Supplemental information for:

Hydrologic regimes drive nutrient export behavior in human impacted watersheds

Galen Gorski and Margaret Zimmer

4 Tables and 4 Figures

S1 Calibration of nitrate probes

For detailed QA/QC protocol see (Garrett, 2019) for USGS sites and (Jones et al., 2018) for IIHR sites. Instruments were calibrated for bias and sensor drift before deployment and during periodic site visits in which hand samples were collected and analyzed to check the sensor accuracy. For USGS sites, a difference of 0.3 mg/L or 5% between consecutive hand samples and sensor data triggered a sensor recalibration, but hand samples show good agreement with sensor data (Pellerin et al., 2014; Zimmer et al., 2019). Hach instruments measure concentrations of NO_3^- and NO_2^- due to the strong absorbance of NO_2^- between 210-220 nm, however, NO_2^- concentrations are generally very low in surface water and therefore sensor measurements are referred to as NO_3^-.

S2 Comparison of nitrate export loads to other studies

Annual NO_3^- export loads compare favorably with estimates by (Jones et al., 2018), who estimated NO_3^- load at 35 sites across Iowa during 2016 including all five sites analyzed here using linear interpolation to fill data gaps. Our results show ≥ 90% agreement in annual load across all five sites with no systematic under or over prediction. Our four-year average annual loads are somewhat higher than those estimated by (Jones et al., 2018) for the period 1987-2016, likely due to higher than average discharge over the four-year period studied.

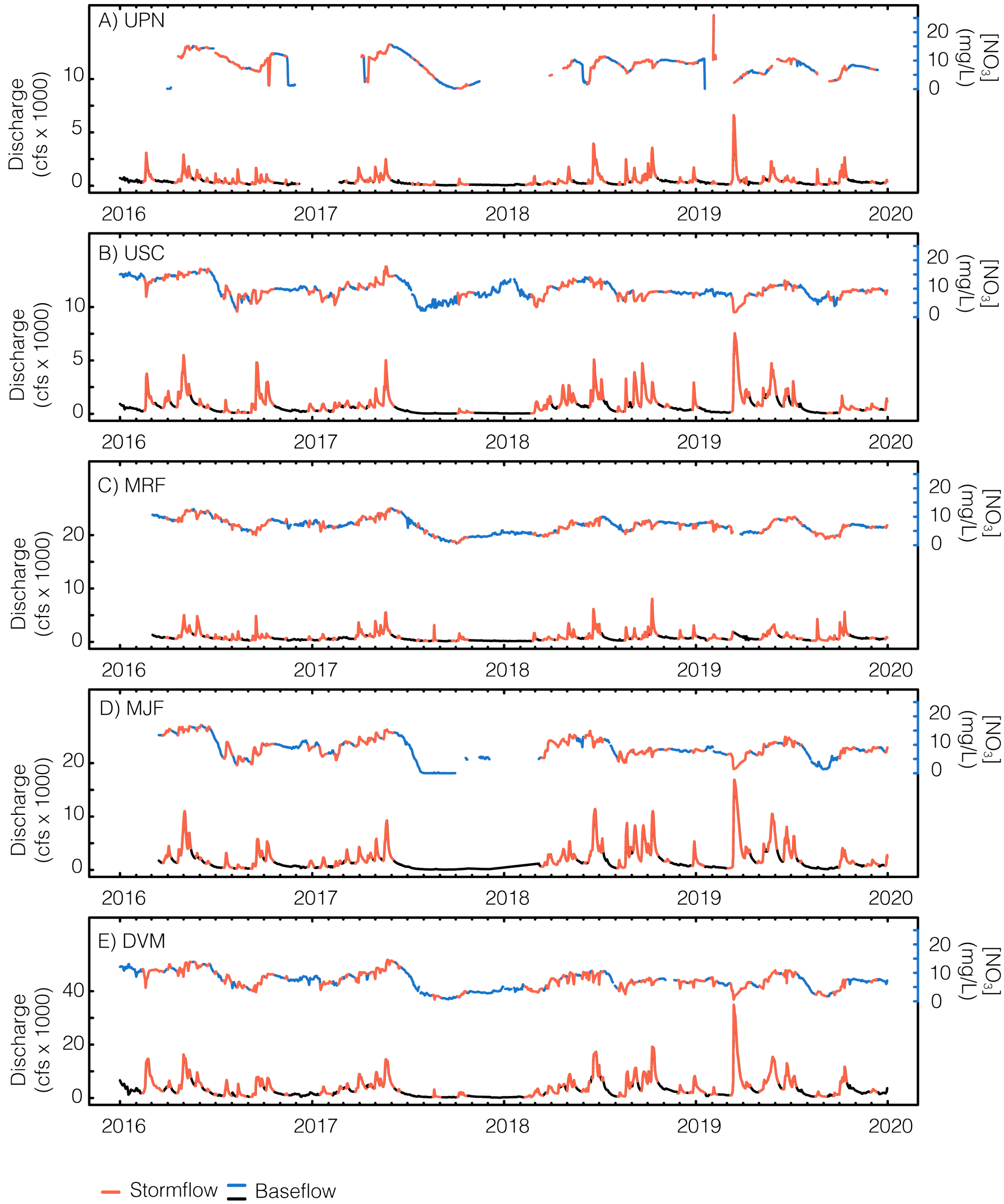

Figure S1 Paired hydrographs and chemographs for the 5 study watersheds with identified events shown in red and baseflow shown in black (hydrograph) and blue (chemograph). Events were identified using the hydrograph, see section 2.3 for details. The record begins in January 2016 and ends in December 2019.

Table S1 – Data coverage by watershed

Watershed	Record start date	Record end date	n obs[a]	coverage[b]	largest gap
				(%)	(days)
UPN	3/31/16	12/13/19	971	71.8	127
USC	1/1/16	12/31/19	1451	99.4	7
MRF	3/3/16	12/31/19	1344	91.9	15
MJF	3/15/16	12/31/19	1229	88.7	94
DVM	1/1/16	12/31/19	1403	96.0	16

[a] Number of paired observations with discharge and [NO_3^-]

[b] Data coverage for discharge was complete for all stations, gaps were [NO_3^-] non-reporting

Table S2 – Watershed land cover characteristics

		Water		Developed		Forest		Crop		
Watershed	Area	Total	100 m buffer of stream	Total	100 m buffer of stream	Total	100 m buffer of stream	Total	100 m buffer of stream	Drainage infrastructure density
	(km^2)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(km/km^2)
UPN	1116	2	45	6	4	5	19	87	32	0.71
USC	1840	2	39	5	5	1	16	92	39	1.11
MRF	2548	2	46	5	3	8	20	85	31	0.37
MJF	4188	2	47	5	3	2	15	91	35	0.93
DVM	8870	2	52	5	3	4	16	88	28	0.70

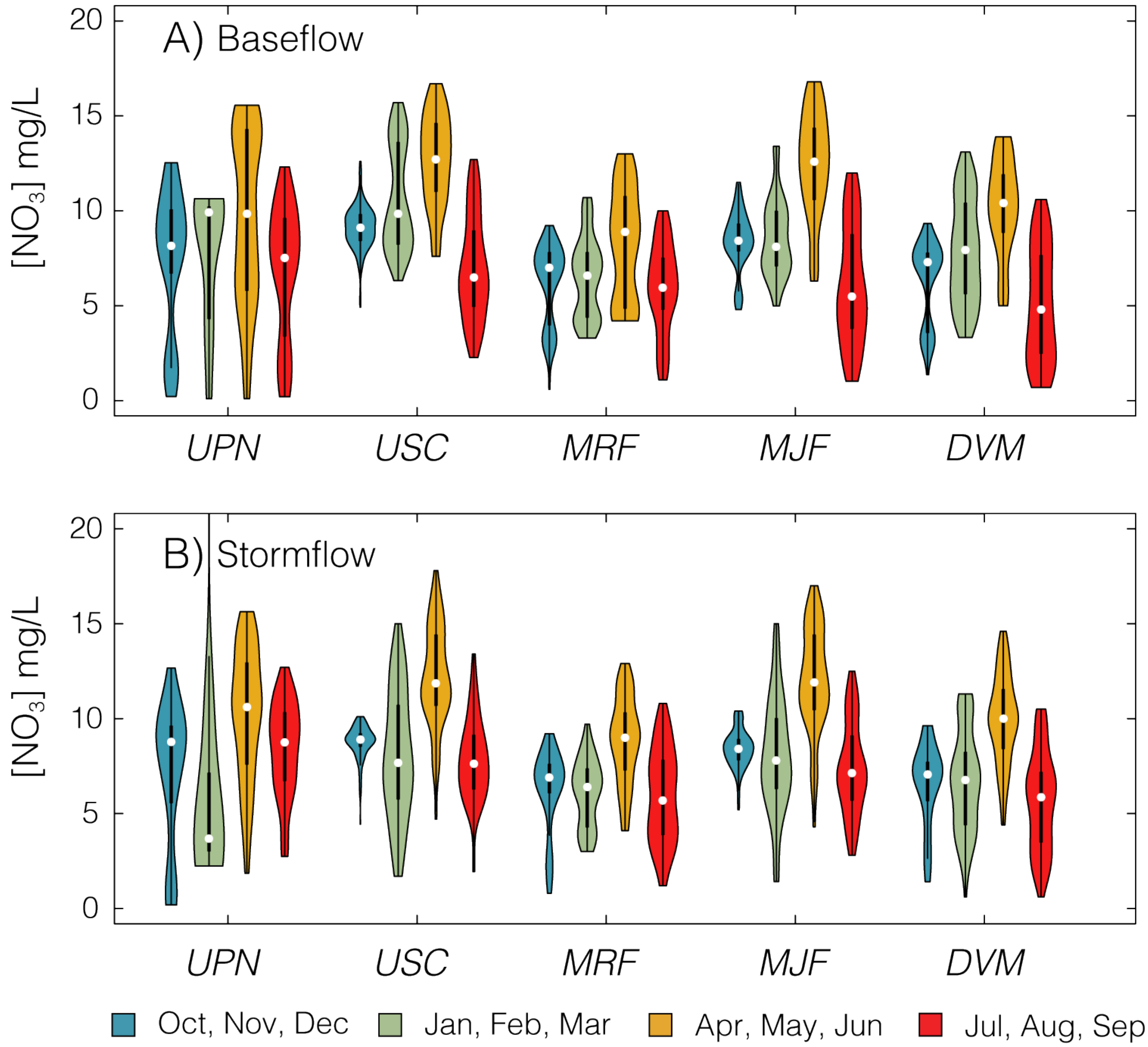

Figure S2 NO_3^- concentration by season for the five watersheds during baseflow (A) and stormflow periods (B).

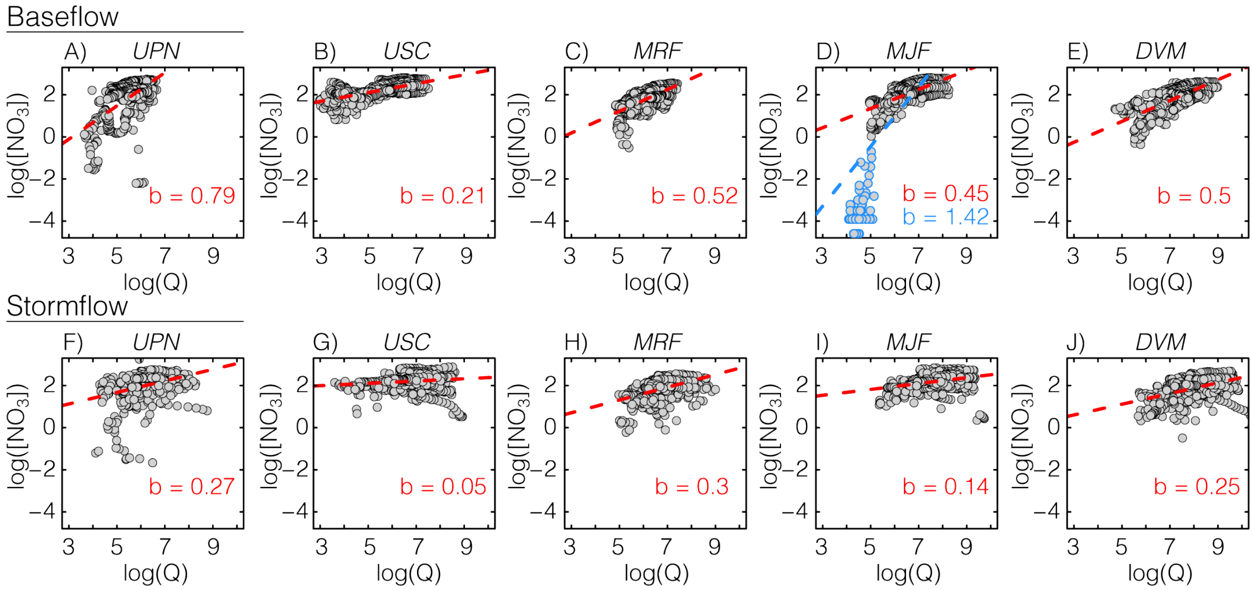

Figure S3 Concentration-discharge plots shown on log-log axes for five studied watersheds during baseflow (A-E) and stormflow (F-J), with the slope shown in red. Panel D shows the baseflow for *MJF* with the low flow period from 7/27/17-10/19/17 when $[NO_3^-] < 0.5$ mg/L included (blue) and excluded (red). All slopes are statistically significant ($p < 0.01$)

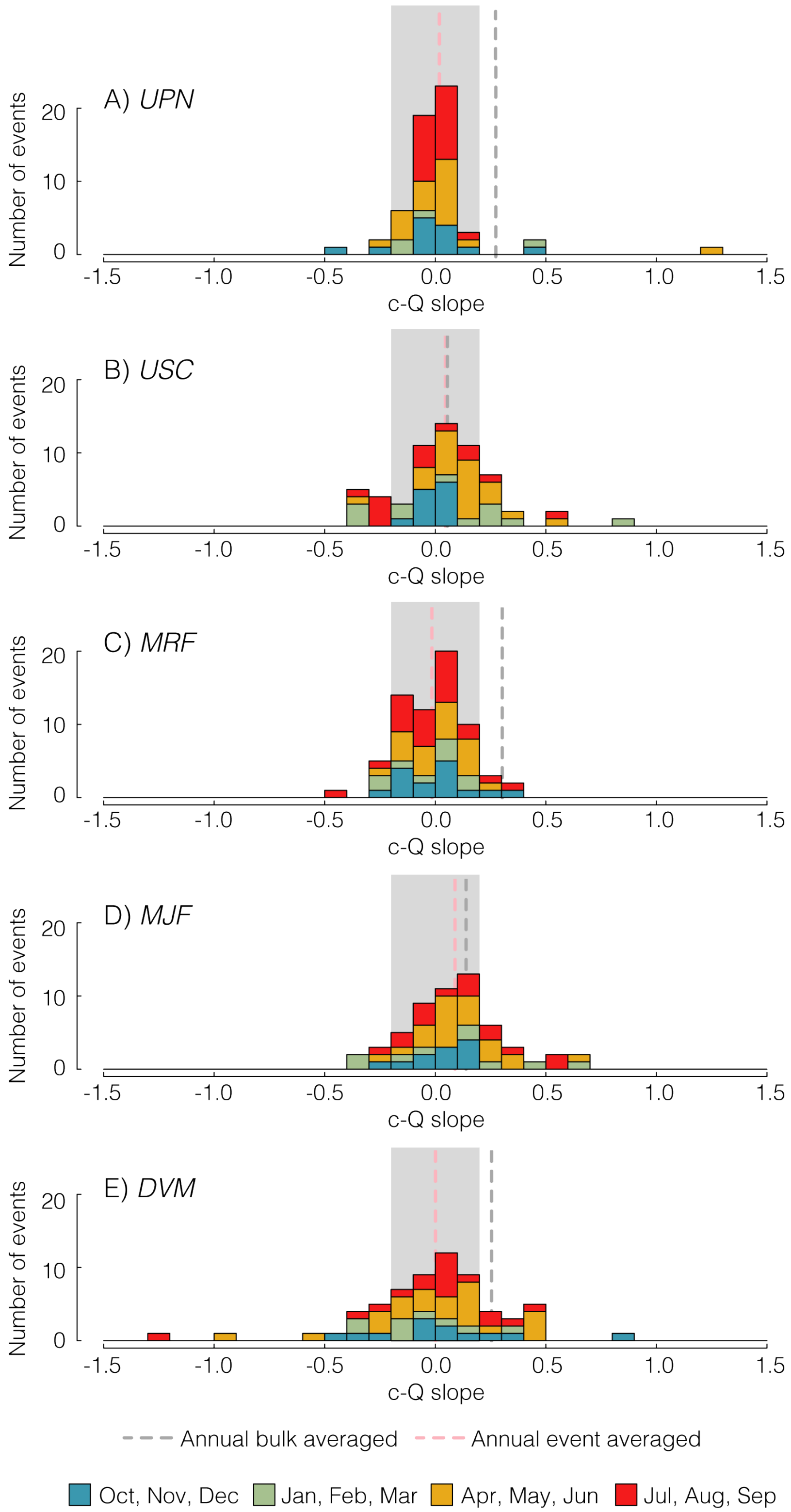

Figure S4 Histograms of individual event c-Q slope for each watershed colored by season. Gray dashed line shows the bulk stormflow c-Q slope and the pink dashed line shows the event-averaged c-Q slope. Gray boxes delineate chemostatic behavior (|c-Q slope| < 0.2).

Table S3 – Nitrate concentration and load for each watershed during baseflow and stormflow

	Baseflow+Stormflow		Baseflow		Stormflow	
Watershed	Nitrate concentration[a]	Cumulative annual load[b]	Nitrate concentration	Cumulative annual load	Nitrate concentration	Cumulative annual load
	mg/L	kg-N/km^2/yr	mg/L	kg-N/km^2/yr	mg/L	kg-N/km^2/yr
UPN	8.27	3457	7.89	953	8.66	2507
	(3.81)	(940)	(4.00)	(162)	(3.57)	(89)
USC	9.56	3799	9.53	1108	9.58	2690
	(3.09)	(1133)	(3.10)	(492)	(3.08)	(675)
MRF	6.77	2222	6.56	813	7.03	1413
	(2.51)	(371)	(2.43)	(208)	(2.59)	(215)
MJF	9.11	4216	8.68	994	9.52	3222
	(3.29)	(768)	(3.32)	(269)	(3.21)	(674)
DVM	7.24	2829	6.94	799	7.55	2031
	(3.07)	(654)	(3.08)	(287)	(3.02)	(412)

[a] mean value is reported for nitrate concentration, numbers in parentheses are the standard deviation

[b] mean annual cumulative load is reported, numbers in parentheses are the standard deviation

Table S4 Pearson correlation coefficient heat map for landscape attributes and nutrient export metrics

			Drainage infrastruct. density (km/km2)	Cropped area within 100 m of stream (%)	Cropped area within 1 km of stream (%)	Total watershed cropped area (%)	Watershed area (km2)
Load	Stormflow +Baseflow	Complete Record	0.87	0.69	-0.35	0.88	-0.21
		OND	0.18	0.10	-0.44	0.07	-0.49
		JFM	0.86	0.49	-0.97	0.81	0.14
		AMJ	0.96	0.79	-0.30	0.99	-0.08
		JAS	0.77	0.64	-0.13	0.81	-0.20
	Stormflow	Complete Record	0.84	0.61	-0.32	0.86	-0.14
		OND	0.34	0.23	-0.49	0.24	-0.48
		JFM	0.89	0.42	-0.86	0.89	0.28
		AMJ	0.94	0.74	-0.26	0.99	0.00
		JAS	0.71	0.55	-0.08	0.76	-0.15
	Baseflow	Complete Record	0.87	0.95	-0.47	0.79	-0.56
		OND	-0.14	-0.16	-0.31	-0.25	-0.46
		JFM	0.58	0.49	-0.92	0.45	-0.15
		AMJ	0.94	0.95	-0.42	0.89	-0.37
		JAS	0.90	0.97	-0.38	0.84	-0.44
c-Q slope	Stormflow +Baseflow	Complete Record	-0.76	-0.80	0.08	-0.80	0.03
		OND	-0.53	-0.54	-0.25	-0.65	-0.26
		JFM	-0.54	-0.32	0.68	-0.43	0.38
		AMJ	-0.79	-0.50	0.13	-0.89	-0.41
		JAS	-0.64	-0.88	-0.01	-0.66	0.27
	Stormflow	Complete Record	-0.93	-0.89	0.31	-0.93	0.16
		OND	-0.42	-0.49	-0.41	-0.56	-0.23
		JFM	-0.64	-0.38	0.70	-0.54	0.33
		AMJ	-0.69	-0.42	0.01	-0.81	-0.49
		JAS	-0.73	-0.88	0.57	-0.59	0.73
	Baseflow	Complete Record	-0.57	-0.64	-0.03	-0.62	-0.11
		OND	-0.58	-0.51	-0.15	-0.69	-0.34
		JFM	-0.23	-0.23	0.70	-0.04	0.64
		AMJ	-0.92	-0.52	0.39	-0.97	-0.30
		JAS	-0.56	-0.65	-0.07	-0.62	-0.09

1.0 0.0 -1.0

Pearson correlation coefficient

REFERENCES

Garrett, J. D. (2019). *The use of continuous water-quality time-series data to compute nutrient loadings for selected Iowa streams, 2008–17*. *Scientific Investigations Report*. https://doi.org/10.3133/sir20195054

Jones, C. S., Schilling, K. E., Simpson, I. M., & Wolter, C. F. (2018). Iowa Stream Nitrate, Discharge and Precipitation: 30-Year Perspective. *Environmental Management*, *62*(4), 709–720. https://doi.org/10.1007/s00267-018-1074-x

Pellerin, B. A., Bergamaschi, B. A., Gilliom, R. J., Crawford, C. G., Saraceno, J., Frederick, C. P., et al. (2014). Mississippi river nitrate loads from high frequency sensor measurements and regression-based load estimation. *Environmental Science and Technology*, *48*(21), 12612–12619. https://doi.org/10.1021/es504029c

Zimmer, M. A., Pellerin, B., Burns, D. A., & Petrochenkov, G. (2019). Temporal variability in nitrate-discharge relationships in large rivers as revealed by high-frequency data. *Water Resources Research*. https://doi.org/10.1029/2018WR023478