TECHNICAL REPORT

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Surface Water Quality

Nitrate losses across 29 Iowa watersheds: Measuring long-term trends in the context of interannual variability

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Abstract

In the U.S. Corn Belt, annual croplands are the primary source of nitrate loading to waterways. Long periods of fallow cause most nitrate loss, but there is extreme interannual variability in the magnitude of nitrate loss due to weather. Using mean annual (2001–2018) flow-weighted nitrate-N concentration (FWNC; mg NO₃⁻-N L⁻¹), load (kg NO₃⁻–N), and yield (kg NO₃⁻–N ha⁻¹ cropland) for 29 watersheds, our objectives were (a) to quantify the magnitude and interannual variability of 5-yr moving average FWNC, load, and yield; (2) to estimate the probability of measuring 41% reductions in nitrate loss after isolating the effect of weather on nitrate loss by quantifying the interannual variability of nitrate loss in watersheds where there was no trend in 5-yr moving average nitrate loss (Iowa targets a 41% nitrate loss reduction from croplands); and (c) to identify factors that, in the absence of long-term trends in nitrate loss, best explain the interannual variability in nitrate loss. Averaged across all watersheds, the mean probability of measuring a statistically significant 41% reduction in FWNC across 15 yr, should it occur, was 96%. However, the probabilities of measuring 41% reductions in nitrate load and yield were only 44 and 32%. Across watersheds, soil organic matter, tile drainage, interannual variability of precipitation, and watershed area accounted for interannual variability in these nitrate loss indices. Our results have important implications for setting realistic timelines to measure nitrate loss reductions against the background of interannual weather variation and can help to target monitoring intensity across diverse watersheds.

Sotirios V. Archontoulis¹

INTRODUCTION 1

The Mississippi Atchafalaya River basin (MARB) is the thirdlargest river basin in the world. Thirty-one states plus two Canadian provinces drain into the MARB, totaling 41% of the contiguous land area of the United States and 15% of North America (Alexander et al., 2008). These lands also play a major role in the production of various crops, such as maize (Zea mays L.), soybean [Glycine max (L.) Merr.], wheat (Triticum aestivum L.), rice (Oryza sativa L.), and cotton (Gossypium hirsutum L.) (USDA-NASS, 2017). In this region, the introduction of synthetic N fertilizer was coincident with a 50-300% increase in crop productivity and enabled the widespread adoption of a cropping system that includes only two warm-season annual crops: maize and

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Science Society of America.

Abbreviations: FWNC, flow-weighted nitrate-nitrogen concentration; MARB, Mississippi Atchafalaya River basin; SOM, soil organic matter.

soybean (Hatfield et al., 2009). Together, synthetic N fertilizer inputs and fallow periods when soil N mineralization occurs in the absence of plant N uptake have led to a large increase in nitrate losses that impairs local and regional waterways (David et al., 2010; Martinez-Feria et al., 2018).

Locally, high nitrate losses cause high nitrate concentrations in surface water and groundwater that harm aquatic ecosystems and challenge water utilities by exceeding the USEPA drinking water standard of 10 mg NO₃⁻–N L⁻¹ (USEPA, 2015). Regionally, nitrate losses from corn and soybean croplands in the upper Midwest are the leading cause of a hypoxic zone in the Gulf of Mexico. The size of the annually occurring hypoxic zone, which is associated with the annual nitrate load (kg NO₃⁻–N yr⁻¹) and flow-weighted nitrate concentration (FWNC; mg NO₃⁻–N L⁻¹), fluctuates from <500 to >22,730 km² yr⁻¹ (National Oceanic and Atmospheric Administration, 2021). The USEPA has set a goal to reduce the average annual size of the hypoxic zone from ~15,000 to ~5,000 km² by 2035.

Recognizing that weather and discharge are large drivers of the interannual variability in the size of the hypoxic zone (Lu et al., 2020), the USEPA evaluates progress toward this goal by using the 5-yr moving average of the size of the hypoxic zone. The moving average helps to control for the large effect of interannual weather variability on the size of the hypoxic zone and thus allows trends in size to be more accurately attributed to changes in MARB land use and management. Consistent with this approach, total water flow rather than nitrate concentration explains most variation in nitrate losses from croplands across space and time (Martinez-Feria et al., 2018). However, land use is the primary mechanism through which weather influences nitrate losses. In perennial vegetation, nitrate losses are low, and the impact of weather on interannual variation in nitrate losses is very small (Randall et al., 1997). In contrast, under annual crops, nitrate losses are high, and the impact of weather is substantial; most nitrate losses occur during long fallows when maize or soybean water and N demand is low or zero, but microbes are transforming soil organic matter (SOM) N to ammonium and subsequently, via nitrification, to nitrate (Christianson et al., 2012; Dietzel et al., 2016; Martinez-Feria et al., 2018).

Despite little change in land use over the last 20–30 yr in the MARB, annual nitrate loading to the Gulf of Mexico has varied by ~500%. Although annual cropping systems are the reason nitrate loads are high (Alexander et al., 2008; David et al., 2010), much of the interannual variation in nitrate loads can be attributed to weather (Wan et al., 2017). For example, in the month of May (which is most predictive of the size of the hypoxic zone), dissolved nitrite plus nitrate flux to the Gulf of Mexico during the drought of 2012 was ~60,000 Mg and increased by nearly 300% to ~175,000 Mg in 2013 (Loecke et al., 2017). Across the same two years, average FWNC across the 29 Iowa watersheds stud-

Core Ideas

- Nitrate losses in annual crop systems are high owing to long periods of fallow.
- Interannual variability in nitrate losses is high due to interannual variability in weather.
- Interannual weather variability challenges our ability to measure long-term trends in nitrate loss.
- Our ability to measure long-term trends is best with flow-weighted nitrate concentration.
- The probability of measuring long-term trends owing to changes in management varies across watersheds.

ied herein increased by 83% from 5.4 to 9.9 mg NO_3^- –N L⁻¹. Moreover, the effect of weather can vary across space owing to differences in land use and physiography. For example, the percentage of cultivated area and hydrological features (e.g., discharge and soil texture) can affect FWNC and loads (David et al., 2010).

High year-to-year variability in nitrate loss can lead to spurious conclusions about land-use-related increases or decreases (Spijker et al., 2021). For example, the load may significantly increase or decrease over some number of years owing solely to interannual weather patterns (Øygarden et al., 2014); indeed, this is why the size of the hypoxic zone is evaluated using a 5-yr moving average. By quantifying and explaining the interannual variation in FWNC, load, and yield—in the absence of land-use change—we can identify watersheds that may require more or less time to detect an effect of land-use change on nitrate loss and set realistic timelines to measure changes in nitrate loss owing to land use and management.

There is a critical need to quantify and understand interannual variation in nitrate loss associated with weather variability. The interannual variation in nitrate loss due to weather has a direct effect on the ability to detect the effect of changes in land use and management on nitrate loss (Figure 1). The greater the interannual variation in nitrate losses due to weather, the more difficult it will be to detect trends that result from changes in land use and management. To this end, the ability to observe non-weather-related changes in nitrate loss is affected by three variables: the mean and standard deviation of nitrate loss metrics (FWNC, load, and yield) in the absence of non-weather-related changes, the amount of non-weather-related change in mean annual nitrate loss (increase or decrease), and the amount of time during which that change occurs. Our objectives were (a) to quantify the interannual variability of the average annual FWNC (mg $NO_3^{-}-NL^{-1}$), load (Gg $NO_3^{-}-N$ watershed⁻¹), and yield (kg NO₃⁻–N ha⁻¹ cropland) across 29 watersheds in Iowa from

FIGURE 1 The challenge associated with measuring reductions in nitrate loss. Squares are the annual nitrate load; blue circles are the 5-yr moving average nitrate load. The solid line is the mean 5-yr moving average; dashed lines are 1 and 2 SD of the mean. The continued lines beyond 2018 represent a simulated 41% reduction in the mean 5-yr moving average load over 15 yr. Data are from watershed ID 2 (Supplemental Figure S2). Given a lack of change in watershed land use or trend in 5-yr moving average nitrate load from 1980 to 2018, we attribute the interannual variability in nitrate load from 1980 to 2018 to interannual variability in weather. If a change in land use beginning in 2018 produces a 41% reduction in the 5-yr moving average nitrate load over 15 yr, in 2025 it would be possible to observe an increase (red circle) or >41% decrease (green circle) in load due to the random effect of weather on load (i.e., "the luck of the draw"). We estimate the probability of these outcomes using Monte Carlo simulation

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2006 to 2018; (b) to estimate the probability of measuring 41% reductions in FWNC, load, and yield, should they occur, across periods of 5, 10, and 15 yr against the background of interannual weather variation; and (c) to identify factors that best explain the interannual variability in nitrate losses across the watersheds. We selected a 41% reduction because this is the target reduction for non-point source N loads in the Iowa Nutrient Reduction Strategy (IDNR, 2017). The 41% reduction in the size of the hypoxic zone of 45% and the fact that 91% of Iowa's contribution to nitrate load (i.e., 41 of 45%) is from non-point sources, which in Iowa are maize and soybean croplands.

2 | MATERIALS AND METHODS

We analyzed a comprehensive long-term water quality and quantity dataset that includes NO_3^- –N concentration and discharge (*Q*) for 29 watersheds in Iowa from 2001 to 2018 (Figure 2; Supplemental Materials). The 29 watersheds cover 63.5% of Iowa's total surface area and 64% of Iowa's croplands. They range in size from 89 to 20,155 km².

Using monthly data and daily data when and where available, we calculated annual flow-weighted average NO_3^--N concentration (mg NO_3^--N L⁻¹), annual NO_3^--N load (Gg NO_3^--N watershed⁻¹ yr⁻¹), and NO_3^--N yield (kg NO_3^--N ha⁻¹ cropland). Nitrate-N yields were estimated using only maize and soybean croplands, which were the major crops cultivated in each watershed (mean = 95% of cropland, across all years and watersheds). The dataset includes 6,379 monthly measurements and 10,325 daily measurements.

Next, using 5-yr moving averages of the three variables, we analyzed each of the 29 watersheds for statistically significant linear trends (a linear model fit to the data with p < .05) in the three nitrate loss variables from 2006 to 2018. We used the 5-yr moving averages to be consistent with the established method for for evaluating causal effects (i.e., nonweather-related) associated with the size of the Gulf of Mexico Hypoxic Zone. We tested for significant linear trends in the 5-yr moving averages of the three nitrate loss variables from 2006 to 2018 because our objective was to determine the interannual variation in these variables owing to interannual variation in weather and the probabilities of measuring temporal trends in reductions in FWNC, load, and yield, should they occur. Hence, we eliminated watersheds with significant changes in the nitrate loss variables from analyses of Monte Carlo simulations (see below). After eliminating watersheds with significant linear trends in nitrate loss variables, we retained 17 watersheds without trends in FWNC and load and 26 watersheds without trends in yield. In an attempt to explain why there were significant trends in FWNC and load for 12 watersheds, we quantified the changes in land use (percent corn and soybean croplands) and discharge for each watershed using 5-yr moving averages from 2006 to 2018. Neither explained the significant trends in FWNC. Although the rate of change in land use did not explain the rate of change in load, the rate of change in discharge explained a large proportion of the across-watershed variation in the change in load $(R^2 = .94;$ Supplemental Materials).



FIGURE 2 Watersheds evaluated in this study. Yellow circles indicate the sample locations. Different colors within each watershed indicate the hydrographic network. The watershed number corresponds to Supplemental Table S1. The dataset was curated by the Iowa Department of Natural Resources Ambient Water Monitoring Program (IDNR, 2017). Daily discharge is taken from USGS stream gauges. The $NO_3^{-}-N$ concentration was measured during the first week of the month in 16 watersheds from 2001 to 2018 and in 13 watersheds from 2001 to 2008. In the 13 watersheds with monthly measurements from 2001 to 2008, the installation of automatic sensors allowed daily measurements from 2012 to 2018; the sensors are operated and maintained by the USGS and the University of Iowa. In watersheds with monthly measurements, water was sampled during the first week of the month was not frozen or dry. In watersheds with monthly sampling, linear interpolation between the samplings during the first week of consecutive months was used to estimate daily $NO_3^{-}-N$ concentration such that concentration measurements of 2 mg $NO_3^{-}-N L^{-1}$ on 1 March and 4 mg $NO_3^{-}-N L^{-1}$ on 1 April would result in a linear daily increase of 0.0645 mg $NO_3^{-}-N L^{-1}$ d⁻¹ across the 31 unmonitored days. In watersheds with daily measurements, sensors were removed just before freezing and installed shortly after thawing. Most watersheds and years include measurements from April through October. We used watersheds and years with daily measurements, to quantify how daily vs. monthly sampling affects the estimate of mean annual flow-weighted $NO_3^{-}-N$ concentration (FWNC). Although estimates of mean annual FWNC for individual watersheds did not significantly differ with the two sampling approaches, the difference in mean annual FWNC ranged from -15 to 22%

Nevertheless, significant trends in nitrate loss variables over time do not necessarily indicate that changes in land use and management were the cause of the trend because the significant linear trends could represent Type I statistical errors (i.e., rejection of the null hypothesis that there is no trend in the 5-yr moving average of the three nitrate loss variables from 2006 to 2018 when in fact the null hpothesis was true; there was no temporal trend [see Figure 1]). Still, we eliminated these watersheds from further analyses because our main objective was to quantify the interannual variability in FWNC, load, and yield that are associated with interannual weather variability. We measured the interannual variation in FWNC, load, and yield in each of the remaining watersheds as the CV of the 5-yr moving average of each of these variables across the 13-yr datasets.

2.1 | Monte Carlo analysis

We used Monte Carlo simulations (Raychaudhuri, 2008) following the approach of Parkin et al. (2012) to estimate the probability of measuring a 41% reduction in the 5-yr moving annual average FWNC, NO_3^- –N loads, and NO_3^- –N yield, should they occur, owing to changes in land use and management in the context of interannual variation in these variables that was observed from 2006 to 2018 in the absence of statistically significant linear trends over time. Monte Carlo simulations use the mean and distribution of a population to generate a random draw. For example, using a normally distributed population with a mean of 100 and a standard deviation of 20, 68% of the draws will fall within 80 and 120 and 95% of the draws will fall within 60 and 140; 2.5% of the draws will be <60 and 2.5% of the draws will be >140. Using Monte Carlo simulations with five consecutive draws, one can estimate the probability of drawing 30, 40, 50, 60, 70—data that would result in a good lieanr model fit. We estimated the probability of measuring the 41% reductions in FWNC, load, and yield, should they occur, across periods of 5, 10, and 15 yr into the future such that the rate of reduction was greatest in the 5-yr scenario and least in the 15-yr scenario. To do this, we adjusted the mean and standard deviation of the population every year into the future so that the probability of random draws with high FWNC, load, and yield decreased every year due to progress toward the 41% reduction but remained a possibility due to interannual variation in weather (i.e., "background variability"; Figure 1).

The Monte Carlo simulations were conducted by generating variates from the unit normal distribution using the Box-Muller algorithm (Box & Muller, 1958) and the Microsoft Excel @RAND function. Our analyses assume that the CV of our data does not change with land use-associated reductions in FWNC, NO₃⁻-N loads, or NO₃⁻-N yield (i.e., the standard deviation of FWNC, NO₃⁻-N load, and NO₃⁻-N yield changes in proportion to the mean FWNC, load, and yield). We tested this assumption by exploring relationships between CVs of FWNC, load, and yield and the percent cropland for each watershed. The CV of FWNC was not associated with land use. The CVs of yield and load were negatively associated with percent cropland (see Results). Hence, our results for load and yield may overestimate the probability of measuring a reduction in nitrate load and yield, should it occur, due to a change in land use if the reduction in croplands increases year-to-year variation in NO3--N load and yield. Nevertheless, the relationship between land use and CVs of load and yield may not be causal; some other factor that leads to high percent cropland within a watershed may also cause the relatively low CVs of load and yield in these watersheds (e.g., soil type); in this case the CVs of load and yield may not increase with a decrease in croplands.

In each watershed without temporal trends in nitrate loss indices from 2006 to 2018, we simulated a 41% reduction in mean annual FWNC, load, and yield linearly across time for each of the three time periods (5, 10, and 15 yr) such that in the 10-yr scenario, 20.5% of the reduction was achieved by Year 5 and 41% was achieved by Year 10. We simulated the 41% reductions 5,000 times [(17 watersheds for FWNC + 17 watersheds for load + 26 watersheds for NO₃⁻–N yield) \times 3 time periods = 180 scenarios and 0.9×10^6 simulations]. The number of watersheds differed for each nitrate loss variable because some of these variables displayed significant linear trends in 5-yr moving average losses from 2006 to 2018 for some variables but not others. We assessed the ability to measure a reduction as a linear model (y = mx + b) fit to the simulated 5-yr moving average FWNC, loads, and NO₃⁻-N yields with a statistically significant negative slope (p < .05). Sub5

sequently, we calculated the proportion of the 5,000 simulations that resulted in a significant negative slope for each of the three nitrate loss variables. The proportion that was significant was equal to the probability of measuring the reduction should it actually occur (e.g., 2,500 significant negative linear slopes in 5,000 simulations is a 50% probability of measuring the reduction).

The remaining simulations represented situations where the interannual weather variability overwhelmed the ability to detect the reduction with a linear model (Figure 1), resulting in a Type II statistical error (i.e., nonrejection of the null hypothesis that there was no trend in nitrate loss when indeed there was). We used a linear model because our goal was to identify the clearest indicator of change that can be easily communicated to stakeholders with limited scientific training. There are statistical and process models that are designed to detect trends in nitrate loss despite interannual variation (e.g., weighted regressions on time, discharge, and season [Hirsch et al., 2010]); that is, situations where a reduction occurred but a linear model could not be fit to the data because of the probabilities of a given random draw from the population (e.g., Figure 1).

2.2 | Explanatory variables

To understand which factors best explain the interannual variability in nitrate losses from the Iowa watersheds, we explored a variety of weather, soil, management, and land use variables and conducted a statistical analysis to explain the across-watershed variation in the CVs of FWNC, NO_3^- –N load, and NO_3^- –N yield. We specifically selected variables that are available in public databases. The dominant land use in Iowa is agriculture, comprised primarily of the annual crops corn and soybean. We used USDA land classification data and calculated annual cropland area based on 30-m resolution rasters for the period 2006–2018 (USDA-NASS, 2017). The percentage of croplands in each watershed was deterimed by summing corn and soybean croplands.

Digital soil information was obtained from the Iowa Gridded Soil Survey Geographic (gSSURGO), a GIS grid coverage of statewide soil series available at 10-m resolution. For each watershed we estimated mean percent SOM from 0 to 30 cm of the cultivated area by intersecting the land classification data and soil gridded maps.

Precipitation data for the 2006–2018 period was obtained from Daily Surface Weather and Climatological Summaries (Oak Ridge National Library, 2020). We calculated for each watershed annual precipitation from daily data on a 1 km by 1 km gridded surface. We calculated the interannual variability of precipitation using the coefficient of variation.

We used tile-drained areas, based on 30-m resolution drained lands following Valayamkunnath et al. (2020), who



FIGURE 3 Coefficients of variation of 5-yr moving average flow-weighted NO_3^--N concentration (FWNC, mg NO_3^--N L⁻¹), nitrate load (kg NO_3^--N watershed⁻¹), and nitrate yield (kg NO_3^--N ha⁻¹ cropland). Each point represents the CV of an individual watershed across the 13-yr monitoring period (2006–2018). The horizontal line represents the median; the edges of each notch represent the upper and lower quartile

estimated the area of tile-drained lands based on four criteria: (a) the county-level tile drainage area (ha) from USDA Census of USDA-NASS (2017), (b) the National Land (Homer et al., 2012) cropland mask at 30-m resolution, (c) the mean slope from Shuttle Radar Topography Mission Digital Elevation Model derived slope (%) at 30 m, and (d) the spatial pattern of soil drainage characteristics based on the SSURGO database at 30 m. The percentage of tile-drained areas was calculated for each watershed. The analysis incorporated data on an annual basis, and data were averaged for the 13-yr period from 2006 to 2018.

We used linear regression to quantify acoss-watershed variation in the CVs of nitrate loss metrics that could be accounted for by individual explanatory variables such as soil properties and land uses. The specific variables are described in Supplemental Table S1. We present explanatory variables that were not colinear. We used simple linear regressions to maximize the utility and transferability of our analyses to other watersheds.

3 | RESULTS

3.1 | Magnitude, variability, and trends in nitrate losses

The interannual variability in 5-yr moving average nitrate load was greater than the interannual variability in FWNC or nitrate yield (Figure 3). Mean annual 5-yr moving average FWNC across the 29 watersheds ranged from 0.6 to 15.5 mg NO₃⁻-N L⁻¹ (mean, 6.7; SD, 2.9). The CV of the 5-yr moving average FWNC across the 29 watersheds ranged from 4 to 23.3% (mean, 11.4; SD, 5.2). Mean annual 5-yr moving average NO₃⁻-N load across the 29 watersheds ranged from 0.07 × 10⁶ to 58 × 10⁶ kg NO₃⁻-N yr⁻¹ (mean, 6.1; SD, 9.1). The CV of the 5-yr moving average NO₃⁻-N load across the 29 watersheds ranged from 17.3 to 48.2% (mean, 27.8; SD, 7.9). Mean annual 5-yr moving average NO_3^--N yields across the 29 watersheds ranged from 3.6 to 78.7 kg NO_3^--N ha⁻¹ of maize and soybean croplands (mean, 28.6; SD, 12.15). The CV of of the 5-yr moving average annual NO_3^--N yield across the 29 watersheds ranged from 17.6 to 52.1% (mean, 29.1; SD, 8.7).

Across the 29 watersheds, from 2006 to 2018, there were increases and decreases in the 5-yr moving average FWNC (-0.29 to +0.33 mg NO₃⁻–N L⁻¹ yr⁻¹) and yield (-1.17 to +1.43 kg NO₃⁻–N ha⁻¹ croplands yr⁻¹). In contrast, in 28 of the 29 watersheds over the same period, there was an increase in the 5-yr moving average nitrate load (-0.009 to 1.43×10^{6} kg NO₃⁻–N watershed⁻¹ yr⁻¹). Of these trends in the nitrate loss variables across the 29 watersheds, 12 were significant for FWNC, 12 were significant for load, and 3 were significant for yield (Figure 4). These watersheds were eliminated from further analyses.

3.2 | Monte Carlo simulations

The probability of measuring a 41% reduction in FWNC was greater than the probability of measuring a 41% reduction in load and yield, should they occur, against the background of interannual variation (Figure 5). Across the 17 watersheds included in our simulations of a 41% reduction in FWNC, the probability of measuring a significant (p < .05; see Materials and Methods) 41% reduction over a 5-yr period ranged from 23.4 to 99.8% (mean, 68%; median, 71.2%; SD, 26.3). The probabilities of measuring the same reductions in FWNC across the 17 watersheds over periods of 10 and 15 yr ranged from 51.7 to 100% (mean, 90; median, 100; SD, 15) and from 71.1 to 100% (mean, 95.6; median, 100; SD, 8), respectively (Figure 5).

For the 17 watersheds included in our simulations of a 41% reduction in NO_3^- –N load, the probability of measuring a significant reduction over 5 yr was below 25.5% in all 17

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FIGURE 4 Rate of change in 5-yr moving average annual flow-weighted nitrate concentration (FWNC, mg NO₃⁻–N L⁻¹), nitrate load (kg NO₃⁻–N watershed⁻¹), and nitrate yield (kg NO₃⁻–N ha⁻¹ cropland) across the 29 watersheds calculated as the linear slope of each variable across years (2006–2018). Blue indicates a decrease; red indicates an increase in the nitrate loss variable. Bars with bolded outlines indicate a significant (p < .05) linear model fit to the data. The watershed ID (y axis) corresponds to Figure 2



FIGURE 5 The probability of measuring a significant reduction in flow weighted NO_3^--N concentration (FWNC; mg $NO_3^--N L^{-1}$), nitrate loads (kg $NO_3^--N yr^{-1}$), and nitrate yields (kg $NO_3^--N ha^{-1}$ cropland yr^{-1}) should a change in land use and management produce a 41% reduction in each of the nitrate loss variables over periods of 5, 10, and 15 yr (y axis)

watersheds (mean, 15.4; median, 13.9; SD, 7.5). The probabilities of measuring the same reductions in annual NO_3^--N load over 10 and 15 yr ranged from 13.6 to 55.3% (mean, 31.1; median, 27.5; SD, 13.5) and from 18.3 to 74% (mean, 43.8; median, 38.9; SD, 18.4), respectively.

Across the 26 watersheds included in our simulations of NO_3^--N yield, the probability of measuring a significant reduction over 5 yr ranged from 5.5 to 27.5% (mean, 12.1; median, 9; SD, 6.1). The probabilities of measuring the same

reductions over 10 and 15 yr increased and ranged from 8.7 to 59.7% (mean, 23.1; median, 16.2; SD, 14.3) and from 10.9 to 78.8% (mean, 32.1; median, 23.1; SD, 19.6).

There was a strong relationship between the probability of measuring reductions in FWNC, loads, or yields and the mean annual CV of these variables across the time period of analysis (2006–2018). The larger the CV, the lower the probability of measuring a signinificant reduction. The shorter the time-line to a reduction (e.g., 5 vs. 15 yr), the lower the probability



FIGURE 6 The relationship between the probability of measuring significant reductions in flow-weighted NO_3^- -N concentration (FWNC; mg NO_3^- -N L^{-1}), nitrate loads (kg NO_3^- -N yr⁻¹), and nitrate yields (kg NO_3^- -N ha⁻¹ cropland yr⁻¹), and the CV of these variables calculated as in Figure 1. Second-degree polynomial and power equations were fit to simulated data (lines) for all three scenarios and all three dependent variables

of measuring a significant reduction (Figure 6) due to lower statistical power associated with fewer data (fewer years).

3.3 | Factors that explain the variability in N losses

The across-watershed variability in CVs of FWNC, load, and yield was explained by dynamic and static factors. The acrosswatershed variability in FWNC CVs was best explained by the percentage of SOM from 0 to 30 cm ($R^2 = .46$; data not shown) (Supplemental Materials). In contrast, the acrosswatershed variability in CVs of loads and yields was explained by percentage of the watershed land use in crops, the CV of annual precipitation, and watershed size (Figure 7). The area of corn and soybean croplands, interannual variability of precipitation, and watershed area did not explain across-watershed variability in FWNC CVs.

4 | DISCUSSION

Despite the use of 5-yr moving averages to evaluate changes in nitrate loss, interannual variability in nitrate loads and yields remains mostly explained by interannual variability in weather (Figure 7); hence, the probabilities of measuring large reductions in nitrate loss, should they occur, over periods of 5–15 yr remain low (Figures 5 and 6). This is a critical finding because progress toward water quality improvement goals is often evaluated with 5-yr moving averages of nutrient loss indices (IDNR, 2017; USEPA, 2015). In the watersheds examined herein, background interannual variability in FWNC, nitrate load, and nitrate yield were typically too large to measure statistically significant 41% reductions in these variables on management-relevant timescales; despite larger annual reductions associated with a 41% reduction over 5 vs. 15 yr, it was more difficult to detect the detection across the shorter monitoring period due to lower statistical power and potentially the effects of irregular climate patterns such as the El Niño Southern Osciliation. Hence, in addition to water quality monitoring, which remains critical, evaluations of progress toward water quality goals should include indicators of variables that are known to reduce nutrient loss, such as inventories of land use (e.g., percent arable croplands, pasture, forest, etc.) and land management practices (e.g., denitrification wetlands, cover crops, etc.). Estimates of the implementation of the land use management practices that are known to reduce nitrate loss indicate that implementation requirements are enormous. For example, the Iowa Nutrient Reduction Strategy identifies seven scenarios of practice implementation that could produce the targeted 41% reduction. One scenario includes application of the universityrecommended N fertilizer rate on all corn croplands, 27% of drained croplands treated with denitrification wetlands, and 60% of drained croplands treated with a denitrification bioreactors (IDNR, 2017). Winter cover crops, which are not included in this scenario, can also reduce nitrate loss, but the average reduction produced by cover crops is 31%, whereas the target loss reduction is 41% (IDNR, 2017).

Nevertheless, some nitrate loss metrics were more robust to interannual variability than others. Our results suggest that FWNC is the most responsive indicator of changes in nitrate loss due to land use change and management. This is consistent with the fact that discharge, like precipitation, accounts for much of the variability in nitrate load and none of the variability in FWNC (Figure 7; Supplemental Materials).

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FIGURE 7 Linear and second-degree polynomial regressions were fit to the CV of flow weighted NO_3^--N concentration (FWNC; mg $NO_3^--N L^{-1}$), nitrate loads (kg $NO_3^--N yr^{-1}$), and nitrate yields (kg $NO_3^--N ha^{-1}$ cropland yr^{-1}) as calculated for each watershed in Figure 1. The shaded area represents the 95% confidence intervals

Indeed, FWNC is weighted to control for the rate of discharge. Hence, the magnitude of FWNC may be driven more by land use, although the data we had access to, including change in land use, could not explain changes in FWNC when they occurred (Figure 4). Nevertheless, at the plot scale, FWNC has been successfully used to identify management effects (e.g., N fertilizer rate and timing, crop variety, etc.) on nitrate loss when there was no effect or a lesser effect of management on load (e.g., Lawlor et al., 2008; Randall et al., 2003). Most past research has focused on annual nitrate load because load is the main driver of the size of the hypoxic zone (Goolsby et al., 2000; Rabalais et al., 2002); however, FWNC does explain some variation in the size of the hypoxic zone (Richards et al., 2021).

Future work should aim to understand if near-term changes in FWNC are predictive of long-term changes in nitrate load and yield. The lower CV of mean annual FWNC compared with nitrate load and yield across all watersheds and years (Figure 3) demonstrates that management-related changes in FWNC can be measured more rapidly than changes in nitrate loads and yields. However, an important question remains: Do changes in FWNC, which can be detected relatively rapidly owing to low year-to-year variability, foreshadow corresponding changes in load and yield that take longer to detect owing to high year-to-year variability?

Our results suggest that FWNC may serve as an early indicator of management-related changes in nitrate loss that is relatively robust to year-to-year variability in weather. In a wet year following drought in 2012, the mean FWNC increased by only 83%, in contrast with loads and yields, which increased by 663 and 529%. Moreover, we found that the across-watershed variability in FWNC, loads, and nitrate yields are all explained to some extent by land use, management, and soils (Figure 7).

Nevertheless, in our dataset, we observed inconsistent trends in FWNC, nitrate load, and nitrate yield. In 28 of the 29 watersheds, the 5-yr moving average annual NO_3^- –N load increased from 2006 to 2018, and the increase was significant in 12 of these watersheds. In contrast, the 5-yr moving annual average FWNC and nitrate yield from 2006 to 2018 did not

consistently increase; in the 12 watersheds with significant trends in FWNC, six were increasing and six were decreasing (Figure 4). These results indicate there may be progress toward nitrate loss reductions despite recent increases in loads because FWNC and NO_3^- –N yields reduce the interannual variability of weather and are more closely associated with land use and management within each watershed (Schilling & Libra, 2000, 2004). Indeed, 5-yr moving average discharge from 2006 to 2018 increased in all 29 waterhseds (Supplemental Materials).

We explored watershed-scale properties that are associated with relatively fast or slow timelines to measuring reductions in nitrate loss (i.e., high or low CVs over the 2006-2018 dataset; Figure 6), purposefully selecting variables from publicly available databases to demonstrate the potential to transfer our concepts to other states and watersheds. The FWNC CV was primarily explained by the positive relationship with SOM, indicating that interannual variability in soil N mineralization may explain some of the interannual variability in FWNC. Indeed, isotope tracer studies demonstrate that most N uptake by the crop and N loss to the environment is derived from SOM rather than N fertilizer (Castellano & David, 2014; Gardner & Drinkwater, 2009). Consistent with this concept, nitrate loss from fertilized corn and unfertilized soybean crops is similar (Christianson et al., 2012), likely because most nitrate loss occurs in the spring when N mineralization from SOM exceeds crop N demand (Martinez-Feria et al., 2018). In north-central Iowa, soils have large pools of SOM; hence, there could be large interannual fluctuations in soil N mineralization, especially given the high interannual variability in precipitation in this region (Knapp & Smith, 2001). In southern Iowa, soils have relatively low SOM levels and low FWNC CVs (Figure 5). Interestingly, soils with high SOM also have high area of cropland and N fertilizer inputs, but we did not find a correlation between FWNC CV and area of corn and soybean croplands (Figure 7). In contrast to FWNC, we observed opposite patterns for nitrate loads and yields. For these variables, watershed properties associated with discharge were the major driver. This was no surprise because discharge is well known to be the most important control on total nitrate load (Randall et al., 1997).

Our results are the first to quantify interannual variability in nitrate loss in the absence of long-term directional trends. We attribute this variability to weather and quantified the time required to measure changes in nitrate loss due to other factors, such as changes in land use and management should they occur. Our results can inform required monitoring intensity to measure directional changes in water quality and identify watersheds where we can more quickly measure changes in nitrate loss variables owing to changes in land use (Figure 5). Our approach differs from methods that aim to detect changes in losses that are due to changes in land use but masked by internnaual variability in precipitation and discharge (e.g., Hirsch et al., 2010). Our approach can be applied to set realistic goals for measuring absolute reductions in nitrate load to the Gulf of Mexico and, alternatively, to quantify the probability of measuring spurious increases or decreases in nitrate loss (Type II errors) due to particular weather patterns (e.g., several wet or dry years) rather than changes in land use and management.

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AUTHOR CONTRIBUTIONS

Gerasimos J. N. Danalatos: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Project administration; Validation; Visualization; Writing – original draft; Writing – review & editing. Calvin Wolter: Data curation; Formal analysis; Writing – review & editing. Sotirios V. Archontoulis: Conceptualization; Writing – original draft; Writing – review & editing. Michael J. Castellano: Conceptualization; Methodology; Project administration; Supervision; Writing – review & editing.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

REFERENCES

- Alexander, R. B., Smith, R. A., Schwarz, G. E., Boyer, E. W., Nolan, J. V., & Brakebill, J. W. (2008). Differences in phosphorus and nitrogen delivery to the Gulf of Mexico from the Mississippi River basin. *Environmental Science & Technology*, 42(3), 822–830.
- Box, G. E. P., & Muller, M. E. (1958). A note on the generation of random normal deviates. *Annals of Mathematical Statistics*, 29(2), 610–611. https://doi.org/10.1214/aoms/1177706645
- Castellano, M. J., & David, M. B. (2014). Long-term fate of nitrate fertilizer in agricultural soils is not necessarily related to nitrate leaching from agricultural soils. *Proceedings of the National Academy of Sciences of the United States of America*, https://doi.org/10.1073/pnas. 1321350111
- Christianson, L., Castellano, M., & Helmers, M. (2012). Nitrogen and phosphorus balances in Iowa cropping systems: Sustaining Iowa's soil resource. In *Proceedings of the Integrated Crop Management Confer*ence. Iowa State University Extension.
- David, M. B., Drinkwater, L. E., & Mcisaac, G. F. (2010). Sources of nitrate yields in the Mississippi River basin. *Journal of Environmental Quality*, 39, 1657–1667. https://doi.org/10.2134/jeq2010.0115
- Oak Ridge National Library. (2020). Daily surface weather data on a 1-km Grid for North America, version 4. https://doi.org/10.3334/ ORNLDAAC/1840
- Dietzel, R., Liebman, M., Ewing, R., Helmers, M., Horton, R., Jarchow, M., & Archontoulis, S. (2016). How efficiently do corn and soybeanbased cropping systems use water? A systems modeling analysis. *Global Change Biology*, 22, 666–681. https://doi.org/10.1111/gcb. 13101
- Gardner, J. B., & Drinkwater, L. E. (2009). The fate of nitrogen in grain cropping systems: A meta-analysis of 15N field experiments.

Ecological Applications, *19*(8), 2167–2184. https://doi.org/10.1890/08-1122.1

- Goolsby, D. A., Battaglin, W. A., Aulenbach, B. T., & Hooper, R. P. (2000). Nitrogen flux and sources in the Mississippi River basin. *Science of the Total Environment*, 248, 75–86. https://doi.org/10.1016/ S0048-9697(99)00532-X
- Hatfield, J. L., Mcmullen, L. D., & Jones, C. S. (2009). Nitrate-nitrogen patterns in the Raccoon River basin related agricultural practices. *Journal of Soil Water Conservation*, 64, 190–199. https://doi.org/10. 2489/jswc.64.3.190
- Hirsch, R. M., Moyer, D. L., & Archfield, S. A. (2010). Weighted regressions on time, discharge, and season (WRTDS), with an application to Chesapeake Bay River inputs. *Journal of the American Water Resources Association (JAWRA)*, 46(5), 857–880. https://doi.org/10.1111/j.1752-1688.2010.00482.x
- Homer, C. H., Fry, J. A., & Barnes, C. A. (2012). The National Land Cover database (U.S. Geological Survey Fact Sheet 2012-302). USGS.
- Iowa Department of Natural Resources (IDNR). (2017). *Iowa's* ambient water quality monitoring and assessment program. https://www.iowadnr.gov/Environmental-Protection/Water-Quality/Water-Monitoring/
- Knapp, A. K., & Smith, M. D. (2001). Variation among biomes in temporal dynamics of aboveground primary production. *Science*, 291, 481– 484. https://doi.org/10.1126/science.291.5503.481
- Lawlor, P. A., Helmers, M. J., Baker, J. L., Melvin, S. W., & Lemke, D. W. (2008). Nitrogen application rate effect on nitrate-nitrogen concentration and loss in subsurface drainage for a corn-soybean rotation. *Transactions of the ASABE*, 51(1), 83–94. https://doi.org/10.13031/ 2013.24229
- Loecke, T. D., Burgin, A. J., Riveros-Iregui, D. A., Ward, A. S., Thomas, S. A., Davis, C. A., & St Clair, M. A. (2017). Weather whiplash in agricultural regions drives deterioration of water quality. *Biogeochemistry*, 133, 7–15. https://doi.org/10.1007/s10533-017-0315-z
- Lu, C., Zhang, J., Tian, H., Crumpton, W. G., Helmers, M. J., Cai, W. -J., Hopkinson, C. S., & Lohrenz, S. E. (2020). Increased extreme precipitation challenges nitrogen load management to the Gulf of Mexico. *Communication Earth Environment*, 1, 21. https://doi.org/10.1038/ s43247-020-00020-7
- Martinez-Feria, R., Castellano, M. J., Dietzel, R., Helmers, M. J., Liebman, M., Huber, I., & Archontoulis, S. V (2018). Linking cropand soil-based approaches to evaluate system nitrogen-use efficiency and tradeoffs. *Agriculture, Ecosystems & Environment*, 256, 131–143. https://doi.org/10.1016/j.agee.2018.01.002
- National Oceanic and Atmospheric Administration (2021). Larger-thanaverage Gulf of Mexico "dead zone" measured. National Oceanic and Atmospheric Administration. https://www.noaa.gov/news-release/ larger-than-average-gulf-of-mexico-dead-zone-measured
- Øygarden, J., Deelstra, J., Lagzdins, A., Bechmann, M., Greipsland, I., Kyllmar, K., Povilaitis, A., & Iital, A. (2014). Climate change and the potential effects on runoff and nitrogen losses in the Nordic-Baltic region. Agriculture, Ecosystems & Environment, 198, 114–126. https://doi.org/10.1016/j.agee.2014.06.025
- Parkin, T. B., Venterea, R. T., & Hargreaves, S. K. (2012). Calculating the detection limits of chamber-based soil greenhouse gas flux measurements. *Journal of Environmental Quality*, 41(3), 705–715. https://doi.org/10.2134/jeq2011.0394
- Rabalais, N. N., Turner, R. E., & Wiseman, W. J. (2002). Gulf of Mexico hypoxia, A.K.A. "The Dead Zone." Annual Review of Ecology, Evolu-

tion, and Systematics, 33, 235–263. https://doi.org/10.1146/annurev. ecolsys.33.010802.150513

- Randall, G. W., Huggins, D. R., Russelle, M. P., Fuchs, D. J., Nelson, W. W., & Anderson, J. L. (1997). Nitrate losses through subsurface tile drainage in Conservation Reserve Program, alfalfa, and row crop systems. *Journal of Environmental Quality*, 26, 1240–1247.
- Randall, G. W., Vetsch, J. A., & Huffman, J. R. (2003). Nitrate losses in subsurface drainage from a corn–soybean rotation as affected by time of nitrogen application and use of nitrapyrin. *Journal of Environmental Quality*, 32(6), 1764–1772. https://doi.org/10.2134/jeq2003.1764
- Raychaudhuri, S. (2008). Introduction to Monte Carlo simulation. In 2008 Winter Simulation Conference (pp. 91–100). Institute of Electrical and Electronics Engineers. https://doi.org/10.1109/WSC.2008. 4736059
- Richards, G., Gilmore, T. E., Mittelstet, A. R., Messer, T. L., & Snow, D. D. (2021). Baseflow nitrate dynamics within nested watersheds of an agricultural stream in Nebraska, USA. *Agriculture, Ecosystems & Environment*, 308, 107223.
- Schilling, K. E., & Libra, R. D. (2000). The Relationship of nitrate concentrations in streams to row crop land use in Iowa. *Journal of Environmental Quality*, 29, 1846–1851. https://doi.org/10.2134/jeq2000. 00472425002900060016x
- Schilling, K. E., & Libra, R. D. (2004). Increased baseflow in Iowa during the second half of the 20th century. *Journal of the American Water Resources Association*, 39, 851–860. https://doi.org/10.1111/j.1752-1688.2003.tb04410.x
- Spijker, J., Fraters, D., & Vrijhoef, A. (2021). A machine learning based modelling framework to predict nitrate leaching from agricultural soils across the Netherlands. *Environmental Research Communications*, 3, 045002. https://doi.org/10.1088/2515-7620/abf15f
- USDA National Agricultural Statistics Service (USDA-NASS). (2017). Census of agriculture. www.nass.usda.gov/AgCensus
- USEPA. (2015). Report on the 2015 U.S. Environmental Protection Agency (EPA) International Decontamination Research and Development Conference (EPA/600/R-15/283). USEPA.
- Valayamkunnath, P., Barlage, M., Chen, F., Gochis, D. J., & Franz, K. J. (2020). Mapping of 30-meter resolution tile-drained croplands using a geospatial modeling approach. *Scientific Data*, 7, 257. https://doi. org/10.1038/s41597-020-00596-x
- Wan, Y., Wan, L., Li, Y., & Doering, P. (2017). Decadal and seasonal trends of nutrient concentration and export from highly managed coastal catchments. *Water Research*, 115, 180–194. https://doi.org/10. 1016/j.watres.2017.02.068

SUPPORTING INFORMATION

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

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