HEE NERR Nutrient Metadata
January-December 2023
Latest Update: June 14, 2024

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 consists of 4 official SWMP sites in our watershed. The overall goal is to track the physical and biogeochemical parameters of the Heʻeia 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 Kāneʻohe 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 2022 submission, we report nutrient (nitrate + nitrite, orthophosphate, silicic acid, ammonia) and chlorophyll *a* data from four permanent SWMP stations (Wai 2, Reef 9, Kahoʻokele, and Papahana).

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 2021 to April 2022. The diel sampling program returned to Wai 2 from May 2022 to current, to accommodate a grant project looking at tidal variability in the Heʻeia Stream.

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 by wading or free diving next to the deployed sonde and collecting water into two amber LDPE 500 mL bottles as close to the sensor depth as possible. Prior to collecting the sample water, each bottle is rinsed 3 times with ambient water, including with the cap. Time collected for each amber bottle is noted in our collection log sheet.

For Wai 2, samples collected before _10/10/22____ were collected from the depth of the sensors ~5 ft from the sonde, due to logistics of disturbing the site and impacting water quality parameters (specifically turbidity) when wading into the water to be near the sensor. However, since _10/10/22___, we have decided to stand next to the sonde for _3-5__ min until the conditions settle down, pre-rinse the sample bottles, and open up the bottle at the depth of the sensors.

For Papahana, nutrients were collected monthly since 2018, prior to the SWMP station being deployed in June 2022. Prior to the station being established, grab samples were collected ~8-10 ft away, about a foot beneath the surface, in a freshwater pool that is expected to be homogeneous. Since the establishment of the sonde, nutrient samples have been collected immediately next to the sensors using the same method as described above. As we collect more data, we will determine if there are any statistical differences between samples collected prior to June 2022, and those collected currently.

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 pre-acid 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 24 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. Subsequent analysese of nutrients are expected to occur within a month of receiving the samples.

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 2023 WP-339 Final Report for the WatR™ Pollution Proficiency Testing Results (issued 06/05/2023) can be 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 on June 12, 2023 and the results are reported here.

4) Site location and character –

He'eia (11.5 km^2), 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

Wai 2, 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 quarterly samples of eDNA.

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

Reef 9, 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

Kaho‘okele, 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 Kaho‘okele, which serves as a point of water exchange between He‘eia Stream and Kāne‘ohe 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 Kaho‘okele 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 He‘eia Stream and nearby He‘eia State Park. Additionally, this site may be heavily influenced by groundwater sources of nutrients.

Papahana (PH): 21.40921° N, 157.82323° W

Papahana, installed on June 27, 2022, is located at Ha‘akolea, or nicknamed Ice Pond, in Waipao in the back of the He‘eia ahupua‘a. Access is through the Indigenous organization Papahana Kuaola. The sensor, installed with telemetry, is co-located with a US Geological Survey stream gauge (16275000). It is a strictly freshwater site with no tidal influence. The bottom habitat is smooth river rock and soft sediment, with occasional flooding from seasonal rains. The water depth of the pool that the sonde sits in ranges from ~0.1 m to ~1 m typically, with much deeper conditions during heavy rains.

SWMP Station Timeline

Station Code	SWMP Status	Station Name	Location	Active Dates	Reason Decommissioned	Notes
W2	P	Wai 2	21.43831° N, 157.81093° W	9/18/2019 - present	NA	NA
R9	P	Reef 9	21.44628° N, 157.80183° W	2/13/2020 - present	NA	NA
KK	P	Kahoʻokele	21.43582° N, 157.80524° W	9/29/2020- present	NA	NA
PH	P	Papahana	21.40921° N, 157.82323° W	6/27/2022- present	NA	NA

5) Coded variable definitions –
heew2nut = Heʻeia Wai 2 Nutrients
heer9nut = Heʻeia Reef 9 Nutrients
heekknut = Heʻeia Kahoʻokele Nutrients
heephnut = Heʻeia Papahana Nutrients

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

6) Data collection period –

Wai 2 (W2):
Grab samples:
1/05/2023 8:34 8:35
2/02/2023 8:11 8:12
3/07/2023 7:37 7:38
4/04/2023 6:45 6:46
5/04/2023 6:52 6:53
6/05/2023 7:10 7:11
7/03/2023 6:55 6:56
8/01/2023 6:58 6:59
8/30/2023 6:38 6:39
9/29/2023 6:47 6:48
10/26/2023 6:47 6:48
11/27/2023 8:00 8:01
12/12/2023 7:44 7:45

Diel samples:
1/05/2023 3:30, 5:45, 8:00, 10:15, 12:30, 14:45, 17:00, 19:15, 21:30, 23:45
1/06/2023 2:00, 4:15

2/02/2023 2:45, 5:00, 7:15, 9:30, 11:45, 14:00, 16:15, 18:30, 20:45, 23:00
2/03/2023 1:15, 3:30

3/07/2023 3:45, 6:00, 8:15, 10:30, 12:45, 15:00, 17:15, 19:30, 21:45
3/08/2023 00:00, 2:15, 4:30

4/04/2023 3:00, 5:15, 7:30, 9:45, 12:00, 14:15, 16:30, 18:45, 21:00, 23:15

4/05/2023 1:30, 3:45

5/04/2023 1:45, 4:00, 6:15, 8:30, 10:45, 13:00, 15:15, 17:30, 19:45, 22:00
5/05/2023 00:15, 2:30

6/05/2023 13:15, 15:30, 17:45, 20:00, 22:15
6/06/2023 00:30, 2:45, 5:00, 7:15, 9:30, 11:45, 14:00

7/02/2023 7:45, 10:00, 12:15, 14:30, 16:45, 19:00, 21:15, 23:30
7/03/2023 1:45, 4:00, 6:15, 8:30

8/01/2023 8:30, 10:45, 13:00, 15:15, 17:30, 19:45, 22:00
8/02/2023 00:15, 2:30, 4:45, 7:00, 9:15

8/30/2023 8:30, 10:45, 13:00, 15:15, 17:30, 19:45, 22:00
8/31/2023 00:15, 2:30, 4:45, 7:00, 9:15

9/28/2023 9:15, 11:30, 13:45, 16:00, 18:15, 20:30, 22:45
9/29/2023 1:00, 3:15, 5:30, 7:45, 10:00

10/28/2023 9:15, 11:30, 13:45, 16:00, 18:15, 20:30, 22:45
10/29/2023 1:00, 3:15, 5:30, 7:45, 10:00

11/27/2023 10:30, 12:45, 15:00, 17:15, 19:30, 21:45
11/28/2023 00:00, 2:15, 4:30, 6:45, 9:00, 11:15

12/12/2023 13:15, 15:30, 17:45, 20:00, 22:15
12/13/2023 00:30, 2:45, 5:00, 7:15, 9:30, 11:45, 14:00

Reef 9 (R9):
Grab samples:
1/06/2023 8:21 8:22
2/03/2023 8:31 8:32
3/08/2023 8:52 8:53
4/05/2023 7:37 7:38
5/05/2023 7:21 7:22
6/06/2023 7:52 7:55
7/05/2023 8:31 8:32
8/02/2023 8:09 8:10
8/31/2023 7:45 7:46
9/28/2023 7:18 7:19
10/27/2023 7:03 7:04
11/28/2023 8:32 8:33
12/11/2023 7:48 7:49

Kaho‘okele (KK):
Grab samples:
1/05/2023 8:28 8:29
2/02/2023 8:24 8:25
3/07/2023 7:40 7:41
4/04/2023 6:49 6:50
5/04/2023 6:56 6:57

6/05/2023 7:10 7:11
7/03/2023 6:56 6:57
8/01/2023 7:04 7:05
8/30/2023 6:45 6:46
9/29/2023 6:52 6:53
10/26/2023 6:46 6:47
11/27/2023 7:58 8:00
12/12/2023 8:02 8:03

Papahana (PH):
Grab samples:
1/05/2023 10:00 10:01
2/02/2023 9:43 9:44
3/07/2023 8:44 8:45
4/04/2023 7:57 7:58
5/04/2023 8:30 8:31
6/05/2023 8:16 8:17
7/03/2023 8:03 8:04
8/01/2023 8:06 8:07
8/30/2023 7:49 7:50
9/29/2023 8:13 8:14
10/26/2023 7:39 7:40
11/27/2023 9:21 9:22
12/12/2023 8:45 8:46

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.

In addition to the SWMP stations, 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 processed 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 2022.

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.

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 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 Parameters:			
	Silicate, Filtered	SiO4F	mg/L as SI
Field Parameters:			
	Water Temperature	WTEM_N	ºC
	Specific Conductance	SCON_N	mS/cm
	Salinity	SALT_N	ppt
	% Dissolved Oxygen Saturation	DO_S_N	%
	Dissolved Oxygen	DO_N	mg/L

pH	PH_N	SU
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 EPA protocols. The MDLs used for each nutrient and chlorophyll *a* were calculated June 2023 and the results are reported here. As the results were reported in µM, they were multiplied by 0.014007, 0.03097, and 0.02809 to yield concentrations in mg/L as N, P, and Si, respectively Additionally the chlorophyll MDL was conducted by running a 3x(15n) of the standard blank, and documenting the deviation (0.023). These values are reviewed and revised annually.

Parameter	Start Date	End Date	MDL	Revisited
NH4F	01/01/23	12/31/23	0.00112	
NO23F	01/01/23	12/31/23	0.00140	
PO4F	01/01/23	12/31/23	0.00031	
SiO4F	01/01/23	12/31/23	0.00253	
CHLA_N	01/01/23	12/31/23	0.024	

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 NO_2 and NO_3 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 Hawaii Ocean Time-series program. 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 redactor 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 ℃ up to 30 days.*

14) Field and Laboratory QAQC programs –

a. **Precision**

i. **Field variability** –

Field replicates:

Nutrients: 52 replicates / 104 total samples =50%

Chlorophyll: 52 replicates / 104 total samples =50%

For both nutrients and chlorophyll, true field replicates were collected for all sites for all months in 2023, by collecting successive grab samples (separate sample in another sample bottle from the field at a different time than the first replicate).

			Nutrients			Chlorophyll		
Site	**Date**	**Collection times**	**Sample**	**Split**	**Replicate**	**Sample**	**Split**	**Replicate**
Wai 2	1/05/2023	8:34 8:35	1		1	1		1
	2/02/2023	8:11 8:12	1		1	1		1
	3/07/2023	7:37 7:38	1		1	1		1
	4/04/2023	6:45 6:46	1		1	1		1
	5/04/2023	6:52 6:53	1		1	1		1
	6/05/2023	7:10 7:11	1		1	1		1
	7/03/2023	6:55 6:56	1		1	1		1
	8/01/2023	6:58 6:59	1		1	1		1
	8/30/2023	6:38 6:39	1		1	1		1
	9/29/2023	6:47 6:48	1		1	1		1
	10/26/2023	6:47 6:48	1		1	1		1
	11/27/2023	8:00 8:01	1		1	1		1
	12/12/2023	7:44 7:45	1		1	1		1
	1/05/2023	3:30	1			1		
	1/05/2023	5:45	1			1		
	1/05/2023	8:00	1			1		
	1/05/2023	10:15	1			1		
	1/05/2023	12:30	1			1		

1/05/2023	14:45	1			1		
1/05/2023	17:00	1			1		
1/05/2023	19:15	1			1		
1/05/2023	21:30	1			1		
1/05/2023	23:45	1			1		
1/06/2023	2:00	1			1		
1/06/2023	4:15	1			1		
2/02/2023	5:00	1			1		
2/02/2023	7:15	1			1		
2/02/2023	9:30	1			1		
2/02/2023	11:45	1			1		
2/02/2023	14:00	1			1		
2/02/2023	16:15	1			1		
2/02/2023	18:30	1			1		
2/02/2023	20:45	1			1		
2/02/2023	23:00	1			1		
2/03/2023	1:15	1			1		
2/03/2023	3:30	1			1		
3/07/2023	3:45	1			1		
3/07/2023	6:00	1			1		
3/07/2023	8:15	1			1		
3/07/2023	10:30	1			1		
3/07/2023	12:45	1			1		
3/07/2023	15:00	1			1		
3/07/2023	17:15	1			1		
3/07/2023	19:30	1			1		
3/07/2023	21:45	1			1		
3/08/2023	00:00	1			1		
3/08/2023	2:15	1			1		
3/08/2023	4:30	1			1		
4/04/2023	3:00	1			1		
4/04/2023	5:15	1			1		
4/04/2023	7:30	1			1		
4/04/2023	9:45	1			1		
4/04/2023	12:00	1			1		
4/04/2023	14:15	1			1		
4/04/2023	16:30	1			1		
4/04/2023	18:45	1			1		

4/04/2023	21:00	1			1		
4/04/2023	23:15	1			1		
4/05/2023	1:30	1			1		
4/05/2023	3:45	1			1		
5/04/2023	1:45	1			1		
5/04/2023	4:00	1			1		
5/04/2023	6:15	1			1		
5/04/2023	8:30	1			1		
5/04/2023	10:45	1			1		
5/04/2023	13:00	1			1		
5/04/2023	15:15	1			1		
5/04/2023	17:30	1			1		
5/04/2023	19:45	1			1		
5/04/2023	22:00	1			1		
5/05/2023	0:15	1			1		
5/05/2023	2:30	1			1		
6/05/2023	13:15	1			1		
6/05/2023	15:30	1			1		
6/05/2023	17:45	1			1		
6/05/2023	20:00	1			1		
6/05/2023	22:15	1			1		
6/06/2023	0:30	1			1		
6/06/2023	2:45	1			1		
6/06/2023	5:00	1			1		
6/06/2023	7:15	1			1		
6/06/2023	9:30	1			1		
6/06/2023	11:45	1			1		
6/06/2023	14:00	1			1		
7/02/2023	7:45	1			1		
7/02/2023	10:00	1			1		
7/02/2023	12:15	1			1		
7/02/2023	14:30	1			1		
7/02/2023	16:45	1			1		
7/02/2023	19:00	1			1		
7/02/2023	21:15	1			1		
7/02/2023	23:30	1			1		
7/03/2023	1:45	1			1		
7/03/2023	4:00	1			1		

7/03/2023	6:15	1			1		
7/03/2023	8:30	1			1		
8/01/2023	8:30	1			1		
8/01/2023	10:45	1			1		
8/01/2023	13:00	1			1		
8/01/2023	15:15	1			1		
8/01/2023	17:30	1			1		
8/01/2023	19:45	1			1		
8/01/2023	22:00	1			1		
8/02/2023	0:15	1			1		
8/02/2023	2:30	1			1		
8/02/2023	4:45	1			1		
8/02/2023	7:00	1			1		
8/02/2023	9:15	1			1		
8/30/2023	8:30	1			1		
8/30/2023	10:45	1			1		
8/30/2023	13:00	1			1		
8/30/2023	15:15	1			1		
8/30/2023	17:30	1			1		
8/30/2023	19:45	1			1		
8/30/2023	22:00	1			1		
8/31/2023	0:15	1			1		
8/31/2023	2:30	1			1		
8/31/2023	4:45	1			1		
8/31/2023	7:00	1			1		
8/31/2023	9:15	1			1		
9/28/2023	9:15	1			1		
9/28/2023	11:30	1			1		
9/28/2023	13:45	1			1		
9/28/2023	16:00	1			1		
9/28/2023	18:15	1			1		
9/28/2023	20:30	1			1		
9/28/2023	22:45	1			1		
9/29/2023	1:00	1			1		
9/29/2023	3:15	1			1		
9/29/2023	5:30	1			1		
9/29/2023	7:45	1			1		
9/29/2023	10:00	1			1		

	10/28/2023	9:15	1			1		
	10/28/2023	11:30	1			1		
	10/28/2023	13:45	1			1		
	10/28/2023	16:00	1			1		
	10/28/2023	18:15	1			1		
	10/28/2023	20:30	1			1		
	10/28/2023	22:45	1			1		
	10/29/2023	1:00	1			1		
	10/29/2023	3:15	1			1		
	10/29/2023	5:30	1			1		
	10/29/2023	7:45	1			1		
	10/29/2023	10:00	1			1		
	11/27/2023	10:30	1			1		
	11/27/2023	12:45	1			1		
	11/27/2023	15:00	1			1		
	11/27/2023	17:15	1			1		
	11/27/2023	19:30	1			1		
	11/27/2023	21:45	1			1		
	11/28/2023	0:00	1			1		
	11/28/2023	2:15	1			1		
	11/28/2023	4:30	1			1		
	11/28/2023	6:45	1			1		
	11/28/2023	9:00	1			1		
	11/28/2023	11:15	1			1		
	12/12/2023	13:15	1			1		
	12/12/2023	15:30	1			1		
	12/12/2023	17:45	1			1		
	12/12/2023	20:00	1			1		
	12/12/2023	22:15	1			1		
	12/13/2023	0:30	1			1		
	12/13/2023	2:45	1			1		
	12/13/2023	5:00	1			1		
	12/13/2023	7:15	1			1		
	12/13/2023	9:30	1			1		
	12/13/2023	11:45	1			1		
	12/13/2023	14:00	1			1		

			Nutrients			Chlorophyll		
Site	**Date**	**Collection times**	**Sample**	**Split**	**Replicate**	**Sample**	**Split**	**Replicate**
Reef 9	1/06/2023	8:21 8:22	1		1	1		1
	2/03/2023	8:31 8:32	1		1	1		1
	3/08/2023	8:52 8:53	1		1	1		1
	4/05/2023	7:37 7:38	1		1	1		1
	5/05/2023	7:21 7:22	1		1	1		1
	6/06/2023	7:52 7:55	1		1	1		1
	7/05/2023	8:31 8:32	1		1	1		1
	8/02/2023	8:31 8:32	1		1	1		1
	8/31/2023	7:45 7:46	1		1	1		1
	9/28/2023	7:18 7:19	1		1	1		1
	10/27/2023	7:03 7:04	1		1	1		1
	11/28/2023	8:32 8:33	1		1	1		1
	12/11/2023	7:48 7:49	1		1	1		1

			Nutrients			Chlorophyll		
Site	**Date**	**Collection times**	**Sample**	**Split**	**Replicate**	**Sample**	**Split**	**Replicate**
Kaho‘okele	1/05/2023	8:28 8:29	1		1	1		1
	2/02/2023	8:24 8:25	1		1	1		1
	3/07/2023	7:40 7:41	1		1	1		1
	4/04/2023	6:49 6:50	1		1	1		1
	5/04/2023	6:56 6:57	1		1	1		1
	6/05/2023	7:10 7:11	1		1	1		1
	7/03/2023	6:56 6:57	1		1	1		1
	8/01/2023	7:04 7:05	1		1	1		1
	8/30/2023	6:45 6:46	1		1	1		1
	9/29/2023	6:52 6:53	1		1	1		1
	10/26/2023	6:46 6:47	1		1	1		1
	11/27/2023	7:58 8:00	1		1	1		1
	12/12/2023	8:02 8:03	1		1	1		1

			Nutrients			Chlorophyll		
Site	**Date**	**Collection times**	**Sample**	**Split**	**Replicate**	**Sample**	**Split**	**Replicate**
Papahana	1/05/2023	10:00 10:01	1		1	1		1
	2/02/2023	9:43 9:44	1		1	1		1
	3/07/2023	8:44 8:45	1		1	1		1
	4/04/2023	7:57 7:58	1		1	1		1
	5/04/2023	8:30 8:31	1		1	1		1
	6/05/2023	8:16 8:17	1		1	1		1
	7/03/2023	8:03 8:04	1		1	1		1
	8/01/2023	8:06 8:07	1		1	1		1
	8/30/2023	7:49 7:50	1		1	1		1
	9/29/2023	8:13 8:14	1		1	1		1
	10/26/2023	7:39 7:40	1		1	1		1
	11/27/2023	9:21 9:22	1		1	1		1
	12/12/2023	8:45 8:46	1		1	1		1

ii. **Laboratory variability** – 0 Laboratory replicates / 946 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 2023 ERA's WP-339 WatR™Pollution Proficiency Testing using standards was conducted April to June 2023 is found here.
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

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
PLR light rain
PHR heavy rain
PSQ squally
PFQ frozen precipitation (sleet/snow/freezing rain)
PSR mixed rain and snow

Tide stage

TSE ebb tide
TSF flood tide
TSH high tide
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 to > 1.0 meters
WH4 1.0 to 1.3 meters
WH5 1.3 or greater meters

Wind direction

N from the north
NNE from the north northeast
NE from the northeast
ENE from the east northeast
E 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 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.

Sample hold times for 2023: 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, plus allows for up to 5 days for collecting, processing, and shipping samples. Samples held beyond that time period are flagged suspect <1>and coded (CHB). If measured values were below MDL, this resulted in <-4> [SBL] (CHB) flagging/coding.

*Sample held longer than allowed by NERRS protocols

	Date of analysis				
Sample Descriptor	**PO4F**	**NH4F**	**NO23F**	**CHLA_N**	**SiO4F**
1/05, 1/06/2023, grab samples	1/13/2023	1/13/2023	1/13/2023	1/19/2023	1/13/2023
1/05, 1/06/2023, diel samples	4/12/2023*	4/12/2023*	4/12/2023*	1/19/2023	4/12/2023*
2/02, 2/03/2023, grab samples	2/9/2023	2/9/2023	2/9/2023	2/15/2023	2/9/2023
2/02, 2/03/2023, diel samples	2/15/2023	2/15/2023	2/15/2023	2/15/2023	2/15/2023
03/07, 3/08/2023, all grab and diel samples	4/4/2023	4/4/2023	4/4/2023	4/4/2023	4/4/2023
4/04, 4/05/2023, grab samples	4/6/2023	4/6/2023	4/6/2023	5/17/2023*	4/6/2023
4/04, 4/05/2023, diel samples	5/2/2023	5/2/2023	5/2/2023	5/17/2023*	5/2/2023
5/04, 5/05/2023, grab samples	11/21/2023*	11/21/2023*	11/21/2023*	11/16/2023*	11/21/2023*
5/04, 5/05/2023, diel samples	11/21/2023*	11/21/2023*	11/21/2023*	11/17/2023*	11/21/2023*

6/05, 6/06/2023 grab samples	11/21/2023*	11/21/2023*	11/21/2023*	11/16/2023*	11/21/2023*
6/05, 6/06/2023 diel samples	11/21/2023*	11/21/2023*	11/21/2023*	11/17/2023*	11/21/2023*
7/03, 7/05/2023, grab samples	12/5/2023*	12/5/2023*	12/5/2023*	12/8/2023*	12/5/2023*
7/03, 7/05/2023, diel samples	12/5/2023*	12/5/2023*	12/5/2023*	11/17/2023*	12/5/2023*
8/01, 8/02/2023, grab samples	12/5/2023* (R9, KK) 12/6/2023* (W2, PH)	12/5/2023* (R9, KK) 12/6/2023* (W2, PH)	12/5/2023* (R9, KK) 12/6/2023* (W2, PH)	12/8/2023*	12/5/2023* (R9, KK) 12/6/2023* (W2, PH)
8/01, 8/02/2023, diel samples	12/7/2023*	12/7/2023*	12/7/2023*	12/13/2023*	12/7/2023*
8/30, 8/31/2023, grab samples	1/8/2024*	1/8/2024*	1/8/2024*	12/8/2023*	1/8/2024*
8/30, 8/31/2023, diel samples	1/8/2024*	1/8/2024*	1/8/2024*	1/19/2024*	1/8/2024*
9/28, 9/29/2023, grab samples	1/8/2024*	1/8/2024*	1/8/2024*	12/8/2023*	1/8/2024*
9/28, 9/29/2023, diel samples	1/8/2024*	1/8/2024*	1/8/2024*	1/19/2024*	1/8/2024*
10/26, 10/27/2023, grab samples	2/14/2024*	2/14/2024*	2/14/2024*	1/21/2024*	2/14/2024*
10/26, 10/27/2023, diel samples	2/9/2024*	2/9/2024*	2/9/2024*	1/30/2024*	2/9/2024*
11/27, 11/28/2023, grab samples	2/14/2024*	2/14/2024*	2/14/2024*	1/21/2024*	2/14/2024*
11/27, 11/28/2023, diel samples	2/9/2024 * (replicate 1) 2/20/2024* (replicate 2)	2/9/2024* (replicate 1) 2/20/2024* (replicate 2)	2/9/2024* (replicate 1) 2/20/2024* (replicate 2)	1/30/2024*	2/9/2024* (replicate 1) 2/20/2024* (replicate 2)
12/11, 12/12/2023, grab samples	2/14/2024*	2/14/2024*	2/14/2024*	1/21/2024*	2/14/2024*
12/11, 12/12/2023, diel samples	2/9/2024* (replicate 1) 2/20/2024* (replicate 2)	2/9/2024* (replicate 1) 2/20/2024* (replicate 2)	2/9/2024* (replicate 1) 2/20/2024* (replicate 2)	1/30/2024*	2/9/2024* (replicate 1) 2/20/2024* (replicate 2)

Notes

For 2023, samples were held longer at the processing laboratory as there was a major backlog in the sample queue. We have continued to work with the facility to adhere to the 28 day hold timeline per our SOP.

Site: Wai 2

Date	Code	Note
01/05/2023	{CSM}	Somewhat higher PO4, NO23, CHLA due to proximity of recent rain https://waterdata.usgs.gov/monitoring-location/16275000/#parameterCode=00060&showMedian=false&startDT=2023-01-01&endDT=2023-01-07
8/1/2023-8/30/2023	{CSM}	Higher than normal NH4 and DIN, potentially due to summer time low flow and buildup of organic material.

Site: Reef 9

Date	Code	Note
02/03/2023	<-4> [SBL] <0> [SRD]	PO4, NH4, SiO4, NO23, DIN all have higher standard deviation than samples throughout the year. NH4, SiO4, NO23 where all bellow detection limit. Additionally, there was a large rain event happened right after sampling. Here.
04/05/2023	{CRE}	Small rain event before sampling. Shows an increase of SiO4 and PO4. Here.

Site: Kaho‘okele

No flags.

Site: Papahana

No flags.