

*Water Resources Research*

Supporting Information for

**Land Use and Season Influence Event-scale Nitrate and Soluble Reactive Phosphorus Exports and Export Stoichiometry from Headwater Catchments**

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**Introduction**

Here we provide supplementary figures and tables. Figures provide (1) an example of unsmoothed and smoothed predicted soluble reactive phosphorus (SRP) time series at all three study sites, (2) site-specific examples of event time series for discharge and nitrate (NO3-) and SRP concentrations, and (3) an alternate figure for Figure 6 depicting data colored by season instead of site. Tables provide (1) model details and statistics for partial least squares regression models used to predict NO3- and SRP time series from absorbance spectral data, (2) parameter values used in the HydRun package to optimize event delineations, and (3) summary of least square linear regressions between event NO3- or SRP and water yield as shown in Figure 4.

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| **Figure S1.** Example of unsmoothed and smoothed predicted soluble reactive P time series at all three sites. Unsmoothed concentrations were predicted from absorbance spectra using calibration models developed with the partial least squares regression method. Smoothed data were produced by using a simple moving average of the unsmoothed data with a rolling window of 2.25 hrs to better capture patterns in hysteresis loops. |

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| A picture containing screenshot  Description automatically generated |
| **Figure S2.** Examples of event time series of discharge (Q), nitrate (NO3), and soluble reactive phosphorus (SRP) for the agricultural (a), urban (b), and forested (c) sites. Each time series is an example of the dominant hysteretic behavior for nitrate (positive hysteresis index and negative flushing index) and SRP (negative hysteresis index and positive flushing index) as shown in Figure 3. |

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| **Figure S3.** Molar ratio of nitrate (NO3-) to soluble reactive P (SRP) yield for each storm. The dashed horizontal line shows the 16:1 molar N:P ratio. Not shown are 8 outliers with ratios from 1517 to 27,105 between 0.11 and 3.03 mm event water yield. |

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|  | **Grab samples** | |  | **PLSR models** | | | | |
| **Site** | **Median concentration (mg N L-1)** | **Range of concentrations (mg N L-1)** |  | **Observations** | **Components** | **RMSE (mg N L-1)** | **R2** |
| All sites | 0.381 | 0.000 – 7.350 |  | 365-421 | 3 | 0.219-0.233 | 0.96-0.97 |

Table S1. Results of partial least squares regression (PLSR) relating lab analyses of nitrate (NO3-) concentrations of grab samples to absorbance spectra of the same samples measured using the s::can spectro::lyser UV-Visible spectrophotometers. A detailed description of our approach can be found in Etheridge et al., (2014) and Vaughan et al., (2017). Briefly, we used PLSR to generate a single calibration model (Mevik et al., 2016) for all sites. Separate calibration models were developed for 2014-2017 and 2018. We report the number of components used for each PLSR model. We also report the ranges of the root mean square errors (RMSE) and R2 for the correlation between predicted and lab measured NO3- concentrations for each PLSR model. Observations indicate the number of grab samples used for the calibration.

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|  | **Grab samples** | |  | **PLSR models** | | | | | |
| **Site** | **Median concentration (μg P L-1)** | **Range of concentrations (μg P L-1)** |  | **Observations** | **Components** | **Training adj. *R2*** | **Training**  **RMSE**  **(μg P L-1)** | **Validation adj. *R2*** | **Validation RMSE (μg P L-1)** |
| Agricultural | 34.10 | 3.04 – 1239.00 |  | 153 | 9 | 0.81 | 55 | 0.54 | 106 |
| Urban | 16.40 | 0.34 – 231.00 |  | 109 | 9 | 0.88 | 18 | 0.65 | 30 |
| Forested | 3.59 | 0.60 – 22.80 |  | 126 | 8 | 0.83 | 2.0 | 0.76 | 2.4 |

Table S2. Results of partial least squares regression (PLSR) relating lab analyses of soluble reactive phosphorus (SRP) concentrations to absorbance spectra of the same samples measured using the s::can spectro::lyser UV-Visible spectrophotometers. A detailed description of our approach can be found in Vaughan et al., (2018). Briefly, training and validation prediction sets were generated for each site using all data from that site (i.e., all years). For each training dataset, 85% of available observations were selected randomly to generate a model. The training model was then used to predict a validation set, which was comprised of the remaining 15% of observations that were randomly withheld. This process was repeated 1000 times with replacement, and predictions and statistics for each model were collected and aggregated. Sensor performance was evaluated by performing linear correlations on the mean predicted value for training and validation sets vs. the corresponding lab-measured values. Adjusted R2 values are presented to compare goodness of fit for regressions to remove the bias associated with differing sample sizes, and root mean square errors (RMSEs) are presented as estimates of model error.

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| **Site** | **Peaking threshold (minimum peak discharge in m3s-1)** | **Baseflow separation filtering coefficient** | **Return ratio (0 to 1)** | **Minimum duration (hours)** |
| Agricultural | 0.10 | 0.996 | 0.18 | 6 |
| Urban | 0.05 | 0.996 | 0.18 | 4 |
| Forested | 0.12 | 0.996 | 0.20 | 4 |

Table S3. Parameter values used in the HydRun package to optimize event delineations.

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| **Site** | **Season** | **Regression formula** | **Slope** | **Standard error** | **p-value** | **Adjusted R2** |
| Agricultural | All | event NO3 yield ~ event water yield | 3.204 | 0.1643 | < 0.0001 | 0.75 |
| Urban | All | event NO3 yield ~ event water yield | 0.295 | 0.0235 | < 0.0001 | 0.63 |
| Forested | All | event NO3 yield ~ event water yield | 0.218 | 0.0132 | < 0.0001 | 0.60 |
| Agricultural | All | event SRP yield ~ event water yield | 0.149 | 0.0163 | < 0.0001 | 0.39 |
| Urban | All | event SRP yield ~ event water yield | 0.086 | 0.0044 | < 0.0001 | 0.80 |
| Forested | All | event SRP yield ~ event water yield | 0.007 | 0.0002 | < 0.0001 | 0.86 |
| Agricultural | Summer | event NO3 yield ~ event water yield | 4.158 | 0.2527 | < 0.0001 | 0.83 |
| Agricultural | Fall | event NO3 yield ~ event water yield | 4.143 | 0.2649 | < 0.0001 | 0.87 |
| Agricultural | Spring | event NO3 yield ~ event water yield | 2.085 | 0.0997 | < 0.0001 | 0.93 |
| Urban | Summer | event NO3 yield ~ event water yield | 0.128 | 0.0191 | < 0.0001 | 0.60 |
| Urban | Fall | event NO3 yield ~ event water yield | 0.234 | 0.0282 | < 0.0001 | 0.67 |
| Urban | Spring | event NO3 yield ~ event water yield | 0.522 | 0.0217 | < 0.0001 | 0.96 |
| Forested | Summer | event NO3 yield ~ event water yield | 0.048 | 0.0042 | < 0.0001 | 0.63 |
| Forested | Fall | event NO3 yield ~ event water yield | 0.103 | 0.0104 | < 0.0001 | 0.66 |
| Forested | Spring | event NO3 yield ~ event water yield | 0.305 | 0.0218 | < 0.0001 | 0.80 |
| Agricultural | Summer | event SRP yield ~ event water yield | 0.217 | 0.0181 | < 0.0001 | 0.72 |
| Agricultural | Fall | event SRP yield ~ event water yield | 0.274 | 0.0349 | < 0.0001 | 0.63 |
| Agricultural | Spring | event SRP yield ~ event water yield | 0.039 | 0.0073 | < 0.0001 | 0.45 |
| Urban | Summer | event SRP yield ~ event water yield | 0.114 | 0.0050 | < 0.0001 | 0.95 |
| Urban | Fall | event SRP yield ~ event water yield | 0.097 | 0.0051 | < 0.0001 | 0.91 |
| Urban | Spring | event SRP yield ~ event water yield | 0.050 | 0.0045 | < 0.0001 | 0.82 |
| Forested | Summer | event SRP yield ~ event water yield | 0.009 | 0.0003 | < 0.0001 | 0.93 |
| Forested | Fall | event SRP yield ~ event water yield | 0.006 | 0.0005 | < 0.0001 | 0.76 |
| Forested | Spring | event SRP yield ~ event water yield | 0.006 | 0.0003 | < 0.0001 | 0.90 |

Table S4. Summary of least square linear regressions between event NO3- or soluble reactive P (SRP; kg N or P km-2) and water yield (mm) as shown in Figure 4.