Deschutes River
Continuous Nitrate Monitoring

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Cover photo: The Deschutes River near the E. Street Bridge in Tumwater, WA.
Photo taken by Brandon Sackmann.

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Deschutes River Continuous Nitrate Monitoring

by

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Waterbody Number: WA-13-1010

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Abstract

From October 21, 2009 through November 22, 2010, the Washington State Department of Ecology deployed a Submersible Ultraviolet Nitrate Analyzer (SUNA; Satlantic, Inc.) in the Deschutes River at the E. Street Bridge in Tumwater, Washington. The Deschutes River is high in nitrate and discharges to the South Puget Sound basin which is known to be sensitive to eutrophication.

The SUNA met all predetermined performance specifications and, after post-processing, provided nitrate estimates within 0.05 mg/L of coincident laboratory values. The high-resolution SUNA nitrate time series was used to develop statistical methods to quantify uncertainties associated with annual nitrate loading estimates derived from more coarsely sampled time series.

The cost-benefit of different sampling strategies was evaluated. The results suggest that a doubling of sampling effort did not yield estimates for the total annual load of nitrate that were twice as accurate (i.e., the slope of the cost-benefit relationship was <1). In general, a monthly sampling strategy was able to provide estimates of the total annual nitrate load that was within 10% of the true value, whereas a 10-day sampling strategy reduced the uncertainty to 5%.

The statistical techniques developed here can (1) be applied generally with other measured water quality parameters and (2) help evaluate uncertainty associated with other statistical metrics of interest.

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Introduction

From October 21, 2009 through November 22, 2010, the Washington State Department of Ecology (Ecology) deployed a Submersible Ultraviolet Nitrate Analyzer (SUNA; Satlantic, Inc.) in the Deschutes River at the E. Street Bridge in Tumwater, Washington. This location is both a long-term U.S. Geological Survey (USGS) gaging site (station 12080010) and an Ecology ambient monitoring site (station 13A060; Figure 1). The Deschutes River is high in nitrate and discharges to the South Puget Sound basin which is known to be sensitive to eutrophication.

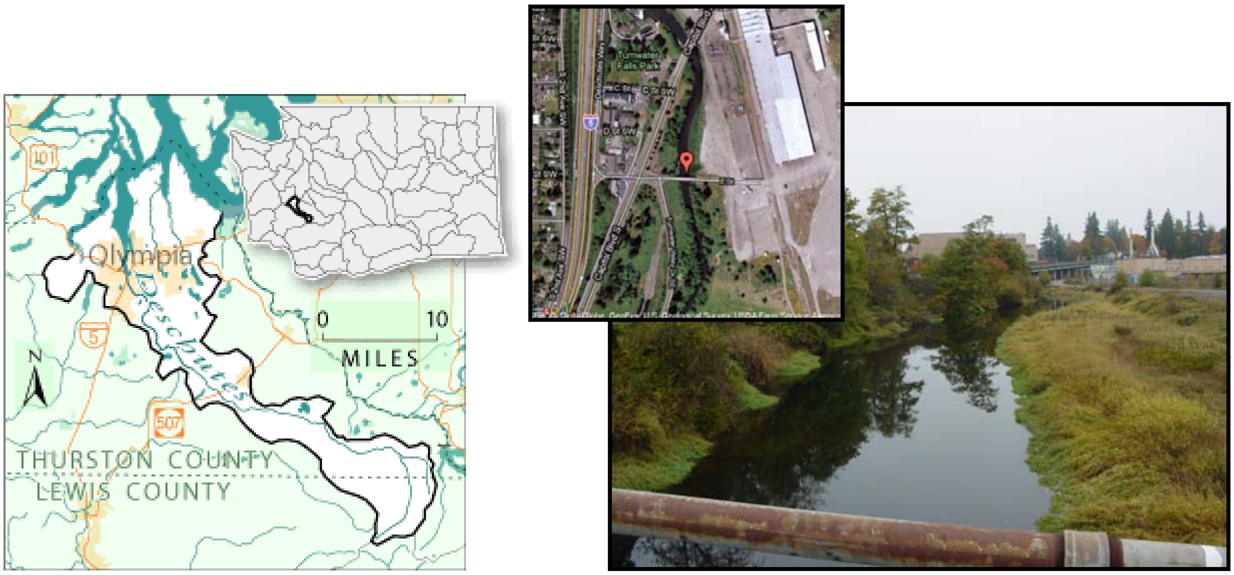

Figure 1. Location of study site on the Deschutes River at the E. Street Bridge, Tumwater, WA.

The SUNA is a real-time, chemical-free sensor designed to overcome the traditional challenges associated with reagent-based nitrate analysis in aquatic environments (Figure 2). The sensor uses advanced ultraviolet (UV) absorption technology to provide accurate nitrate concentration measurements in the sometimes highly turbid, high colored dissolved organic matter (CDOM) waters of rivers, lakes, and estuaries (Johnson and Coletti, 2002; Sakamoto et al., 2009).

Figure 2. Satlantic's Submersible Ultraviolet Nitrate Analyzer (SUNA).

Nutrient (e.g., nitrogen) pollution is considered one of the largest threats to Puget Sound. Inputs from oceanic sources, tributary inflows, point source discharges, nonpoint source inputs, sediment-water exchange, and atmospheric deposition determine the amount of nitrogen delivered to Puget Sound. Recognized nation-wide, the following characteristics of nitrogen pollution apply equally and imperatively to Puget Sound (Glibert et al., 2005; Howarth, 2006; Howarth and Marino, 2006):

- Human acceleration of the nitrogen cycle over the past 40 years is far more rapid than almost any other aspect of global change.
- Nutrient pollution leads to hypoxia and anoxia, degradation of habitat quality, loss of biotic diversity, and increased harmful algal blooms.
- Technical solutions exist and should be implemented, but further scientific work can best target problems and solutions, leading to more cost-effective solutions.

While eutrophication can be a natural process, anthropogenic nutrient pollution can cause *cultural eutrophication* which is the process of amplified eutrophication resulting from human activity. Both natural and cultural eutrophication occur when a body of water becomes enriched with nutrients which, in turn, stimulate excessive algal growth. Oxygen consumption results from the subsequent decomposition and respiration of the excess algae by bacteria. This leads to dissolved oxygen depletion in areas that are not well ventilated (e.g., quiescent bays and near-bottom waters).

Future marine Total Maximum Daily Load (TMDL; water cleanup) studies and water quality modeling projects in Puget Sound require highly resolved time series of nitrate discharge from fluvial sources. Currently, daily loads of nitrate are estimated statistically from monthly observations of nitrate concentration and multiple linear regressions (MLR) that are functions of measured flow and time of year (Roberts and Pelletier, 2001; Mohamedali et al., 2011; Roberts et al., 2011). The continuous nitrate time series collected for this study allowed Ecology to:

- Assess the performance of the SUNA over a one-year deployment in a freshwater stream.
- Quantify many uncertainties implicit in the MLR approach for estimating nitrate loads.
- Define strategies to quantitatively assess the cost-benefit of different nitrate sampling strategies.
- Explore the benefits of high-resolution SUNA nitrate estimates for instream process studies.

Methods and Experimental Design

The Quality Assurance (QA) Project Plan for this project (Sackmann, 2009) was carefully followed to ensure that data collection efforts were conducted according to standard Ecology protocols. While the following section includes a brief overview of the methods and experimental design, much of the discussion focuses on topics that were not included in the QA Project Plan.

Continuous Sampling

Ecology sampled sensor-derived water quality parameters continuously every 15 minutes (on the quarter-hour), approximately one meter off the streambed, from October 21, 2009 through November 22, 2010. The station was established as a telemetry station with the capability to transmit data every three hours to Ecology Headquarters in Olympia where the data were automatically imported into the streamflow database and published to Ecology's website.

Figure 3. Sensor installation at E. Street Bridge location.

Left: data logger, automatic refrigerated sampler, batteries, and telemetry equipment.
Middle: in-situ sensors installed in protective aluminum housing alongside intake to automatic pump sampler.
Right: sensors deployed in the Deschutes River; pump intake and sensor were positioned approximately one meter off the streambed.

Discrete Sampling

Field Sampling

Discrete grab samples from the near-surface were collected at the E. Street Bridge site three times per month (approximately every 10 days). Manchester Environmental Laboratory (MEL) analyzed the samples for both total and dissolved nitrate, nitrite, and nitrite+nitrate. Duplicate samples and field blanks were collected for QA/quality control (QC) purposes. During each site visit, optical windows were cleaned to reduce the effects of bio-fouling, and sensors were visually inspected for damage that may have been caused by instream debris, especially after high-flow events. Beginning in January 2010, samples were also collected from the Henderson Street Bridge and analyzed for total nitrite+nitrate. This second site is approximately 3.79 km upstream from the primary E. Street Bridge site, just above the Tumwater Valley Golf Course.

Automatic Pump Sampling

Field staff used a 14-bottle refrigerated sequential pump sampler to automatically collect and preserve water samples for determination of nitrite+nitrate. Samples were harvested and transported to MEL as part of the three site visits per month. The 950-ml sample bottles were pre-acidified and prepared with the recommended quantity of preservative (sulfuric acid; H2SO4). Because sample preservation was required, it was necessary to limit laboratory analyses to total nitrite+nitrate. To characterize systematic biases that may exist between collection methods, the automatic pump sampler was manually triggered to collect a sample during each site visit for comparison with coincident discrete grab samples. Pump intake was positioned approximately one meter off the streambed.

The sampling logic for the sequential pump sampler was refined over the course of the deployment. The final configuration ensured that samples were collected *when*:

1. The absolute difference between the previous and current SUNA nitrate value was < 0.1 mg/L; this validation procedure was used to evaluate new data for outliers, AND

2. The absolute difference between the approximate median SUNA nitrate value (0.7 mg/L) and the current value climbed above one of the following thresholds (steps): 0.10, 0.15, 0.20, 0.25, 0.30, and 0.35 mg/L. To limit the number of samples collected at each step, it was necessary to *lock out* a step until a new result triggered the step +2 above or the topmost step had been reached. All steps were reset when the calculated difference dropped to < 0.05 mg/L, OR

3. The elapsed time since the last sample was > 72 hours.

This robust sampling design ensured that pumped samples were collected as SUNA nitrate values both climbed and fell. It also ensured that samples would be collected every three days during periods of little nitrate variability.

Freshwater Ambient Monitoring Sampling

The deployment location in the Deschutes River at the E. Street Bridge in Tumwater is both a long-term USGS gaging site (station 12080010) and an Ecology ambient monitoring site (station 13A060). By deploying at an active ambient monitoring site, project staff were able to incorporate the monthly discrete values of dissolved nitrite+nitrate that were collected. Sampling was performed according to the protocols outlined in Ward (2007).

Sensor Maintenance and Servicing

Sensor Performance Checks

Field staff performed five sensor performance checks with the SUNA at Ecology's Operations Center. Optical windows were cleaned using cotton swabs, and the sensor was inspected for any signs of damage. The SUNA was placed in a calibration bath to measure the nitrate concentration in ultra-clean de-ionized water to verify that values were below the sensor's minimum detection threshold (±0.028 mg/L). Readings between ±0.028 mg/L indicate that the instrument response had not drifted.

While de-ionized water values rose systematically over the one-year deployment, all values were within the recommended range, and it was not necessary to update the instrument's internal reference spectrum (Table 1). In general, the amount of drift is expected to be proportional to the amount of time used on the lamp.

Table 1. Summary of SUNA ultra-clean de-ionized water blank readings.
Values calculated from 50 discrete scans (n = 50); readings between ±0.028 mg/L indicate the instrument response has not drifted. SUNA UV lamps are rated to last approximately 1000 hrs.

Date	Lamp Time Used (hr; % Remaining)	De-ionized Water Blank (mg/L)
October 15, 2009 (pre-deployment)	41.6 (96%)	-0.021
January 19, 2010	90.8 (91%)	-0.020
April 15, 2010	140 (86%)	-0.005
July 19, 2010	193 (81%)	0.003
November 22, 2010 (post-deployment)	276 (72%)	0.018

After verification that nitrate concentrations in de-ionized water were below the detection threshold, standard solutions ranging from 0 to ~3 mg/L were prepared using dissolved potassium nitrate. Subsamples of each standard solution were sent to MEL for laboratory determination of dissolved nitrate. Coincident SUNA average nitrate and relative standard deviation (%RSD) were calculated from 50 discrete instrument scans (i.e., n = 50).

Laboratory tests revealed that SUNA nitrate estimates were ~2.2% higher than MEL nitrate across the range of environmental nitrate concentrations observed during the study (i.e., <1.2 mg/L), and %RSD was <1% when SUNA nitrate exceeded 0.5 mg/L. Correlation between MEL nitrate and SUNA nitrate measurements was >0.99 (Figure 4). Variability was markedly more pronounced at nitrate concentrations >1.2 mg/L. This increased variability could be due, in part, to MEL's additional dilutions and sample handling to get sample nitrate concentrations into the proper range for analysis.

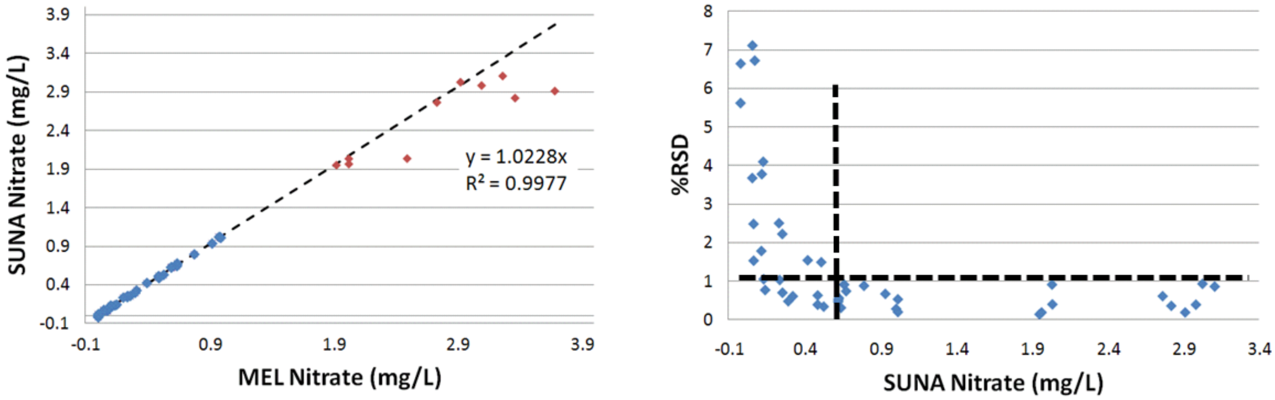

Figure 4. Results of SUNA sensor performance checks.

Left: comparison of MEL dissolved nitrate and average SUNA nitrate.
Right: %RSD calculated from 50 discrete SUNA scans across a range of average SUNA nitrate concentrations.

Lamp Degradation

Over the course of the one-year deployment there was a time-varying increase in the amount of high-frequency variability associated with the SUNA nitrate estimates (Figure 5). A 1-hr high pass filter was used to highlight the observed pattern. This increased variability is consistent with the expected decay of ultraviolet lamp used by the SUNA.

The integration time on the SUNA was set to 250 milliseconds and held constant. In general, as an ultraviolet lamp ages, it will be necessary to concomitantly increase the sensor's integration time to achieve a reasonable signal-to-noise ratio. The choice to not adjust the integration time during this study was deliberate, as we were specifically interested in the effects of lamp degradation on sensor performance. The raw SUNA signal measured at 220 nanometers can be used as a guideline to assess lamp health, and it is recommended that the value stay above 15,000 counts. All SUNA nitrate measurements were first smoothed using a one-hour high pass filter before being used in any statistical analyses.

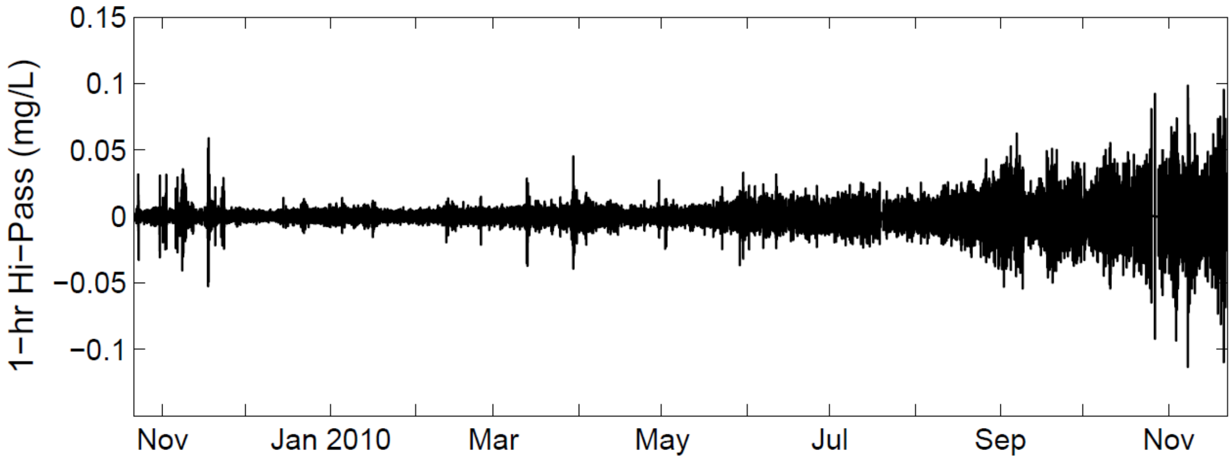

Figure 5. Results from a one-hour high pass filter of SUNA nitrate measurements showing a time-varying increase in signal variability associated with lamp degradation.

Interference Species and Nitrite Sensitivity

Various dissolved and particulate substances in the water can interfere with the UV spectra sampled by the SUNA. To this end, a Forest Technology Systems DTS-12 turbidity/temperature sensor and a Wetlab's Colored Dissolved Organic Matter (CDOM) fluorometer were used to continuously monitor both turbidity levels and concentrations of CDOM, respectively, in the vicinity of the SUNA. While some unexplained residual nitrate variability remained after post-processing and adjustment of the SUNA data to match coincident lab results, the differences were generally observed to be <5% and showed no obvious pattern with either turbidity levels or CDOM fluorescence.

Due to similar UV absorption spectra, the SUNA may also be sensitive to dissolved nitrite if present in large concentrations. To mitigate the influence of nitrite, the optical algorithms provided with the instrument have been designed to produce accurate estimates of nitrate in mixed standard solutions of nitrite+nitrate at similar molar ratios, as well as in ambient waters where nitrite concentrations are much lower than nitrate. Fortunately, nitrite concentrations were very low at the location chosen for this study and, in all cases, were below the analytical detection limit of 0.01 mg/L.

Data Post-Processing and Adjustment

The geometric mean Model II regression technique (reduced major axis method) was used to quantify the relationship between MEL nitrite+nitrate and SUNA nitrate. This method is preferred when neither dataset is controlled or free of error. The resulting slope minimizes the absolute value of the sum of the products of the deviations between the observations and the regression line in both the X and Y directions (Ricker, 1973; Laws and Archie, 1981). Correlation between MEL nitrite+nitrate and SUNA nitrate measurements was used to assess the strength and statistical significance (p-value <0.05) of a linear relationship between the observations.

Bootstrap Technique for Estimating Loading Uncertainties

Ecology has developed a statistical method for estimating daily loads of nitrate from more coarsely sampled time series of nitrate concentrations and multiple linear regressions (MLR) that are functions of measured flow and time of year (Cohn et al., 1989; 1992; Roberts and Pelletier, 2001; Mohamedali et al., 2011; Roberts et al., 2011).

To evaluate the performance of the MLR approach, a simple statistical bootstrapping technique was used to develop many alternative estimations of the average annual nitrate load. The complete 15-minute SUNA nitrate dataset was randomly sub-sampled (with replacement) to create a large number of datasets that *could have been* observed. For each subset, the MLR approach was used to estimate daily nitrate loads which were then compared to the observed time series and average annual load estimate of 678 kg/d. Different sampling strategies were simulated to determine how sampling frequency influenced the level of uncertainty associated with the MLR estimates of average annual nitrate loads. This procedure was repeated 10,000 times for each sampling scenario that was evaluated.

Sampling scenarios were defined by an interval ± time window (e.g., monthly sampling; 30 ± 3 days). For example, one might want to sample monthly (every 30 days), but due to logistical constraints an individual sampling event may be offset by as much as 3 days from when a particular sample was scheduled to be collected. In this case, the sampling interval is 30 days, and the time window is 3 days. Using a similar logic, the bootstrap sampling simulated intervals ranging from 3-45 days with a constant time window of 3 days.

Random sampling of the 15-minute SUNA nitrate dataset was carried out as follows:

1. A random sample was selected from within the first time interval of the time series; this defined the sampling start date. All subsequent sampling events were initialized based on the chosen start date and sampling interval.
2. For each sampling event following the start date, a random sample was chosen from within the chosen time window surrounding each scheduled sampling event. In this way a random subsample of data, with a desired sampling interval, could be extracted from the complete high-resolution SUNA nitrate time series.

Results and Discussion

Without exception, SUNA nitrate estimates and laboratory results from manually collected discrete samples met or exceeded data quality and usability objectives defined in the QA Project Plan. A systematic bias was observed with the laboratory results associated with the automatic pump sampler. This bias limited the utility of these data for the purposes of validating SUNA nitrate estimates.

Laboratory Result Inter-Comparison

A total of 591 discrete samples (955 lab results) and ~38,000 SUNA nitrate measurements were collected for this study (Table 2; Figure 6). All blanks were below the analytical detection limit of 0.01 mg/L with respect to nitrate, nitrite, and nitrite+nitrate. The average percent difference between duplicate samples was 0.44% (*n* = 28).

Table 2. Sampling summary (includes duplicates).

Type of Sample	Total			Dissolved		
	NO3	NO2	NO2+NO3	NO3	NO2	NO2+NO3
Automatic pump (auto)	-	-	298*	-	-	-
Discrete grab	35	34	36	52	51	52
Automatic pump (manual)	-	-	37	-	-	-
Freshwater ambient monitoring	-	-	-	-	-	14
Henderson Street Bridge	1	1	19	-	-	-
Sensor performance checks	-	-	-	40	40	40
Field and calibration blanks	-	-	36	56	55	56
Runoff/rain	-	-	2	-	-	-
Total	36	35	428	148	146	162
Grand Total						*955*
--*SUNA nitrate measurements*	*~38K*					

* Holding times ranged from 0 to 10 days inside refrigerated sampler.
NO3 = nitrate; NO2 = nitrite; NO2+NO3 = nitrite+nitrate

Ecology protocols require filtration of field samples that are to be analyzed for nitrate, nitrite, and/or nitrite+nitrate (Ward, 2007). Since samples from the automatic pump sampler could not be automatically filtered, it was necessary to quantify any systematic differences between dissolved and total nitrate and nitrite+nitrate. The average percent error between total and dissolved nitrate and nitrite+nitrate was -0.85% (*n* = 71; Figure 7). This small but consistent bias is likely due to residual nitrate uptake within unfiltered samples. These differences are of a sufficiently small magnitude as to have little influence on efforts to use discrete field samples to validate SUNA nitrate estimates. For the purposes of this study, total and dissolved results have been used interchangeably.

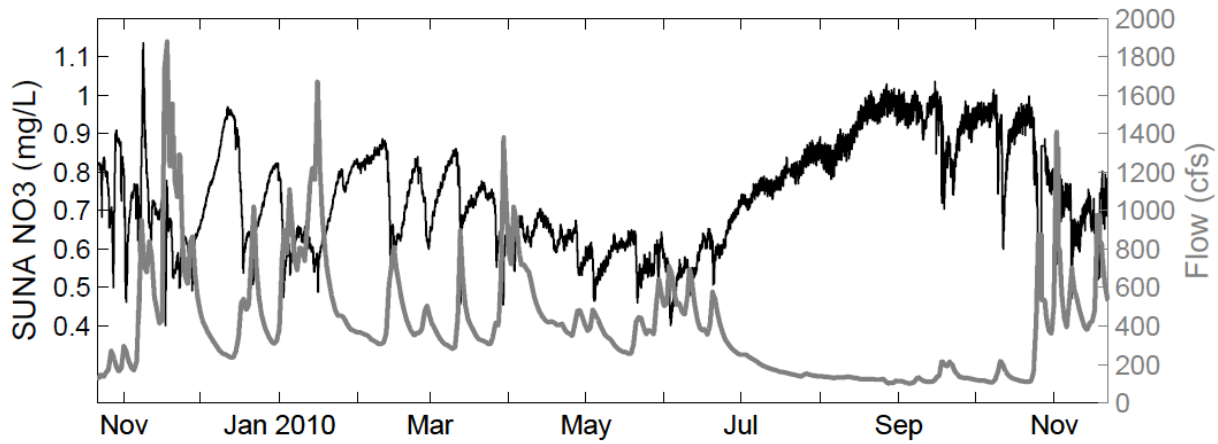

Figure 6. 15-minute unadjusted SUNA nitrate estimates from the E. Street Bridge site.

Daily flow estimates were provided by the USGS and validated using Ecology's on-site stage height measurements.

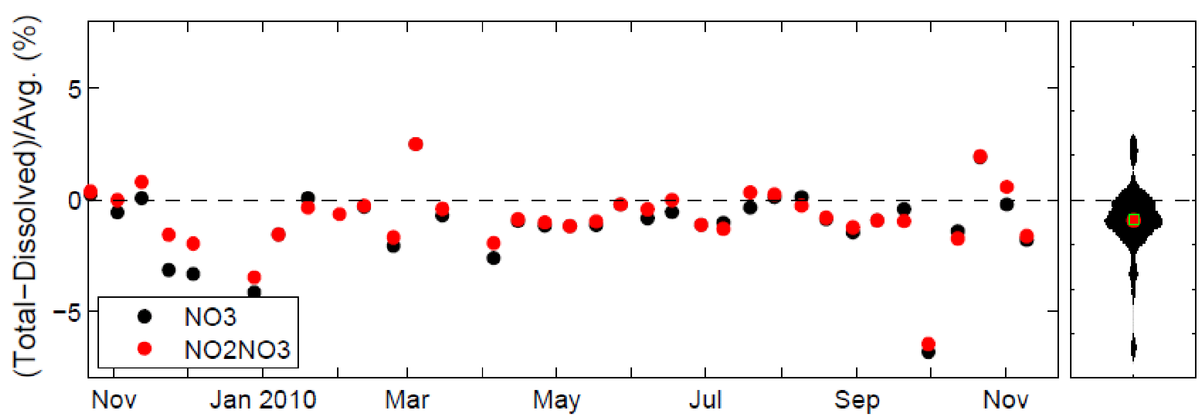

Figure 7. Time series of the percent error between coincident total and dissolved nitrate and nitrite+nitrate.

Average value was -0.85% (n = 71).

Historically, nitrite values have been very low (usually below detection) in the Deschutes River. Results from this 2009-10 study were consistent with this historical trend (Figure 8), thereby allowing for the direct comparison between SUNA nitrate estimates and MEL estimates of nitrate and/or nitrite+nitrate. Values of nitrite were below analytical detection limits, and the average percent error between nitrite+nitrate and nitrate was 0.31% (*n* = 87; total and dissolved results combined, see above).

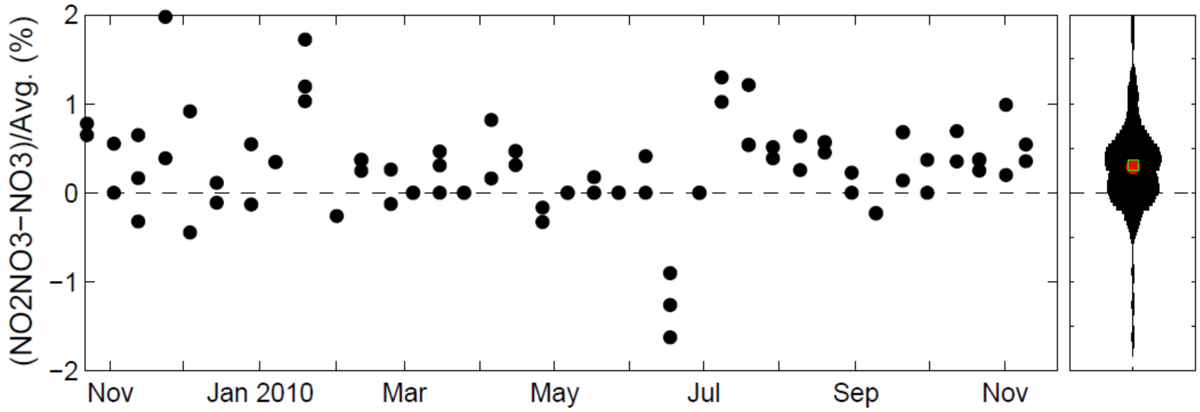

Figure 8. Time series of the percent error between coincident nitrite+nitrate and nitrate (both total and dissolved).
Average value was 0.31% (n = 87).

Comparison between grab samples and automatic pump samples revealed a small, systematic bias. The configuration of the sensor installation dictated that the intake for the automatic pump sampler be held at a fixed depth approximately one meter above the streambed. As such, the samples taken by the automatic sampler were collected from a deeper depth than could be achieved with the discrete grab samples at the surface. It is believed that the difference in precise sampling location is at least partially responsible for the systematic bias observed between coincident grab and automatic pumped samples (Figure 9).

In general, nitrate values from the automatic pumped sampler were anywhere from 0 – 5% lower than the near-surface grab sample. This is consistent with more instream algal production and nitrate uptake at the sediment-water interface.

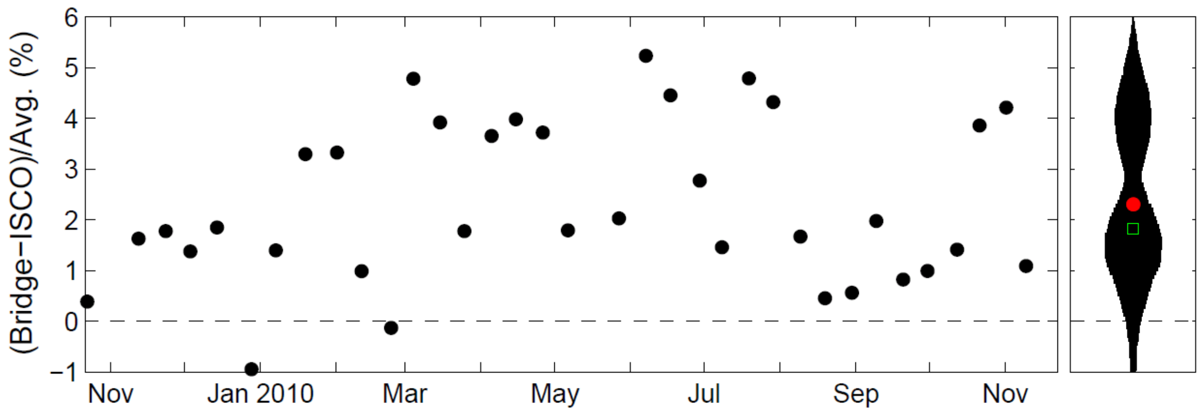

Figure 9. Time series of percent error between coincident discrete grab samples and automatic pumped samples (ISCO) analyzed for total nitrite+nitrate.
Average value was 1.82% (n = 36).

SUNA Nitrate Validation and Sensor Performance

SUNA nitrate measurements were adjusted to match discrete field measurements of nitrite+nitrate using a geometric mean Model II regression (Figures 10-11). For the purposes of adjusting the SUNA nitrate data, only surface grab samples collected as part of this study were used. SUNA nitrate measurements were approximately 7.7% higher than what was measured by MEL, and the measurements displayed excellent linearity ($r^2 = 0.96$). The bias between SUNA and MEL nitrate estimates was higher in the field than what was observed from the quarterly sensor performance checks, 7.7% vs. 2.2%, respectively. This is likely due to additional interfering species present in the field environment that were not replicated in the lab.

Results from Ecology's freshwater ambient monitoring and *coincident* automatic pump samples revealed very similar patterns. The automatic pumped samples were systematically lower, as described above, but the overall pattern was similar to the other datasets evaluated. That said, the automatic pumped samples collected throughout the 10-day interval between site visits revealed much lower nitrite+nitrate values than was otherwise predicted by the Model II regression. Even though these samples were refrigerated and stored with the proper amount of sulfuric acid preservative, it is believe that these precautions were not sufficient to arrest all biological activity within the samples, allowing for some residual nitrate uptake.

Adjusted SUNA nitrate estimates in the Deschutes River ranged from approximately 0.4 – 1.0 mg/L and averaged 0.7 mg/L. These values are well within the range of historical values reported for the site (Sackmann, 2009; their Figure 3). As expected, nitrate showed a strong inverse relationship with flow, consistent with groundwater sources that become diluted with increased surface runoff and river flow (Figure 6). The only time when the inverse relationship between nitrate and flow was not observed was during the first high-flow event captured in November 2009. Nitrate concentrations associated with this event increased as flow increased and provided the maximum nitrate concentration observed.

This initial flushing of nitrate (Figure 11) in 2009 was likely the result of nitrate accumulation in the adjacent watershed over the previous year, but was not observed with the first major flow events of 2010. The spring and early summer of 2010 were particularly wet, and river flows were well above normal. Increased rainfall may have facilitated the prolonged mobilization of nitrate and reduced the overall accumulation of nitrate in soils in 2010 as compared with 2009.

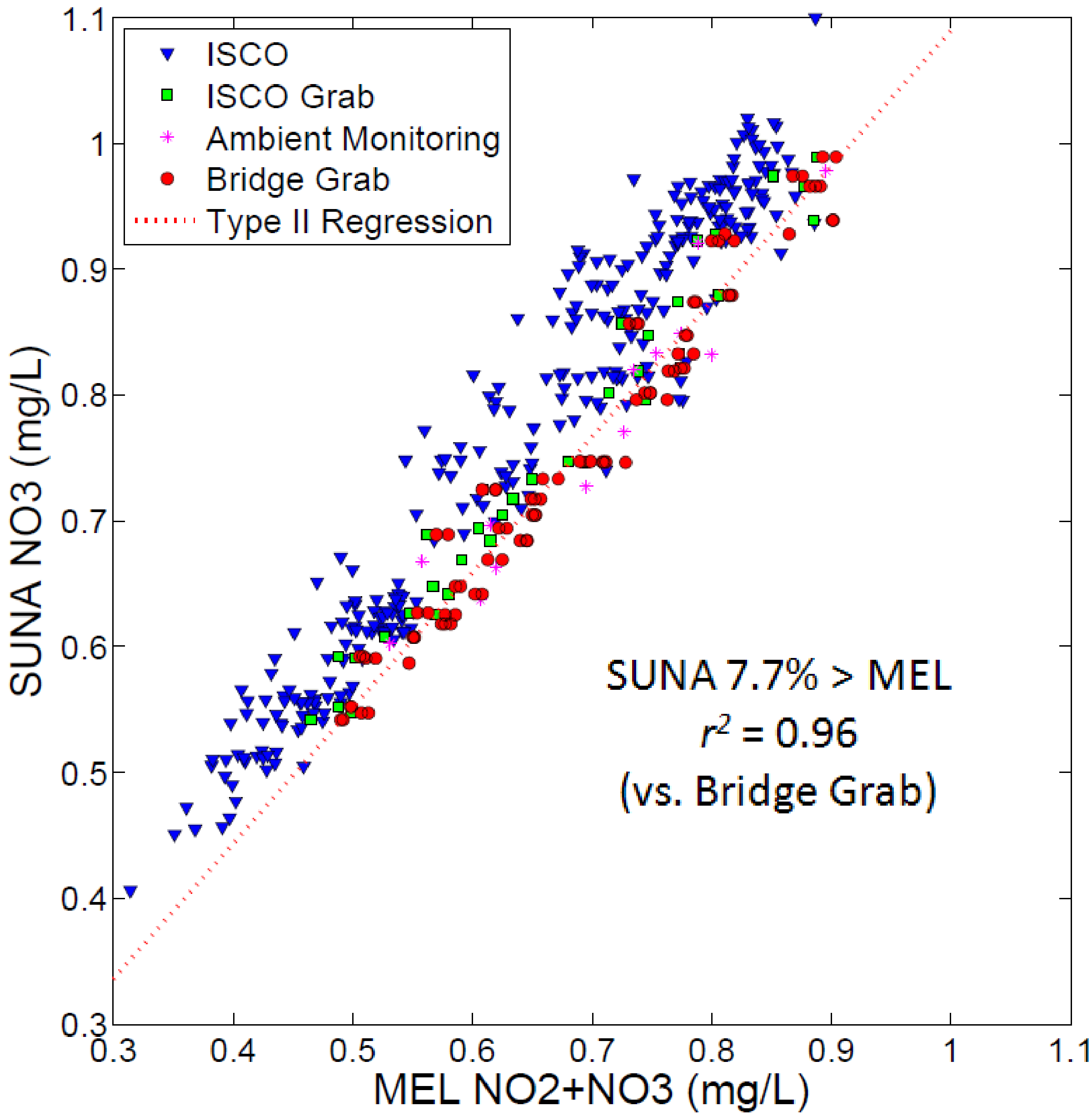

Figure 10. Model II regression results used to adjust SUNA nitrate to match MEL nitrite+nitrate.

ISCO = automatic pumped samples.
*SUNA = 1.0768*MEL + 0.012825.*

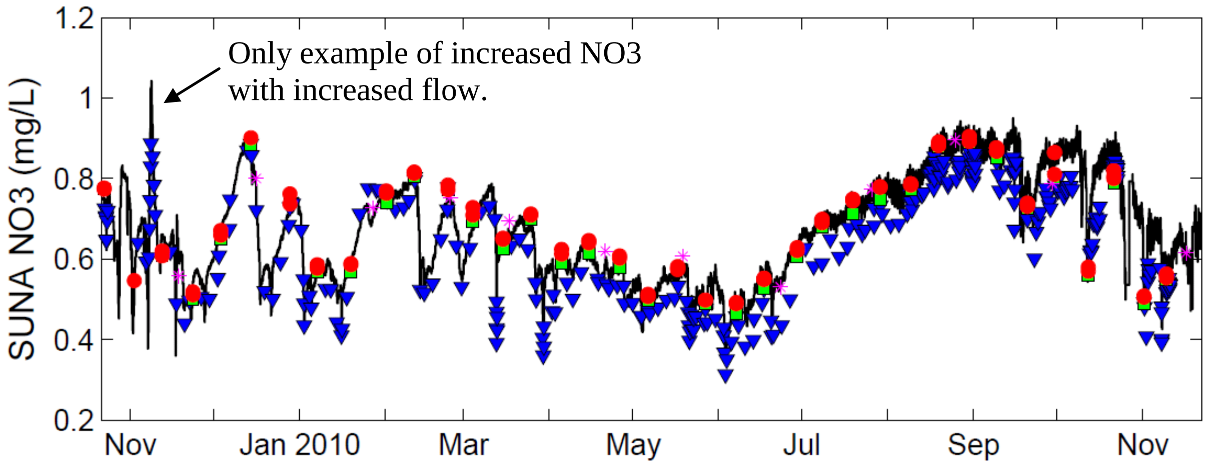

Figure 11. Time series of laboratory-adjusted SUNA nitrate values.
Legend same as in Figure 10.

Adjusted SUNA values were found to be within 0.05 mg/L of coincident laboratory values (Figure 12). On average, these values are well within the specifications outlined in the QA Project Plan. Patterns in the residual differences suggest that the adjusted SUNA values have a tendency to be more negatively biased during the winter, perhaps due to differences in the type and quantity of the interfering materials present.

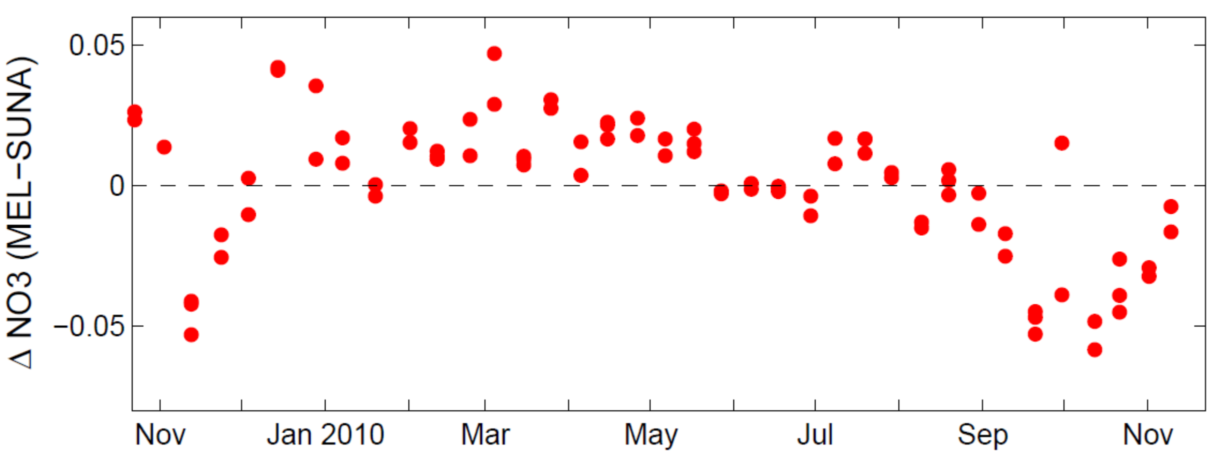

Figure 12. Time series of residual nitrate difference between the SUNA and coincident MEL values.

Loading Uncertainty as a Function of Sampling Strategy

The statistical bootstrapping technique outlined above was used to simulate sampling intervals ranging from 3 to 45 days with a time window of ±3 days. Figure 13 shows representative results from the 30-day and 10-day simulations, respectively. For brevity, only 100 out of the total 10,000 simulations are shown.

As expected, when a smaller dataset (30-day sampling) was used to develop the MLR for predicting daily nitrate concentrations, the difference between observed and predicted concentrations increased. That said, even a 30-day sampling interval managed to capture the most salient features of the true nitrate time series and the strong inverse relationship with flow. Even MLRs developed with samples collected every 10 days were not able to accurately predict the more extreme nitrate variations. This is a manifestation of the smoothing effect that is to be expected with an MLR-based approach.

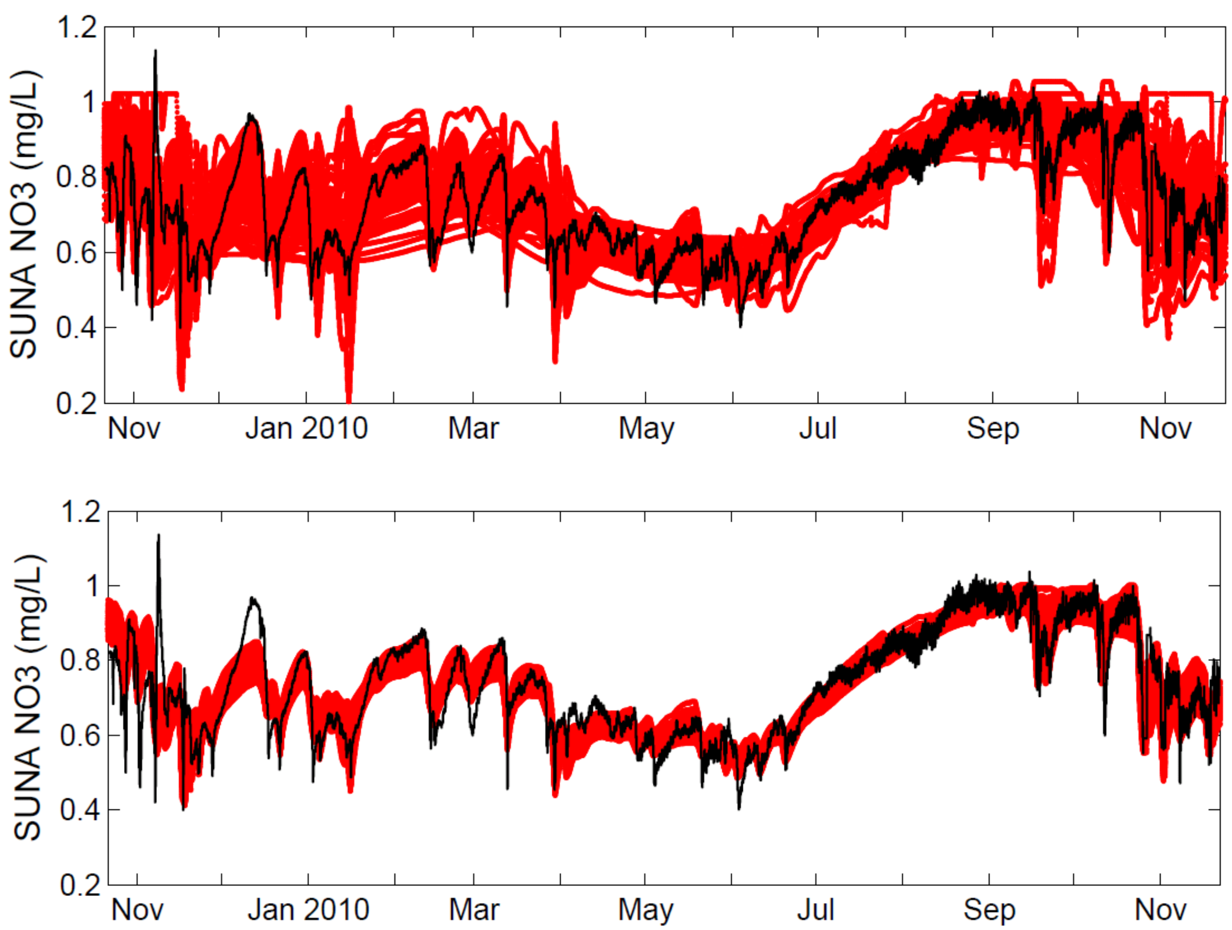

Figure 13. Bootstrapping simulations using a 30-day (top) and 10-day (bottom) sampling interval, each with +/- 3-day time window.

The annual average nitrate load estimated from the complete SUNA time series equaled 678 kg/d. Comparison values from the 10,000 bootstrap stimulations for the 10- and 30-day sampling intervals are presented in Figure 14. A standard 30-day sampling design, similar to the one used by Ecology's freshwater ambient monitoring program, yielded estimates of average annual nitrate load that were within 10% of the true value over 95% of the time. In contrast, a 10-day sampling design, similar to the one used for this study, yielded an average nitrate load that was within 5% of the true value over 95% of the time.

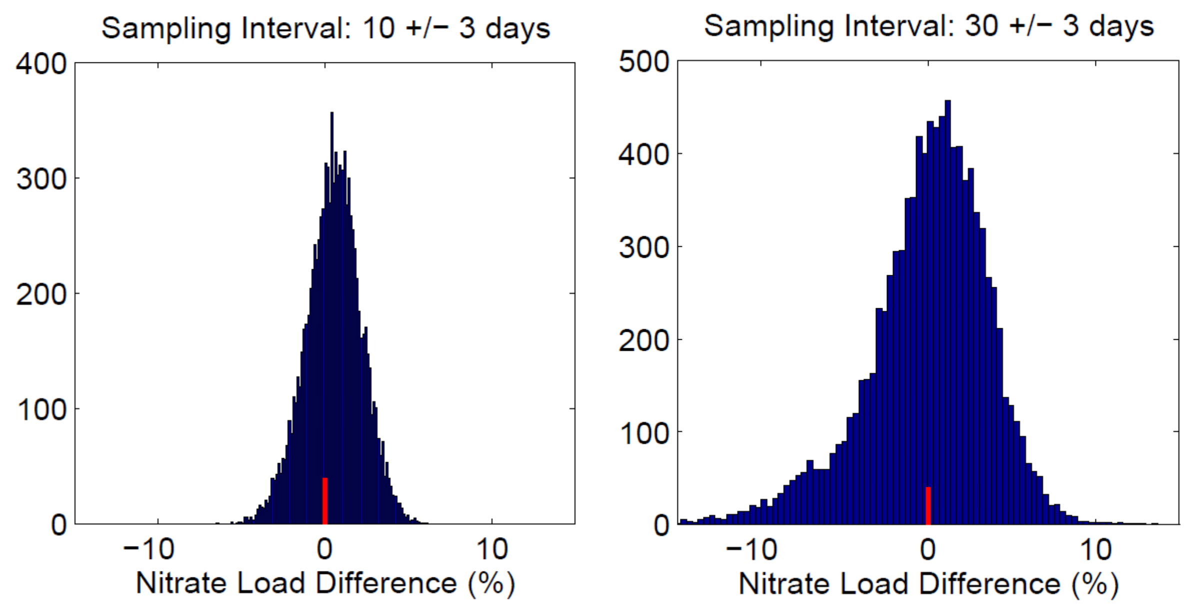

Figure 14. Histograms of percent differences between observed and simulated annual nitrate load estimates for 10-day (left) and 30-day (right) sampling intervals.

The cost-benefit of different sampling strategies with intervals ranging from 3-45 days was evaluated and characterized (Figure 15). The slope of the empirical cost-benefit relationship was <1. This suggests that doubling the sampling effort did not yield estimates for the total annual load of nitrate that were twice as accurate. In general, a monthly sampling strategy was able to provide estimates of the total annual nitrate load that were within 10% of the true value, whereas a 10-day sampling strategy reduced the uncertainty to only 5%.

The statistical techniques developed here can be applied generally with other measured water quality parameters and can also help evaluate uncertainty associated with other statistical metrics of interest. The results can be very useful when designing new studies, allowing for the efficient use of resources to implement sampling programs that have a greater chance of achieving a particular level of accuracy in the desired outputs.

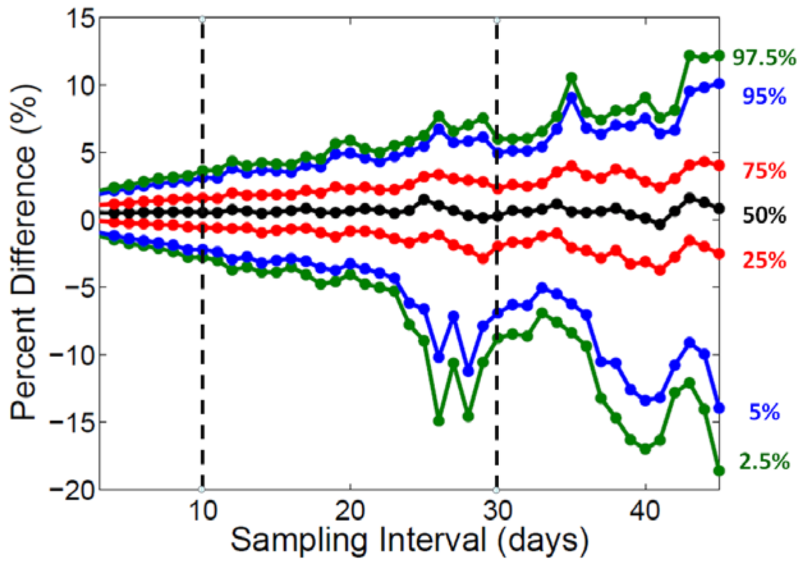

Figure 15. Histograms of percent difference from 10,000 simulations carried out for sampling intervals ranging from 3-45 days that define an empirical cost-benefit relationship between sampling effort and accuracy in the total annual load of nitrate.
Lines denote standard percentiles.

Diurnal Variability and Relationships with Instream Processes

The SUNA was sensitive enough to resolve subtle diurnal patterns reflecting instream biological processes (e.g., uptake and (de)nitrification). The strong inverse relationship between water temperature and nitrate concentration is likely due to increased algal uptake at warmer temperatures and/or increased rates of denitrification relative to nitrification (Pellerin et al., 2009; Heffernan and Cohen, 2010).

The amplitude of the diurnal nitrate variability was time-varying, with the largest amplitudes observed in late summer and early fall (Figure 16). In an attempt to compare upstream and downstream nitrate concentrations, additional grab samples were taken from the Henderson Street Bridge approximately 3.79 km upstream from the E. Street Bridge. These samples were consistently collected 1-2 hours after the samples from the E. Street Bridge, closer to the mid-day maximum nitrate concentration.

On average, the Henderson Street Bridge samples were 16% higher than those collected at the E. Street Bridge (n = 19), with larger differences observed in late summer and early fall. These results provide analytical confirmation of the strong diurnal patterns observed in the high-resolution SUNA nitrate time series. The ability to collect high-resolution nitrate time series extends Ecology's ability to perform detailed instream process studies, especially if the SUNA were to be deployed as part of a larger suite of sensors (e.g., dissolved oxygen, pH, solar radiation).

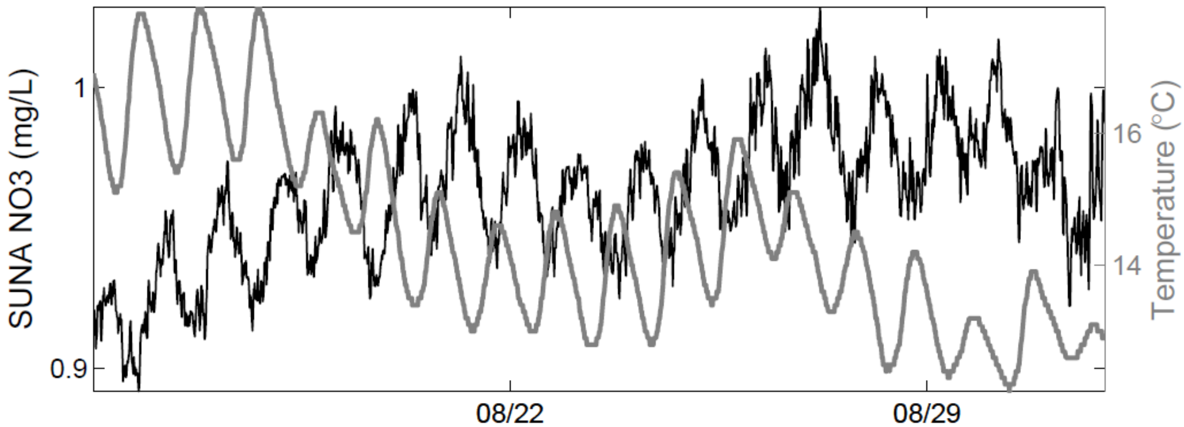

Figure 16. Example of diurnal nitrate variability from August 2010 showing a strong inverse relationship with water temperature.

Conclusions

The Submersible Ultraviolet Nitrate Analyzer (SUNA) performed well within the specifications outlined in the QA Project Plan, and the 2009-10 study accomplished each of the three goals that had been identified for the study:

- Continuously monitor dissolved nitrate concentrations in the context of other environmental conditions in the Deschutes River for a period of one year.
- Analyze coincident field grab samples for dissolved nitrate to quantify the accuracy and precision of SUNA nitrate estimates.
- Use a continuous time series of nitrate concentrations to develop new or refined statistical methods for predicting continuous daily loads of nitrate from a limited number of discrete observations.

The statistical techniques developed during this study can be applied generally with other measured water quality parameters and can help evaluate uncertainty associated with other statistical metrics of interest. This approach can also be used to perform cost-benefit analyses to evaluate different sampling designs.

Results of this study support the following conclusions:

- High-resolution time series of key water quality parameters (e.g., nitrate), even with only a single complete annual cycle, provide a wealth of information that is difficult to extract from more coarsely sampled time series.
- The multiple linear regression (MLR) approach for estimating the total annual load of nitrate entering Puget Sound from the Deschutes River (and other similar streams and watersheds) is likely robust to within 10%. This knowledge helps define uncertainties associated with nitrate loading estimates presented in the recent Puget Sound loading reports (Mohamedali et al., 2011; Roberts et al., 2011).
- The cost-benefit of the sampling strategies evaluated in this study was <1. In other words, a doubling of sampling effort did not yield estimates for the total annual load of nitrate that were twice as accurate. The relationship presented here is not expected to be universal; it will likely vary with different sampling designs (e.g., uniform sampling vs. event-based sampling) and water quality parameters.

Recommendations

As a result of this 2009-10 study, the following recommendations are made:

The performance of the SUNA in this study is encouraging, and consideration of this technology for use in future studies is recommended. In particular, it would be beneficial to deploy similar sensors in both larger and smaller streams to provide a sense of daily nitrate variation by stream size. Additional statistical tests should also be developed using the existing data collected as part of this study to evaluate the cost-benefit of alternate sampling strategies (e.g., event-based sampling).

The SUNA is sensitive enough to resolve subtle diurnal patterns that likely reflect instream biological processes (e.g., uptake and (de)nitrification). This ability extends Ecology's ability to perform detailed instream process studies, especially if the SUNA were to be deployed as part of a larger suite of sensors (e.g., dissolved oxygen, pH, solar radiation).

It is anticipated that in 2011, the SUNA will be integrated into Ecology's marine flight monitoring program to achieve higher spatial and vertical resolution nitrate sampling. Increased resolution is required to (1) assess the time-varying nitrate inventory in Puget Sound and (2) improve our understanding of how nitrate concentrations vary in response to distributed point and nonpoint pollutant sources and to seasonal and longer-term climatic perturbations.

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Appendix. Glossary, Acronyms, and Abbreviations

Glossary

Ambient: Background or away from point sources of contamination.

Anthropogenic: Human-caused.

Anoxia: Depleted of oxygen.

Biotic: Produced or caused by living organisms.

Diurnal: Daytime only, as opposed to nocturnal or crepuscular.

Diel: Of, or pertaining to, a 24-hour period.

Dissolved oxygen (DO): A measure of the amount of oxygen dissolved in water.

Eutrophication: An increase in productivity resulting from nutrient loads from human conditions such as fertilizer runoff and leaky septic systems.

Fluvial: Relating to or happening in a river.

Grab sample: A discrete sample from a single point in the water column or sediment surface.

Hypoxia: Low oxygen.

Loading: The input of pollutants into a waterbody.

Nitrate (nitrate): A measure of the amount of nitrate dissolved in water.

Nonpoint source: Unconfined and diffuse sources of contamination. Pollution that enters water from dispersed land-based or water-based activities. This includes, but is not limited to, atmospheric deposition, surface-water runoff from agricultural lands, urban areas, or forest lands, subsurface or underground sources, or discharges from boats or marine vessels not otherwise regulated under the National Pollutant Discharge Elimination System program.

Parameter: Water quality constituent being measured (analyte). A physical, chemical, or biological property whose values determine environmental characteristics or behavior.

Point source: Source of pollution that discharges at a specific location.

Pollution: Contamination or other alteration of the physical, chemical, or biological properties of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state. This definition assumes that these changes will, or are likely to, create a nuisance or render such waters harmful, detrimental, or injurious to (1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

Stormwater: The portion of precipitation that does not naturally percolate into the ground or evaporate but instead runs off roads, pavement, and roofs during rainfall or snow melt. Stormwater can also come from hard or saturated grass surfaces such as lawns, pastures, playfields, and from gravel roads and parking lots.

Total Maximum Daily Load (TMDL): Water cleanup plan. A distribution of a substance in a waterbody designed to protect it from not meeting (exceeding) water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a Margin of Safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

Acronyms and Abbreviations

CDOM	Colored dissolved organic matter
DO	Dissolved oxygen
DTS	Digital turbidity sensor
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
MEL	Manchester Environmental Laboratory
MLR	Multiple linear regression
N	number
NO2	Nitrite
NO3	Nitrate
NO2+NO3	nitrite plus nitrate
QA	Quality assurance
RSD	Relative standard deviation
SUNA	Submersible Ultraviolet Nitrate Analyzer
TMDL	(See Glossary above)
USGS	U.S. Geological Survey
UV	Ultraviolet

Units of Measurement

°C	degrees centigrade
cfs	cubic feet per second
kg/d	kilograms per day
km	kilometer, a unit of length equal to 1,000 meters
mg/L	milligrams per liter (parts per million)