ALGORITHM THEORETICAL BASIS DOCUMENT (ATBD):

SURFACE WATER NITRATE

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See configuration management system for approval history.

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Change Record

REVISION	DATE	ECO #	DESCRIPTION OF CHANGE
A	09/12/2017	ECO-04874	Initial Release
B	01/03/2019	ECO-05951	Revised averaging window per configuration change
C		ECO-06279	Revised burst timestamp handling, data regularization, null, and gap flagging to better align with other IS data products.

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LIST OF TABLES AND FIGURES

1 DESCRIPTION

Contained in this document are details concerning temperature measurements made at all NEON sites. Specifically, the processes necessary to convert "raw" sensor measurements into meaningful scientific units and their associated uncertainties are described. Nitrate will be continuously monitored at all core and relocatable sites via a submersible ultraviolet nitrate analyzer.

1.1 Purpose

This document details the algorithms used for creating NEON Level 1 data products for Surface Water Nitrate from Level 0 data, and ancillary data as defined in this document (such as calibration data) obtained via instrumental measurements made by the Nitrate Analyzer. It includes a detailed discussion of measurement theory and implementation, appropriate theoretical background, data product provenance, quality assurance and control methods used, approximations and/or assumptions made, and a detailed exposition of uncertainty resulting in a cumulative reported uncertainty for this product.

1.2 Scope

The theoretical background and entire algorithmic process used to derive Level 1 data from Level 0 data for Surface Water Nitrate is described in this document. The Nitrate Analyzer employed is the SUNA V2 Submersible Ultraviolet Nitrate Analyzer manufactured by SeaBird Coastal. This document does not provide computational implementation details, except for cases where these stem directly from algorithmic choices explained here.

2 RELATED DOCUMENTS, ACRONYMS AND VARIABLE NOMENCLATURE

2.1 Applicable Documents

AD[01]	NEON.DOC.000001	NEON OBSERVATORY DESIGN
AD[02]	NEON.DOC.002652	NEON Level 1, Level 2 and Level 3 Data Products Catalog
AD[03]	NEON.DOC.000782	ATBD QA/QC Data Consistency
AD[04]	NEON.DOC.011081	ATBD QA/QC Plausibility Tests
AD[05]	NEON.DOC.000783	ATBD De-spiking and Time Series Analyses
AD[06]	NEON.DOC.000746	Calibration Fixture and Sensor Uncertainty Analysis (CVAL)
AD[07]	NEON.DOC.000785	TIS Level 1 Data Products Uncertainty Budget Estimation Plan
AD[08]	NEON.DOC.000927	NEON Calibration and Sensor Uncertainty Values[1]
AD[09]	NEON.DOC.001113	Quality Flags and Quality Metrics for TIS Data Products
AD[10]	NEON.DOC.001570	NEON Sensor Command, Control and Configuration Document: SUNA Nitrate Analyzer, Wadeable Streams
AD[11]	NEON.DOC.000597	STCDD – 0329950000 – Sensor, Suna Nutrient with Integrated Wiper
AD[12]	NEON.DOC.003808	NEON Sensor Command, Control and Configuration Document: Buoy Meteorological Station and Submerged Sensor Assembly
AD[13]	NEON.DOC.003824	STCDD – 0329950100 – Sensor, Buoy, SUNA Nitrate with Integrated Wiper, Titanium Housing

[1] Note that CI obtains calibration and sensor values directly from an XML file maintained and updated by CVAL in real time. This report is updated approximately quarterly such that there may be a lag time between the XML and report updates.

2.2 Reference Documents

RD[01]	NEON.DOC.000008	NEON Acronym List
RD[02]	NEON.DOC.000243	NEON Glossary of Terms

2.3 Acronyms

Acronym	Explanation
AIS	Aquatic Instrument System
ATBD	Algorithm Theoretical Basis Document
CI	NEON Cyberinfrastructure
CVAL	NEON Calibration, Validation, and Audit Laboratory
DAS	Data Acquisition System
DP	Data Product

FDAS	Field Data Acquisition System
GRAPE	Grouped Remote Analog Peripheral Equipment
Hz	Hertz
L0	Level 0
L1	Level 1
PRT	Platinum resistance thermometer
QA/QC	Quality assurance and quality control

2.4 Variable Nomenclature

The symbols used to display the various inputs in the ATBD, e.g., calibration coefficients and uncertainty estimates, were chosen so that the equations can be easily interpreted by the reader. However, the symbols provided will not always reflect NEON's internal notation, which is relevant for CI's use, and/or the notation that is used to present variables on NEON's data portal. Therefore a lookup table is provided in order to distinguish what symbols specific variables can be tied to in the following document.

Symbol	**Internal Notation**	**Description**
u_{A1}	U_CVALA1	Combined, standard uncertainty of the SUNA nitrate sensor (µM)
u_{A3}	U_CVALA3	Combined, relative uncertainty of the SUNA nitrate sensor (%)
H	Parse from L0 string (field 271)	Internal humidity of sensor
$SpAv_L$	Parse from L0 string (field 8)	Spectrum average during light frame
$SpAv_D$	Parse from L0 string (field 9)	Spectrum average during dark frame
NO_3	Parse from L0 string (field 3)	Nitrate Value in micromoles per liter (µM)

3 DATA PRODUCT DESCRIPTION

3.1 Variables Reported

The Surface Water Nitrate-related L1 DPs provided by the algorithms documented in this ATBD are displayed in the accompanying file: swn_datapub_NEONDOC004046.txt.

3.2 Input Dependencies

Table 1 details the Surface Water Nitrate-related L0 DPs used to produce L1 Surface Water Nitrate DPs in this ATBD.

Table 1. List of Surface Water Nitrate-related L0 DPs that are transformed into L1 Surface Water Nitrate DPs in this ATBD.

Description	Sample Frequency	Units	Data Product Number
Nitrate in surface water	burst of 1 dark frame and 20 light frames	NA	NEON.DOM.SITE.DP0.20033.001.02242.HOR.VER.000

3.3 Product Instances

One Nitrate Analyzer will be deployed at each AQU site. At wadeable stream sites the SUNA will be installed in the stream channel at the S2 location and will be mounted onto the in-stream infrastructure that is shared with other submerged aquatic sensors (multisonde, prt and LevelTroll). At lake and river sites, the SUNA will be deployed off of the buoy approximately 0.5 m below the surface.

3.4 Temporal Resolution and Extent

L0 data will be collected in burst measurements every 15 minutes, where each burst consists of 1 dark frame and 20 light frames. A portion of the sampling window is averaged and treated as a single instantaneous point measurement every 15 minutes to form L1 DPs.

3.5 Spatial Resolution and Extent

The spatial resolution and extent represented by the SUNA will vary depending on the aquatic feature the sensor is placed in. In streams the SUNA will be located at only S2 and deployed at a fixed depth. This position will be chosen to represent the bulk water mass in the stream. In rivers and lakes the SUNA will be located at a fixed depth to monitor relative changes; however extrapolation to the broader aquatic system will require additional observational measurements.

During aquatic infrastructure redesign efforts, more than one SUNA may be temporarily deployed at a site simultaneously for data comparability testing.

4 SCIENTIFIC CONTEXT

Nitrate is a form of nitrogen, one of the primary nutrients (carbon, nitrogen, and phosphorous) in aquatic and terrestrial ecosystems. It is formed during the breakdown of organic material, the production of nitrogen fixing-plants, and industrial production. Figure 1 illustrates how nitrate is formed and utilized in aquatic environments relative to other forms of nitrogen. While nitrogen is often the limiting nutrient for primary production in marine environments, it also can be (but is not always) a limiting nutrient in freshwater. Runoff of excess fertilizer or animal wastes in agricultural areas, or discharge of effluent from septic tanks or wastewater treatment plants in urban areas can lead to excess nitrate in surface and ground waters.

Levels of nutrients in the environment can indicate the health of the ecosystem. Excess nutrients in the system can stimulate rapid primary production (growth of plants and algae), which can include blooms of toxic algae. As the plants and algae die they are decomposed by microbes in the water which consume oxygen. This reduction in dissolved oxygen can be harmful to fish and other aquatic organism and lower the overall health of the ecosystem.

Measuring nitrate in aquatic systems is critical to understanding the biogeochemical cycle and mechanisms in the ecosystem. Changes in the concentration of nitrate over time may be an indication of shifts in the trophic structure and community composition of the aquatic ecosystem.

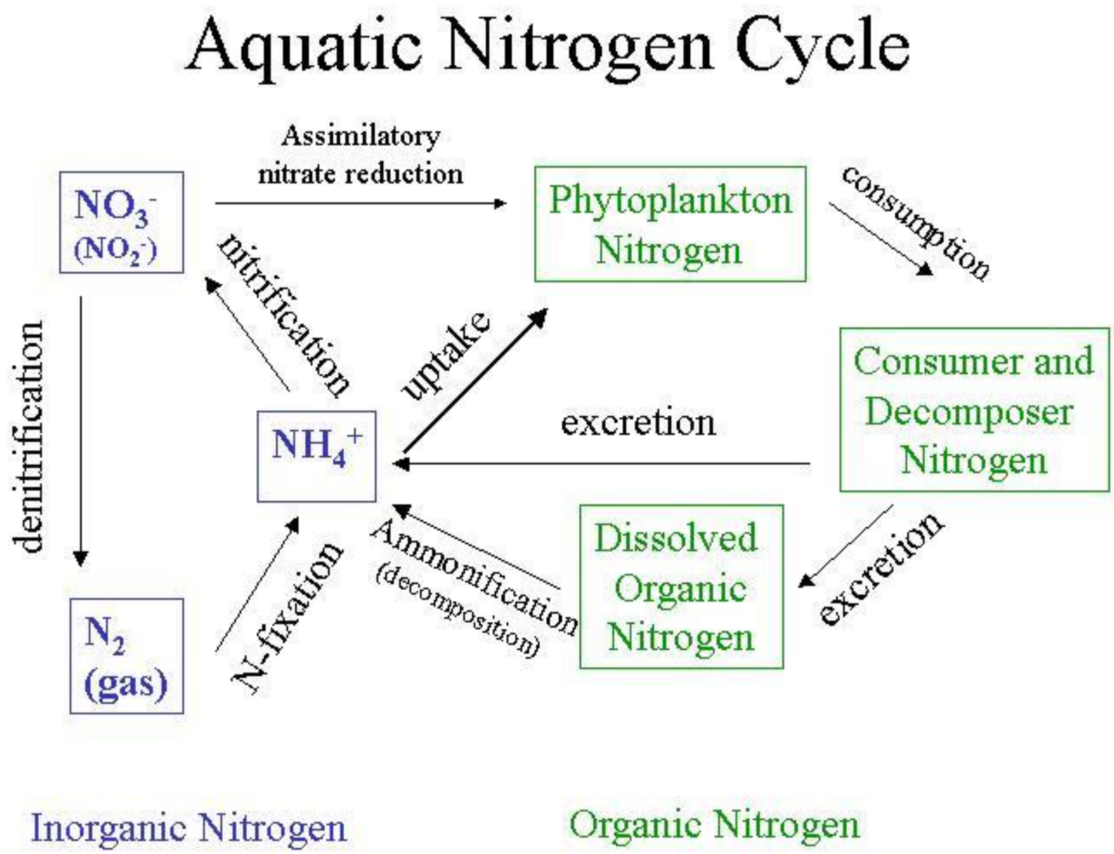

Figure 1. Schematic of nitrogen cycle in aquatic environments.

4.1 Theory of Measurement

Nitrate is one of several inorganic chemical species that strongly absorb ultraviolet light (wavelength <280nm). Other species of importance include bromide and hydrogen sulfide and some organic compounds (see Figure 2). Measuring nitrate in aquatic systems using UV spectroscopy can be difficult because of the overlapping absorbance bands of different chemical species.

The principle of the measurement consists of applying a UV light source across the water sample; the nitrate (and other species) absorb energy from the light in the state of it electrons; a spectrometer then measures how much light passed through the sample at each wavelength. The absorbance signal due to nitrate in the water is proportional to its concentration in the sample. It is critical to have a stable light source and a spectrometer capable of resolving the spectra for the nitrate in the water.

The SUNA consists of a high-resolution spectrometer that is optimized for UV range wavelengths, a stable deuterium lamp, an on-board controller and a data storage device. The SUNA internally converts all signals to digital data and applies algorithms developed by MBARI and SeaBird specific to this instrument prior to output.

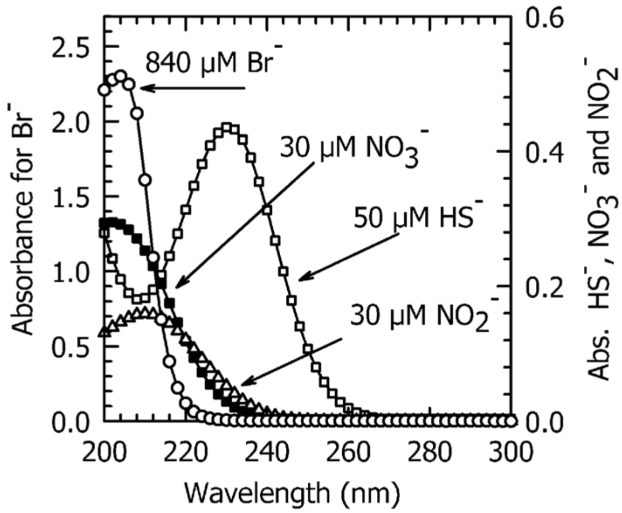

Figure 2. Absorbance spectra for bromide, nitrate, hydrogen sulfide and nitrite in the ultraviolet range.

4.2 Theory of Algorithm

The SUNA nitrate sensor produces an ASCII file that contains 286 data fields. To accommodate this large number of fields, the data fields are concatenated such that each measurement is reported as a single string of characters, where the fields are identified by the numeric field ID followed by a colon and the measurement value. Each field is delimited by commas. This data transmission scheme is illustrated in Equation 1. The identification of the data fields is given in Table 2.

Measurement string#0 = {0: <value>, 1: <value>,…285:<value>} **Equation 1**

Where each field has a numerical index followed by the measurement value.

Table 2. Data fields and position that are captured with the SUNA and placed into the concatenated string, L0 data stream, identified in **Table 1** above.

L0 Data Stream Field Position	Full ASCII Data Fields
0	Light Frame/Dark Frame
1	Date field (numeric)
2	Time field (numeric)
3	Nitrate concentration in micromolar
4	Nitrogen as nitrate in mg/L
5	Absorbance at 254 nm
6	Absorbance at 350 nm
7	Bromide trace
8	Spec Average or SW Average(Dark Correction Method)
9	Dark Signal Average (average dark intensity)

10	Integration Time Factor
11	spectrometer intensity at wavelength #1
12	spectrometer intensity at wavelength #2
13	spectrometer intensity at wavelength #3
14	spectrometer intensity at wavelength #4
15	spectrometer intensity at wavelength #5
16	spectrometer intensity at wavelength #6
17	spectrometer intensity at wavelength #7
18	spectrometer intensity at wavelength #8
19	spectrometer intensity at wavelength #9
20	spectrometer intensity at wavelength #10
21	spectrometer intensity at wavelength #11
22	spectrometer intensity at wavelength #12
23	spectrometer intensity at wavelength #13
24	spectrometer intensity at wavelength #14
25	spectrometer intensity at wavelength #15
26	spectrometer intensity at wavelength #16
27	spectrometer intensity at wavelength #17
28	spectrometer intensity at wavelength #18
29	spectrometer intensity at wavelength #19
30	spectrometer intensity at wavelength #20
31	spectrometer intensity at wavelength #21
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34	spectrometer intensity at wavelength #24
35	spectrometer intensity at wavelength #25
36	spectrometer intensity at wavelength #26
37	spectrometer intensity at wavelength #27
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40	spectrometer intensity at wavelength #30
41	spectrometer intensity at wavelength #31
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51	spectrometer intensity at wavelength #41
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55	spectrometer intensity at wavelength #45
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264	spectrometer intensity at wavelength #254
265	spectrometer intensity at wavelength #255
266	spectrometer intensity at wavelength #256
267	Temperature of sensor in ^oC
268	Spectrometer temperature in ^oC
269	Lamp temperature in ^oC
270	Cumulative lamp time in seconds
271	Relative humidity in %
272	Main voltage in Volts
273	Lamp voltage in Volts
274	Internal voltage in Volts
275	Main current in milliAmps

276	Fit aux 1
277	Fit aux 2
278	Fit base 1
279	Fit base 2
280	Fit RMSE
281	CTD Time
282	CTD Salinity
283	CTD Temperature
284	CTD Pressure
285	Check sum of data stream

The nitrate value and other relevant fields for a given measurement are identified in Equations 2 – 5:

$$\boldsymbol{NO_{3,i}} = \{(\boldsymbol{field})\boldsymbol{3}, <\boldsymbol{value}>\}_i \quad \textbf{Equation 2}$$

$$\boldsymbol{H_i} = \{(\boldsymbol{field})\boldsymbol{271}, <\boldsymbol{value}>\}_i \quad \textbf{Equation 3}$$

$$\boldsymbol{SpAv_L} = \{(\boldsymbol{field})\boldsymbol{8}, <\boldsymbol{value}>\}_i \quad \textbf{Equation 4}$$

$$\boldsymbol{SpAv_D} = \{(\boldsymbol{field})\boldsymbol{9}, <\boldsymbol{value}>\}_i \quad \textbf{Equation 5}$$

For each burst of measurements, the first measurement is a dark measurement in which the UV lamp is off (dark frame: {(field)0 = 0}), followed by 20 consecutive light measurements in which the UV lamp is on (light frame: {(field)0 = 1}). If non-consecutive dark or light frames are encountered, implement the error tracking system since the sensor is not functioning properly. After the dark frame, the first 9 light frames allow for the sensor to stabilize. The 10^{th} through 20^{th} light frames (frames 11-21 overall) will be averaged to provide the 15-minute L1 nitrate DP according to Equation 6.

$$\overline{\boldsymbol{NO_3}} = \frac{\boldsymbol{1}}{\boldsymbol{n}} \sum_{\boldsymbol{i=11}}^{\boldsymbol{i=21}} \boldsymbol{NO_{3,i}} \quad \textbf{Equation 6}$$

Where:

$i = 11 \ldots 21$ for each measurement in the burst, any measurements beyond the 21^{st} frame (20^{th} light frame) should be ignored.

n = number of light measurements used to calculate average. This will normally be 11 (frames 11-21) however it may be less because measurement which receive a QA/QC or despike quality flag will not be used to calculate the burst average, details below.

$NO_{3,i}$ = individual nitrate measurements (light frames)

$\overline{\boldsymbol{NO_3}}$ = average nitrate per burst measurement

The time between the initiation of bursts as indicated by the presence of a dark frame ($i = 1$) should be 00:15:00. The exact timing of a given burst may vary based on hardware and/or environmental conditions. Therefore, no assumptions should be made about the exact time between the end of one burst (last light frame) and the beginning of the next (next dark frame).

The averaged L0 data will be regularized to 15-minute intervals for publication as L1 data. The beginning timestamp of a burst will dictate the start and end dates associated with the regularized data. For example, if the beginning of a burst (12:14 PM) and end of a burst (12:16 PM) are in different 15-minute bins, the start and end dates for the mean nitrate concentration will be 12:00 PM and 12:15 PM, respectively, even though some of the burst data was collected during the next bin.

A dark frame will be used to find the beginning of each burst since all bursts start with one dark frame and should be followed by multiple light frames.

5 ALGORITHM IMPLEMENTATION

Data flow for signal processing of L1 DPs will be treated in the following order.

1. Extract L0 values from the appropriate fields of the concatenated data stream for each instantaneous light or dark frame according to Eq. 1.
2. Find the beginning of the burst measurement according to Section 4.
3. QA/QC sensor flags will be applied to the data stream values within the averaging window defined in Eq. 6, details below.
4. QA/QC Plausibility tests will be applied to the nitrate measurements (field 3 only) within the averaging window defined in Eq. 6 in accordance with AD[04], details are provided below.
5. Signal de-spiking will be applied to the nitrate measurements (field 3 only) using the algorithm described in AD[05] except within a fixed averaging window defined in Eq. 6.
6. Nitrate measurement averages will be calculated using Eq. 6.
7. Descriptive statistics, i.e. minimum, maximum, and variance, will be determined for each burst measurement of surface water nitrate.
8. Quality metrics, quality flags, and the final quality flag will be produced for each nitrate measurement according to AD[09].

<u>**QA/QC Procedure**</u>:

1. **Plausibility Tests** AD[04] – All plausibility tests will be determined for the nitrate analyzer. Test parameters will be provided by AIS and maintained in the CI data store. All plausibility tests will be applied to the sensor's converted L0 DPs and associated quality flags (QFs) will be generated for each test. The lamp may not have been properly warmed up during the beginning of the burst and data from the first 9 light frames should not be used for QA/QC procedures.

2. **Sensor Flags** – Recently it was found that the internal humidity of this sensor can reach levels that impair the both the health and operation of the sensor. Therefore, we will check the humidity level for each measurement and measurements taken when the humidity is above the threshold of 40% will be flagged accordingly.

   Additionally, the spectral average measured during light frames should far exceed the value of the spectral average measured during dark frames. The dark frames are taken with the lamp off and provide the background signal of the detector. If the spectral average of the light frame is not greater than at least twice that of the dark frames that measurement shall be flagged accordingly. The dark and spectral averages are calculated internally by the SUNA and no averaging is done by CI for this. Only the output values for a given measurement are compared for data quality assurance.

   a. Spectral Average:

$$\text{SpecQF} = \begin{cases} 1 \text{ if } SpAv_L \leq 2 \times SpAv_D \\ 0 \text{ otherwise} \end{cases} \quad \text{Equation 7}$$

   b. Internal Humidity:

$$\text{humidityQF} = \begin{cases} 1 \text{ if } H_i \geq 40 \\ 0 \text{ otherwise} \end{cases} \quad \text{Equation 8}$$

3. **Signal Despiking** Time segments and threshold values for the automated despiking QA/QC routine will be specified by AIS and maintained in the CI data store. QFs from the despiking analysis will be applied according to AD[05] with a modification to use a static window rather than a sliding window. Despiking will occur only within the burst data used for calculating mean nitrate values. The lamp may not have been properly warmed up during the beginning of the burst and should not be used for QA/QC procedures.
4. **Quality Flags (QFs) and Quality Metrics (QMs)** AD[09] – If a datum fails one of the following tests it will not be used to create a L1 DP, ***sensor test, despiking, range***, ***persistence***, and ***step***. α and β QFs will be determined for each measurement using the flags in Table 3, as detailed in AD[09]. Measurements which raise a QF will not be used to calculate burst averages or be used in statistics (max, min, etc…). QFs for individual measurements will be used to calculate α and β Quality

Metrics (QMs) and a Final QF for each burst, as detailed in AD[09]. Ancillary information needed for the algorithm and other information maintained in the CI data store is shown in Table 4. The final quality flag for surface water nitrate will be determined accordingly.

Table 3. Flags associated with Surface Water Nitrate measurements.

Tests
Null
Gap
Range
Persistence
Signal Despiking
Step
Sensor Test – Internal Humidity
Sensor Test – Spectral Average
Alpha
Beta
Final Quality Flag

Table 4. Information maintained in the CI data store for Surface Water Nitrate.

Tests/Values	CI Data Store Contents
Null	Test limit
Gap	Test limit
Range	Minimum and maximum values
Persistence	Window size, threshold values and maximum time length
Step	Threshold values

Tests/Values	CI Data Store Contents
Signal Despiking	Time segments and threshold values
Sensor Test – Internal Humidity	Humidity threshold of 40 %
Sensor Test – Spectral Average	Light / Dark Spectral Average Ratio minimum of 2
Uncertainty	AD[07]
Final Quality Flag	AD[09]

6 UNCERTAINTY

Uncertainty of measurement is inevitable (JCGM 2008, 2012; Taylor 1997). It is crucial that uncertainties are identified and quantified to determine statistical interpretations about mean quantity and variance structure; both are important when constructing higher level data products (e.g. L1 DP) and modeled processes. Uncertainty related to the Surface Water Nitrate and associated data products is provided in detail in the Aquatics Uncertainty Document AD[07], which serves to identify, evaluate, and quantify sources of uncertainty relating to L1 surface water nitrate and L1 surface water nitrate DPs. It is a reflection of the information described in AD[07] and is explicitly described for the nitrate sensor in AD[08].

6.1 Uncertainty of Surface Water Nitrate

Uncertainty of the SUNA nitrate analyzer assembly is discussed in this section. The section is broken down into two topics. The first informs the sources of *measurement* uncertainty, i.e., those associated with *individual nitrate measurements*. The second details uncertainties associated with temporally averaged data products. A diagram detailing the data flow and known sources of uncertainty are displayed in Figure 04.

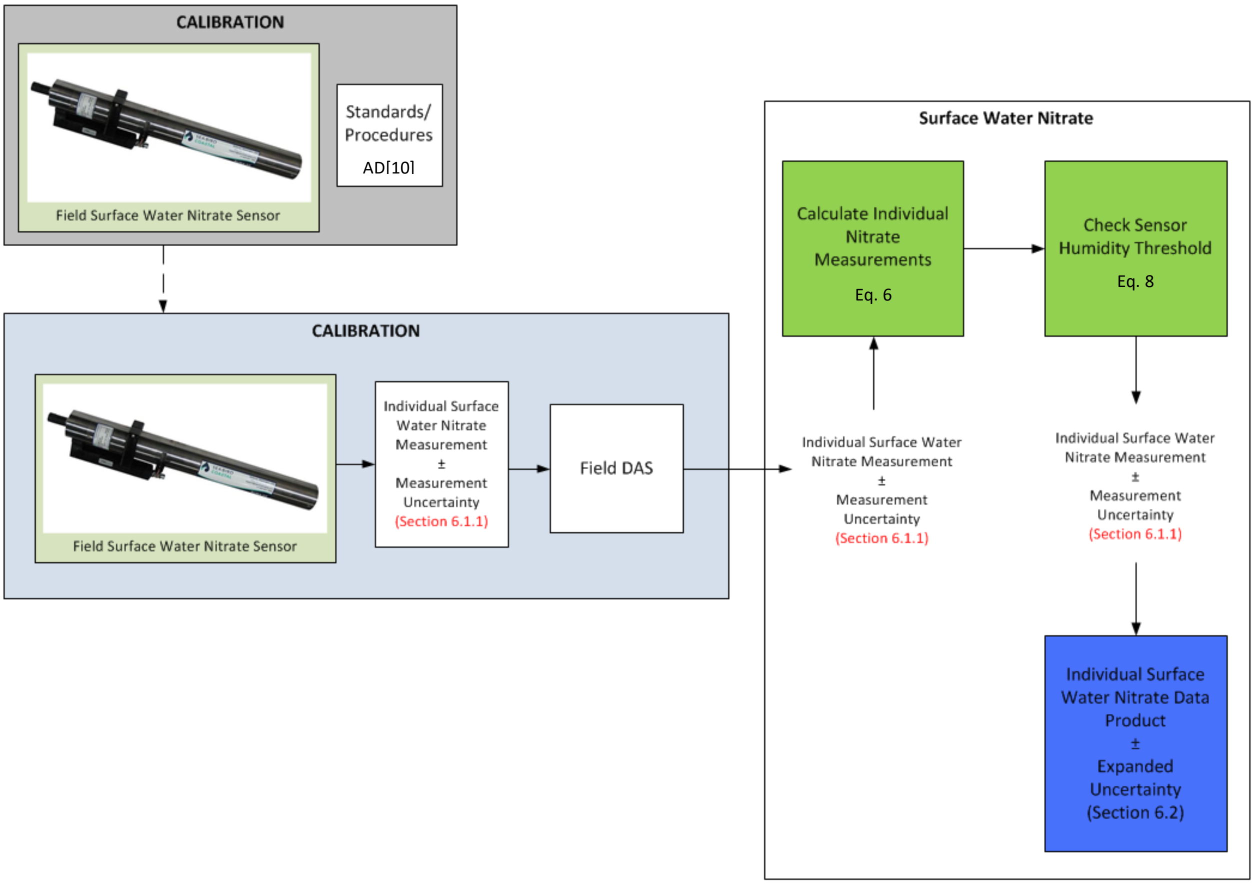

Figure 3. Displays the data flow and associated uncertainties of individual measurements of surface water nitrate and associated L1 DPs.

6.1.1 Measurement Uncertainty

The following subsections present the uncertainties associated with *individual observations*. It is important to note that the uncertainties presented in the following subsections are *measurement uncertainties*, that is, they reflect the uncertainty of an *individual* measurement. These uncertainties should not be confused with those presented in Section 6.1.2. We urge the reader to refer to AD[07] for further details concerning the discrepancies between quantification of measurement uncertainties and L1 uncertainties.

NEON calculates measurement uncertainties according to recommendations of the Joint Committee for Guides in Metrology (JCGM) 2008. In essence, if a measurand *y* is a function of *n* input quantities

$x_i\ (i = 1, \dots, n),\ i.e., y = f(x_1, x_2, \dots, x_n)$, the combined measurement uncertainty of *y*, assuming the inputs are independent, can be calculated as follows:

$$u_c(y) = \left(\sum_{i=1}^{N}\left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i)\right)^{\frac{1}{2}} \quad \textbf{Equation 9}$$

where

$\frac{\partial f}{\partial x_i}$ =partial derivative of *y* with respect to x_i

$u(x_i)$ =combined standard uncertainty of x_i.

Thus, the uncertainty of the measurand can be found be summing the input uncertainties in quadrature. For surface water nitrate measurements, the sources of uncertainty are discussed below.

6.1.1.1 DAS

The SUNA V2 nitrate sensor has an internal Analog to Digital (A/D) converter and outputs data in digital form. Therefore, no data conversions occur within the DAS, and uncertainty introduced by the DAS can be considered negligible.

6.1.1.2 Calibration

The SUNA V2 is calibrated by the manufacturer SeaBird Scientific and is no additional calibration is currently performed by CVAL. The accuracy of calibrated measurements are given by the manufacturer. Additionally the sensor baseline (blank) is calibration in the field. If the sensor is properly field-calibrated, the nitrate concentration should have an accuracy as follows:

$$\text{Measurement Accuracy} = \begin{cases} 2\ \mu M & \text{if } \overline{NO_3} \leq 20\ \mu M \\ \overline{NO_3} \times 10\% & \text{if } 20\ \mu M < NO_{3,i} \leq 1000\ \mu M \end{cases} \quad \text{Equation 10}$$

The values 0-1000 μM represent the expected environmental range across the NEON Aquatic Sites. The uncertainty is assumed to be the manufactures reported accuracy divided by 3. Therefore, the uncertainty will be 0.666 μM (u_{A1}) or 3.33% (u_{A3}) of the measurement, depending on the concentration of the individual measurements. These values will be given by CVAL as $\{u_{A1}\}$ and $\{u_{A3}\}$ (see Section 2.4) representing i) the repeatability and reproducibility of the sensor and ii) uncertainty of the calibration procedures and coefficients including uncertainty in the standard (truth). This will be provided by CVAL, stored in the CI data store, and applied to all *individual nitrate measurements.* CI will need to use the appropriate uncertainty value for individual measurements based on the concentration as follows:

Individual measurement uncertainty $\{u_{An}\}$ =

$$\begin{cases} u_{A1} \text{ if } \overline{NO_3} \le 20\ \mu M \\ u_{A3}, \text{ if } 20\ \mu M < \overline{NO_3} \le 1000\ \mu M \end{cases}$$

Equation 11

6.1.1.3 Combined Measurement Uncertainty

Because the only known quantifiable uncertainties are those provided by the manufacturer, the combined uncertainty of nitrate is simply a product to the standard uncertainty value given by the manufacturer and provided by CVAL, u_{A1}, (See Sections 2.4 and 6.1.1.2).

$$\boldsymbol{u_{CAL}}(\overline{NO_3}) = \begin{cases} u_{An} \text{ if } \overline{NO_3} \le 20\ \mu M \\ u_{An} \times \overline{NO_3} \text{ if } 20\ \mu M < \overline{NO_3} \le 1000\ \mu M \end{cases}$$

Equation 12

Where,

$u_{CAL}(\overline{NO_3})$ = standard calibration uncertainty of an individual measurement (µM)

u_{An} = u_{A1} or u_{A3}, depending on concentration range as identified in 6.1.1.2, calibration uncertainty provided by CVAL (%, from manufacturer)

$\overline{NO_3}$ = averaged nitrate measurements (µM)

6.1.2 Uncertainty of the L1 Mean Data Products

The following subsections discuss uncertainties associated with temporally averaged, i.e., L1 mean data products. As stated previously, it is important to note the differences between the *measurement uncertainties* presented in Section 6.1.1 and the uncertainties presented in the following subsections. The uncertainties presented in the following subsections reflect the uncertainty of a time-averaged mean value, that is, they reflect the uncertainty of a distribution of measurements collected under non-controlled conditions (i.e., those found in the field), as well as any uncertainties in the form of *Truth* and *Trueness* related to the accuracy of the field assembly.

6.1.2.1 Repeatability (Natural Variation)

To quantify the uncertainty attributable to random effects, the distribution of the individual measurements is used. Specifically, the *estimated standard error of the mean (natural variation)* is computed. This value reflects the repeatability of measurements for a specified time period:

$$\boldsymbol{u_{NAT}\left(\overline{NO_3}\right) = \sqrt{\frac{\sigma^2}{n}}} \qquad \textbf{Equation 13}$$

Where

$\overline{NO_3}$ = averaged nitrate measurements (μM)

$u_{NAT}(\overline{NO_3})$ = standard error of the mean (natural variation)

σ = standard deviation of individual within the averaging window (of the burst)

n = number of observations made within the averaging window (of the burst)

6.1.2.2 Calibration

The calibration uncertainty for a L1 mean DP is similar to that described in Section 6.1.1.1. However, the uncertainties provided by CVAL (see Section 2.4) do not account for i) individual sensor repeatability, or ii) the variation of sensors' responses over a population (reproducibility). These components estimate the uncertainties due to the accuracy of the instrumentation in the form of *Truth* and *Trueness*, a quantity that is not captured by the standard error of the mean. This is a constant value that will be provided by CVAL and stored in the CI data store. Please refer to AD[07] for further justification regarding evaluation and quantification of this combined uncertainty.

6.1.2.3 Combined Uncertainty

The combined uncertainty for L1 data products are computed by summing the uncertainties from Section 6.1.2.1 and the CVAL provided uncertainties in quatrature:

$$\boldsymbol{u_c(\overline{NO_3}) = \left[u_{NAT}^2(\overline{NO_3}) + u_{CAL}^2(\overline{NO_3})\right]^{\frac{1}{2}}} \qquad \textbf{Equation 14}$$

6.1.2.4 Communicating Precision

L1 mean surface water nitrate data products will be reported to 0.1 μM. The sensor is capable of measuring nitrate at a precision of 0.3 μM. The resolution of individual nitrate measurements is 0.1 μM, as this maintains the proper significant figures, despite the reported resolution being greater than the 0.3 μM precision and limit of detection.

6.2 Expanded Uncertainty

We assume the measurement variability is normally distributed (Gaussian). The combined uncertainty represents plus or minus one standard deviation or a confidence interval of 68%. This confidence level is below the industry standard and is therefore expanded to a 95% confidence interval. This is typically calculated by multiplying the combined uncertainty, $u_{c,r}(y)$, by a coverage factor, k_p.

$$\boldsymbol{U_p = k_p\, u_{c,r}(y)} \qquad \textbf{Equation 15}$$

Where $k_{95} = 1.96$ for $p = 95$ for a given degrees of freedom. k_p is approximated by a t-distribution with an effective degrees of freedom, v_{eff}, obtained from the Welch-Saterwaite formula:

$$\boldsymbol{v_{eff}} = \frac{u_c^4(y)}{\sum_{i=1}^{n} \frac{u_i^4(y)}{v_i}} \qquad \textbf{Equation 16}$$

The coverage factor then becomes $k_p = t_p(v_{eff})$, where $t_p(v_{eff})$ is obtained from a table.

However to simplify the calculations further, we can conservatively estimate the expanded uncertainty at a 95% confidence level to be two times the combined uncertainty.

$$\boldsymbol{U_{Expanded} = 2 \times u_c} \qquad \textbf{Equation 17}$$

This expansion is to be applied to all combined uncertainties for the L1 DP described herein.

6.1 Uncertainty Budget

The uncertainty budget is a visual aid detailing i) quantifiable sources of uncertainty, ii) means by which they are derived, and iii) the order of their propagation. Uncertainty values denoted in this budget are either derived within this document or are provided by other NEON teams (e.g., CVAL), and stored in the CI data store.

Table 5. Uncertainty budget for individual measurements. Shaded rows denote the order of uncertainty propagation (from lightest to darkest).

Source of Measurement Uncertainty	Measurement uncertainty Component $u(x_i)$	Measurement Uncertainty Value	$\frac{\partial f}{\partial x_i}$	$u_{x_i}(Y) \equiv \left\|\frac{\partial f}{\partial x_i}\right\| u(x_i)$
Nitrate	$u_{CAL}(NO_{3,i})$	AD[08]	n/a	Eq. 12

Table 6. Uncertainty budget for L1 mean DPs. Shaded rows denote the order of uncertainty propagation (from lightest to darkest).

Source of Uncertainty	Uncertainty Component $u(x)$	Uncertainty Value	$\frac{\partial f}{\partial x_i}$	$u_{u_{x_i}}(Y) \equiv \left\|\frac{\partial f}{\partial x_i}\right\| u(x_i)$

Nitrate	$u_c(\overline{NO}_3)$	Eq. (14)	n/a	Eq. 14
Calibration	$u_{CAL}(NO_{3,i})$	AD[08]	n/a	Eq. 12
Natural variation	$u_{NAT}(\overline{NO}_3)$	Eq. 13	n/a	Eq. 13

7 FUTURE PLANS AND MODIFICATIONS

Future system flags may be incorporated into the data stream and included in the QA/QC summary DP ($Qsum_{5min}$) that summarizes any flagged data that went into the computation of the L1 DP.

It is planned to add another sensor flag that will identify when the internal temperature of the sensor has exceeded 35°C. At this temperature, the sensor shuts off. Providing this additional sensor flag will provided clarity when expected data is missing and no other flags are thrown.

Future implementation of an additional data filter pass for quality control over longer temporal scales is planned.

It is planned that CVAL will provide and internal, independent calibration for performance of the SUNA in freshwater and at low concentrations. Once implemented CVAL will perform a three-point calibration with the associated coefficients.

In the future, ATBD specific flags will be added for unexpected frame counts. If greater than 10 light frames are available for averaging or if less than 10 light frames are available for averaging the data will be flagged to indicate long or short burst readings.. Similarly, if greater than 1 dark frame is present or less than 1 dark frames is present, the data will be flagged, meaning that there were more or less measurements than expected.

Because of the relatively unique "burst" mode of sampling, in the future additional burstStartDate and burstEndDate fields will be added to the publication WB so that users will know more accurate timestamp information for the nitrate L0 readings in addition to the regularized startDate and endDates currently published with the mean L1 data.

In the future, a specific flag may be added for error codes ("-1") indicating the inability of the SUNA to make measurements in optically dense water where less than 10 wavelength channels within the nitrate absorbance range have an absorbance value below the standard absorbance cutoff value of 1.3. At present, busts populated with only "-1" values should be flagged by the persistence test. However an additional flag will indicate to NEON science team that these measurements need to be reprocessed using a larger absorbance cutoff.

8 BIBLIOGRAPHY

Sea-Bird Scientific. (2018) User manual for SUNA V2. Sea-Bird Scientific, Bellevue, WA. Pp. 56, Manual No. SUNA180725, v.F.

JCGM (2012) International vocabulary of metrology – Basic and general concepts and associated terms (VIM). 3rd Edition. pp. 92

Taylor, J. R. (1997) An Introduction to Error Analysis: The Study of Uncertainties in Physical Measurements. University Science Books, Mill Valley, California. 2nd Ed. pp. 327.