Quality Assurance Project Plan

Deschutes River
Continuous Nitrate Monitoring

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Cover photo: The Deschutes River near the E Street Bridge (taken by Zachary Holt).

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Continuous Nitrate Monitoring

October 2009

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Signatures are not available on the Internet version.
EAP - Environmental Assessment Program.
EIM - Environmental Information Management system.

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Abstract

Future marine Total Maximum Daily Load (TMDL; water cleanup) studies and water quality modeling projects in Puget Sound will need accurate and highly resolved time series of nitrate discharge from fluvial sources.

For this study, a Submersible Ultraviolet Nitrate Analyzer (SUNA) will be deployed in the Deschutes River at the E. Street Bridge in Tumwater from November 1, 2009 through October 31, 2010. The Deschutes River is high in nitrate and discharges to the sensitive South Puget Sound basin.

Satlantic's SUNA is a real-time, chemical-free sensor designed to overcome the traditional challenges associated with reagent-based nitrate analysis in aquatic environments.

The SUNA 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. Data collected will be analyzed statistically to determine how nitrate concentrations (and other measured water quality parameters) behave throughout the year, with special attention being paid to patterns observed during winter storm events. This knowledge will be synthesized in the form of new or refined methods for predicting continuous daily loads of nitrate from a limited number of discrete observations.

After the stormwater fluctuation pattern of the Deschutes River is characterized, it is anticipated that the sensor will be deployed in both larger and smaller streams to provide a sense of daily nitrate variation by stream size.

Each study conducted by the Washington State Department of Ecology must have an approved Quality Assurance Project Plan. The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completion of the study, a final report describing the study results will be posted to the Internet.

Acknowledgement

Funding for this study is provided by a 104(b)(3) grant from the U.S. Environmental Protection Agency.

Background

Future marine Total Maximum Daily Load (TMDL; water cleanup) studies and water quality modeling projects in Puget Sound will need accurate and 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 that are functions of measured flow and time of year (Roberts and Pelletier, 2001). Unfortunately, monthly monitoring chronically under-samples episodic events and these multiple linear regressions can break down during high-flow (and sometimes low-flow) conditions.

Higher frequency sampling is required to:

- Better characterize nitrate concentrations during storm events.
- Improve stormwater wasteload allocations for nitrate.
- Refine, validate, and establish error estimates for statistical methods used to predict continuous daily loads of nitrate from a limited number of discrete observations.

Why Do We Care About Nitrate in Water?

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 loads 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 enhanced 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 (DO) depletion in areas that are not well ventilated (e.g., quiescent bays and near-bottom waters).

Project Description

Satlantic's SUNA (Submersible Ultraviolet Nitrate Analyzer) is a real-time, chemical-free sensor designed to overcome the traditional challenges associated with reagent-based nitrate analysis in aquatic environments. The SUNA 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).

From November 1, 2009 through October 310, 2010, a SUNA will be deployed 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 Washington State Department of Ecology (Ecology) ambient monitoring site (station 13A060; Figure 1).

The Deschutes River is high in nitrate and discharges to the sensitive South Puget Sound basin. The daily nitrate fluctuation pattern with storm events is currently unknown. After the stormwater fluctuation pattern of the Deschutes River is characterized, it is anticipated that the sensor will be deployed in both larger and smaller streams to provide a sense of daily nitrate variation by stream size.

By initially deploying at an active ambient monitoring site, the monthly discrete values can be used as partial quality assurance comparisons, to be supplemented by additional quality assurance measures described below.

After sufficient data have been collected, they will be analyzed statistically to determine how nitrate concentrations (and other measured water quality parameters) behave throughout the year, with special attention being paid to patterns observed during winter storm events. This knowledge will be further synthesized in the form of new or refined methods for predicting continuous daily loads of nitrate from a limited number of discrete observations. These new statistical methods will be documented to facilitate their use in future marine TMDL studies and water quality modeling projects in Puget Sound.

Field validation efforts for SUNA-type sensors have been successful, even in the presence of relatively strong interfering species such as suspended particulate material (turbidity) and CDOM. However, to ensure the highest quality data, a variety of optical characteristics will be monitored in the environment in which the SUNA is deployed. If necessary, the manufacturer's calibration will be refined using discrete samples that will be analyzed for nitrate using standard laboratory protocols.

Coincident estimates of CDOM concentration and turbidity will be provided by a WETLabs FLCDRT (FLuorometer-CDOM-RealTime) CDOM fluorometer and a Forest Technology Systems DTS-12 turbidity/temperature sensor, respectively. While these ancillary measurements are useful water quality indicators in their own right, they serve a dual purpose in terms of aiding the Quality Assurance/Quality Control of the SUNA-nitrate data.

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

Site is denoted with a yellow arrow.

Organization and Schedule

The following people are involved in this project. All are employees of Ecology's Environmental Assessment Program (EAP).

Table 1. Organization of project staff and responsibilities.

Staff	Title	Responsibilities
Brandon Sackmann MIS Unit Statewide Coordination Section Phone: (360) 407-6684	Project Manager and Principal Investigator	Writes the QAPP. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data, analyzes and interprets data, and enters data into EIM. Writes the draft report and final report.
Christopher Moore MIS Unit Statewide Coordination Section Phone: (360) 407-0067	Field Assistant and EIM Data Lead	Collects samples and records field information. Enters data into EIM.
Carolyn Lee MIS Unit Statewide Coordination Section Phone: (360) 407-6430	EIM Quality Assurance Lead	Confirms correct EIM data entry.
Zackary Holt Freshwater Monitoring Unit Western Operations Section Phone: (360) 407-6022	Instrument Setup Lead	Configures and deploys sensors and sampling equipment at study site.
Karol Erickson MIS Unit Statewide Coordination Section Phone: (360) 407-6694	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Will Kendra Statewide Coordination Section Phone: (360) 407-6698	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Robert F. Cusimano Western Operations Section Phone: (360) 407-6596	Section Manager for the Study Area	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP. Keeps Ecology's Southwest Regional Water Team apprised of project status.
Stuart Magoon Manchester Environmental Laboratory Phone: (360) 871-8801	Director	Approves the final QAPP.
William R. Kammin Phone: (360) 407-6964	Ecology Quality Assurance Officer	Reviews the draft QAPP and approves the final QAPP. Has delegated authority from EPA to approve EPA grant-funded project QAPPs.

MIS – Modeling and Information Support.
QAPP – Quality Assurance Project Plan.
EIM – Environmental Information Management system.
EPA – U.S. Environmental Protection Agency.

Table 2. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	Due date	Lead staff
Field work completed	October 2010	Christopher Moore
Laboratory analyses completed	December 2010	
Environmental Information System (EIM) database		
EIM user study ID	BSAC0001	
Product	Due date	Lead staff
EIM data loaded	January 2011	Christopher Moore
EIM quality assurance	February 2011	Carolyn Lee
EIM complete	March 2011	Christopher Moore
Final report		
Author lead / Support staff	Brandon Sackmann / Christopher Moore	
Schedule		
Draft due to supervisor	February 2011	
Draft due to client/peer reviewer	March 2011	
Draft due to external reviewer(s)	NA	
Final (all reviews done) due to publications coordinator	May 2011	
Final report due on web	June 2011	

SUNA Nitrate Sensor Description

Many dissolved inorganic compounds, including, nitrate, nitrite, bi-sulfide, and bromide, absorb light at UV wavelengths. The SUNA uses the UV (200-400 nm) absorption spectra to provide *in situ* measurements of dissolved nitrate.

The sensor contains three key components:

- Stable UV light source.
- 256 channel UV spectrometer.
- Processing computer.

The components are housed within two pressure cases, connected with a rigid coupler containing the sample volume (Figure 2). By illuminating a sample of water with UV light onto a spectrometer, the absorption spectra can be measured.

The factory calibration of the SUNA uses standard solutions of dissolved potassium nitrate (KNO_3) over a range of salinity conditions and temperatures to compute instrument-specific extinction coefficients for nitrate and bromide.

Figure 2. Diagram of the Satlantic SUNA nitrate sensor.

Sampling Process Design (Experimental Design)

Installation of sensors and other equipment at the study site will follow the *Standard Operating Procedures for Turbidity Threshold Sampling* (Estrella, 2008). The sensor suite will be expanded to include both a Satlantic SUNA and WETLabs FLCDRT CDOM fluorometer. Installation of the SUNA will adhere to the manufacturer's guidelines for a moored sensor deployment.

Sensor-derived water quality parameters will be sampled continuously every 15 minutes (on the quarter-hour) in the Deschutes River at the E. Street Bridge in Tumwater, from November 1, 2009 to October 31, 2010. The station will be established as a telemetry station with the capability to transmit data every three hours to Ecology Headquarters in Olympia where the data will be automatically imported into the streamflow database and published to Ecology's website. The data will be transmitted via either a GOES satellite transmitter or a standard dial-up modem.

Goals and Objectives

The goals of the project are to:

- 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.

Quality Objectives

Measurement quality objectives for freshwater ambient monitoring, including both laboratory and *in situ* measurements, are summarized in Tables 3 and 4. The laboratory objectives are based on historical performance of Ecology's Manchester Environmental Laboratory (MEL) for these parameters (Hallock, 2007). Staff-collected and automated pump samples that satisfy these objectives will be adequate to meet the study objectives.

Table 3. Measurement quality objectives for laboratory parameters.

Analyte	Precision (% relative standard deviation)	Bias (% Recovery)	Lower Reporting Limit
Nitrate-N, total and dissolved	10%	80-120	0.01 mg/L
Nitrite-N, total and dissolved	10%	80-120	0.01 mg/L
Nitrite+Nitrate-N, total and dissolved	10%	80-120	0.01 mg/L

Accuracy objectives for the continuous *in situ* sensor measurements are based on the accuracy of a given sensor as reported by the manufacturer. One of the outcomes of this project will be a better understanding of SUNA accuracy, precision, and bias under a range of ambient and laboratory conditions. A post-data collection sensitivity analysis will be conducted to quantify how the performance of the SUNA affected the estimated nitrate loads for the Deschutes River. Accuracy of SUNA-derived nitrate estimates should not affect final load estimates by more than 20%.

While ancillary measurements of the secondary parameters listed in Table 4 are useful water quality indicators in their own right, their primary purpose will be to aid the Quality Assurance/Quality Control of the SUNA-nitrate data. The measurement quality objectives listed for the secondary parameters will be assessed through comparison with available ambient monitoring data (see below) when possible, but a more rigorous validation of these data is not planned as part of this study.

Table 4. Measurement quality objectives for continuous *in situ* sensor measurements.

Analyte	Accuracy (deviation or % deviation from true or replicate value)	Precision (% relative standard deviation)	Lower Reporting Limit	Upper Reporting Limit
Primary Parameters				
Nitrate-N (Satlantic SUNA)	±0.028 mg/L or ±10% of reading, whichever is greater (under laboratory conditions)	10%	0.028 mg/L	56 mg/L
Secondary Parameters				
CDOM fluorescence (WETLabs FLCDRT CDOM fluorometer [ex/em: 370/460 nm])	±0.09 QSU (1 QSU = 1 µg quinine equivalent)	15%	0.09 QSU	500 QSU
Turbidity (Forest Technology Systems DTS-12 turbidity sensor)	±2% (1-499 NTU), ±4% (500-1600 NTU)	15%	1 NTU	1600 NTU
Temperature (Forest Technology Systems DTS-12 temperature sensor)	±0.2 °C	10%	NA	NA

Sampling Procedures

Discrete Samples

Discrete grab samples will be collected three times per month (approximately every 10 days) and analyzed for nitrate as follows (Table 5):

- Visit 1 – Dissolved and total nitrate.
- Visit 2 – Dissolved and total nitrate.
- Visit 3 – Duplicate dissolved nitrate.

Table 5. Estimated sample counts.

Analyte	SUNA	Grab Samples	Pump Samples	Ambient Monitoring
Nitrate-N (dissolved)	35,040	36*	-	-
Nitrate-N (total)	-	24*	-	-
Nitrite-N (dissolved)	-	36*	-	-
Nitrite-N (total)	-	24*	-	-
Nitrite+Nitrate-N (dissolved)	-	36*	-	-
Nitrite+Nitrate-N (total)	-	24*	~144**	12**

* Unpreserved samples (48-hour holding time).
** Preserved samples (28-day holding time).

Nitrate is determined by analyzing the same unpreserved sample for nitrite+nitrate and nitrite separately. Calculating the difference between these two results yields the result for nitrate. Samples will be collected and handled according to standard Ecology protocols (Joy, 2006). Ecology personnel will fill collection bottles, and samples will be kept on ice until delivered to MEL for analysis.

Systematic differences between total and dissolved nitrate concentrations are not expected. However, without data to validate this assumption for the Deschutes River it will be necessary to monitor both fractions simultaneously. Samples will be collected on the quarter-hour to ensure that the grab samples coincide with a continuous *in situ* measurement. It is also anticipated that it will be possible to manually trigger and collect an automatic pump sample while on-site (see below) to properly synchronize the discrete sampling efforts.

Automatic Pump Samples

A 14-bottle refrigerated sequential pump sampler will be used to automatically collect and preserve water samples for determination of nitrite+nitrate by MEL. The 950 ml sample bottles will be pre-acidified and prepared with the recommended quantity of preservative (sulfuric acid; H_2SO_4). Pumped samples will be regularly harvested and transported to MEL as part of the three site visits per month. The maximum holding period for nitrite+nitrate samples is 28 days; MEL requires 14 of those days to ensure sufficient time to analyze the samples. The sample recovery schedule for this project is designed so that no more than 14 days will elapse between sample collection and delivery to MEL, leaving MEL with the requisite 14 days for sample analyses.

Because sample preservation is required, it is necessary to limit laboratory analyses to total nitrite+nitrate. As noted above, systematic differences between dissolved and total nitrate concentrations are not expected, and nitrite values have historically been very low. If these assumptions prove valid in the Deschutes River during this study, dissolved nitrate should approximately equal total nitrite+nitrate.

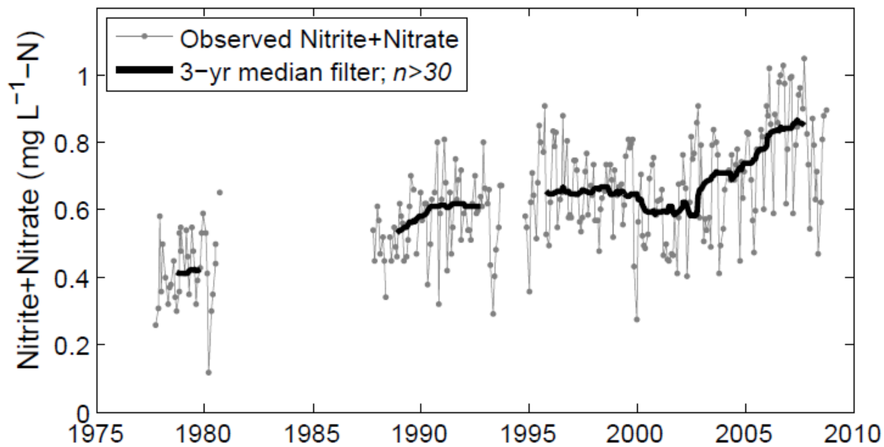
An analysis of the historical nitrite+nitrate data from the study site suggested that the maximum variability associated with any given 30-day period is 0.57 mg/L (calculated as the range containing the central 95% of the available observations; Figure 3). This value represents an estimate for the maximum variability that has been observed historically at any particular time of year (centered on year day 278). Unfortunately, there are no available data with which to characterize nitrate variability over short time scales (e.g. < 30 days) within a given year. While one might expect the variability within a year to be less than the maximum variability observed throughout the entire period of record, it must be noted that extreme episodic events are often under-sampled and are likely not well represented in the historical data.

Based on this limited information, pumped samples will initially be collected as follows in an attempt to distribute the 14 available samples across a sufficiently large range.

A pumped sample will be collected *if*:

1. The absolute difference between the last 4 SUNA-nitrate readings and the SUNA-nitrate reading associated with the last water sample are all > 0.1 mg/L,
   OR
2. The elapsed time since the last sample is > 72 hour.

This sampling strategy will likely be refined after the fluctuation pattern of nitrate is better constrained.



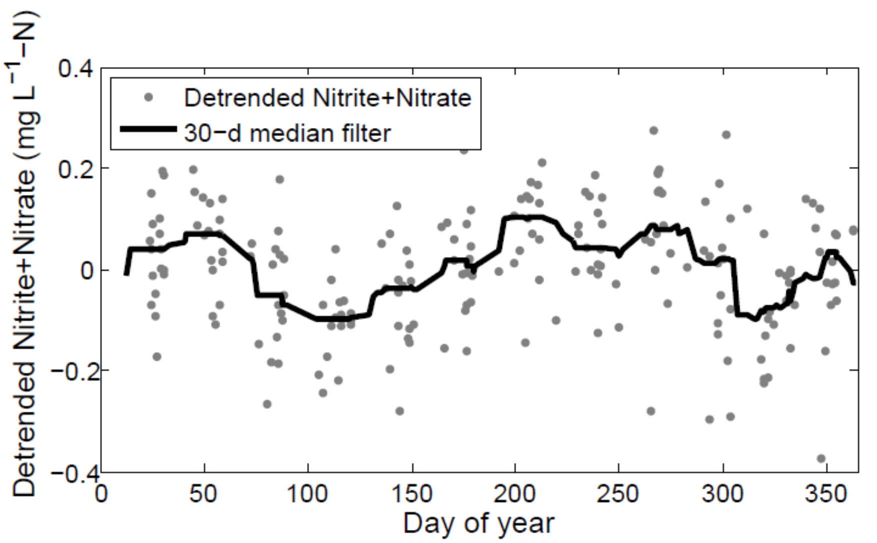


Figure 3. Historical nitrite+nitrate observations at the study site.

Data in the upper panel are shown with results from the 3-year median filter that was used to detrend the dataset. Data in the lower panel illustrate the range of residual variability observed throughout the year. Results from a 30-day median filter are used to highlight the annual pattern of variability. The maximum range of variability observed for any 30-day period was centered near year day 278 (0.57 mg/L).

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, the project can incorporate the monthly discrete values of total nitrite+nitrate and other water quality indicators (Table 6) that are routinely collected. These data will be used to establish context for the continuous water quality data that are collected and for additional QA comparisons. Sampling is performed according to the protocols outlined in Ward (2007).

Table 6. Routinely measured indicators of water quality (and methods).

Indicator	Method
Ammonia (NH4)	SM4500NH3H
Nitrate plus nitrite (NO2+NO3)	SM4500NO3I
Total nitrogen (TN)	SM4500NB
Soluble reactive phosphorus (SRP)	SM4500PG
Total phosphorus (TP)	SM4500PF
Conductivity	SM2510B
Temperature	Thermistor
pH	EPA150.1
Dissolved Oxygen	SM4500OC
Suspended Solids	SM2540D
Turbidity	SM2130

SM = APHA, 2000.
EPA = U.S. Environmental Protection Agency, 1983.

Measurement Procedures

All field samples collected as part of this study will be processed using the same methods currently employed by Ecology's Freshwater Ambient Monitoring Program. Also, sampling will follow the procedures being developed to minimize the spread of invasive species in areas of moderate concern (Ward, 2009).

Quality Control Procedures

Completeness

In order to develop new or refine existing statistical methods for predicting continuous daily loads of nitrate from a limited number of discrete observations, a relatively complete time series of nitrate concentrations must be obtained. EPA has defined *completeness* as a measure of the amount of valid data needed to be obtained from a measurement system to meet study objectives. The completeness objective for this study is to collect 90% of the data as described in this QA Project Plan.

Following are reasons why all data may not be collected:

1. Dry streambed (cannot be mitigated, but unlikely at the chosen study site).
2. Flooding streambeds (unlikely at the chosen study site). To mitigate this, we may sample dates during the month to avoid flooding conditions.
3. Severe weather that restricts field activities. To mitigate this, we will schedule backup field dates when feasible.
4. Malfunctioning equipment. To minimize this risk, we will use auxiliary equipment whenever feasible, ensure equipment is well maintained, and check functionality prior to starting field work. Establishing the site as a telemetered station will allow remote confirmation that equipment is working properly.
5. Access problems for the study site. This problem will be mitigated to the extent possible by coordinating activities with existing site stewards and by maintaining communication with local property owners and authorities as necessary.

Comparability

A variety of comparisons will be made between data sets to isolate sources of variability. Notable examples will include:

- Nitrate (dissolved) to SUNA-nitrate. Staff-collected grab samples of nitrate (dissolved) will be compared to the nearest continuous SUNA-derived nitrate value three times per month.

- Nitrate (dissolved) (total variation; field plus lab). Duplicate staff-collected grab samples will be compared once per month.
- Nitrate (dissolved) to nitrite+nitrate (total) (variability due to fractionation and the presence of nitrite). Staff-collected samples of both nitrate (dissolved) and nitrite+nitrate (total) will be compared twice per month.
- Nitrite+nitrate (total) (variability due to methodological differences in sample collection and preparation). Staff-collected grab samples will be compared to the nearest automatic pump collected samples.

Results from these comparisons will be used to assess whether the various measurement quality objectives were met. If the objectives were not met, the data will be qualified. In addition, MEL routinely analyzes duplicate samples in the laboratory for quality control purposes. The difference between the field and laboratory variability is a measure of the sample field variability.

Manchester Laboratory's full quality control procedures are documented in their Lab Users Manual and Quality Assurance Manual (MEL, 2008; MEL, 2006). The laboratory will be able to assess laboratory bias in sample results. Bias from field procedures will not be able to be assessed directly. However, bias will be minimized by strictly following standard protocols.

Representativeness

Monitoring once a month consistently under-samples episodic events. Higher frequency sampling is required (1) to better characterize nitrate concentrations during storm events, (2) improve stormwater wasteload allocations for nitrate, and (3) refine, validate, and establish error estimates for statistical methods used to predict continuous daily loads of nitrate from a limited number of discrete observations.

It is anticipated that the continuous SUNA-nitrate data collected as part of this project will result in more complete and representative estimates of nitrate concentrations and loads for the Deschutes River.

SUNA Laboratory Calibration Checks

Laboratory calibration checks will be used to characterize the performance of the SUNA nitrate sensor. A pre-deployment calibration check will be completed in advance of sensor deployment, and periodic calibration checks will be done quarterly thereafter. Quarterly calibration checks will require recovery of the SUNA from the study site. However, it is anticipated that re-installation of the instrument will be performed on the same day, immediately following the laboratory calibration check, thereby minimizing the amount of missed data. More frequent calibration checks may be necessary depending on sensor behavior and performance.

Two types of instrument offsets are possible with SUNA nitrate sensors. One is associated with a long-term drift in the instrument response caused by changes in the transmission properties in the internal optical components. The other is associated with interfering species present in the water.

To check for instrument drift, the SUNA will be submerged in a recirculating water bath of ultra-clean deionized water and allowed to warm up for 8-10 minutes. If the nitrate reading is >-0.028 mg/L or <+0.028 mg/L, the instrument response has not drifted significantly. If it has drifted, the linearity of the instrument response across the expected sampling range should be characterized. The drift must then be removed by refreshing the water bath with pure deionized water and updating the reference spectrum. This is done using the Update Calibration function in the instrument software. After the reference spectrum has been updated, the linearity of the instrument should be reassessed.

Instrument linearity can be characterized by adding crystalline KNO_3 to the deionized water bath to artificially increase the dissolved nitrate concentrations so that they bracket the expected sampling range. Subsamples must be taken periodically from the water bath and sent to MEL for determination of dissolved nitrate.

Interfering Species

Various dissolved and particulate substances in the water can interfere with the UV spectra sampled for nitrate analysis. Particulate matter, if suspended in the water column (i.e. not settled in the sample chamber), generally has the effect of increasing noise slightly with little reduction in accuracy. Because the spectral signature of many particulate sediments between 220 and 240 nm is relatively flat, the results are generally good as long as a significant signal is still reaching the spectrometer. A Forest Technology Systems DTS-12 turbidity/temperature sensor will be used to continuously monitor turbidity levels in the vicinity of the SUNA.

Colored dissolved organic matter (CDOM) on the other hand does have a spectral component to its absorption curve and thus may have a greater effect on the end calculation of nitrate concentration. The baseline correction method of the absorption curve-fitting algorithms partially compensates for changes in CDOM concentrations. In extreme cases with very high CDOM, a linear offset may affect the nitrate data. In such cases, the manufacturer recommends taking discrete samples for independent verification at periodic intervals to "reality check" the SUNA-nitrate output. These samples can then be used to calculate an offset that can be applied to the SUNA-generated time series data.

The fluctuation pattern of CDOM in the Deschutes River is presently unknown. In this study, coincident output from a WETLabs FLCDRT CDOM fluorometer will be used as a proxy for CDOM concentration. Discrepancies between laboratory and SUNA-derived nitrate estimates will be evaluated as a function of CDOM fluorescence to determine the extent to which CDOM influences the integrity of SUNA-nitrate estimates.

Nitrite Sensitivity

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 nitrate+nitrite at similar molar ratios, as well as in ambient waters where nitrite concentrations are much lower than nitrate. Fortunately, nitrite concentrations are very low at the location chosen for this study.

Analysis of the available historical data revealed a maximum nitrite concentration of 0.02 mg/L, and only 1.3% of the available data were above the analytical detection limit of 0.01 mg/L. Despite the low risk of interference, nitrite concentrations will be monitored monthly as part of this study.

Biofouling

The SUNA Biofouling Guard (Figure 4) is a semi-circular piece of perforated copper attached to a plastic armature. The armature isolates the copper from the stainless steel coupler, preventing galvanic corrosion issues. The copper discourages biological growth, while the perforations allow passive flushing of the sample volume. The biofouling guard is intended for use in moored applications without an active pumping system.

When using the biofouling guard, the SUNA will be mounted so that the optical chamber is mounted at 90 degrees to the vertical. This orientation helps to prevent air bubbles and sediment from becoming trapped in the optical chamber.

Routine preventative maintenance and cleaning procedures will be followed as outlined in the instrument's operations manual.

Figure 4. SUNA Biofouling Guard.

Data Management Procedures

Field data will initially be recorded in field notebooks and then entered into Excel spreadsheets for conducting the QA analysis. Data will then be loaded into Ecology's Environmental Information Management (EIM) System.

Audits and Reports

Good communication, strict adherence to standard protocols, and documentation of any deviation from standard protocols will be essential. A QA assessment will be conducted prior to using the data for analysis. The QA assessment will be included in the final report for this project.

Data Verification

Manchester Laboratory will provide verified data packages for all data analyzed. To assure accurate entry of data into EIM, 10% of all values will be checked against the source data. If errors are found, an additional 10% of values will be checked; the process will continue in this way until no errors are found or all values have been verified.

Data Quality (Usability) Assessment

Data will be evaluated for obvious errors, and quality will be evaluated against the objectives described in this document for precision and accuracy. The usability of the data will be confirmed by its ability to aid in developing new statistical methods for predicting continuous daily loads of nitrate from a limited number of discrete observations.

Study Budget

A summary of the sample numbers and laboratory costs are presented in Table 7. The total laboratory cost for the project is estimated at $5,304.

All analyses will be conducted by MEL. The cost estimates reflect a 50% discount for analyses conducted by MEL.

Table 7. Summary of Laboratory Costs.

Analysis	Number of Samples	Cost
Nitrate (dissolved); grab samples	48	$1248
Nitrate (dissolved); calibration samples	48	$1248
Nitrate (total); grab samples	24	$936
Nitrite+Nitrate (total); pump samples	144	
Total Project Lab Cost:		$5304

References

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Appendix. Glossary, Acronyms, and Abbreviations

Ambient: Background or away from point sources of contamination.

Anthropogenic: Human-caused.

Conductivity: A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

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

Fluvial: Relating to or happening in a river.

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

Parameter: A physical chemical or biological property whose values determine environmental characteristics or behavior.

pH A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

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.

Study site: For this study, it is the Deschutes River at the E. Street Bridge in Tumwater, Washington.

Total Maximum Daily Load (TMDL): Water cleanup plan. A distribution of a substance in a waterbody designed to protect it from 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.

Total suspended solids (TSS): Portion of solids retained by a filter.

Turbidity: A measure of water clarity. High levels of turbidity can have a negative impact on aquatic life.

Wasteload allocation: The portion of a receiving water's loading capacity allocated to existing or future point sources of pollution. Wasteload allocation constitutes one type of water quality-based effluent limitation.

Water year: October 1 through September 30. For example, WY07 is October 1, 2006 through September 30, 2007.

Acronyms and Abbreviations

CDOM	Colored dissolved organic matter
DTS	Digital turbidity sensor
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
FLCDRT	FLuorometer-CDOM-RealTime
GOES	Geostationary Operational Environmental Satellite
MEL	Manchester Environmental Laboratory
QA	Quality assurance
SOP	Standard operating procedures
SUNA	Submersible ultraviolet nitrate analyzer
TMDL	(See Glossary above)
TSS	(See Glossary above)
UV	Ultraviolet

Units of Measurement

mg/L	milligrams per liter (parts per million)
mm	millimeter
nm	nanometer
QSU	quinine sulfate unit
µg	microgram