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Nitrogen in the Nooksack River Watershed: Comparing Models to Monitoring

David U. Hooper
Western Washington University

Nitrogen in the Nooksack: Real-time sensors are a gold standard – except when they fail

Madeline Mikles[1], David U. Hooper [1], Beatrice Macagno [1], Craig Senter[2], Nichole Embertson[3], Richard W. Sheibley[2], Jana E. Compton[4]

Author Affiliations
1- Department of Biology, Western Washington University, Bellingham, WA
2- Washington Water Science Center, U.S. Geological Survey, Tacoma, WA
3- Whatcom Conservation District, Lynden, WA
4- Pacific Ecological Systems Division, U.S. EPA, Corvallis, OR

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INTRODUCTION

- Nitrogen (N) inputs help maintain agricultural productivity, however N waste in the watershed threatens both human communities and natural ecosystems. Contaminated drinking water, eutrophication, and toxic algal blooms can all result from enhanced N loading to streams and nearshore marine systems (Compton et al. 2011).
- Agriculture contributes greatly to the lowland economy of the Nooksack River watershed in northwest Washington State and southwest British Columbia (Fig 1).
- Nitrogen imports in animal feed for dairy cattle (WA) and poultry (BC) and inputs through fertilizer, manure and deposition in major crops, such as berries, likely contribute to losses to groundwater and streams (Lin et al. 2020).
- Accurate monitoring of nitrate loads will help better understand nutrient sources and dynamics to make mitigation actions more strategic, both ecologically and economically.
  - Common practice uses monthly grab sample measurements, often combined with continuous flow monitoring and modeling using the LOAD ESTimator (LOADEST) model (Runkel et al. 2004), to estimate nutrient fluxes.
  - However, new automated nitrate sensors are available for real-time monitoring that may provide greater accuracy.
- The Nooksack River and two of its lowland tributaries, Kamm and Fishtrap Creeks provided opportunities to compare these methods in different stream environments. The Nooksack encompasses a large watershed, while Kamm and Fishtrap have varying land use and groundwater influence.

QUESTIONS

- How well do grab sample and LOADEST modeling reflect continuous measurements of nitrate loading using SUNA Seabird and OTT Hydromet ecoN sensors?
- How do LOADEST and grab-sample accuracy for estimating nitrate flux vary across seasons and across different stream environments?

METHODS

Taking measurements at Fishtrap Creek near the Canadian border.

Taking measurements at Kamm Creek. Levelogger pictured behind OTT.

Installation of OTT ecoN sensor for testing in Fishtrap Creek, Lynden, WA, October 2018.

Initial testing of SUNA (left) and OTT (right) sensors in Fishtrap Creek, Lynden, WA.

Grab Sample | **LOADEST** | **Automated**

Grab Sample Method

- Instantaneous discharge (Q) measured using water depth and flow meter.
- $[NO_3^- + NO_2^-]$ (mg N/L) measured using filtered water grab sample and SMARTCHEM 200
- Calculate flux (Kg/day)

$$\frac{\left\{inst.Q\left(\frac{m^3}{s}\right) \times conc\left(\frac{g}{m^3}\right) \times 86400\left(\frac{s}{day}\right)\right\}}{1000\left(\frac{g}{Kg}\right)} = flux\left(\frac{Kg}{day}\right)$$

- Average the flux (Kg/day) for months with more than one day of grab sample and inst. Q measurements.
- Scale daily values up to monthly flux (Kg/mo = Kg/day x day/mo)

*Conversion: mg/L is equal to g/m3

$$\frac{mg}{L} \times \frac{1\ g}{1000\ mg} \times \frac{1000\ L}{1\ m^3} = \frac{g}{m^3}$$

LOADEST Modeling Method

- LOADEST (Runkel et al. 2004) calibration file created using $[NO_3^- + NO_2^-]$ grab samples and continuous Q
- LOADEST estimates daily N flux using model of best fit with calibration file
- Outputs one daily average flux (Kg/day) and (+/-) 95% confidence intervals (CI) for each month
- Scale daily values up to monthly flux (Kg/mo = Kg/day x day/mo)

Automated Sensor Method

- SUNA and OTT sensors measures $[NO_2 + NO_3]$ every 15 min.
- USGS gauging stations (Fishtrap Creek=12212050 and Nooksack River at Ferndale= 12213100) and Levelogger (Kamm Creek) continuously measure water height, which was used to calculate discharge (Q) using rating curves.
- [NO3] and water height data can be manually downloaded or available in real-time with telemetry
- Calculate flux (Kg/s)

$$\frac{\left\{cont.Q\left(\frac{m^3}{s}\right) \times conc\left(\frac{g}{m^3}\right)\right\}}{1000\left(\frac{g}{Kg}\right)} = flux\left(\frac{Kg}{s}\right)$$

- Calculate average daily flux (Kg/day)
- Where missing, fill gaps in [N] concentration using a regression model between daily Q and daily flux values.
- Sum daily flux measurements up to monthly flux

Figure 2. Methods for measuring discharge and concentration and calculating flux .

Table 1. Pros and cons of using grab sample, LOADEST modeling and automated sensors to estimate flux.

	Pros	Cons
Grab Sample	• Captures seasonal trends but may miss peak flows. • Cheapest method of sampling. • Measurements needed to validate sensors and calibrate LOADEST.	• Lowest temporal resolution and accuracy: monthly fluxes are estimated from just 1-3 samples taken per month. • Time and labor intensive, restricting number of monthly measurements.
LOADEST modeling	• Captures monthly and annual trends at a higher resolution and accuracy than grab samples using time series regression. • Cheaper than an automated nitrate sensor.	• Needs continuous discharge measurements • Needs sufficient data, including full range of flows, to develop calibration curve, esp. in highly variable stream environments. • May need multiple years of data • The longer the sampling project, the more accurate LOADEST estimates will be.
Automated sensors	• High resolution: takes measurements every 15 minutes. • Sensor captures extreme flow events, eliminating biases. • Most data per effort: after initial setup, needs monthly validation and periodic maintenance. • With telemetry, data can be available in real-time (e.g., agency data portals). • Real-time data assist with troubleshooting.	• Maintenance issues can take sensors out for days-months, missing data if other forms of monitoring are not in place. • Most costly of the three methods (sensor, telemetry, installation). • High resolution may not be needed for monthly or annual loading estimates.

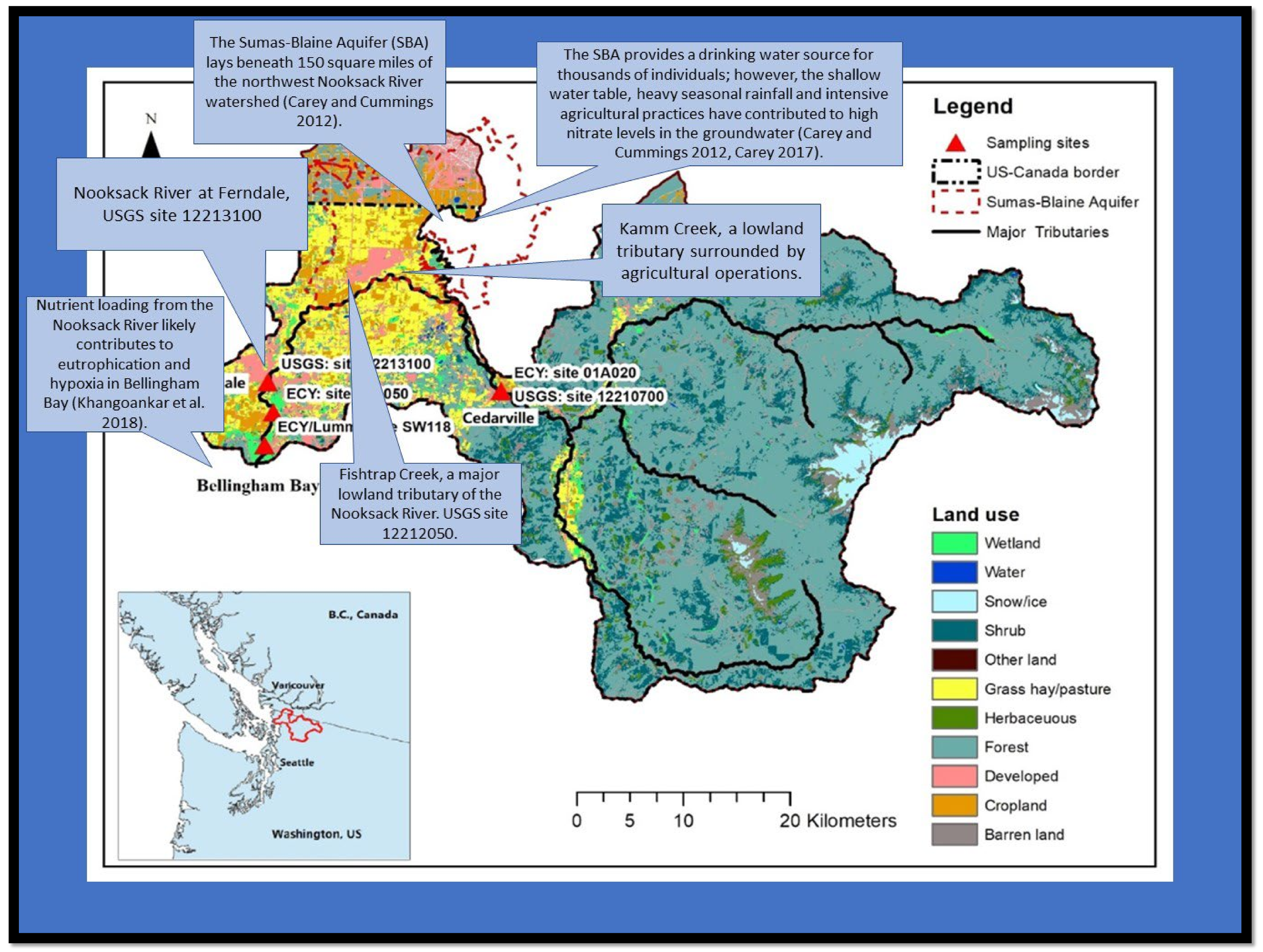

Figure 1. The Nooksack Watershed (figure from Lin et al. 2020). Most of the watershed sits within Whatcom County, WA, with some groundwater and surface water inputs from southern British Columbia (Carey 2017). Headwaters are largely forest and alpine glaciers; lowlands are largely agricultural and developed.

NOOKSACK RIVER

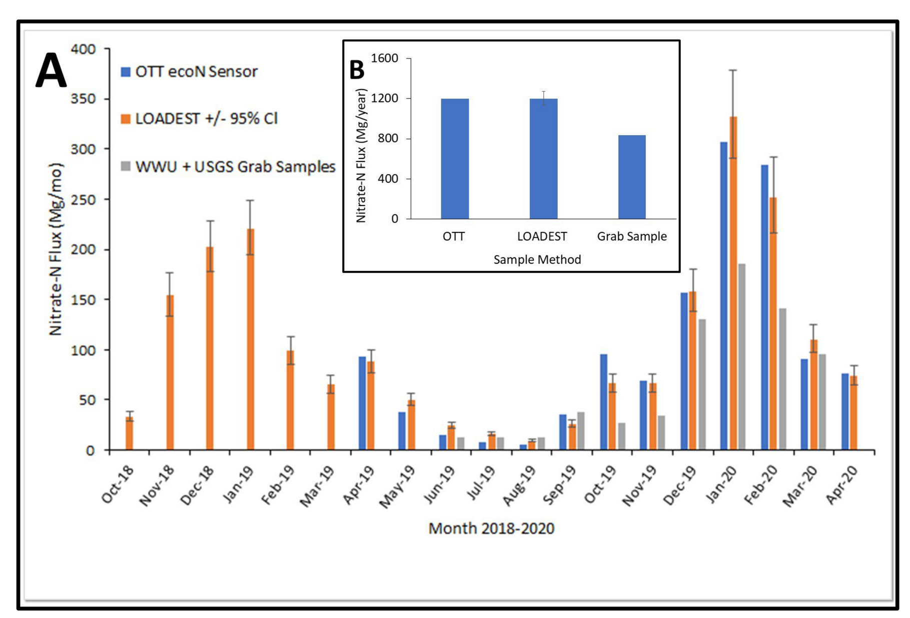

Figure 3. Estimates of nitrate-N flux measured by three different sampling methods in the Nooksack River: A) Monthly estimates from October 2018 to April 2020; B) Annual estimates from April 2019 through March 2020. OTT ecoN automatic nitrate sensor installed April 2019, gap in grab samples from June 2018 through May 2019. LOADEST model calibrated with monthly samplings by WA Dept. of Ecology from 2000 – 2018, shown with 95% CIs (A & B). We calculated annual estimates by summing monthly fluxes.

Seasonal Trends (Figure 3)

- More flow and N flux in the winter (Fig. 3A).
- **Differences among methods were greatest in winter high flows.**

Comparing Across Methods

- Grab samples underestimated fluxes during the rainy season. (Fig. 3A).
- Monthly LOADEST was close to sensor measurements, but not always within the 95% CI.
- **Annually, LOADEST did not differ from sensor fluxes (Fig. 3B).**
- **Grab samples underestimated the annual total by 30%.**

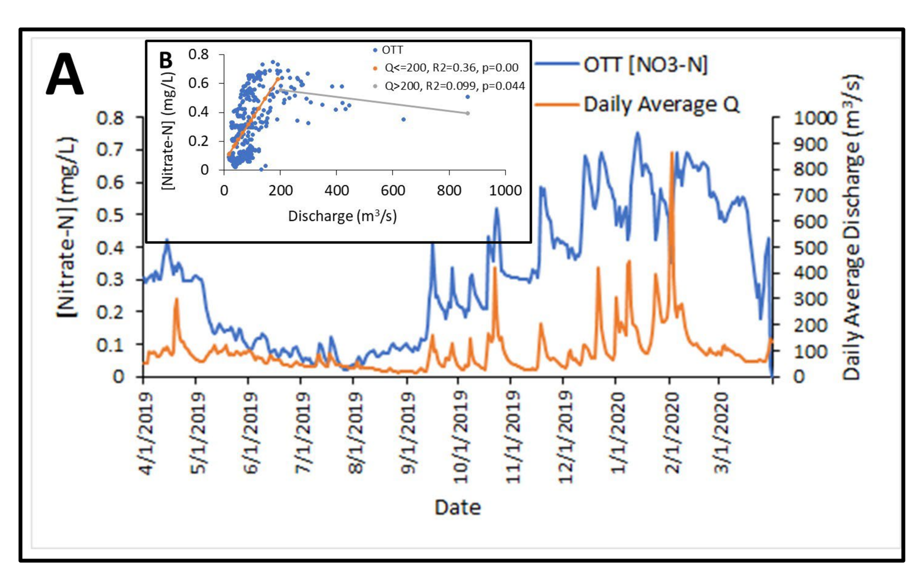

Figure 4. A) Nitrate concentration (mg N/L) measured by the real-time OTT sensor and daily average discharge (Q; m3/s) in the Nooksack River from April 1st, 2019 through March 31st, 2020. B) Nooksack River nitrate concentrations (mg/L, from OTT sensor) vs. discharge (Q; m3/s) from same time period.

Nitrate Concentrations (Fig. 4)

- Positive correlation between [nitrate-N] and discharge across seasons (Fig. 4A).
- However, N concentrations decreased during winter peak flow events, likely due to soil flushing and dilution (Lee 2004) (Fig. 4B)

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KAMM CREEK

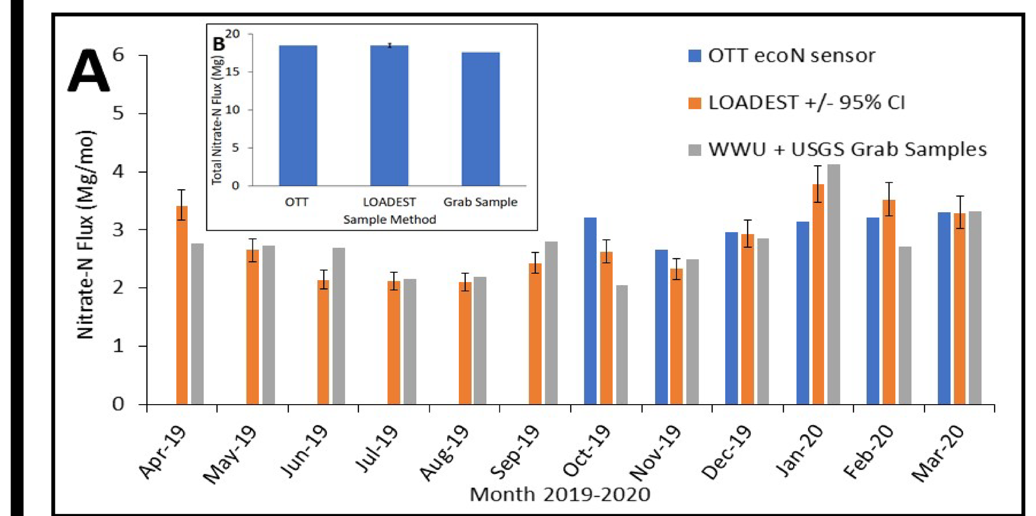

Figure 5. Estimates of nitrate-N flux measured by three different sampling methods in Kamm Creek: A) Monthly estimates from April 2019 to March 2020. OTT sensor data were reliable from October 2019, LOADEST and grab sample estimates were available from April 2019. B) Total nitrate- N fluxes (Mg/year) from October 2019 through March 2020, calculated by summing monthly fluxes. LOADEST model calibrated with monthly samples from WA State Dept. of Ecology and Hooper Lab at WWU from 9/2015 – 2/2020, shown with 95% CIs (A & B).

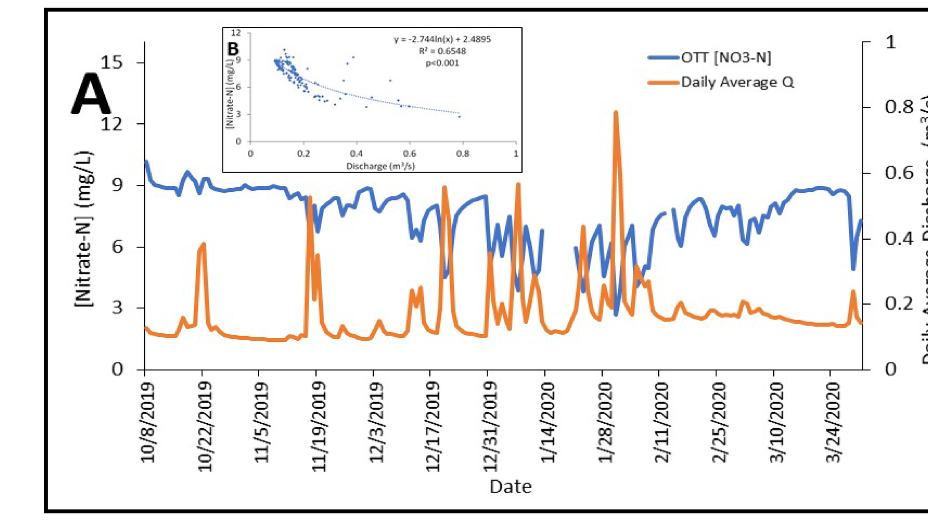

Figure 6. A) Nitrate concentration (mg/L) measured by OTT ecoN sensor and daily average discharge (Q, m^3/day) calculated from Levelogger in Kamm Creek from October 2019 to March 2020. OTT sensor data had gaps at the beginning of October 2019, and in January and February 2020, which we filled using regressions. We converted Levelogger instantaneous stream height measurements to discharge (Q) using a location-specific rating curve ($R^2 = 0.92$, $p << 0.001$, data not shown). B) Kamm Creek nitrate concentrations (daily average, mg/L, from OTT sensor) vs discharge (daily average, m^3/s) from October 2019 to March 2020.

Seasonal Trends (Figure 5)

- Kamm Creek had less seasonal variability in N flux, discharge, and [N], than did the Nooksack River or Fishtrap Creek.
- Our 5-year calibration data set for LOADEST in Kamm Creek resulted in better flux estimates than those seen for Fishtrap Creek.
- **More consistent discharge and [N] in Kamm Creek resulted reasonable estimates of N export with LOADEST and grab samples.**

Nitrate Concentrations (Figure 6)

- In Kamm Creek, discharge and nitrate concentrations had low seasonal variability (Fig. 6A), and concentrations consistently decreased with increasing flow (Fig. 6B).
- These trends that suggest high inputs from nitrate-laden groundwater (Carey 2017).

Comparing Across Methods

- **OTT technical difficulties caused data loss from Apr – Sep 2019.**
- Grab samples and LOADEST both under and overestimated monthly loads measured by the continuous sensor (Fig. 5A).
- However, across six months of available data, **sums were similar across methods**.

FISHTRAP CREEK

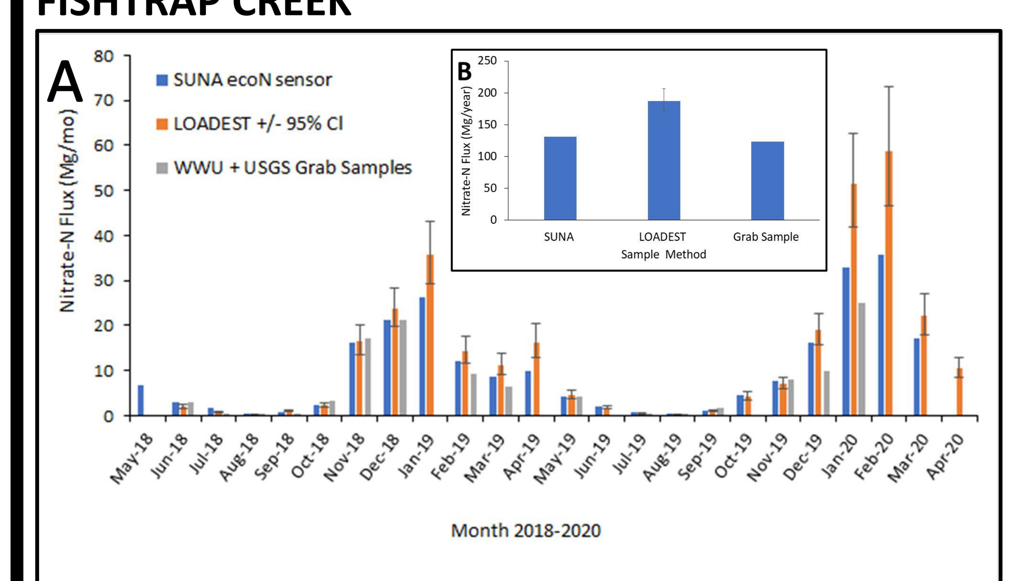

Figure 7. Estimates of nitrate-N flux measured by three different sampling methods in Fishtrap Creek: A) Monthly estimates from May 2018 to April 2020; B) Annual estimates from April 2019 to March 2020. LOADEST calibrated with monthly samples from WA State Dept. of Ecology and Hooper Lab at WWU from 6/2018 – 1/2020, shown with 95% CIs (A & B). We calculated annual estimates by summing monthly fluxes.

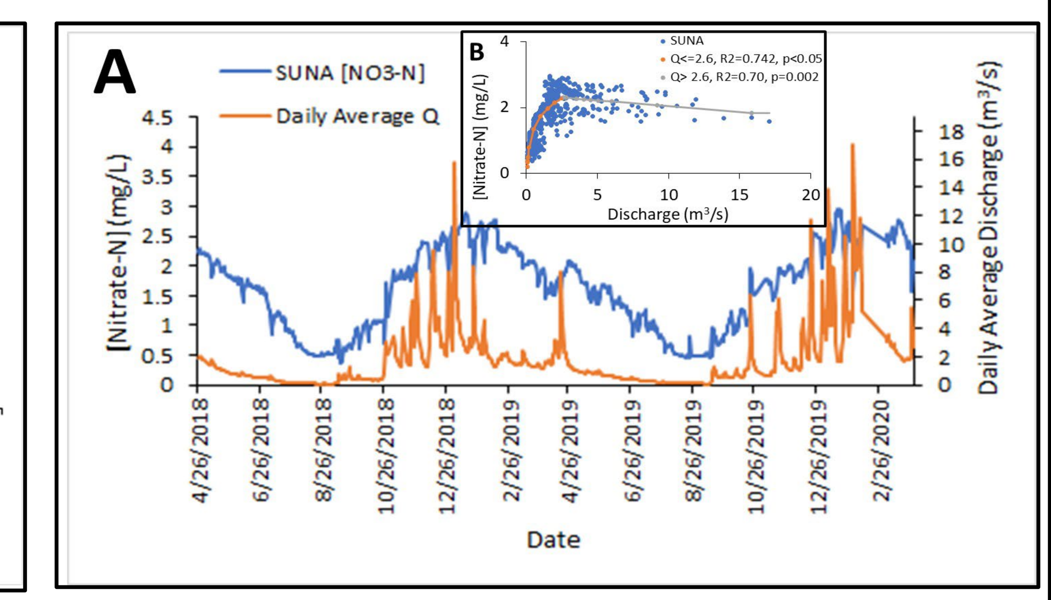

Figure 8. A) Nitrate concentration in mg/L measured by the real-time SUNA sensor and daily average discharge (Q; m^3/s) measured by USGS gauging station 12212050 in Fishtrap Creek from April 26th, 2018 to March 31st, 2020. B) Fishtrap Creek nitrate concentrations (mg/L, from SUNA sensor) vs. discharge (Q; m^3/s) from April 26th, 2019 to March 31st, 2020.

Seasonal Trends and Comparing Methods (Figure 7)

- Winter rainfall led to **high seasonal variability** in both discharge and nitrate flux in Fishtrap Creek (Fig. 7A).
- All three sampling methods captured the seasonal pattern; however, **the greatest differences among methods occurred during high winter flows**.
- LOADEST had limited calibration data at this site (~2 years), leading to extrapolation outside the calibration range and over-estimation of winter and spring fluxes (Fig. 7A): **more than 40% higher annually**.

Nitrate Concentrations (Figure 8)

- N concentrations increased seasonally with discharge, except large winter rainfall events created spikes in discharge that decreased N concentrations(Fig. 8A, 8B).
- These data suggest more limited input of groundwater to Fishtrap than Kamm:

Conclusions

- Real-time nitrate sensors are a gold standard for estimating fluxes – except when they fail.
- Accuracy of LOADEST modeling depended on a large calibration dataset for streams with highly variable flow.
- Accuracy of grab sample estimates depended on the stability of the stream flows.