Book 9, Chaps. A1–A10. http://pubs.water.usgs.gov/twri9A.

Ueda, M.U., E. Mizumachi, and N. Tokuchi. 2010. "Winter Nitrate Uptake by the Temperate Deciduous Tree Quercus Serrata." *Journal of Forest Research* 15: 411–14. https://doi.org/10.1007/s10310-010-0219-4.

Valayamkunnath, P., M. Barlage, F. Chen, D. Gochis, and K.J. Franz. 2020. "Mapping of 30-Meter Resolution Tile-Drained Croplands Using a Geospatial Modeling Approach." *Scientific Data* 7: 257 10.1038/s41597-020-00596-x.

Wallander, S., D. Smith, M. Bowman, and R. Claassen. 2021. "Cover Crop Trends, Programs, and Practices in the United States." U.S. Department of Agriculture Economic Research Service, Economic Information Bulletin Number 222.

Welsh, M.K., S.K. McMillan, and P.G. Vidon. 2017. "Denitrification along the Streamriparian Continuum in Restored and Unrestored Agricultural Streams." *Journal of Environmental Quality* 46(5): 1010–19. https://doi.org/10.2134/jeq2017.01.0006.

White, D., K. Johnston, and M. Miller. 2005. *Ohio River Basin*. Burlington, MA: Rivers of North America, Academic Press.

White, D.S., and S.P. Hendricks. 2022. "Ohio River Basin." In *Rivers of North America* (Second Edition), edited by M. Delong, T. Jardine, and A.C. Benke. Burlington, MA: Elsevier.

Williams, M.R., K.W. King, W. Ford, and N.R. Fausey. 2016. "Edge-of-Field Research to Quantify the Impacts of Agricultural Practices on Water Quality in Ohio." *Journal of Soil and Water Conservation* 71(1): 9A–12A.

Woo, D.K., and P. Kumar. 2016. "Mean Age Distribution of Inorganic Soil-Nitrogen." *Water Resources Research* 52(7): 5516–36.

Woo, D.K., and P. Kumar. 2017. "Role of Micro-Topographic Variability on the Distribution of Inorganic Soil-Nitrogen Age in Intensively Managed Landscape." *Water Resources Research* 53(10): 8404–22.

Woo, D.K., and P. Kumar. 2019. "Impacts of Subsurface Tile Drainage on Age—Concentration Dynamics of Inorganic Nitrogen in Soil." *Water Resources Research* 55(2): 1470–89.

Wu, Z., N.E. Huang, and C. Peng. 2007. "On the Trend, Detrending, and Variability of Nonlinear and Nonstationary Time Series." *Proceedings of the National Academy of Sciences of the United States of America* 104(38): 14889–94.

Zimmer, M.A., B. Pellerin, D.A. Burns, and G. Petrochenkov. 2019. "Temporal Variability in Nitrate-Discharge Relationships in Large Rivers as Revealed by High-Frequency Data." *Water Resources Research* 55: 973–89. https://doi.org/10.1029/2018WR023478.

SUPPORTING INFORMATION

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

How to cite this article: Gerlitz, Morgan, Jimmy Fox, William Ford, Admin Husic, Tyler Mahoney, Mindy Armstead, Susan Hendricks et al; 2023. "Instream sensor results suggest soil–plant processes produce three distinct seasonal patterns of nitrate concentrations in the Ohio River Basin." *JAWRA Journal of the American Water Resources Association* 00 (0): 1–17. https://doi.org/10.1111/1752-1688.13107.