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Research Letter

Carbon, Nitrogen, and Phosphorus Stoichiometric Response to Hydrologic Extremes in a Tributary to Lake Erie, USA

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Core Ideas

- C/N/P stoichiometry at the 5th and 95th percentile of discharge was compared.
- Extreme low-flow stoichiometry was N or P limited relative to other nutrients.
- Extreme high-flow N contributions from tile push stoichiometry toward the Redfield ratio.
- Wastewater outflow pushes third-order stream to the Redfield ratio for low and high flow.

Abstract: Anthropogenic activities are a major cause of water quality impairment. We evaluated how hydrologic extremes (5th and 95th percentile of flow) affect carbon (C), nitrogen (N), and phosphorus (P) stoichiometry in a tile-drained agricultural tributary to Lake Erie. Water samples collected (2003–2009) from three sites along one agricultural drainage ditch and its receiving third-order stream were analyzed for C, N, and P. The C/N/P concentrations were transformed to compare against the Redfield ratio (106:16:1 C/N/P), ideal for algal proliferation. Nitrogen was depleted relative to C and P at two sites on the agricultural ditch during extreme low-flow conditions, whereas P was depleted to C and N at the third. Tile drainage N and P losses during high flows shifted stoichiometry toward the Redfield ratio. Stoichiometry in the third-order stream was near the Redfield ratio at both hydrologic extremes, likely from wastewater treatment plant effluent.

Increasing global population increases the demand for fresh water to support uses, such as drinking water, recreation, and irrigation (Lal, 2015; O'Connor et al., 2008). However, just as the growing population needs an ever-increasing volume of fresh water to support these uses, anthropogenic land uses such as urbanization and intensive agricultural production may lead to impaired water quality. Losses of N and P from agriculture and urban areas can lead to eutrophication of surface waters that diminish their ability to be used for recreation or drinking water (Jarvie et al., 2017; 2018); such has been the case with the Chesapeake Bay (Boesch et al., 2001) and Lake Erie (Baker et al., 2017).

Redfield (1958) established the Redfield ratio as 106:16:1 C/N/P, values that have since been used to evaluate the potential for eutrophication of surface waters (Hecky et al., 1993). Recently, stoichiometric ratios of C, N and P in rivers and how they relate to water quality have been of considerable interest (Jarvie et al., 2018; Singer and Battin, 2007; Smith et al., 2017; Soares et al., 2017).

Hydrology plays a major role in nutrient fate and transport. In tile-drained landscapes, such as the Western Lake Erie Basin (WLEB), storms are known to increase N and P transport (Smith et al., 2015; King et al., 2017). The objective of this work was to evaluate the potential role of hydrologic extremes on C/N/P stoichiometry along a stream continuum within the WLEB. For this study, we used the upper and lower 5% of hydrologic conditions to represent disparate flow conditions to evaluate how hydrology affects stoichiometry.

Site Description

This work uses data collected from the St. Joseph River watershed in northeast Indiana, which conveys water to the Maumee River in Fort Wayne, IN. This watershed is a major contributor of nutrients to the highly

Abbreviations: TDC, total dissolved carbon; TDN, total dissolved nitrogen; TDP, total dissolved phosphorus; WLEB, Western Lake Erie Basin.

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eutrophic WLEB (Jarvie et al., 2017). A nested series of watersheds was monitored, with sites draining 310 ha (AME), 1900 ha (ALG), 4500 ha (AXL) and 19,000 ha (F34). Row crop agriculture was the dominant land use in all watersheds, and there were no observed major shifts in agricultural management between the watersheds (Smith, 2009). For a full description, see Smith et al. (2008) and Smith (2009). The AME site represents the headwaters of this artificially drained system and has a streambed very high in organic matter, clay, and silt. The ALG site is the first monitoring site in the stream continuum with a coarse sand ditch bed. The AXL site represents the largest site on the drainage ditch, capturing 95% of the 12-digit hydrologic unit code (HUC) watershed. This water is conveyed to the F ditch approximately 1.25 km upstream from the F34 site.

Procedures

The sites were monitored as part of the St. Joseph River Conservation Effects Assessment Project–Watershed Assessment Study (CEAP-WAS). For more details on sampling and analysis protocols, see Smith et al. (2008). Briefly, water samples were pulled daily at each site with ISCO 6712 autosamplers. Samples were processed using common techniques for total dissolved C (TDC), total dissolved N (TDN), and total dissolved P (TDP). Samples were only analyzed for TDC in 2003 and from 2006 to 2009. From that dataset, daily measures of discharge at each site were used to discriminate data based on the 5th and 95th percentile of discharge to represent extreme low and high flow, respectively.

Stoichiometric analysis was performed according to Smith et al. (2017). In short, TDC, TDN, and TDP molar concentrations (mM) were transformed to represent relative Redfield concentrations. This was done by multiplying N by 6.625 and P by 106 to adjust both relative to C. Redfield ratio values for C, N, and P were calculated by summing the transformed data and then dividing the relative Redfield concentration by the sum of the three constituents. These values were then plotted on a ternary plot as described by Smith et al. (2017).

Results and Discussion

Only TDC showed a consistent trend in concentrations along the stream continuum: TDC was highest at the upstream AME site and decreased as the water was conveyed downstream (Table 1). At each site, TDN concentrations more than doubled when comparing extreme high-flow to extreme low-flow observations. This result is not surprising given that the predominant land use in these watersheds is row crop agriculture and the soils are tile drained, which is known to be a primary pathway for N loss (Woodley et al., 2018). The impact of hydrology on TDP was inconsistent across sites. At AME, there was a 35% decrease in TDP at extreme high flows (from 0.81 to 0.51 mg L^{-1}), whereas at ALG, TDP increased more than 500% from 0.075 to 0.50 mg L^{-1}, when comparing extreme low flows to high flows.

Previous work at the A ditch sites showed similar results with respect to P. In an assessment of ditch sediment P dynamics, Smith et al. (2006) observed sediment exchangeable P to be higher at the AME and AXL sites than at ALG. The ALG sediments have been shown to have a very high affinity for P in other studies as well. For example, ALG was shown to have a lower equilibrium P concentration and a greater P removal flux (from the water to the sediment) than the other sites (Smith, 2009). The latter study indicated lower levels of Al and Fe, suggesting that benthic biota instead of abiotic processes may be responsible for P uptake.

When the Redfield C/N/P stoichiometric ratios were plotted for the 5th and 95th percentile of discharge for the AME watershed, there was a shift toward greater Redfield N at the higher discharge (Fig. 1A). The extreme low-flow AME samples were predominantly situated below 20% Redfield N, which approximates to an “N depleted zone” relative to C and P (Smith et al., 2017). At the highest flows, the AME samples tended to congregate near the central zone where C/N/P approaches the Redfield ratio. Mean Redfield C did not change significantly between the extreme low and high flows (Table 1). However, there was a shift in Redfield N and P from 13 and 38% at lowest flows, respectively, to 33 and 25% at highest flows at the AME site.

Table 1. Hydrology influenced total dissolved C (TDC), N (TDN), and P (TDP) concentrations and Redfield C/N/P stoichiometric ratios from a watershed continuum in northeast Indiana. Column n represents the number of values in the 5th and 95th percentile from each watershed.

Catchment	Area	Response period	*n*	*Q*†	TDC	TDN	TDP	Redfield C	Redfield N	Redfield P
	ha			L s^{-1}	mg L^{-1}			%		
AME	310	5th	24	2.5	34.5 ab‡	1.84 cd	0.808 a	49.2 b	13.1 d	37.7 a
		95th	23	164	35.9 a	4.59 b	0.512 b	42.3 bc	33.2 b	24.5 cd
ALG	1,900	5th	20	22.8	29.3 abcd	2.23 cd	0.075 c	64.2 a	29.6 bc	6.2 e
		95th	21	1,920	30.2 abc	7.90 a	0.501 b	34.6 cde	46.5 a	18.9 d
AXL	4,300	5th	24	47.3	27.1 cd	1.17 d	0.413 b	61.5 a	11.3 d	27.3 c
		95th	24	2,740	27.9 bcd	6.89 a	0.349 bc	32.8 de	48.3 a	19.0 d
F34	19,000	5th	18	177	24.5 cd	2.95 c	0.572 ab	40.3 bcd	24.7 c	35.0 sb
		95th	18	11,300	22.3 d	6.90 a	0.629 ab	26.3 e	44.3 a	29.5 bc

† *Q* = discharge.

‡ Values within a column followed by different letters are significantly different at $P < 0.05$. Comparisons of means was performed in JMP v. 11.2.0 using Analysis of Variance and mean separation with Student’s *t* test.

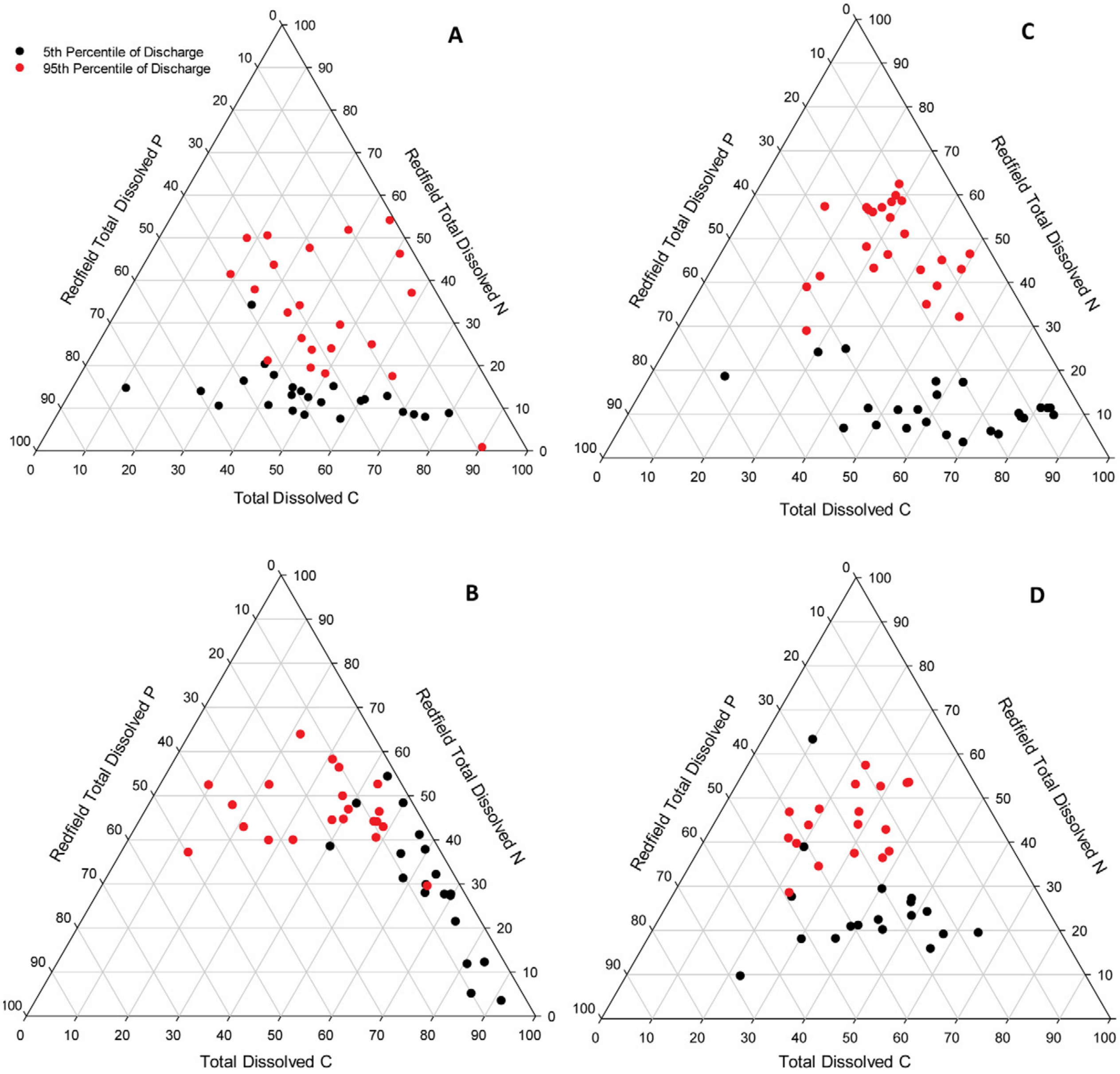

Fig. 1. Total dissolved carbon, nitrogen, and phosphorus stoichiometry in water samples from the 5th and 95th percentile of flow from the (A) AME, (B) ALG, (C) AXL, and (D) F34 sites.

At the ALG site, extreme low-flow stoichiometry was P depleted relative to C and N, with most observations below 10% Redfield P (Fig. 1B) and mean Redfield P of 6% (Table 1). With extreme high flows, Redfield N and P increased toward the central zone, thus approaching the Redfield ratio (35% Redfield C, 37% Redfield N, and 19% Redfield P). While tile drainage N losses are well documented, tile drainage losses of P (Smith et al., 2015) and persistent losses of P from legacy sources (King et al., 2017) during storms have been documented in the WLEB.

The AXL extreme low-flow stoichiometry was generally in the N depleted zone relative to C and P, with Redfield N values near 11% (Fig. 1C). Extreme high flows increased the proportion of N relative to C and P to a mean of 48% Redfield N, while the relative contribution of P declined from 27% Redfield P at lowest flow to 19% at highest flow (Table 1). Thus, there was a transition for AXL from the N depleted zone at lowest flow to the border of the P depleted zone and into the central zone approaching the Redfield ratio at extreme high flow (Fig. 1C).

The majority of extreme low-flow and high-flow observations for the F34 site were located close to the central zone (Fig. 1D), although there was a shift to higher Redfield N (25% at lowest flow and 44% at highest flow). Approximately 3.3 km upstream from the F34 site is a wastewater treatment plant serving a town of approximately 2200 residents, which is potentially having an impact on the stream nutrient stoichiometry during both extreme low and high flows. Wastewater treatment plants are well known to elevate N and P concentrations in streams as well as alter resource stoichiometry toward conditions that may drive algal proliferation (Haggard et al., 2001; Neal et al., 2010; Singer and Battin, 2007).

Rattan and Chambers (2018) found that variability in hydrology in a snowmelt-dominated Canadian prairie watershed had a greater impact on particulate-associated nutrients than soluble nutrients. Forests in New Zealand appear to show little stoichiometric shifts due to hydrology; however, P losses relative to C and N increased with higher flows (McGroddy et al., 2008). In the humid climates of the United States, Green and Finlay (2010) observed a positive correlation between discharge and TDN/TDP ratios. In the region represented by the watershed used for this study, hydrology had the greatest impact on nutrient stoichiometry when comparing extreme high to low flows. This is because of the mobility of nitrate N through tile drains.

In summary, hydrology plays an important role in the C/N/P stoichiometry in this agricultural watershed of northeast Indiana. In these watersheds dominated by row crops and tile drainage, storm events greatly increased the Redfield N relative to C and P. Under extreme low-flow conditions, sites along the A ditch were N depleted relative to P and C (AME and AXL) or P depleted relative to N and C (ALG). This likely reflects the converging effects of varying N and P sources at extreme low flow, including instream nutrient cycling, and biological activity. However, the average concentrations of TDN and TDP at extreme low flow remain above levels likely to be limiting to primary producers (Jarvie et al., 2018). While extreme high-flow conditions resulted in stoichiometry approaching the Redfield ratio and elevated concentrations of the most bioavailable nutrient fractions, other factors such as water residence times, light, and temperature can limit algal growth. However, stormwater from this watershed is rapidly conveyed to Lake Erie, which is known to experience hypereutrophic conditions during the late summer, possibly due to runoff with stoichiometry approaching the Redfield ratio during high-flow events.

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