# Long-term temporal variation of nitrate concentration-stream discharge (C-Q) relationship for an agricultural watershed in Midwest USA

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## Introduction

- Nutrients export from agricultural watersheds have long been recognized as a critical cause of eutrophication in receiving surface water bodies.
- Since 1970s, many changes have occurred in intensively managed, agricultural watersheds in U.S., including increased weather extremes, enhanced artificial drainage, timing and rate of fertilizer applications, and implementation of conservation tillage practices.
- Nutrient concentration – discharge relationship (C-Q relationship) can identify periods and locations influencing the change in nutrient export in stream discharge, which could help infer the relationship between observed changes in nutrient export to factors that cause these changes.
- We hypothesize that the long-term pattern of C-Q relationship would change in response to changes in climate, land use, and management practices that happened over the past 40 years.
- To test the hypothesis, we analyzed the long-term variation of nitrate C-Q relationship in an agricultural watershed in Ohio across different time scales, using a dataset of relatively high-frequency measurements of stream flow and nitrate concentrations.

## Watershed description

- Honey Creek Watershed, Ohio, U.S.
- Land use: 84% of agricultural and 10% of forest.
- 90% of soil is classified as poorly drained.
- Data were provided by the Ohio Tributary Monitoring program that is operated by the National Center for Water Quality Research at Heidelberg University.

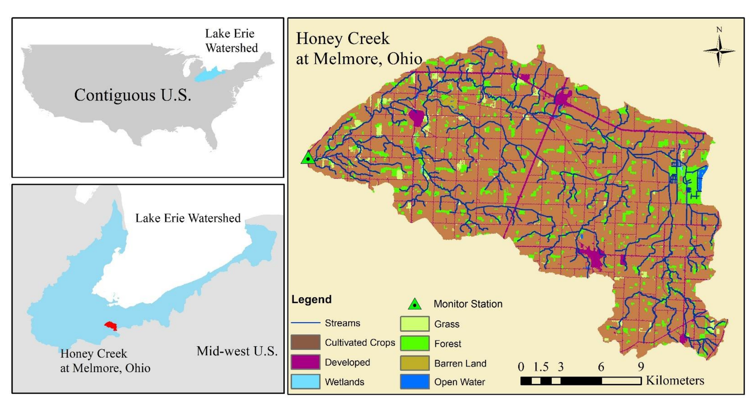



Fig. 1 Honey Creek watershed in OHIO, U.S.

- Measured stream flow data USGS station 04197100 from Jan 1976 to April 2017 was used in this study.
- Nitrate concentration was based on 21,191 water quality samples.
- Water quality samples were taken at least once per day and three or four samples per day during storm events

## Composite C-Q relationship

- Power equation:
  - ❖ $C = aQ^b$ ( $\log C = \log a + b * logQ$ )
  - ❖ Slope (b) represents the chemo -dynamics of C-Q relationship

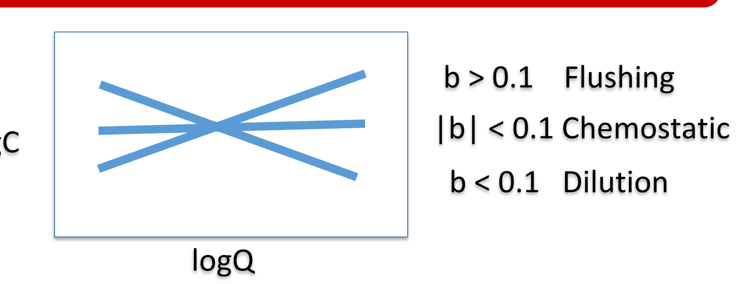
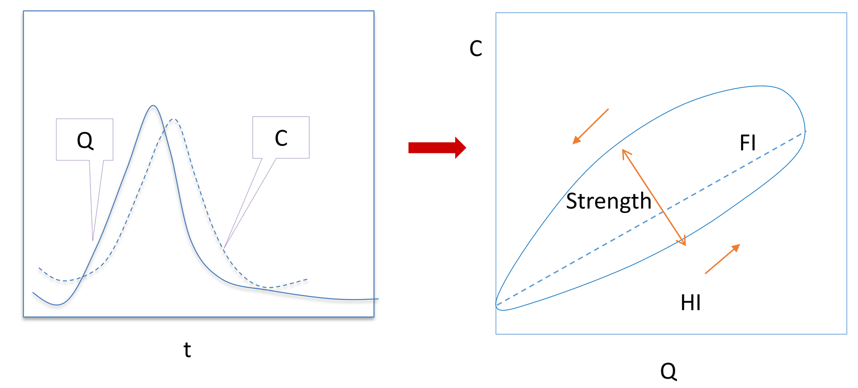



Fig. 2 Demonstration of slope (b)

- Weighted Regressions on Time, Discharge and Season (WRTDS)
  - ❖ $\ln(C_i) = \beta_{0,i} + \beta_{1,i}t_i + \beta_{2,i}\ln(Q_i) + \beta_{3,i}\sin(2\pi t_i) + \beta_{4,i}Cos(2\pi t_i) + \varepsilon_i$
  - ❖ $\beta_2$ as an indicator of C-Q relationship (similar to slope).
  - ❖ Decompose overall C-Q relationship into different years, discharge ranges and seasons.

## Metrics to characterize hysteresis patterns




a) Time series data b) Non-linear C-Q relationship

Fig. 3 The demonstration of non-linear C-Q relationship and associated hysteresis metrics.
a) shows the time series data of drainage/stream flow and nitrate concentration. b) is the plot of nitrate concentration against drainage/stream flow

- Hysteresis Index (HI):
  - ❖ Quantifies the direction and strength of hysteresis loop.
  - HI > 0 clockwise loop
  - HI < 0 anti-clockwise loop
- Flushing Index (FI):
  - ❖ Quantifies the concentration or dilution of nitrate at the rising limb.
  - FI > 0 Nitrate flushing during events
  - FI < 0 Nitrate dilution during events

## Preliminary results and discussion

- Long-term inter-annual pattern of C-Q relationship:
  - ❖ Relatively stable at decadal scales.
  - ❖ No significant change in storm hysteresis patterns at decadal scales.
  - ❖ 75% of nitrate export contributed by flow greater than 5 m³/s.

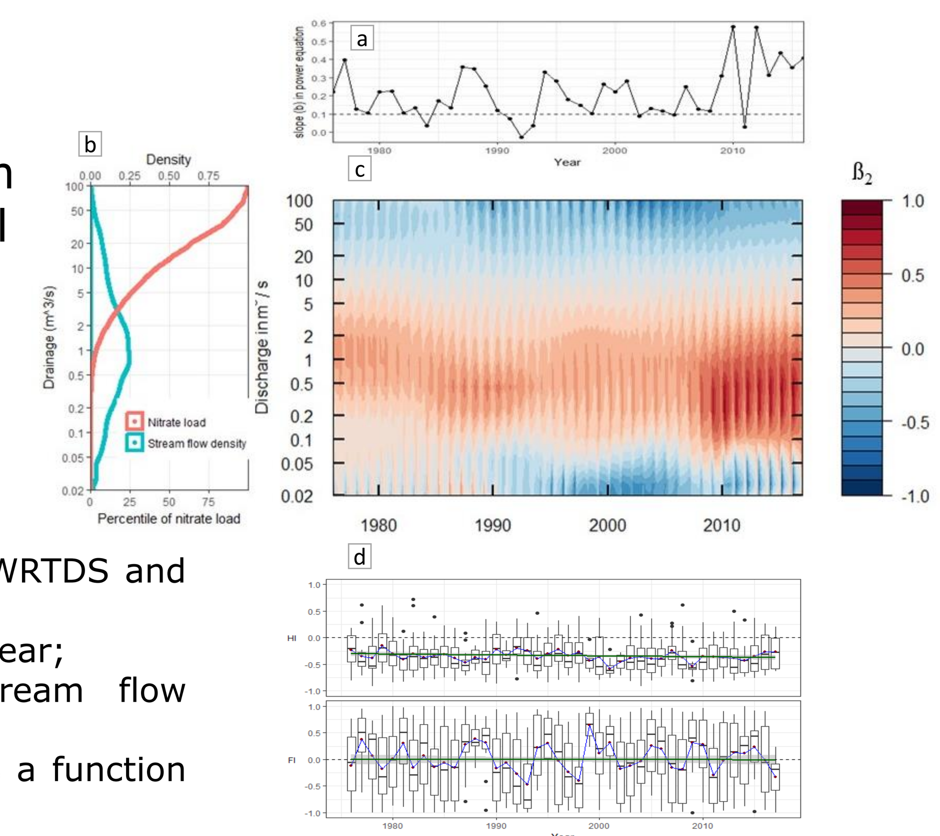



Fig. 4 Long-term C-Q relationship from WRTDS and storm hysteresis patterns.
a) Slope (b) in power equation for each year;
b) Cumulative nitrate loading and stream flow distributions;
c) Long-term temporal variation of $\beta_2$ as a function of time and stream discharge;
d) Long-term inter-annually hysteresis patterns.

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- We hypothesize that the constant long-term C-Q relationship is attributed to the relatively constant relationship between nitrate availability and hydraulic connectivity.
  - ❖ Artificial Drainage will increase the flashiness of stream water generation.
  - ❖ Fertilization will enhance the nitrate availability in watershed.
  - ❖ These two factors cancelled each other during the measuring periods.

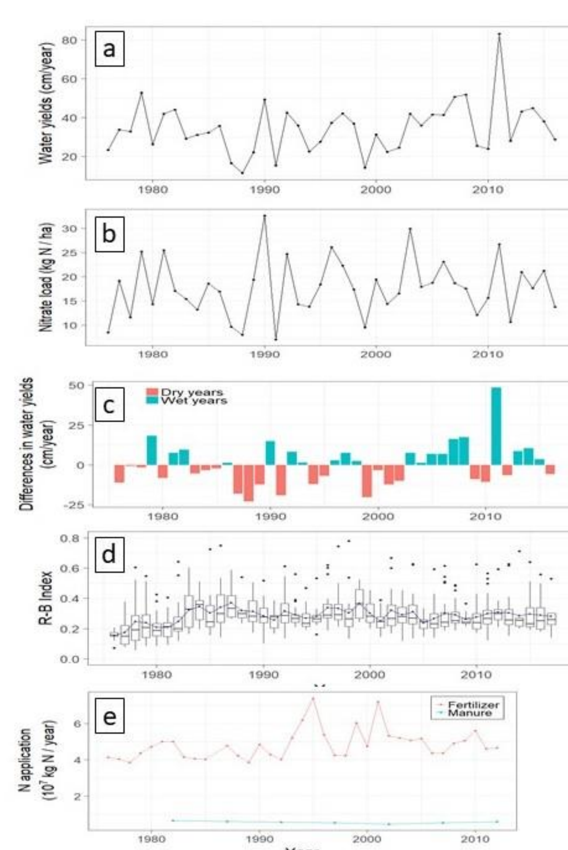


Fig. 5 Long-term variation of water yields (a), nitrate export (b), dry and wet years (c), Richards - Baker flashiness Index (R-B Index) (d) and estimated nitrogen input as commercial fertilizer and manure application (e)

## Results and discussion Cont'd

- Long-term inner-annual variation of C-Q relationship:
  - ❖ Significant seasonality in long-term C-Q relationship.
  - ❖ Shifted seasonality observed in composite C-Q relationship.
  - ❖ Possibly caused by changed fertilizer timing.
    - ❖ Timing: Fall to late spring.

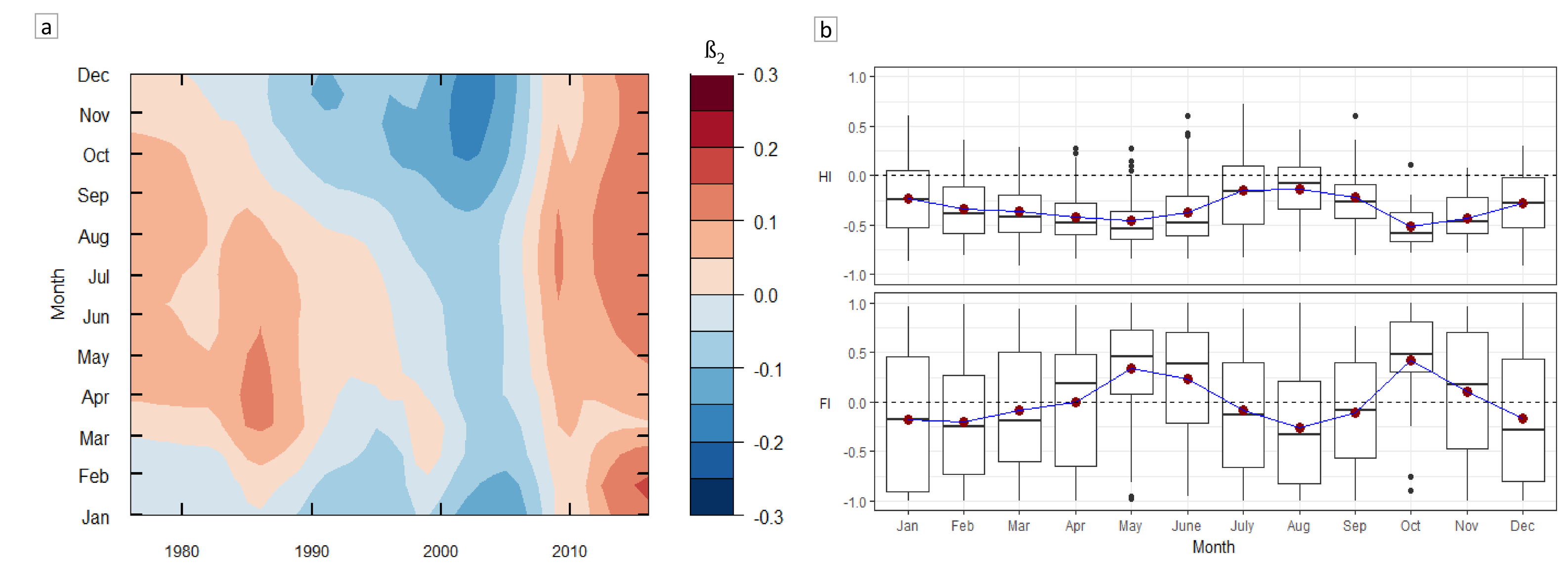


Fig. 6 Long-term seasonality of C-Q relationship from WRTDS (a) and storm hysteresis metrics (b).

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- Insights from the seasonality of C-Q relationship:
  - ❖ Take corn as an example.
  - ❖ Primarily driven by climatically conditions and agricultural activities.
  - ❖ Spring to early summer is the most vulnerable period.
  - ❖ Adapted fertilizer timing and types changed the seasonal patterns of C-Q relationship.

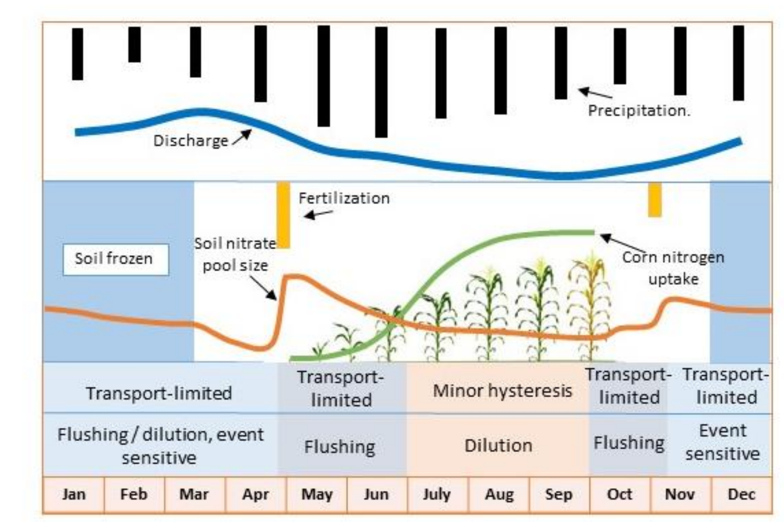


Fig. 7 Conceptual model for fate, transport and pathways of nitrate in different seasons.

## Summary

- Long-term C-Q relationship remained relatively stable during the observation period, primarily due to enhanced artificial drainage and increased fertilization quantity.
- Seasonal pattern of C-Q relationship indicated that late spring to early summer is the most sensitive period for nitrate export.
- Seasonal pattern shifted due to adaption of fertilizer management.

## Acknowledgement

The valuable long-term daily water quality data were provided by the Ohio Tributary Monitoring program that is operated by the National Center for Water Quality Research at Heidelberg University.