LETTER

Temporal scaling of long-term co-occurring agricultural contaminants and the implications for conservation planning

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Abstract

Stemming the export of agricultural contaminants such as nitrogen, phosphorus, sediment, and bacteria in rivers is needed to improve water quality in agricultural regions. However, patterns and trends of these co-occurring agricultural contaminants are relatively unexplored owing to the lack of long-term and high-frequency data sets needed to capture their fluctuations over different time scales. Using a dataset measured at the Raccoon River in west-central Iowa for more than 17 years, spectral analyses were used to characterize the variability and temporal scaling of co-occurring nutrients, sediment, and bacteria in long-term monitoring data in a water-supply river draining a highly agricultural watershed. Results showed that scaling exponents of pollutant concentrations gradually increased from bacteria (0.27) to sediment (0.64), chloride (1.02), orthophosphate (0.75), and nitrate (1.73). The smaller scaling exponents of bacteria and sediment indicate transport primarily by surface water runoff whereas the larger exponents of nutrients indicate transport by groundwater and subsurface tile drainage. Nitrate export exhibits a chemostatic behavior whereas the other constituents deviate from the chemostatic behavior, indicating that the agricultural watershed has a large reservoir of nitrogen relative to the other pollutants. The results are seen to provide guidance for implementation of conservation practices in agricultural watersheds by helping watershed managers more correctly match the appropriate practice to the dominant hydrologic transport pathway.

1. Introduction

Stemming the loss of nutrients, sediment and bacteria from agricultural regions has been an intractable world-wide problem for 50 years, degrading water quality at the local, regional and continental scales (Mee 1992, Nixon 1995, Howarth et al. 1996, Diaz 2001, Ward et al. 2005, Sprague et al. 2011, Rabalais et al. 2014). Preventing the contaminants sourced to the U.S. Cornbelt from entering the stream network of the Mississippi River Basin (MRB) has been particularly challenging and improvements have been difficult to realize despite years of conservation efforts and U.S. government programs (USEPA 2017, Feng et al. 2019, Secchi and McDonald 2019).

The State of Iowa, with a large fraction of its land in corn and soybean production along with a dense population of food animals, is a disproportionately large contributor of agricultural pollutants to the MRB. Recent assessments show that Iowa contributes 29% of the nitrate-nitrogen (NO$_3^-$-N) load (Jones et al. 2018) and 14.9% of the total phosphorus (TP) load to the Gulf (Schilling et al. 2020), despite occupying only 4.5% of the basin and contributing only 5.9% of the water. Regionally, the Upper MRB that includes Iowa is a significant contributor of total suspended solids (TSS), NO$_3^-$-N, silica and total organic carbon
to the MRB (Turner and Rabalais 2004). Other pollutants sourced to agricultural land use in the MRB include fecal contamination, traditionally measured by fecal indicator bacteria (Schilling et al. 2009). It is likely that any random grab sample of river water flowing through Iowa and the U.S. Cornbelt would contain variable quantities of all of these typical agricultural pollutants at any given time, given the abundance of sources and the quantities of each contaminant that are vulnerable to transport to the stream network in this landscape. How the patterns and processes of transport relate between these contaminants has not been explored in depth. Transport pathways for contaminants in the particulate form (e.g., *Escherichia coli*) will differ from those that in a dissolved state (e.g., NO$_3$−N, and orthophosphate (OP)). Designing strategies to focus on overall water quality improvement will require improved characterization of multiple contaminants’ temporal co-occurrence in river water, so that cost-effective and broadly effective remedial strategies can be developed. While conservation practices targeting a single contaminant such as NO$_3$−N are well-developed (Dinnes et al. 2002), multi-contaminant remediation is not common and the transport processes simultaneously governing multiple contaminants remain largely unquantified.

Spectral analysis has been widely applied to long-term records of hydrological and chemical variables in rivers, soils, and groundwater. A time series is considered to be a temporal fractal or has temporal scaling if its power spectrum follows the power law form (Feder 1988, Turcotte 1992). The spectrum slope is typically called the scaling exponent and it is considered a key parameter to identify the fractal characteristics of a time series. The power spectrum has been adopted to determine the periodic components and to reveal temporal scaling of the rainfall and streamflow (Tessier et al. 1996, Zhang and Schilling 2005), soil moisture (Katul et al. 2007, Yang et al. 2018), groundwater levels (Zhang and Schilling 2004, Zhang and Li 2005, 2006, Bloomfield and Little 2010, Schilling and Zhang 2012, Liang and Zhang 2013, 2015, Yang et al. 2016), NO$_3$−N concentrations in spring (Schilling et al. 2019), and stream chemistry (Kirchner et al. 2000, Godsey et al. 2010, Kirchner and Neal 2013, Aubert et al. 2014, Benettin et al. 2015, Hensley et al. 2018).

In this study, we analyzed the power spectra of river flow and water quality in an Iowa river draining an intensely-agricultural region. Since the river is utilized as a regional water supply source for a large water supply utility, long-term monitoring data available for TSS, chloride (Cl$^-$), OP, NO$_3$−N and *E. coli* allow for characterization of the co-occurrence and spectral signatures of these agricultural contaminants in the same river system over the same period of time. Our study objectives were to (a) quantify the power spectra and scaling exponents of individual agricultural pollutants; (b) compare and contrast the spectra among pollutants to identify characteristic behavior indicative of pollutant sources and hydrologic flow paths; and (c) discuss implications for improved implementation of multi-contaminant remediation strategies to reduce agricultural pollution in agricultural watersheds.

2. Data and methodology

2.1. Study area

The Raccoon River watershed drains a 9389 km$^2$ area in the central part of the U.S. cornbelt state of Iowa (figure S1 available online at stacks.iop.org/ERL/16/094015/mmedia). The three main branches (North, Middle, and South Raccoon Rivers) join near Van Meter, Iowa, and their combined flow discharges into the Des Moines River about 50 km downstream of Van Meter. The largest of the three branches, the North Raccoon River, flows through the recently-glaciated Des Moines Lobe landform (Prior 1991). Low relief and poorly developed natural drainage require networks of buried porous pipes (tiles) and constructed ditches to remove water that might otherwise reduce yields of corn and soybean. The South Raccoon River drains a portion the older pre-Illinoian Southern Iowa Drift Plain, also a glacial landscape but with more relief and well-developed natural drainage (Prior 1991). The Middle Raccoon drains water from both the Des Moines Lobe and the Southern Iowa Drift Plain. Row crop agriculture dominates land cover throughout entire Raccoon basin, with nearly 80% of the area cultivated for corn and soybean (Jones and Schilling 2011) and poultry, hog, and cattle production are common (Jones et al. 2017).

2.2. Water quality and discharge data

All water quality samples were collected from the Raccoon River near its outlet in the City of Des Moines and analyzed by the Des Moines Water Works (DMWW), the public water supply utility serving a metropolitan area of 400,000 people. The DMWW operates a state-certified laboratory where water monitoring is conducted to support plant operation and compliance with regulations. Because of its importance as a source of drinking water, many researchers have used DMWW data to characterize the patterns and processes associated with contaminant loss to the Raccoon River and its tributaries (Lucey and Goolsby 1993, Schilling and Lutz 2004, Jha et al. 2007, Hatfield et al. 2009, Schilling et al. 2009, Feng et al. 2013, Villarini et al. 2016a, Jones et al. 2017). Grab samples were collected daily Monday through Friday from the DMWW’s intake structure by lowering a sample collection apparatus into the flowing water. Samples are immediately delivered to the DMWW laboratory for analysis. This study focused on five water quality parameters: TSS, OP, NO$_3$−N, Cl$^-$ and *E. coli*, all reported as mg l$^{-1}$ except *E. coli* which was reported as Most Probable Number (MPN) 100 ml$^{-1}$.
Method 300.0 (Pfaff 1996) was used to quantify P, NO₃-N, and Cl. TSS was quantified using turbidity as a proxy as has been previously reported by Jones and Schilling (2011). E. coli was quantified using the IDEXX Colilert Quanti-Tray 2000 bacterial enumeration procedure for water samples (IDEXX Laboratories). Daily discharge for the Raccoon River were obtained from the United States Geological Survey gauging station at Van Meter, Iowa. Over the ~17 year monitoring period from 1 January 1997 to 23 June 2014 (6383 d), TSS, OP, NO₃-N, Cl and E. coli were measured on 4341, 2156, 3340, 3266, and 4197 d, respectively (figure 1), about half of all calendar days for most water quality parameters.

2.3. Theory of spectral analysis
The spectral analysis is widely used in the analysis of time series because it provides a frequency decomposition in harmonics the behavior of which can be studied separately. Power spectra $S(f)$ of a continuous time series $x(t)$ is defined as the modulus square of Fourier transform of $x(t)$, i.e.

$$S(f) = |X(f)|^2 = \left[ \int_{-\infty}^{+\infty} x(t) \cos(2\pi ft) dt \right]^2 + \left[ \int_{-\infty}^{+\infty} x(t) \sin(2\pi ft) dt \right]^2$$

where $X(f)$ is the Fourier transform of $x(t)$ and $f$ is frequency. The power spectrum displays the fluctuation intensity or variances per unit frequency of $x(t)$. We usually have a time series measured over a finite period and with a finite sample interval such as the observed stream chemicals of this study. Therefore, the discrete Fourier transform needs to be employed to estimate power spectra of a discrete time series. The measured contaminants of this study contained some data gaps due to variations in sample collection by the DMWW. Analyzing such an irregularly gapped time series requires special Fourier analysis techniques. In this study, we used the software package REDFIT 3.5 (Schulz and Mudelsee 2002) to estimate the power spectra, which was widely used to estimate spectra directly from unevenly spaced time series.

A power spectrum is often used to determine the periodic components of the time series. It is also a powerful tool to analyze temporal scaling or fractal characteristic of a time series. It has been recognized that a time series is a temporal fractal or has temporal scaling if its power spectrum follows the power law form $S(f) \propto f^{-\beta}$, where $\beta$ is the fractal scaling exponent (Feder 1988, Turcotte 1992). The scaling exponent ($\beta$) is a key parameter to identify the fractal characteristics of a time series. The fluctuations of time series behave as the fractional Gaussian noise (fGn) when $0 < \beta < 1$ and the fractional Brownian motion (fBm) when $1 < \beta < 3$ (Mandelbrot and Van Ness 1968). In addition, the scaling exponent is relevant to the auto-correlation of a time series (Zhang and Schilling 2005, Liang and Zhang 2015, Yang et al 2018): the larger the scaling exponent, the
more temporally correlated or persistent is the time series. The correlation scale or persistence reflects the mechanisms of solute release and transport in a watershed (Kirchner et al. 2000, 2001).

Fourier analysis also can be used to gain insight into the chemostatic behaviors of the chemical constituents transported in watersheds by evaluating the ratio for the spectra of chemical loads (L) and stream discharges (Q) (Guan et al. 2011). Chemostatic behavior refers to a condition when the chemical load is a linear function of discharge, meaning that the flow weighted value of concentration was essentially constant. It implies that the chemical constituent has a large accumulated store in watersheds (Godsey et al. 2009). Chemostatic behavior provides an appropriate description of the export dynamics of a range of geologically derived solutes. The chemostatic behavior of solutes in rivers are recognized by several previous studies (Godsey et al. 2009, Basu et al. 2010, Guan et al. 2011). Specifically, the Fourier transform of the chemical loads is given by (Guan et al. 2011)

\[ L(f) = \int_{-\infty}^{\infty} \exp(i2\pi ft) C(t)Q(t) dt = C_c Q(f) \]  

where \( C_c \) is assumed as a constant. The ratio of the spectra of loads and discharge can be written as

\[ C_c^2 = \frac{|L(f)|^2}{|Q(f)|^2} = \frac{S_L}{S_Q} \]  

where \( S_L \) and \( S_Q \) are the spectra of loads and discharges, respectively. The chemical constituent is considered to be chemostatic when the ratio of the spectra \( (C_c^2) \) is close to white noise. In this study, the loads of TSS, CI, OP, NO\textsubscript{3}-N, and \textit{E. coli} are respectively obtained by multiplying their concentrations by the stream discharge. Then the spectra of loads are obtained using equation (1). Finally, the ratios for power spectra of the loads and the stream discharges are determined by equation (3).

3. Results

3.1. Water quality and discharge

Water quality and discharge for the period of 1 January 1997 to 23 June 2014 were displayed in figure 1 and were summarized in table S1. Average values were similar to the medians for the solute parameters of CI, OP and NO\textsubscript{3}-N, but were \sim 3–15 times higher than the median for discharge, TSS and \textit{E. coli}. values were especially variable, ranging from 0 to 130 000 MPN 100 ml\textsuperscript{-1}. Daily discharge \( (Q) \) ranged over three orders of magnitude from 0.9 m\textsuperscript{3} s\textsuperscript{-1} (3 March 2014) to 1130 m\textsuperscript{3} s\textsuperscript{-1} during the historic flood of 2008 (12 June). TSS concentrations ranged from 0 to nearly 7000 mg l\textsuperscript{-1} with an average of 169 mg l\textsuperscript{-1}. NO\textsubscript{3}-N was measured at levels <0.1 mg l\textsuperscript{-1} numerous times during abnormally dry weather conditions, but >24 mg l\textsuperscript{-1} during the wet spring of 2013, which followed a period of extended drought. CI concentrations ranged from 5 to 308 mg l\textsuperscript{-1} with an average of 26 mg l\textsuperscript{-1}, while OP ranged from 0.01 to 1.9 mg l\textsuperscript{-1} with an average of 0.17 mg l\textsuperscript{-1}.

3.2. Spectra of pollutants

The power spectra of the measured TSS, CI, OP, NO\textsubscript{3}-N, \textit{E. coli} and Q are presented in log-log scales in figure 2. It is seen that all of the power spectra exhibit a power law form or can be fitted with the straight lines of different slopes within at least two orders of frequencies, indicating that these time series behave as temporal fractals. However, the slopes of the power spectra or the scaling exponents (\( \beta \)) of the variables are different (table S2). The \textit{E. coli} has the smallest scaling exponent (\( \beta = 0.27 \)) that is closest to the exponent of a white noise (\( \beta = 0 \)). The scaling exponents of TSS and OP are 0.64 and 0.75, respectively, indicating they are f\textsuperscript{Gn}. In contrast, the scaling exponent of CI is close to 1, meaning CI behaves as a 1/f\textsuperscript{Gn} fractal signal, a feature that was recognized in previous studies (Kirchner et al. 2000, Kirchner and Neal 2013, Aubert et al. 2014, Benettin et al. 2015). A crossover point was observed in the power spectrum of NO\textsubscript{3}-N that was fitted with two straight lines. The scaling exponent of the spectrum of high frequencies was 1.76 whereas that of low frequencies was 0.69. Such time series are usually defined as multifractal signals (Tessier et al. 1996, Boufadel et al. 2000, Ivanov et al. 2001). The multifractal NO\textsubscript{3}-N in streams has also been reported in previous studies (Aubert et al. 2014, Hensley et al. 2018). Similar to the NO\textsubscript{3}-N, there was a crossover in the spectrum of the streamflow: the scaling exponent at high-frequencies was 1.80 and that at low frequencies was 0.90 (table S2).

The main periods of the spectra were identified with the spectral analysis. A peak was observed at \( f = 2.74 \times 10^{-3} \) 1/day in each of the spectra of the measured variables except OP (figure 3), i.e. all of the variables except OP have an annual period (\sim 365 d). This indicates that the concentrations of these components fluctuate seasonally (except OP). In addition, there was a peak at \( f = 5.48 \times 10^{-3} \) 1/day or a semi-annual period (\sim 182 d) in the spectra of \textit{E. coli}, NO\textsubscript{3}-N and Q but this peak was absent in the spectra of TSS, OP, and CI. The semi-annual peak for \textit{E. coli} was consistent with previous study by Schilling et al. (2009). Interestingly, there was no annual or semi-annual period in the spectrum of OP; instead its spectrum had a noticeable peak at \( f = 9.96 \times 10^{-2} \) 1/day or a period of \sim 91 d.

In short, the scaling exponents among the agricultural pollutants were observed to gradually increase from \textit{E. coli} to TSS, OP, CI, NO\textsubscript{3}-N and Q (table S2).
All the variables except OP have an annual period and the variables, \textit{E. coli}, NO$_3$-N, and Q also have a semi-annual period. The variable OP has a shorter period of 91 d. Overall, the different scaling exponents and periods of the variables appear to largely relate to the different sources and transport pathways in the watershed.

In addition, the ratios of power spectra of the measured loads for TSS, CI, OP, NO$_3$-N, and \textit{E. coli} are presented in log-log scales in figure 4. It shows that the ratio of power spectra for NO$_3$-N is very close to white noise for all time scales and the CI slightly deviates the white noise, indicating that the export dynamics of both NO$_3$-N and CI could be approximated as chemostatic behaviors. Except for NO$_3$-N and CI, however, the ratios of power spectra of the other substances significantly deviate the white noise, meaning that the exports of these substances do not have chemostatic behaviors.

4. Discussion

4.1. The sources and transport pathways of \textit{E. coli}

With the smallest scaling exponent ($\beta = 0.27$), the fluctuation of the \textit{E. coli} concentration is weakly persistent, which is consistent with the previous study.
by Schilling et al (2009) who found that the correlation scale of the E. coli to be approximately 4 d. The time range of the temporal correlation falls within the typical duration of many surface water runoff events in large watersheds such as the Raccoon River (Schilling et al 2009). In addition, the small scaling exponent of E. coli is close to that of the rainfall which is widely recognized as a white noise (Kirchner et al 2000, Zhang and Schilling 2004). Therefore, the spectrum of E. coli concentrations reflects mainly the transport and delivery of bacteria with surface water runoff. The reason is that in a watershed containing large numbers of concentrated animal feeding operations of primarily swine and poultry, cattle feedlots and grazed pastures, surface water runoff can regularly deliver E. coli sourced from animal waste to the stream network. The two peaks in spectral density of E. coli concentrations in the Raccoon River at 365 and 183 d largely reflect annual and seasonal patterns in precipitation and river discharge. Higher E. coli concentrations are associated with periods of greater precipitation (April through August) and runoff (primarily May and June with smaller peaks in November).

4.2. The sources and transport pathways of TSS
The scaling exponent for TSS (0.64) is larger than that of the E. coli and the temporal fluctuations are considered weakly persistent. Similar to E. coli, TSS is also primarily delivered to streams with surface water runoff but TSS sources include both upland sheet and rill contributions (Schilling et al 2011) as well as in-channel streambed and bank sources (Beck et al 2018). Upland sediment is usually carried into streams by overland flow during heavy rainfall and its travel path is longer than that of E. coli since erosive sediments are everywhere in a watershed. In contrast, in-stream TSS sources have a short travel path and contribute to TSS export whenever geotechnical constraints are met (Wilson et al 2008). We hypothesize that the contributions from both sources and variable long and short-term travel paths increase the scaling exponent beyond a simple E. coli runoff response model. In Midwestern regions, upland sources tend to dominate TSS export during the first flush of rainfall runoff whereas streambank failure and in-channel erosion dominate during the recession period (Wilson et al 2008). Combined, these two sources extend the persistence in the TSS time-series record but it is clear that TSS concentrations similarly respond to seasonal patterns in precipitation and river discharge with one peak in spectral density at annual period (~365 d).

4.3. The sources and transport pathways of OP
The scaling exponent for OP (0.75) is larger than TSS and it appears to reflect the mixing of multiple sources and hydrologic pathways. P losses can occur through highly episodic, event-driven transport or through more continuous groundwater or tile drain discharge (Kleinman et al 2002, Sharpley et al 2002). Episodic P delivery is dominated by P attached to soil particles (particulate P), whereas groundwater or tile drainage sources are typified by soluble P present in the water (typically OP) (Schilling et al 2018). In most Iowa watersheds, particulate P sources dominate TP export so if we had analyzed the spectrum of TP concentrations, we suspect that the spectrum would have been very similar to TSS. However, OP sources include runoff following surface application of liquid swine manure or inorganic P fertilizers (Kleinman et al 2002, Sharpley et al 2002, Allen...
and Mallarino 2008), or leaching from soils with high soil-test P levels that is discharged to rivers from baseflow, either as groundwater seepage or tile drainage. Background concentrations of OP in shallow Iowa groundwater are quite high (Schilling et al 2020) and groundwater discharge of OP to streams contributes to a higher spectral exponent for this parameter. We suspect that the combined surface and subsurface sources of OP reduce the signal of seasonal periodicity in the time-series record.

4.4. The sources and transport pathways of Cl
The scaling exponent of Cl (1.02) is consistent to previous studies (Kirchner et al 2000, Kirchner and Neal 2013, Aubert et al 2014, Benettin et al 2015). These studies have posited that the Cl is primarily sourced from the atmosphere and the fluctuation of Cl concentration in precipitation is close to a white-noise or $\beta = 0$ (Kirchner et al 2000, 2010, Shaw et al 2008, Godsey et al 2010, Kirchner and Neal 2013). Then, in this simple case, the scaling exponent of Cl in the Raccoon River ($\beta = 1.02$) would indicate that the watershed acts as a 1/f fractal filter, converting nearly white-noise atmospheric inputs into fractal streamflow outputs. However, in cold-climate locations, additional Cl inputs are derived from road salt contamination of groundwater which has been recognized in many studies (Williams et al 2000, Jackson and Jobbagy 2005). Road salt (i.e. various Cl salts) is the most widely used deicer in the United States and its use has escalated over the last 70 years (Corsi et al 2015). In one Iowa watershed, urban areas with road salt applications contributed approximately 23% of the Cl loading to the stream despite only occupying 5% of the land area. Thus, like OP, Cl can be delivered to streams in two paths, a surface runoff path during heavier rainfalls and a subsurface groundwater discharge path (baseflow). The surface path is relatively short, resulting in a small scaling exponent (e.g. E. coli) while subsurface path is relatively long and tortuous owing to the nature of porous media, resulting in a larger scaling exponent. Aquifers are known to act as a 1/f$^2$ fractal filter, converting the white-noise recharge into fBm outputs (e.g. groundwater levels and baseflow) (Zhang and Schilling 2004, 2005, Zhang and Li 2005, 2006, Liang and Zhang 2013, 2015, Yang et al 2018). Therefore, the 1/f fractal fluctuations of Cl in the river may be the mixing effects of the surface and subsurface deliveries while the proportion of subsurface path of Cl may be larger than that of OP owing to the larger scaling exponents.

4.5. The sources and transport pathways of NO$_3$-N
NO$_3$-N and streamflow have larger scaling exponents and multifractal characteristics that reflect a more complicated delivery path in the watershed. First, the large scaling exponents of NO$_3$-N and streamflow in high frequencies are the result of subsurface flow that dominates the delivery path of the NO$_3$-N and streamflow in the watershed. It was recognized that the baseflow may contribute as much as two-thirds of the mean annual NO$_3$-N export in the Raccoon River (Schilling and Zhang 2004). In addition, in drained areas, subsurface tiles provide an additional pathway for NO$_3$-N and water transport; Schilling et al (2019) reported that subsurface drainage tiles contributed half of the annual discharge in an Iowa river and accounted for a majority of flow in the river from March to June. Tile drainage is also the main source of NO$_3$-N concentrations to streams, routinely exceeding 20 mg L$^{-1}$ at tile outlets (Tomer et al 2003, Ikenberry et al 2014). NO$_3$-N concentrations primarily derived from fertilizer and manure applications (Jones et al 2018) are damped by the interactions within soils and aquifer materials, resulting larger scaling exponents observed in streams fed by baseflow and tile drainage (Yang et al 2016, 2018, Chen et al 2019). Second, the streambank storage and the dynamic exchange of surface groundwater may also affect the fractal behaviors of the NO$_3$-N and streamflow and cause the multifractal fluctuations. Surface water-groundwater exchanges induced by geomorphology contribute to power law residence time distributions (RTDs) (Cardenas 2008) that result in temporally fractal river chemistry. Liang et al (2018) found that the dynamic surface water-groundwater exchanges may contribute to the power law RTDs as well. Since streambanks are also a biogeochemical hot spot (McClain et al 2003), denitrification in this region will further affect the temporal variations of NO$_3$-N. Both temporal and spatial variations in surface water-groundwater exchanges in streambanks will dampen the exchange of NO$_3$-N and baseflow with streams and steepen their spectra slopes at high-frequencies, resulting in the multifractal signal. Third, river network also contributes the multifractal characteristics of NO$_3$-N due to in-channel damping of solute variability (Riml and Worman 2015, Hensley et al 2018). At network scales, the in-channel damping effects arise from geomorphic dispersion and kinematic dispersion. The effects of river networks steepen the spectra slopes of the solute, nevertheless this effect is limited to the very high-frequency of the spectra owing to the rapid solute transport in stream channels relative to solute transport in the watershed (Hensley et al 2018).

4.6. The chemostatic behaviors
The chemostatic behaviors of NO$_3$-N export from the Raccoon River watershed are similar to conditions recognized in other agricultural watersheds (Godsey et al 2009, Basu et al 2010, Guan et al 2011). The Raccoon River watershed, like most cropped areas Iowa, has a large, accumulated store of N within loamy soils, stemming from of an abundance of N in the natural, organic-rich glacial soils along with continual N replenishment with commercial fertilizer and manure (Jones and Schilling 2011, Jones et al 2018). Fertilizers
such as anhydrous ammonia or urea-ammonium nitrate are applied in the fall or spring to corn rotations (Sawyer et al. 2006), and while fertilization clearly increases the supply of N on the landscape, native soil N levels can exceed 10,000 kg ha$^{-1}$ (Russell et al. 2005, Hernandez-Ramirez et al. 2011). Jones et al. (2017) noted that NO$_3$-N export in Iowa watersheds is often transported limited (not supply) because of the large quantity of N available in the landscape.

Unlike NO$_3$-N, OP significantly deviates from the chemostatic behavior. While recent work suggests that background Iowa groundwater contains OP concentrations around 0.1 mg l$^{-1}$ (Schilling et al. 2020), OP concentrations in rivers will vary with rainfall runoff and discharge (Wang et al. 2016). CI export is close to exhibiting chemostatic behavior but less than NO$_3$-N. CI is primarily sourced from the atmosphere which will cause CI loads to be approximated as a linear function of stream discharge. However, it is important to also note that in cold-climate locations, additional CI inputs are derived from seasonal road salt applications. The seasonal applications provide a finite reservoir of CI that will be depleted by ongoing efflux, arguing against the chemostatic behavior. The exports of both TSS and $E. coli$ significantly deviate from chemostatic behavior, implying that these two constituents have the finite reservoirs which could be depleted by ongoing efflux.

In summary, the diverse sources and delivery paths of the agricultural pollutants in the watershed can be revealed from the long-term and high-frequency time series based on the spectral analysis (figure 2). $E. coli$ sourced from manure application and feedlots and TSS derived from upland and in-channel erosion are mainly delivered to the river by the surface water runoff whereas OP and CI are derived from multiple sources and delivered to streams by both the surface and subsurface flows. NO$_3$-N concentrations are sourced to widespread N applications to agricultural row crop lands and overwhelmingly driven by subsurface groundwater and tile drainage flows to the Raccoon River. In addition, the chemostatic behavior of NO$_3$-N export reflects the presence of a large reservoir of nitrogen in the Raccoon River watershed.

5. Implications for conservation planning

The spectral exponent values of various agricultural pollutants have implications for improving our understanding of pollutant transport and for conservation planning in watersheds (figure 5). The temporal patterns of co-occurring agricultural pollutants in the Raccoon River are very different and signal that multiple strategies may be needed to simultaneously reduce their concentrations such that an overall improvement in downstream water quality is manifested.

In watersheds threatened by pollutants with small exponents such as $E. coli$ and TSS, control of surface flows is critically important. Practices such as no-till, grass waterways, terraces, contour filter strips, and sedimentation basins that serve to slow or capture runoff will reduce downstream delivery of bacteria and sediment. Installation of riparian buffers in sloping landscape areas can also reduce nutrient and sediment delivery to streams (Dosskey 2001). For OP and CI concentrations that have mixed hydrologic pathways and spectral exponents near 1, both runoff and leaching need to be reduced. In addition to practices that reduce runoff, strategies to reduce subsurface OP export include decreasing P applications rates (King et al. 2015) and incorporating fertilizer after application (Kleinman et al. 2009). CI reductions will also require a more specific source control that is focused on reducing the application of road salt deicers in the
region, because its solubility and lack of biological uptake limit options for mitigation. In watersheds dominated by NO$_3$-N with a spectral exponent of 1.7, conservation practices are needed that retain water and nutrients in the soil profile (controlled drainage) (Thorpe et al. 2008) or pass the nutrient-laden water though subsurface carbon filters (bioreactors) (Jaynes et al. 2008), or re-saturated buffers (Jaynes and Isenhart 2014). Use of restored or constructed wetlands to intercept and treat subsurface drainage water is often effective for nitrogen reductions in these poorly drained areas (Dake et al. 2018, Crump ton et al. 2020). Finally, it is important to note that practices such as land use change, cover crops, and other perennial cover that improve soil health (Tomer et al. 2015) can affect all the agricultural pollutants, serving to reduce soil erosion and loss of P (Basche et al. 2016), and sequester soluble NO$_3$-N and OP (Kaspar et al. 2012) across all seasons regardless of their method of delivery and spectral exponents.

6. Conclusions

Common pollutants such as E. coli, TSS, OP, CI, NO$_3$-N co-occur in surface water draining agricultural watersheds. In this study of the Raccoon River in west-central Iowa, we showed that scaling exponents of the power spectra of their concentrations gradually increased from E. coli, to TSS, OP, CI, to NO$_3$-N. The different scaling exponents and correlation periods of the pollutants largely relate to different sources and transport pathways in the watershed, with smaller scaling exponents indicating transport by surface water runoff (E. coli, TSS) whereas larger exponents indicate transport by groundwater and subsurface tile drainage (NO$_3$-N). Intermediate exponents shown by OP and CI indicate both hydrologic transport pathways. The chemostatic behavior of NO$_3$-N export reflects the presence of a large reservoir of nitrogen in the agricultural watershed, whereas other co-occurring pollutants appeared to have a largely finite reservoir. Overall study methodology and results are seen to provide additional guidance for implementation of conservation practices in agricultural watersheds by helping watershed managers more correctly match the appropriate practice to the dominant hydrologic transport pathway.

Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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