HEE NERR Nutrient Metadata January-December 2021

Latest Update: June 17, 2022

Note: This is a provisional metadata document; it has not been authenticated as of its download date. Contents of this document are subject to change throughout the QAQC process and it should not be considered a final record of data documentation until that process is complete. Contact the CDMO (cdmosupport@baruch.sc.edu) or reserve with any additional questions.

I. Data Set and Research Descriptors

1) Principal investigator(s) and contact persons -

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2) Research objectives -

a) Monthly grab sampling program

Our long term monitoring program currently consists of 3 official SWMP sites (1 pending) in our watershed. The overall goal is to track the physical and biogeochemical parameters of the He'eia Stream water that originates in our upper watershed, then move through invasive wetland vegetation, areas undergoing invasive mangrove removal, and restored taro fields, and flow out towards a coastal ancient Hawaiian fishpond and out into Kāne'ohe Bay. The SWMP sites are intended to measure various parameters in real-time representing the emerging wetland/tidal marsh, estuary, coastal/ocean interface, and patch reef in the Bay. This indicates a gradient in salinity, temperature, and land-use change. We designed these SWMP sites to be able to track short- and long-term changes in our watershed through active restoration of habitat using a combination of conventional and Indigenous Native Hawaiian management strategies. As a measure of success, we hope to be able to capture the return to conditions ideal for many of our native species (fish, waterbirds, invertebrates, etc.) that have not been seen in the watershed for decades. We also envision the SWMP stations to serve as data hubs for researchers with various expertise to conduct question-specific research based around our consistent SWMP water quality measurements. Specifically, the SWMP nutrient dataset is designed to illustrate the nutrient consumption in the wetland and the fate of nutrients in the coastal fishpond and nearshore reef environments.

Our monthly grab sampling program consists of sampling for nutrients (nitrate + nitrite, orthophosphate, silicic acid, ammonium, total nitrogen and total phosphorus), total suspended solids, particulate carbon and nitrogen, chlorophyll *a*, and quarterly sampling of environmental DNA (eDNA) for fish.

For this 2021 submission, we report nutrient (nitrate + nitrite, orthophosphate, silicic acid, ammonia) and chlorophyll *a* data from three permanent SWMP stations (Wai 2, Reef 9, and Kahoʻokele).

b) Diel sampling program

We started our diel sampling program in November 2020 at Wai 2. Diel sampling was conducted at Wai 2 for November 2020 to January 2021. To accommodate an experiment looking at Chlorophyll sensors, diel sampling was moved to Kahoʻokele from February to December 2021.

3) Research methods –

a) Monthly grab sampling program

Sample collection and collection intervals: Before sampling, all nutrient bottles are rinsed 3 times with 10% hydrochloric acid and rinsed 3 times with DI water. Samples are collected on a monthly basis during the full moon phase on an outgoing tide (within 3 hours before slack low tide). Physical water parameters are documented using a YSI ProDSS immediately before the sample collection. Sampling is conducted using a horizontal Van Dorn water sampler (2.2 L capacity), and collected near the depth of the YSI sensor faces, within 2 m of the instrument. Small amounts of water (~10 mL) collected in the Van Dorn bottle are used to rinse two amber LDPE 500 ml bottles three times, and then ~250 mL of water are collected into each bottle.

Sample processing: Each amber 500 mL bottle is then processed for both nutrients and chlorophyll a. Using a syringe and a 25 mm GF/F filter in a filter holder, 5 mL of the filtrate is used to rinse the 60 mL LDPE preacid washed bottles twice prior to collecting 40 mL of the filtrate into the bottle for subsequent nutrient analyses. Then, another 50 mL is filtered through the GF/F filter for a total of 100 ml. The GF/F filter is then folded in half and stored in an aluminum foil packet. Both nutrients and chlorophyll samples, post collection, are then kept on ice in a cooler and delivered within 3 hours of field sampling to the University of Hawai'i SOEST Laboratory for Analytical Biogeochemistry (S-LAB), where they are frozen in a laboratory-grade walk-in -20°C freezer for subsequent laboratory processing.

Equipment and analyzers: Nutrients are processed on a Seal Analytical AA3 HR Nutrient Autoanalyzer following these established protocols. Chlorophyll *a* was analyzed on a Turner 10-AU fluorometer using the methods shown here and by Welschmeyer (1994). The 2022 TNI Evaluation Report using standards was conducted February-March 2022 is found here. The Method Detection Limits reported in this submission was analyzed using these EPA protocols. The Method Detection Limits used for each nutrient and chlorophyll *a* were calculated June 2020 and the results are reported here.

4) Site location and character -

He'eia (11.5 km²), O'ahu, Hawai'i, extends from the summit of the Ko'olau mountain range to the fourth largest wetland in the islands containing historically productive flooded taro agroecosystems (lo'i), a coastal loko i'a, and into Kāne'ohe Bay highly valued for marine biodiversity. Ha'ikū and 'Ioleka'a basins contribute ~2.0 cfs perennial flow as He'eia Stream. State-wide, He'eia remains one of the few watersheds actively managed from ridge to reef. The He'eia NERR comprises a 1,385-acre region within the He'eia watershed, spanning the wetland and flooded-field agroecosystems managed by Kāko'o 'Ōiwi, the 800-year-old He'eia Fishpond managed by Paepae o He'eia, the surrounding streams and Kāne'ohe Bay under the jurisdiction of the state of Hawai'i Department of Land and Natural Resources, and Moku o Lo'e, the island on which Hawai'i Institute of Marine Biology, University of Hawai'i at Mānoa resides.

Wai 2 (W2): 21.43831° N, 157.81093° W

W2, installed on September 18, 2019, is a site in He'eia Stream as the water flows out of the wetland area that has recently undergone large-scale mangrove removal. At W2, water either diverts and flows into the He'eia Fishpond, or goes straight towards the stream mouth into Kāne'ohe Bay. There is slight tidal influence, with intrusions of saline water at the peak of high tide when tide is greater than typical values. As a result, the typical salinity is 0.11 psu, but have observed salinity as high as 33.2 psu, very occasionally. Typical water depth is 0.52 m, increasing slightly only when heavy rains coincide with high tide. The bottom habitat is soft, silty, dark (anoxic) sediment. Pollutants in the area may include fecal contaminants from invasive cats, pigs, and mongoose, and potential cesspool contamination from the upper watershed. At W2, we now have an active data logger, and we are collecting monthly grab samples of nutrients, total suspended solids, chlorophyll *a*, and bimonthly samples of eDNA.

Reef 9 (R9): 21.44628° N, 157.80183° W

R9, installed on February 13, 2020, is a site on a patch reef located in Kāne'ohe Bay, a subtropical embayment on the windward coast of O'ahu. The salinity range is 33.7 psu to 35.0 psu, and depth changes ~1 m throughout tidal changes. This is a perpetual ocean site and presumed to have no input of freshwater except

precipitation or during extreme low tide events. The bottom habitat is sandy, coral rubble, the average depth is ~3 m. Pollutants may include motorboat oil and human contaminants from nearby motorboat operators and proximity to He'eia Kea Small Boat Harbor.

Kaho'okele (KK): 21.43582° N, 157.80524W

Kahoʻokele, installed on September 29, 2020, is positioned on the ocean side (makai) of a ~800 year old Native Hawaiian fishpond. It is within close proximity to one of the fishpond sluice gates (mākāhā), also named Kahoʻokele, which serves as a point of water exchange between Heʻeia Stream and Kāneʻohe Bay. These traditional sluice gates are essential for regulating the physical-chemical parameters of the fishpond as well as maintenance of traditional husbandry of resource fish, and Kahoʻokele has been shown to exchange ~25% of the water exchanged through all the gates at the fishpond. The salinity range is 27.2 psu to 35.2 psu, and depth changes ~1 m throughout tidal changes. The bottom habitat is sandy, coral rubble, and pollutants may include pathogens related to domestic animal (i.e. cat, pig, mongoose) and other land-based pollutants coming from Heʻeia Stream and nearby Heʻeia State Park. Additionally, this site may be heavily influenced by groundwater sources of nutrients.

SWMP Station Timeline

Station Code	SWMP Status	Station Name	Location	Active Dates	Reason Decommissioned	Notes
W2	Р	Wai 2	21.43831° N, 157.81093° W	9/18/2019 - present	NA	NA
R9	Р	Reef 9	21.44628° N, 157.80183° W	2/13/2020 - present	NA	NA
KK	Р	Kahoʻokele	21.43582° N, 157.80524° W	9/29/2020- present	NA	NA

5) Coded variable definitions –

heew2nut = He'eia Wai 2 Nutrients heer9nut = He'eia Reef 9 Nutrients heekknut = He'eia Kaho'okele Nutrients

monthly grab sample program = 1 diel grab sample program = 2

6) Data collection period –

Wai 2:

1/28/2021 9:12 9:16

2/26/2021 8:00 8:10

3/30/2021 8:40 8:42

4/27/2021 8:09 8:14

5/27/2021 8:09 8:14

6/25/2021 7:48 7:49

7/23/2021 7:18 7:19

8/24/2021 8:22 8:21

9/21/2021 8:33 8:34

10/21/2021 8:03 8:04

11/18/2021 8:26 8:29

12/17/2021 8:17 8:17

1/13/2021 14:00 16:15 18:30 20:45 23:00

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1/14/2021 1:15 3:30 5:45 8:00 10:15 12:30 14:45
12/5/2021 4:30 6:45
                        9:00
                                11:15 13:30
                                              15:45
                                                       18:00
                                                               20:15
                                                                       22:30
12/6/2021 0:45 3:00
                        5:15
Reef 9:
1/27/2021 8:01 8:15
2/25/2021 7:27 7:37
3/29/2021 7:42 7:48
4/26/2021 7:10 7:13
5/26/2021 6:55 7:09
6/24/2021 6:49 6:53
7/24/2021 7:40 7:41
8/25/2021 9:04 9:05
9/20/2021 7:03 7:19
10/20/2021 8:02 8:03
11/19/2021 8:03 8:02
12/16/2021 7:49 7:50
Kahoʻokele (KK):
1/28/2021 8:41 8:43
2/26/2021 7:13 7:18
3/30/2021 7:44 7:45
4/27/2021 7:21 7:22
5/27/2021 7:16 7:20
6/25/2021 7:08 7:09
7/23/2021 6:41 6:42
8/24/2021 9:17 9:16
9/21/2021 7:59 8:00
10/21/2021 7:30 7:31
11/18/2021 7:42 7:43
12/17/2021 7:37 7:38
2/10/2021 9:30 11:45 14:00 16:15 18:30 20:45 23:00
2/11/2021 1:15 3:30 5:45 8:00 10:15
3/30/2021 9:45 12:00
                       14:15
                                16:30
                                       18:45
                                                21:00
                                                       23:15
3/31/2021 1:30 3:45
                        6:00
                                8:15
                                        10:30
4/27/2021 9:00 11:15
                        13:30
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                                       18:00
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4/28/2021 0:45 2:00
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5/26/2021 8:00 10:15
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6/24/2021 16:15 18:30
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6/25/2021 1:15 3:30
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                                                12:30
7/22/2021 7:00 9:15
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7/23/2021 1:00 3:15 5:30
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8/25/2021 1:45 4:00
                        6:15
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                                8:30
9/21/2021 9:00 11:15
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9/22/2021 0:45 3:00
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10/20/2021 8:30
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                                                       19:45
                        10:45
                                       15:15
                                                                22:00
10/21/2021 0:15
                        2:30
                                4:45
                                       7:00
                                                9:15
12/1/2021 8:00 10:15
                        12:30
                                               19:15
                                14:45
                                       17:00
                                                       21:30
                                                                23:45
12/2/2021 2:00 4:15
                        6:30
                                8:45
12/15/2021 8:00
                        10:15
                               12:30
                                       14:45
                                               17:00
                                                       19:15
                                                               21:30
                                                                       23:45
12/16/2021 2:00
                        4:15
                                6:30
                                        8:45
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7) Associated researchers and projects-

As part of the SWMP long-term monitoring program, He'eia NERR also monitors 15-minute meteorological and water quality data which may be correlated with this nutrient/pigment dataset. These data are available at www.nerrsdata.org.

We have also started collecting nutrients and pigments at 1 other future SWMP station, but we will be reporting those measurements at a later time when the respective SWMP station is established officially.

In addition to the SWMP stations (3 current and 1 future), we also collect nutrients and pigments from 6 other stations in the He'eia watershed, designed to fill knowledge gaps on the fate of nutrients through the watershed. Many of these stations may be added as secondary SWMP stations in the future.

8) Distribution -

NOAA retains the right to analyze, synthesize and publish summaries of the NERRS System-wide Monitoring Program data. The NERRS retains the right to be fully credited for having collected and process the data. Following academic courtesy standards, the NERR site where the data were collected should be contacted and fully acknowledged in any subsequent publications in which any part of the data are used. The data set enclosed within this package/transmission is only as good as the quality assurance and quality control procedures outlined by the enclosed metadata reporting statement. The user bears all responsibility for its subsequent use/misuse in any further analyses or comparisons. The Federal government does not assume liability to the Recipient or third persons, nor will the Federal government reimburse or indemnify the Recipient for its liability due to any losses resulting in any way from the use of this data.

Requested citation format:

NOAA National Estuarine Research Reserve System (NERRS). System-wide Monitoring Program. Data accessed from the NOAA NERRS Centralized Data Management Office website: www.nerrsdata.org; accessed 12 October 2019.

NERR nutrient data and metadata can be obtained from the Research Coordinator at the individual NERR site (please see Principal investigators and contact persons), from the Data Manager at the Centralized Data Management Office (please see personnel directory under the general information link on the CDMO home page) and online at the CDMO home page www.nerrsdata.org. Data are available in comma separated version format.

II. Physical Structure Descriptors

9) Entry verification –

Nutrient data is received by the Research Coordinator from the S-LAB Laboratory Specialist in a Microsoft Excel format. The original nutrient data is then archived in a shared Google Drive folder and an external hard drive. The S-LAB calculates and reports results in µg/L. For purposes of consistency in the NERR System, He'eia NERR converts the concentrations into mg/L by dividing all values by 1000. The SWMP Technician then enters the data from each month into the Microsoft Excel worksheet that will be subsequently processed for QAQC. Prior to running NutrientQAQC, the worksheet is sent to the Research Coordinator for verification.

After verification, nutrient data are entered into a Microsoft Excel worksheet and processed using the NutrientQAQC Excel macro. The NutrientQAQC macro sets up the data worksheet, metadata worksheets, and MDL worksheet; adds chosen parameters and facilitates data entry; allows the user to set the number of significant figures to be reported for each parameter and rounds using banker's

rounding rules; allows the user to input MDL values and then automatically flags/codes measured values below MDL and inserts the MDL; calculates parameters chosen by the user and automatically flags/codes for component values below MDL, negative calculated values, and missing data; allows the user to apply QAQC flags and codes to the data; produces summary statistics; graphs selected parameters for review; and exports the resulting data file to the CDMO for tertiary QAQC and assimilation into the CDMO's authoritative online database.

10) Parameter titles and variable names by category –

Required NOAA NERRS System-wide Monitoring Program nutrient parameters are denoted by an asterisk "**"

Data Category	Parameter	Variable Name	Units of Measure
Phosphorus and	d Nitrogen:		
•	*Orthophosphate, Filtered	PO4F	mg/L as P
	*Ammonium, Filtered	NH4F	mg/L as N
	*Nitrite + Nitrate, Filtered	NO23F	mg/L as N
	Dissolved Inorganic Nitrogen	DIN	mg/L as N
Plant Pigments:			
	*Chlorophyll a	CHLA_N	μg/L
Other Lab Para			
	Silicate, Filtered	SiO4F	mg/L as SI
Field Parameter	rs:		
	Water Temperature	WTEM_N	°C
	Specific Conductance	SCON_N	mS/cm
	Salinity	SALT_N	ppt
	% Dissolved Oxygen Saturation	DO_S_N	0/0
	Dissolved Oxygen	DO_N	mg/L
	рН	PH_N	SÜ
	Turbidity – Nephelometer Turbidity Units	TURB_N	NTU

Notes:

- 1. Time is coded based on a 2400 clock and is referenced to Standard Time.
- 2. NO2 and NO3 are not reported individually and are reported together as NO23, as NO2 is a minor component (in the 0-1 nanomolar range) in Hawai'i's ocean and rain-fed systems relative to NO3 (https://hahana.soest.hawaii.edu/hot/hot-dogs/interface.html).

11) Measured or calculated laboratory parameters –

a) Parameters measured directly

Nitrogen species: NH4F, NO23F

Phosphorus species: PO4F

Other: CHLA_N, SiO4F

b) Calculated parameters

DIN NO23F+NH4F

12) Limits of detection –

Method Detection Limits (MDL), the lowest concentration of a parameter that an analytical procedure can reliably detect, have been established by the S-LAB using these <u>EPA protocols</u>. The MDLs used for each

nutrient and chlorophyll a were calculated June 2022 and the results are reported <u>here</u>. As the results were reported in μ M, they were multiplied by 0.014007, 0.03097, and 0.02809 to yield concentrations in mg/L as N, P, and Si, respectively. These values are reviewed and revised annually.

Parameter	Start Date	End Date	MDL	Revisited
NH4F	01/01/21	12/31/21	0.00028	
NO23F	01/01/21	12/31/21	0.00014	
PO4F	01/01/21	12/31/21	0.00028	
SiO4F	01/01/21	12/31/21	0.00169	
CHLA_N	01/01/20	12/31/20	0.03	

CHLA MDL values may change, as we are still awaiting 2021 MDL values from S-LAB.

13) Laboratory methods -

All dissolved nutrient samples are stored frozen until analysis. Samples are thawed overnight in a refrigerator. Standards are made from concentrated stock solutions daily. For determination of NO23F and TN, a NO2 and NO3 is included in the run to determine efficiency of cadmium column reduction. For TN and TP determination an organic TN and TP sample is included in the run to determine efficiency of UV digestion. Every 15 samples the following sequence is completed: deionized baseline, deionized water blank, low nutrient seawater blank, two replicate standards at the middle concentration (to determine consistent recovery and accuracy), a low concentration QA/QC sample, a high concentration QA/QC sample, and finally, the high standard (to determine instrument drift).

QA/QC samples analyzed throughout the run are collected by the <u>Hawaii Ocean Time-series program</u>. These are collected with the CTD-Niskin bottles at 250 m and 4000 m. The 250 m sample acts as the high concentration sample for total dissolved nitrogen and total dissolved phosphorus and acts as the low concentration sample for the suite of inorganic dissolved nutrients. The 4000 m sample acts as the low concentration sample for total dissolved nitrogen and total dissolved phosphorus and acts as the high concentration sample for the suite of inorganic dissolved nutrients.

Refer to document "S-LAB Description of Procedures" on file with CDMO for specific procedures and references.

a) Parameter: NH4F

S-LAB Laboratory Method: S-LAB Description of Procedures

Method Reference: Kerouel and Aminot (1997)

Method Descriptor: The sample is reacted with o-phthaladehyde (OPA) at 75°C in the presence of borate buffer and sodium sulfite to form a fluorescent species proportional to the ammonia concentration. The fluorescence is measured at 460 nm following excitation at 370 nm.

Preservation Method: Samples filtered and stored at -20 °C up to 28 days.

b) Parameter: NO23F

S-LAB Laboratory Method: S-LAB Description of Procedures

Method Reference: Armstrong et al. (1967); Grasshof (1969); Grasshof et al. (1983)

Method Descriptor: The determination of nitrate and nitrite uses a procedure whereby nitrate is reduced to nitrite by a copper-cadmium reductor column. The nitrite then reacts with sulfanilamide under acidic conditions to form a diazo compound. This compound then couples with N-1-napthylethylene diamine dihydrochloride to form a purple azo dye. The method is based on the nitrate determination in Standard Methods and in the DIN/ISO Standards for automatic nitrate measurements. Detection is at 520 nm.

Preservation Method: Samples filtered and stored frozen at -20 °C up to 28 days.

c) Parameter: PO4F

S-LAB Laboratory Method: S-LAB Description of Procedures

Method Reference: Grasshoff (1965)

Method Descriptor: Automated procedure for the determination of orthophosphate based on the colorimetric method in which blue color is formed by the reaction orthophosphate, molybdate ion and antimony ion followed by reduction with ascorbic acid at a pH<1. The reduced blue phosphor-molybdenum complex is

colorimetrically read at 880 nm.

Preservation Method: Samples filtered and stored at -20 °C up to 28 days.

d) Parameter: SiO4F

S-LAB Laboratory Method: S-LAB Description of Procedures

Method Reference: Grasshoff et al. (1983)

Method Descriptor: This automated procedure for the determination of soluble silicates is based on the reduction of silicomolybdate in acidic solution to molybdenum blue by ascorbic acid. Oxalic acid is introduced to the sample stream before the addition of ascorbic acid to minimize interference from phosphates. Detection is at 820 nm.

Preservation Method: Samples filtered and stored at -20 °C up to 28 days.

e) Parameter: CHLA_N

S-LAB Laboratory Method: S-LAB Description of Procedures

Method Reference: Welschmeyer (1994)

Method Descriptor: Samples are extracted with a 90% acetone solution at the end of the day (after 3 PM). They are stored in the freezer overnight for extraction. Sample extraction ranges between 16-19 hours. Sample extraction is never less than 2 hours or greater than 24 hours. Samples are brought to room temperature prior to analysis. At the start and end of each day a high and low solid standard is analyzed on the Turner 10AU fluorometer to monitor any long-term instrument drift. The Turner 10 AU fluorometer is calibrated every 6 months or as needed based on solid standard drift (not to exceed 5 %). A blank of 90% acetone is analyzed at the start and end of each day. Samples are homogenized and the 90% acetone solution is decanted into a new borosilicate test tube for analysis. If dilution is required, a known volume of the original sample is pipetted into a new test tube, diluted with a known volume of 90% acetone, homogenized, and analyzed. The Turner 10 AU is equipped with a non-acidification module that does not require acidification to account for chlorophyll b and pheopigments

Preservation Method: Samples filtered and stored at -20 °C up to 30 days.

14) Field and Laboratory QAQC programs -

a) Precision

i) Field variability -

Field replicates: 36 replicates / 72 total samples =50%

Nutrients: True field replicates were collected for all sites for all months in 2021. Chlorophyll *a*. True field replicates were collected for all sites for all months in 2021.

*S indicates "Split" sample.

			Nutrients			Chlorophyll		
Site	Date	Collection times	Sample	Split	Replicate	Sample	Split	Replicate
Wai 2	1/28/2021	9:12 9:16	1		1	1		1
	2/26/2021	8:00 8:10	1		1	1		1
	3/30/2021	8:40 8:42	1		1	1		1

4/27/2021	8:09 8:14	1	1	1	1
5/27/2021	8:09 8:14	1	1	1	1
6/25/2021	7:48 7:49	1	1	1	1
7/23/2021	7:18 7:19	1	1	1	1
8/24/2021	8:22 8:21	1	1	1	1
9/21/2021	8:33 8:34	1	1	1	1
10/21/2021	8:03 8:04	1	1	1	1
11/18/2021	8:26 8:29	1	1	1	1
12/17/2021	8:17 8:17	1	1	1	1
1/13/2021	14:00	1		1	
1/13/2021	16:15	1		1	
1/13/2021	18:30	1		1	
1/13/2021	20:45	1		1	
1/13/2021	23:00	1		1	
1/14/2021	1:15	1		1	
1/14/2021	3:30	1		1	
1/14/2021	5:45	1		1	
1/14/2021	8:00	1		1	
1/14/2021	10:15	1		1	
1/14/2021	12:30	1		1	
1/14/2021	14:45	1		1	
12/5/2021	4:30	1		1	
12/5/2021	6:45				
12/5/2021	9:00				
12/5/2021	11:15				
12/5/2021	13:30				
12/5/2021	15:45				
12/5/2021	18:00				
12/5/2021	20:15				
12/5/2021	22:30				
12/6/2021	0:45				
12/6/2021	3:00				
12/6/2021	5:15				

			Nutrients			Chlorophyll		
Site	Date	Collection times	Sample	Split	Replicate	Sample	Split	Replicate

Reef 9	1/27/2021	8:01 8:15	1		1	
	2/25/2021	7:27 7:37	1		1	
	3/29/2021	7:42 7:48	1	1	1	1
	4/26/2021	7:10 7:13	1	1	1	1
	5/26/2021	6:55 7:09	1	1	1	1
	6/24/2021	6:49 6:53	1	1	1	1
	7/24/2021	7:40 7:41	1	1	1	1
	8/25/2021	9:04 9:05	1	1	1	1
	9/20/2021	7:03 7:19	1	1	1	1
	10/20/2021	8:02 8:03	1	1	1	1
	11/19/2021	8:03 8:02	1	1	1	1
	12/16/2021	7:49 7:50				

				Nutrients		Chlorophyll			
Site	Date	Collection times	Sample	Split	Replicate	Sample	Split	Replicate	
Kahoʻokele	1/28/2021	8:41 8:43	1		1	1		1	
	2/26/2021	7:13 7:18	1		1	1		1	
	3/30/2021	7:44 7:45	1		1	1		1	
	4/27/2021	7:21 7:22	1		1	1		1	
	5/27/2021	7:16 7:20	1		1	1		1	
	6/25/2021	7:08 7:09	1		1	1		1	
	7/23/2021	6:41 6:42	1		1	1		1	
	8/24/2021	9:17 9:16	1		1	1		1	
	9/21/2021	7:59 8:00	1		1	1		1	
	10/21/2021	7:30 7:31	1		1	1		1	
	11/18/2021	7:42 7:43	1		1	1		1	
	12/17/2021	7:37 7:38	1		1	1		1	
	2/10/2021	9:30	1			1			
	2/10/2021	11:45	1			1			
	2/10/2021	14:00	1			1			
	2/10/2021	16:15	1			1			
	2/10/2021	18:30	1			1			
	2/10/2021	20:45	1			1			
	2/10/2021	23:00	1			1			
	2/11/2021	1:15	1			1			
	2/11/2021	3:30	1			1			
	2/11/2021	5:45	1			1			

2/11/2021	8:00	1		1	
2/11/2021	9:30	1		1	
2/11/2021	10:15	1		1	
3/30/2021	9:45	1		1	
3/30/2021	12:00	1		1	
3/30/2021	14:15	1		1	
3/30/2021	16:30	1		1	
3/30/2021	18:45	1		1	
3/30/2021	21:00	1		1	
3/30/2021	23:15	1		1	
3/31/2021	1:30	1		1	
3/31/2021	3:45	1		1	
3/31/2021	6:00	1		1	
3/31/2021	8:15	1		1	
3/31/2021	10:30	1		1	
4/27/2021	9:00	1		1	
4/27/2021	11:15	1		1	
4/27/2021	13:30	1		1	
4/27/2021	15:45	1		1	
4/27/2021	18:00	1		1	
4/27/2021	20:15	1		1	
4/27/2021	22:30	1		1	
4/28/2021	0:45	1		1	
4/28/2021	2:00	1		1	
4/28/2021	4:15	1		1	
4/28/2021	6:30	1		1	
4/28/2021	8:45	1		1	
5/26/2021	8:00	1		1	
5/26/2021	10:15	1		1	
5/26/2021	12:00	1		1	
5/26/2021	14:45	1		1	
5/26/2021	17:00	1		1	
5/26/2021	19:15	1		1	
5/26/2021	21:30	1		1	
5/26/2021	23:45	1		1	
5/27/2021	2:00	1		1	
5/27/2021	4:15	1		1	
5/27/2021	6:30	1		1	
5/27/2021	8:45	1		1	

6/24/2021	16:15	1	1	
6/24/2021	18:30	1	1	
6/24/2021	20:45	1	1	
6/24/2021	23:00	1	1	
6/25/2021	1:15	1	1	
6/25/2021	3:30	1	1	
6/25/2021	5:45	1	1	
6/25/2021	8:00	1	1	
6/25/2021	10:15	1	1	
6/25/2021	12:30	1	1	
6/25/2021	14:45	1	1	
6/25/2021	17:00	1	1	
7/22/2021	7:00	1	1	
7/22/2021	9:15	1	1	
7/22/2021	11:30	1	1	
7/22/2021	13:45	1	1	
7/22/2021	16:00	1	1	
7/22/2021	18:15	1	1	
7/22/2021	20:30	1	1	
7/22/2021	22:45	1	1	
7/23/2021	1:00	1	1	
7/23/2021	3:15	1	1	
7/23/2021	5:30	1	1	
7/23/2021	7:45	1	1	
8/24/2021	10:00	1	1	
8/24/2021	12:15	1	1	
8/24/2021	14:30	1	1	
8/24/2021	16:45	1	1	
8/24/2021	19:00	1	1	
8/24/2021	21:15	1	1	
8/24/2021	23:30	1	1	
8/25/2021	1:45	1	1	
8/25/2021	4:00	1	1	
8/25/2021	6:15	1	1	
8/25/2021	8:30	1	1	
8/25/2021	10:45	1	1	
9/21/2021	9:00	1	1	
9/21/2021	11:15	1	1	
9/21/2021	13:30	1	1	

9/21/2021	15:45	1		1	
9/21/2021	18:00	1		1	
9/21/2021	20:15	1		1	
9/21/2021	22:30	1		1	
9/22/2021	0:45	1		1	
9/22/2021	3:00	1		1	
9/22/2021	5:15	1		1	
9/22/2021	7:30	1		1	
9/22/2021	9:45	1		1	
10/20/2021	8:30	1		1	
10/20/2021	10:45	1		1	
10/20/2021	13:00	1		1	
10/20/2021	15:15	1		1	
10/20/2021	17:30	1		1	
10/20/2021	19:45	1		1	
10/20/2021	22:00	1		1	
10/21/2021	0:15	1		1	
10/21/2021	2:30	1		1	
10/21/2021	4:45	1		1	
10/21/2021	7:00	1		1	
10/21/2021	9:15	1		1	
12/1/2021	8:00	1		1	
12/1/2021	10:15	1		1	
12/1/2021	12:30	1		1	
12/1/2021	14:45	1		1	
12/1/2021	17:00	1		1	
12/1/2021	19:15	1		1	
12/1/2021	21:30	1		1	
12/1/2021	23:45	1		1	
12/2/2021	2:00	1		1	
12/2/2021	4:15	1		1	
12/2/2021	6:30	1		1	
12/2/2021	8:45	1		1	
12/15/2021	8:00	1		1	
12/15/2021	10:15	1		1	
12/15/2021	12:30	1		1	
12/15/2021	14:45	1		1	
12/15/2021	17:00	1		1	
12/15/2021	19:15	1		1	

12/15/2021	21:30	1		1	
12/15/2021	23:45	1		1	
12/16/2021	2:00	1		1	
12/16/2021	4:15	1		1	
12/16/2021	6:30	1		1	
12/16/2021	8:45	1		1	

- ii) Laboratory variability 0 Laboratory replicates / 72 total samples = 0%
- iii) Inter-organizational splits Samples were not split and analyzed by two different labs.

b) Accuracy

- i) Sample spikes Standards utilized are "spiked" low nutrient seawater (LNSW), though no samples are spiked. Middle LNSW spiked standards are evaluated in the same way, the % recovery of this is reported every 15 samples (duplicate Cal 3 on each run file), and % recovery is typically 100% +/- 5%.
- ii) **Standard reference material analysis** Certified reference materials (NMIJ Seawater Standards) are analyzed during each nutrient run, and the S-LAB values are consistently within the accepted ranges. The 2019 TNI Evaluation Report using standards was conducted February-March 2019 is found here. We are working with S-LAB to obtain an updated TNI Evaluation Report.
- iii) **Cross calibration exercises** –He'eia NERR has not participated in any cross calibration exercises.

15) QAQC flag definitions -

QAQC flags provide documentation of the data and are applied to individual data points by insertion into the parameter's associated flag column (header preceded by an F_). QAQC flags are applied to the nutrient data during secondary QAQC to indicate data that are out of sensor range low (-4), rejected due to QAQC checks (-3), missing (-2), optional and were not collected (-1), suspect (1), and that have been corrected (5). All remaining data are flagged as having passed initial QAQC checks (0) when the data are uploaded and assimilated into the CDMO ODIS as provisional plus data. The historical data flag (4) is used to indicate data that were submitted to the CDMO prior to the initiation of secondary QAQC flags and codes (and the use of the automated primary QAQC system for WQ and MET data). This flag is only present in historical data that are exported from the CDMO ODIS.

- -4 Outside Low Sensor Range
- -3 Data Rejected due to QAQC
- -2 Missing Data
- -1 Optional SWMP Supported Parameter
- 0 Data Passed Initial QAQC Checks
- 1 Suspect Data
- 4 Historical Data: Pre-Auto QAQC
- 5 Corrected Data

16) QAQC code definitions -

QAQC codes are used in conjunction with QAQC flags to provide further documentation of the data and are also applied by insertion into the associated flag column. There are three (3) different code categories, general, sensor, and comment. General errors document general problems with the sample or sample collection, sensor errors document common

sensor or parameter specific problems, and comment codes are used to further document conditions or a problem with the data. Only one general or sensor error and one comment code can be applied to a particular data point. However, a record flag column (F_Record) in the nutrient data allows multiple comment codes to be applied to the entire data record.

General errors

GCM	Calculated value could not be determined due to missing data
GCR	Calculated value could not be determined due to rejected data
GDM	Data missing or sample never collected
GQD	Data rejected due to QA/QC checks
GQS	Data suspect due to QA/QC checks
GSM	See metadata

Sensor errors

SBL	Value below minimum limit of method detection
SCB	Calculated value could not be determined due to a below MDL component
SCC	Calculation with this component resulted in a negative value
SNV	Calculated value is negative
SRD	Replicate values differ substantially
SUL	Value above upper limit of method detection

Parameter Comments

CAB	Algal bloom
CDR	Sample diluted and rerun
CHB	Sample held beyond specified holding time
CIP	Ice present in sample vicinity
CIF	Flotsam present in sample vicinity
CLE	Sample collected later/earlier than scheduled
CRE	Significant rain event
CSM	See metadata
CUS	Lab analysis from unpreserved sample

Record comments

lecora comm	lents
CAB	Algal bloom
CHB	Sample held beyond specified holding time
CIP	Ice present in sample vicinity
CIF	Flotsam present in sample vicinity
CLE	Sample collected later/earlier than scheduled
CRE	Significant rain event
CSM	See metadata
CUS	Lab analysis from unpreserved sample
Cloud cover	
CCL	clear (0-10%)
CSP	scattered to partly cloudy (10-50%)
CPB	partly to broken (50-90%)
COC	overcast (>90%)
CFY	foggy
CHY	hazy
CCC	cloud (no percentage)
Precipitation	
PNP	none
PDR	drizzle

light rain

heavy rain

PLR PHR

```
PSQ
            squally
  PFQ
            frozen precipitation (sleet/snow/freezing rain)
  PSR
            mixed rain and snow
Tide stage
  TSE
            ebb tide
  TSF
            flood tide
            high tide
  TSH
  TSL
            low tide
Wave height
  WH0
            0 to < 0.1 meters
  WH1
            0.1 to 0.3 meters
  WH2
            0.3 to 0.6 meters
  WH3
            0.6 \text{ to} > 1.0 \text{ meters}
  WH4
            1.0 to 1.3 meters
  WH5
            1.3 or greater meters
Wind direction
            from the north
  N
  NNE
            from the north northeast
  NE
            from the northeast
  ENE
            from the east northeast
  Е
            from the east
  ESE
            from the east southeast
  SE
            from the southeast
  SSE
            from the south southeast
  S
            from the south
  SSW
            from the south southwest
  SW
            from the southwest
  WSW
            from the west southwest
  W
            from the west
  WNW
            from the west northwest
  NW
            from the northwest
  NNW
            from the north northwest
Wind speed
  WS0
            0 to 1 knot
  WS1
            > 1 to 10 knots
  WS2
            > 10 to 20 knots
  WS3
            > 20 to 30 knots
  WS4
            > 30 to 40 knots
  WS5
            > 40 \text{ knots}
```

17) Other remarks/notes -

Data may be missing due to problems with sample collection or processing. Laboratories in the NERRS System submit data that are censored at a lower detection rate limit, called the Method Detection Limit or MDL. MDLs for specific parameters are listed in the Laboratory Methods and Detection Limits Section (Section II, Part 12) of this document. Concentrations that are less than this limit are censored with the use of a QAQC flag and code, and the reported value is the method detection limit itself rather than a measured value. For example, if the measured concentration of NO23F was 0.0005 mg/l as N (MDL=0.0008), the reported value would be 0.0008 and would be flagged as out of sensor range low (-4) and coded SBL. In addition, if any of the components used to calculate a variable are below the MDL, the calculated variable is removed and flagged/coded -4 SCB. If a calculated value is negative, it is rejected and all measured components are marked

suspect. If additional information on MDL's or missing, suspect, or rejected data is needed, contact the Research Coordinator at the reserve submitting the data.

Note: The way below MDL values are handled in the NERRS SWMP dataset was changed in November of 2011. Previously, below MDL data from 2007-2010 were also flagged/coded, but either reported as the measured value or a blank cell. Any 2007-2011 nutrient/pigment data downloaded from the CDMO prior to November of 2011 will reflect this difference.

Date	Codes	Description
January, February, Nov,	Dec	Wai 2 might be displaying seasonally elevated NO23, with Reef 9 and KK displaying decrease in SiO4 during the winter months.
3/29/21		High CHLA at Reef 9 and Kaho'okele, possibly due to delayed effect of storm on 3/22?
May – September		Elevated PO4 in diel samples at Kahoʻokele during the summer, high light months
6/25/21		High NH4 at Wai 2 – is this due to something? King tide/full moon
8/24/21		Elevated CHLA at Wai 2, possibly due to King tide effects?
11/19/21 8:02	SRD	Reef 9 replicate variation of 0.0055 for PO4.
12/16/21	SRD	For Reef 9, NH4, NO23, and DIN replicates vary significantly, possibly caused by a storm event that occurred 12/7/21.
		https://nwis.waterdata.usgs.gov/hi/nwis/uv/?cb_00060=on&cb_00065=on&format=gif_default&site_no=1627500 0.=&begin_date=2021-12-01&end_date=2021-12-16

Sample hold times for 2021: Samples are held at -20°C. NERRS SOP allows nutrient samples to be held for up to 28 days (CHLA for 30) at -20°C.

*Sample held longer than allowed by NERRS protocols

	Date Analyzed				
Sample Descriptor	PO4F	NH4F	NO23F	CHLA_N	SiO4F
1/27, 1/28/2021, all grab	1/29/2021	1/29/2021	1/29/2021	2/3/2021	1/29/2021

samples					
2/10, 2/11/2021, and 2/26, 2/27/2021 all grab samples	3/9/2021	3/9/2021	3/9/2021	3/5/2021	3/9/2021
03/29, 3/30, 03/31/2021, all grab samples	4/7/2021	4/7/2021	4/7/2021	4/9/2021	4/7/2021
4/26, 04/27, 04/28, all grab samples	4/28/2021	4/28/2021	4/28/2021	4/30/2021	4/28/2021
5/26, 5/27/2021 all grab samples	6/8/2021	6/8/2021	6/8/2021	6/3/2021	6/8/2021
6/24, 6/25/2021 all grab samples	7/8/2021	7/8/2021	7/8/2021	6/30/2021	7/8/2021
7/22, 7/24/2021, all grab samples	7/28/2021	7/28/2021	7/28/2021	7/28/2021	7/28/2021
8/24, 8/25/2021, all grab samples	8/30/2021	8/30/2021	8/30/2021	8/28/2025	8/30/2021
9/20, 9/22/2021, all grab samples	10/11/2021	10/11/2021	10/11/2021	9/24/2021	10/11/2021
10/20, 10/21/2020, all grab samples	10/29/2021	10/29/2021	10/29/2021	10/27/2021	10/29/2021
11/18, 11/19, 12/1, 12/2/2021, all grab samples	12/13/2021 1/19/2022	12/13/2021 1/19/2022	12/13/2021 1/19/2022	12/3/2021 1/14/2022	12/13/2021 1/19/2022
12/15, 12/17/2021, all grab samples	1/19/2022*	1/19/2022*	1/19/2022*	1/14/2022	1/19/2022