ALGORITHM THEORETICAL BASIS DOCUMENT (ATBD):

SURFACE WATER NITRATE

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See configuration management system for approval history.

Change Record

REVISION	DATE	ECO #	DESCRIPTION OF CHANGE
	MM/DD/YYYY	ECO-XXXXX	Initial Release

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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 Satlantic LP. 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.005003	NEON Scientific Data Products Catalog
AD[03]	NEON.DOC.002652	NEON Level 1, Level 2 and Level 3 Data Products Catalog
AD[04]	NEON.DOC.005005	NEON Level 0 Data Products Catalog
AD[05]	NEON.DOC.000782	ATBD QA/QC Data Consistency
AD[06]	NEON.DOC.011081	ATBD QA/QC Plausibility Tests
AD[07]	NEON.DOC.000783	ATBD De-spiking and Time Series Analyses
AD[08]	NEON.DOC.000746	Calibration Fixture and Sensor Uncertainty Analysis (CVAL)
AD[09]	NEON.DOC.000785	TIS Level 1 Data Products Uncertainty Budget Estimation Plan
AD[10]	NEON.DOC.000927	NEON Calibration and Sensor Uncertainty Values[1]
AD[11]	NEON.DOC.001113	Quality Flags and Quality Metrics for TIS Data Products
AD[12]	NEON.DOC.001113	Quality Flags and Quality Metrics for TIS Data Products
AD[13]	NEON.DOC.001570	NEON Sensor Command, Control and Configuration Document: SUNA Nitrate Analyzer, Wadeable Streams
AD[14]	NEON.DOC.000597	STCDD – 0329950000 – Sensor, Suna Nutrient with Integrated Wiper
AD[15]	NEON.DOC.003808	NEON Sensor Command, Control and Configuration Document: Buoy Meteorological Station and Submerged Sensor Assembly
AD[16]	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 3-1: 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	0.00111	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 1.5m 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 51 samples collected at approximately 0.5 Hz for nearly 2 minutes. 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.

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 nitrate is often the limiting nutrient for photosynthesis in marine environments it is not the limiting nutrient in freshwater. Human activities and various land-uses such as agriculture, urban and industrial areas can lead to excess nitrate in surface and ground waters.

Levels of nutrients in the environment indicate the health of the ecosystem. Excess nutrients in the system stimulate rapid primary production (growth by 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.

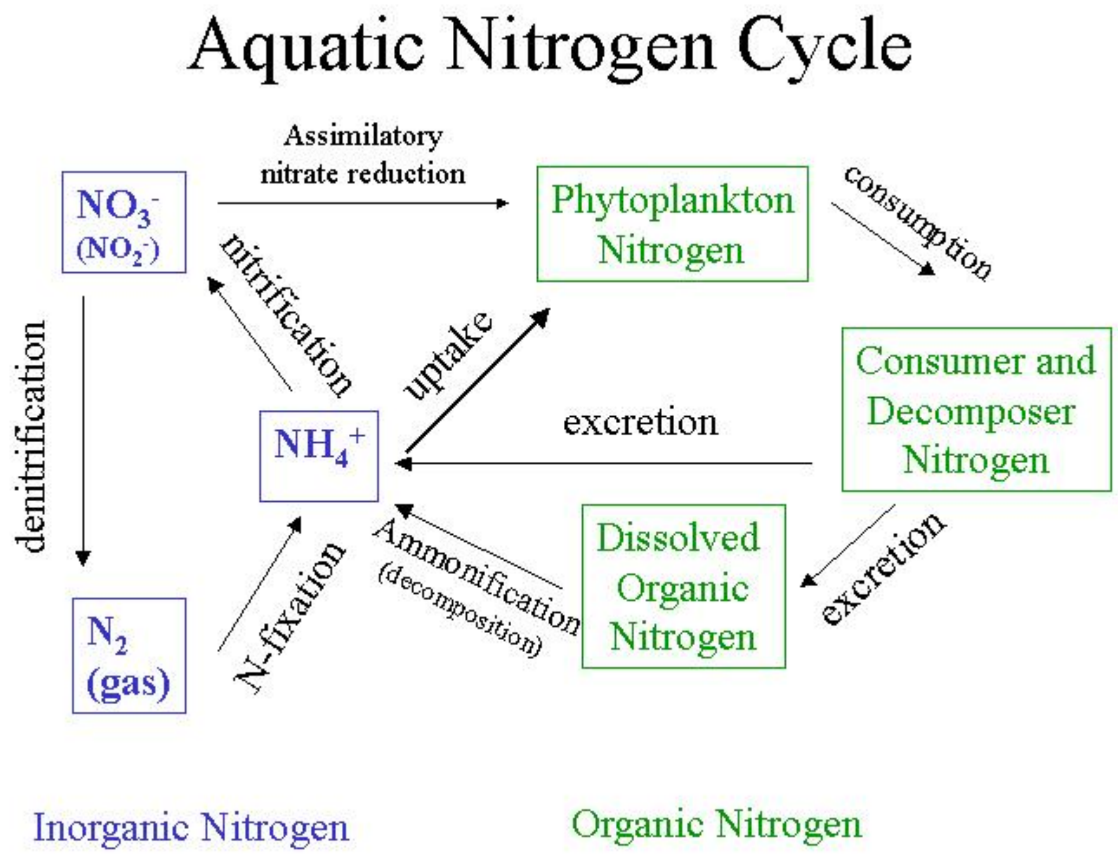

Figure 1. Schematic of nitrogen cycle in aquatic environments.

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 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 Satlantic specific to this instrument prior to output.

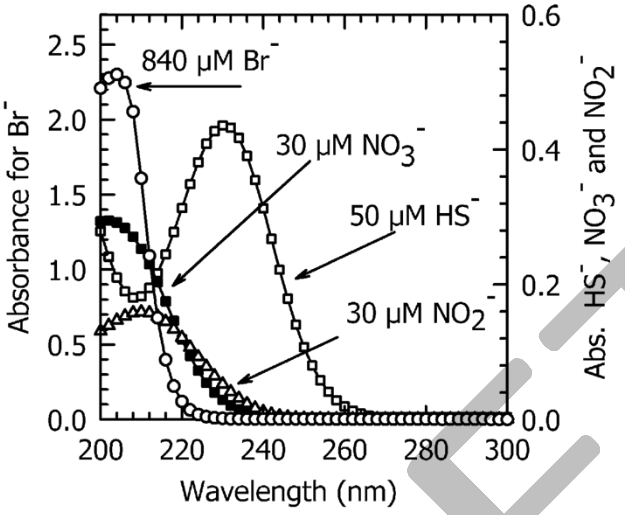

Figure 2. Absorbance spectra for bromide, nitrate, hydrogen sulfide and nitrite in the ultraviolet range.

4.2 Theory of Algorithm

The SUNA nitrate sensor produces an ASCII file that contains 285 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.

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

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

The identification of the data fields is given in Table 2.

Table 2. Data fields and position that are captured with the SUNA and placed into the concatenated string, L0 data stream, identified in Table 3-1 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 as micromolar
4	Nitrogen in nitrate as 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 189.29 nm
12	spectrometer intensity at wavelength 190.08 nm
13	spectrometer intensity at wavelength 190.87 nm
14	spectrometer intensity at wavelength 191.67 nm
15	spectrometer intensity at wavelength 192.46 nm
16	spectrometer intensity at wavelength 193.26 nm
17	spectrometer intensity at wavelength 194.05 nm
18	spectrometer intensity at wavelength 194.85 nm
19	spectrometer intensity at wavelength 195.64 nm
20	spectrometer intensity at wavelength 196.44 nm
21	spectrometer intensity at wavelength 197.23 nm
22	spectrometer intensity at wavelength 198.03 nm
23	spectrometer intensity at wavelength 198.83 nm
24	spectrometer intensity at wavelength 199.62 nm
25	spectrometer intensity at wavelength 200.42 nm
26	spectrometer intensity at wavelength 201.22 nm
27	spectrometer intensity at wavelength 202.02 nm
28	spectrometer intensity at wavelength 202.81 nm
29	spectrometer intensity at wavelength 203.61 nm
30	spectrometer intensity at wavelength 204.41 nm
31	spectrometer intensity at wavelength 205.21 nm
32	spectrometer intensity at wavelength 206.01 nm
33	spectrometer intensity at wavelength 206.81 nm
34	spectrometer intensity at wavelength 207.61 nm
35	spectrometer intensity at wavelength 208.41 nm
36	spectrometer intensity at wavelength 209.21 nm
37	spectrometer intensity at wavelength 210.01 nm
38	spectrometer intensity at wavelength 210.81 nm
39	spectrometer intensity at wavelength 211.61 nm
40	spectrometer intensity at wavelength 212.41 nm
41	spectrometer intensity at wavelength 213.21 nm
42	spectrometer intensity at wavelength 214.01 nm
43	spectrometer intensity at wavelength 214.82 nm
44	spectrometer intensity at wavelength 215.62 nm
45	spectrometer intensity at wavelength 216.42 nm
46	spectrometer intensity at wavelength 217.22 nm

47	spectrometer intensity at wavelength 218.03 nm
48	spectrometer intensity at wavelength 218.83 nm
49	spectrometer intensity at wavelength 219.63 nm
50	spectrometer intensity at wavelength 220.43 nm
51	spectrometer intensity at wavelength 221.24 nm
52	spectrometer intensity at wavelength 222.04 nm
53	spectrometer intensity at wavelength 222.85 nm
54	spectrometer intensity at wavelength 223.65 nm
55	spectrometer intensity at wavelength 224.46 nm
56	spectrometer intensity at wavelength 225.26 nm
57	spectrometer intensity at wavelength 226.06 nm
58	spectrometer intensity at wavelength 226.87 nm
59	spectrometer intensity at wavelength 227.68 nm
60	spectrometer intensity at wavelength 228.48 nm
61	spectrometer intensity at wavelength 229.29 nm
62	spectrometer intensity at wavelength 230.09 nm
63	spectrometer intensity at wavelength 230.9 nm
64	spectrometer intensity at wavelength 231.71 nm
65	spectrometer intensity at wavelength 232.51 nm
66	spectrometer intensity at wavelength 233.32 nm
67	spectrometer intensity at wavelength 234.13 nm
68	spectrometer intensity at wavelength 234.93 nm
69	spectrometer intensity at wavelength 235.74 nm
70	spectrometer intensity at wavelength 236.55 nm
71	spectrometer intensity at wavelength 237.36 nm
72	spectrometer intensity at wavelength 238.16 nm
73	spectrometer intensity at wavelength 238.97 nm
74	spectrometer intensity at wavelength 239.78 nm
75	spectrometer intensity at wavelength 240.59 nm
76	spectrometer intensity at wavelength 241.4 nm
77	spectrometer intensity at wavelength 242.21 nm
78	spectrometer intensity at wavelength 243.01 nm
79	spectrometer intensity at wavelength 243.82 nm
80	spectrometer intensity at wavelength 244.63 nm
81	spectrometer intensity at wavelength 245.44 nm
82	spectrometer intensity at wavelength 246.25 nm
83	spectrometer intensity at wavelength 247.06 nm
84	spectrometer intensity at wavelength 247.87 nm
85	spectrometer intensity at wavelength 248.68 nm
86	spectrometer intensity at wavelength 249.49 nm

87	spectrometer intensity at wavelength 250.3 nm
88	spectrometer intensity at wavelength 251.11 nm
89	spectrometer intensity at wavelength 251.92 nm
90	spectrometer intensity at wavelength 252.73 nm
91	spectrometer intensity at wavelength 253.55 nm
92	spectrometer intensity at wavelength 254.36 nm
93	spectrometer intensity at wavelength 255.17 nm
94	spectrometer intensity at wavelength 255.98 nm
95	spectrometer intensity at wavelength 256.79 nm
96	spectrometer intensity at wavelength 257.6 nm
97	spectrometer intensity at wavelength 258.41 nm
98	spectrometer intensity at wavelength 259.23 nm
99	spectrometer intensity at wavelength 260.04 nm
100	spectrometer intensity at wavelength 260.85 nm
101	spectrometer intensity at wavelength 261.66 nm
102	spectrometer intensity at wavelength 262.48 nm
103	spectrometer intensity at wavelength 263.29 nm
104	spectrometer intensity at wavelength 264.1 nm
105	spectrometer intensity at wavelength 264.91 nm
106	spectrometer intensity at wavelength 265.73 nm
107	spectrometer intensity at wavelength 266.54 nm
108	spectrometer intensity at wavelength 267.35 nm
109	spectrometer intensity at wavelength 268.17 nm
110	spectrometer intensity at wavelength 268.98 nm
111	spectrometer intensity at wavelength 269.79 nm
112	spectrometer intensity at wavelength 270.61 nm
113	spectrometer intensity at wavelength 271.42 nm
114	spectrometer intensity at wavelength 272.23 nm
115	spectrometer intensity at wavelength 273.05 nm
116	spectrometer intensity at wavelength 273.86 nm
117	spectrometer intensity at wavelength 274.68 nm
118	spectrometer intensity at wavelength 275.49 nm
119	spectrometer intensity at wavelength 276.31 nm
120	spectrometer intensity at wavelength 277.12 nm
121	spectrometer intensity at wavelength 277.93 nm
122	spectrometer intensity at wavelength 278.75 nm
123	spectrometer intensity at wavelength 279.56 nm
124	spectrometer intensity at wavelength 280.38 nm
125	spectrometer intensity at wavelength 281.19 nm
126	spectrometer intensity at wavelength 282.01 nm

127	spectrometer intensity at wavelength 282.82 nm
128	spectrometer intensity at wavelength 283.64 nm
129	spectrometer intensity at wavelength 284.45 nm
130	spectrometer intensity at wavelength 285.27 nm
131	spectrometer intensity at wavelength 286.08 nm
132	spectrometer intensity at wavelength 286.9 nm
133	spectrometer intensity at wavelength 287.71 nm
134	spectrometer intensity at wavelength 288.53 nm
135	spectrometer intensity at wavelength 289.35 nm
136	spectrometer intensity at wavelength 290.16 nm
137	spectrometer intensity at wavelength 290.98 nm
138	spectrometer intensity at wavelength 291.79 nm
139	spectrometer intensity at wavelength 292.61 nm
140	spectrometer intensity at wavelength 293.42 nm
141	spectrometer intensity at wavelength 294.24 nm
142	spectrometer intensity at wavelength 295.06 nm
143	spectrometer intensity at wavelength 295.87 nm
144	spectrometer intensity at wavelength 296.69 nm
145	spectrometer intensity at wavelength 297.51 nm
146	spectrometer intensity at wavelength 298.32 nm
147	spectrometer intensity at wavelength 299.14 nm
148	spectrometer intensity at wavelength 299.95 nm
149	spectrometer intensity at wavelength 300.77 nm
150	spectrometer intensity at wavelength 301.59 nm
151	spectrometer intensity at wavelength 302.4 nm
152	spectrometer intensity at wavelength 303.22 nm
153	spectrometer intensity at wavelength 304.04 nm
154	spectrometer intensity at wavelength 304.85 nm
155	spectrometer intensity at wavelength 305.67 nm
156	spectrometer intensity at wavelength 306.49 nm
157	spectrometer intensity at wavelength 307.3 nm
158	spectrometer intensity at wavelength 308.12 nm
159	spectrometer intensity at wavelength 308.93 nm
160	spectrometer intensity at wavelength 309.75 nm
161	spectrometer intensity at wavelength 310.57 nm
162	spectrometer intensity at wavelength 311.38 nm
163	spectrometer intensity at wavelength 312.2 nm
164	spectrometer intensity at wavelength 313.02 nm
165	spectrometer intensity at wavelength 313.83 nm
166	spectrometer intensity at wavelength 314.65 nm

167	spectrometer intensity at wavelength 315.47 nm
168	spectrometer intensity at wavelength 316.28 nm
169	spectrometer intensity at wavelength 317.1 nm
170	spectrometer intensity at wavelength 317.92 nm
171	spectrometer intensity at wavelength 318.73 nm
172	spectrometer intensity at wavelength 319.55 nm
173	spectrometer intensity at wavelength 320.37 nm
174	spectrometer intensity at wavelength 321.18 nm
175	spectrometer intensity at wavelength 322 nm
176	spectrometer intensity at wavelength 322.82 nm
177	spectrometer intensity at wavelength 323.63 nm
178	spectrometer intensity at wavelength 324.45 nm
179	spectrometer intensity at wavelength 325.27 nm
180	spectrometer intensity at wavelength 326.08 nm
181	spectrometer intensity at wavelength 326.9 nm
182	spectrometer intensity at wavelength 327.72 nm
183	spectrometer intensity at wavelength 328.53 nm
184	spectrometer intensity at wavelength 329.35 nm
185	spectrometer intensity at wavelength 330.17 nm
186	spectrometer intensity at wavelength 330.98 nm
187	spectrometer intensity at wavelength 331.8 nm
188	spectrometer intensity at wavelength 332.62 nm
189	spectrometer intensity at wavelength 333.43 nm
190	spectrometer intensity at wavelength 334.25 nm
191	spectrometer intensity at wavelength 335.06 nm
192	spectrometer intensity at wavelength 335.88 nm
193	spectrometer intensity at wavelength 336.7 nm
194	spectrometer intensity at wavelength 337.51 nm
195	spectrometer intensity at wavelength 338.33 nm
196	spectrometer intensity at wavelength 339.14 nm
197	spectrometer intensity at wavelength 339.96 nm
198	spectrometer intensity at wavelength 340.78 nm
199	spectrometer intensity at wavelength 341.59 nm
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201	spectrometer intensity at wavelength 343.22 nm
202	spectrometer intensity at wavelength 344.04 nm
203	spectrometer intensity at wavelength 344.85 nm
204	spectrometer intensity at wavelength 345.67 nm
205	spectrometer intensity at wavelength 346.48 nm
206	spectrometer intensity at wavelength 347.3 nm

207	spectrometer intensity at wavelength 348.12 nm
208	spectrometer intensity at wavelength 348.93 nm
209	spectrometer intensity at wavelength 349.75 nm
210	spectrometer intensity at wavelength 350.56 nm
211	spectrometer intensity at wavelength 351.38 nm
212	spectrometer intensity at wavelength 352.19 nm
213	spectrometer intensity at wavelength 353.01 nm
214	spectrometer intensity at wavelength 353.82 nm
215	spectrometer intensity at wavelength 354.63 nm
216	spectrometer intensity at wavelength 355.45 nm
217	spectrometer intensity at wavelength 356.26 nm
218	spectrometer intensity at wavelength 357.08 nm
219	spectrometer intensity at wavelength 357.89 nm
220	spectrometer intensity at wavelength 358.71 nm
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229	spectrometer intensity at wavelength 366.03 nm
230	spectrometer intensity at wavelength 366.84 nm
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232	spectrometer intensity at wavelength 368.47 nm
233	spectrometer intensity at wavelength 369.28 nm
234	spectrometer intensity at wavelength 370.09 nm
235	spectrometer intensity at wavelength 370.91 nm
236	spectrometer intensity at wavelength 371.72 nm
237	spectrometer intensity at wavelength 372.53 nm
238	spectrometer intensity at wavelength 373.34 nm
239	spectrometer intensity at wavelength 374.15 nm
240	spectrometer intensity at wavelength 374.97 nm
241	spectrometer intensity at wavelength 375.78 nm
242	spectrometer intensity at wavelength 376.59 nm
243	spectrometer intensity at wavelength 377.4 nm
244	spectrometer intensity at wavelength 378.21 nm
245	spectrometer intensity at wavelength 379.02 nm
246	spectrometer intensity at wavelength 379.83 nm

247	spectrometer intensity at wavelength 380.64 nm
248	spectrometer intensity at wavelength 381.45 nm
249	spectrometer intensity at wavelength 382.27 nm
250	spectrometer intensity at wavelength 383.08 nm
251	spectrometer intensity at wavelength 383.89 nm
252	spectrometer intensity at wavelength 384.7 nm
253	spectrometer intensity at wavelength 385.51 nm
254	spectrometer intensity at wavelength 386.32 nm
255	spectrometer intensity at wavelength 387.13 nm
256	spectrometer intensity at wavelength 387.93 nm
257	spectrometer intensity at wavelength 388.74 nm
258	spectrometer intensity at wavelength 389.55 nm
259	spectrometer intensity at wavelength 390.36 nm
260	spectrometer intensity at wavelength 391.17 nm
261	spectrometer intensity at wavelength 391.98 nm
262	spectrometer intensity at wavelength 392.79 nm
263	spectrometer intensity at wavelength 393.6 nm
264	spectrometer intensity at wavelength 394.4 nm
265	spectrometer intensity at wavelength 395.21 nm
266	spectrometer intensity at wavelength 396.02 nm
267	Temperature of sensor
268	Spectrometer temperature
269	Lamp temperature
270	Cumulative lamp time
271	Relative humidity
272	Main voltage
273	Lamp voltage
274	Internal voltage
275	Main current
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:

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

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

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

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

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 50 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 20 light frames allow for the sensor to stabilize. The final 30 frames will be averaged to provide the 15-minute L1 nitrate DP according to Equation 6.

$$\boldsymbol{\overline{NO_3} = \frac{1}{30}\sum_{n-29}^{n} NO_{3,i}} \qquad \textbf{Equation 6}$$

Where:

n = 51 ± 0 total number of measurements (light and dark frames)

$i = 1 \ldots n$ for each measurement in the burst

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

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

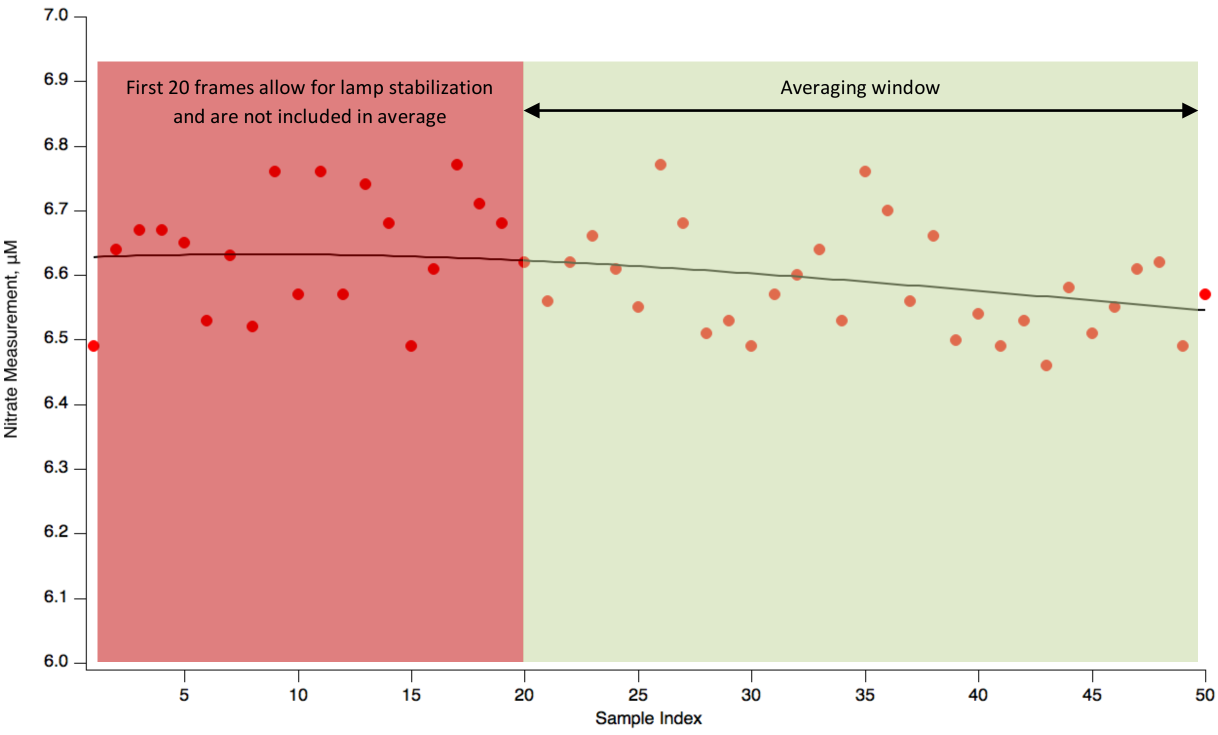

Figure 3. Example of data showing the stabilization of the lamp and the nitrate measurements to be averaged.

If greater than 30 light frames are available for averaging, flag the data with a gap test value of 2, meaning that there were more measurements than expected. If less than 30 light frames are available for averaging, flag the data with a gap test value of 1, meaning that there were fewer measurements than expected. Similarly, if greater than 1 dark frames are present, flag the data with gap test value of 3, meaning that there were more measurements than expected. If less than 1 dark frames are present, flag the data with gap test value of 4, meaning that there were less measurements than expected.

The time between the initiation of bursts ($i = 1$) should be 00:15:00. Each burst should last a maximum of $51 \times 1.5s = 00{:}01{:}16.5$. Therefore, the total time step between the end of a burst and the beginning of the next burst should be $t \geq 00{:}13{:}00$.

Each L1 15-minute nitrate measurement value shall have a timestamp according to Equation 7.

$$\boldsymbol{t_{\overline{NO_3}} = t_1 + \ 00{:}53.0} \qquad \textbf{Equation 7}$$

where:

$t_{\overline{NO_3}}$ = the timestamp for the averaged nitrate value for each burst

t_1 = the timestamp of the first measurement in each burst

00:00:53.0 = the average duration between $t_1$and t_{36}

The timestamp of individual measurements may be used to find the beginning of each burst. The measurement index is then reset to 1 at the beginning of each burst as follows:

$While\ i \leq n$

$$i = \left| \begin{array}{l} 1 \text{ if } \ t_{i+1} - t_i > 00{:}10{:}00.0 \\ \\ i + 1 \text{ otherwise} \end{array} \right.$$

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 0.5 to 0.667 Hz 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. 6in accordance with AD[06], details are provided below.
5. Signal de-spiking will be applied to the nitrate measurements (field 3 only) within the averaging window defined in Eq. 6 in accordance with AD[07].
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[12].

QA/QC Procedure:

1. **Plausibility Tests** AD[06] – 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.
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:

   $$\text{SpecQF=}\left|\begin{array}{l} 1 \text{ if } SpAv_L \ \leq 2 \times SpAv_D \\ \\ 0 \text{ otherwise} \end{array}\right.$$

   b. Internal Humidity:

   $$\text{humidityQF=}\left|\begin{array}{l} 1 \text{ if } H_i \geq 40 \\ \\ 0 \text{ otherwise} \end{array}\right.$$

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[07].
4. **Quality Flags (QFs) and Quality Metrics (QMs)** AD[12] – 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 and QMs will be determined for nitrate using the flags in Table 3. In addition, nitrate L1 DPs will have a QA/QC report and quality metrics associated with each flag listed in Table 4, as detailed in AD[12]. 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 5-1: 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 5-2: Information maintained in the CI data store for Surface Water Nitrate.

Tests/Values	CI Data Store Contents

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
Signal Despiking	Time segments and threshold values
Sensor Test – Insternal Humidity	Humidity threshold of 40 %
Sensor Test – Spectral Average	Light / Dark Spectral Average Ratio minimum of 2
Uncertainty	AD[09]
Final Quality Flag	AD[12]

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 [09], 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[08] and is explicitly described for the nitrate sensor in AD [09].

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.

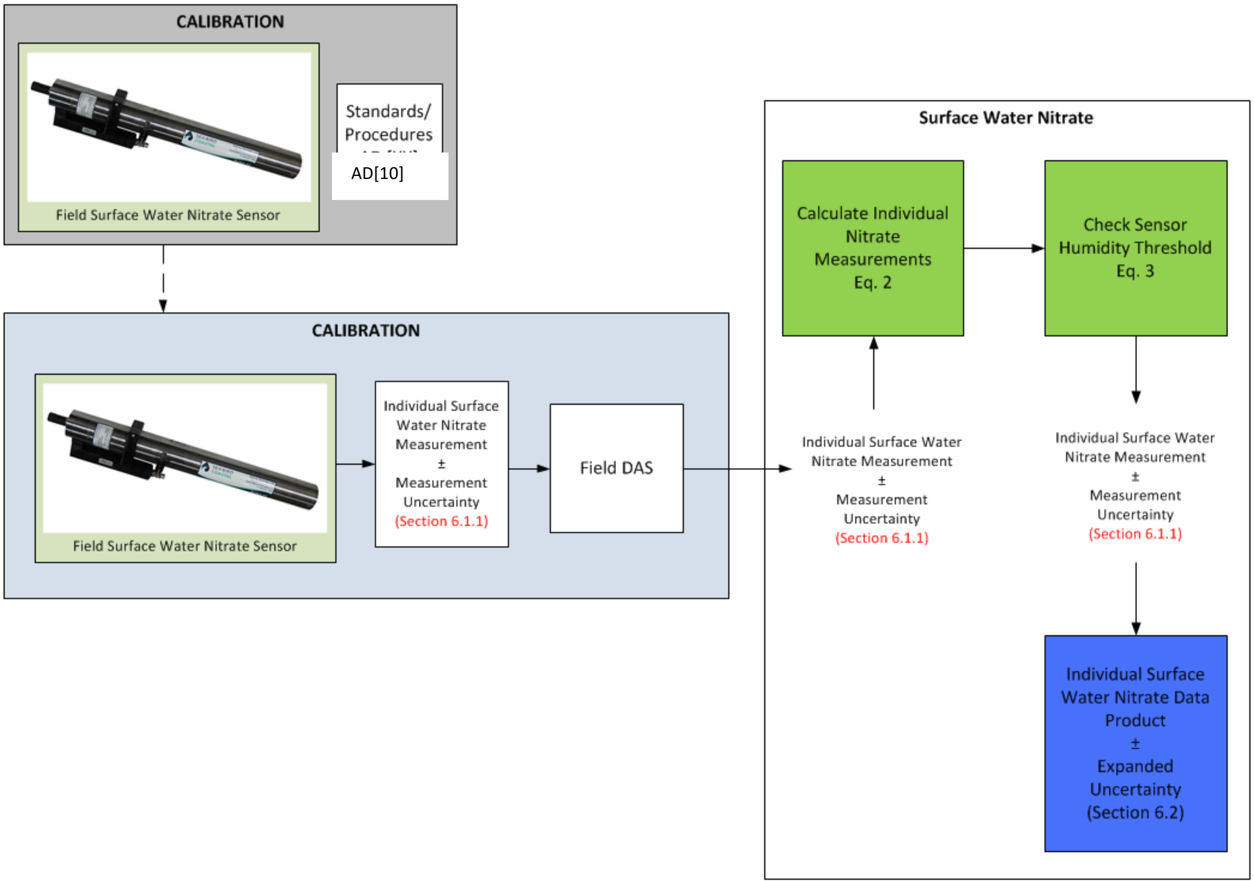

Figure 4. Displays the data flow and associated uncertainties of individual measurements of surface water nitrate and associated L1 DPs.

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[11] 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:

$$u_c(y) = \left(\sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i)\right)^{\frac{1}{2}} \qquad \textbf{Equation 8}$$

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 pressure 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 Satlantic LP 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:

$$\text{Measurement Accuracy=} \left| \begin{array}{l} 2\ \mu M \quad \text{if} \quad \overline{NO_3} \ \leq 20\ \mu M \\ \\ \overline{NO_3} \times 10\% \quad \text{if} \quad 20\ \mu M \ < \ NO_{3,i} \ \leq 1000\ \mu M \end{array} \right.$$

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:

$$\text{Individual measurement uncertainty} \left| \begin{array}{l} u_{A1} \ \text{if} \quad \overline{NO_3} \ \leq 20\ \mu M \\ \\ \\ \end{array} \right.$$

$$\{u_{An}\} = \left| \begin{array}{l} \\ u_{A3}, \text{ if } \quad 20\ \mu M < \overline{NO_3} \leq 1000\ \mu M \end{array} \right.$$

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).

$$\boldsymbol{u_{CAL}}(\overline{NO_3}) = \left| \begin{array}{l} u_{An} \text{ if } \quad \overline{NO_3} \leq 20\ \mu M \\ \\ u_{An} \times \overline{NO_3} \text{ if } \quad 20\ \mu M < \overline{NO_3} \leq 1000\ \mu M \end{array} \right. \qquad \textbf{Equation 9}$$

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:

$$\boldsymbol{u_{NAT}(\overline{NO_3}) = \sqrt{\frac{\sigma^2}{n}}}$$ **Equation 10**

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[10] 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:

$$\boldsymbol{u_c(\overline{NO_3}) = \left[u_{NAT}^2(\overline{NO}_3) + u_{CAL}^2(\overline{NO_3})\right]^{\frac{1}{2}}}$$ **Equation 11**

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.

$$\boldsymbol{U_p = k_p\, u_{c,r}(y)}$$ **Equation 12**

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:

$$\boldsymbol{v_{eff}} = \frac{\boldsymbol{u_c^4(y)}}{\sum_{i=1}^{n}\frac{\boldsymbol{u_i^4(y)}}{\boldsymbol{v_i}}}$$ **Equation 13**

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.

$$\boldsymbol{U_{Expanded}} = \boldsymbol{2 \times u_c}$$ **Equation 14**

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

Source of Measurement Uncertainty	**Measurement uncertainty Component** $\boldsymbol{u(x_i)}$	**Measurement Uncertainty Value**	$\boldsymbol{\frac{\partial f}{\partial x_i}}$	$\boldsymbol{u_{x_i}(Y) \equiv \left\lvert\frac{\partial f}{\partial x_i}\right\rvert u(x_i)}$
Nitrate	$u_{CAL}(NO_{3,i})$	AD[11]	n/a	Eq. 9

Table 4. Uncertainty budget for L1 mean DPs. Shaded rows denote the order of uncertainty propagation (from lightest to darkest).

Source of Uncertainty	**Uncertainty Component** $\boldsymbol{u(x)}$	**Uncertainty Value**	$\boldsymbol{\frac{\partial f}{\partial x_i}}$	$\boldsymbol{u_{u_{x_i}}(Y) \equiv \left\lvert\frac{\partial f}{\partial x_i}\right\rvert u(x_i)}$
Nitrate	$u_c(\overline{NO_3})$	Eq. (11)	n/a	Eq. 11
Calibration	$u_{CAL}(NO_{3,i})$	AD[11]	n/a	Eq. 9
Natural variation	$u_{NAT}(\overline{NO_3})$	Eq. 10	n/a	Eq. 10

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 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.

8 BIBLIOGRAPHY

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9 CHANGELOG