

Elkhorn Slough (ELK) NERR Nutrient Metadata
January 2023 to December 2023
Latest Update: June 6, 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

a) Primary Contact Reserve, Data management + Laboratory
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Field Code Changed

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2) Research objectives

Elkhorn Slough (ESNERR) is a unique estuary along the central Californian coast. ESNERR has fresh water inputs during the wet season (October through May) causing a brackish environment, while during the dry season (June through September) there is very little freshwater input resulting in a much more saline environment. The surrounding area is mostly farmlands, which causes concern, as farms may be a considerable

source of large amounts of nutrients entering the slough possibly causing eutrophication. With the monthly monitoring program we are able to quantify the variability of nutrients in different areas of the slough and possibly correlate any changes in land use with changes in nutrient concentrations.

a) Monthly grab sampling program

To quantify the spatial variability of nutrient concentrations in Elkhorn Slough we collect monthly grab samples in the water column. The sampled sites represent the estuarine endpoints from the head to the mouth of Elkhorn Slough estuary and sites throughout the estuary.

b) Diel sampling program (mention if samples were taken over a lunar day)

To quantify the temporal variability of important nutrients in the water column as a function of tidal forcing we collect 14 water samples through a 24-hour tidal cycle once per month, at a permanent water quality station, South Marsh. Sample collection dates are January to December.

3) Research methods

During 2023 we continued to filter all samples at Elkhorn Slough Reserve. We also stored and analyzed all chlorophyll-a samples at Elkhorn Slough Reserve. All nutrient samples were stored and analyzed at Moss Landing Marine Laboratory. The 2023 samples were analyzed for phosphate, nitrate, nitrite, ammonia, and silica at Moss Landing. For additional detail on QAQC of the equipment and data, send an inquiry to rikke@elkhornslough.org and ask for APP4_SOP_MLML.pdf and nutrient SOP official_2022.docx

Monthly grab sampling program

Diel sampling program

a) Monthly grab sampling program

Monthly grab samples were taken at four stations within the Elkhorn Slough estuary. Samples were taken at the four principle ESNERR data sonde stations (Azevedo Pond, North Marsh, South Marsh and Vierra Mouth). All grab samples were taken on the same day in the time window of -4 to 0 hours before low tide. At each station either replicate samples were taken (n = 2) or at one of the four stations, a triplicate samples was taken (n = 3) and then only a single sample was taken at one of the other four stations. Each month, we grabbed a total of n = 8 samples at the four stations collectively. No distinction was made between neap and spring tide conditions. Grab samples were collected by hand at an approximate depth of 10 cm. At the time of sample collection, water temperature, salinity, specific conductivity, pH, chlorophyll, and dissolved oxygen was measured with a YSI EXO2 sonde and a hand held YSI unit. These field data are not included in this dataset, but are available directly through the Reserve if you contact John Haskins or Rikke Jeppesen. All samples were collected in amber, narrow-mouth, 250 mL Nalgene sample bottles that were previously acid washed (10% HCL), rinsed (3x) with deionized water, dried, and followed by rinsing (3x) with ambient water prior to collection of the sample. Samples were immediately placed on ice in the dark and returned to the laboratory. Once in the laboratory, samples were inverted, filtered and processed for nutrient and Chl-a analysis. The filtrate was transferred to 50mL Falcon tubes, refrigerated, and delivered to Moss Landing Marine Lab within a few hours after the last ISCO sample was filtered. The filter was placed in 90% acetone, in a 5ml test tube, shaken, and stored in the freezer until the sample was analyzed, less than 30 days later. Rikke Jeppesen or Melany Scannell was responsible for the chlorophyll analysis, Steven Cunningham or Elizabeth Allen at Moss Landing Marine Labs were responsible for the phosphate, nitrate, nitrite, ammonia, and silica analyses.

b) Diel sampling program

Within the same 24-hour period of grab sample collection, we deploy an ISCO water sampler from the bank of the marsh at South Marsh. This device automatically samples 500 ml of water every 2 hrs (Jan.-Dec). All samples are pumped into polyethylene sample bottles that were previously acid washed (10% HCL), rinsed (3x) with distilled-deionized water and dried. Samples are kept cold with ice until the end of the 24 hr period; the 14 samples are collected within 1 hr after the last sample has been dispensed returned to the laboratory for immediate filtering,

unless there are problems with any equipment. After sampling, if the can't be analyzed immediately, they are stored in a freezer at -4 C. From January to December, samples were collected every other hour through a 24-hour tidal cycle. Rikke Jeppesen or Melany Scannell was responsible for the chlorophyll analysis. Steven Cunningham or Elizabeth Allen at Moss Landing Marine Labs were responsible for the phosphate, nitrate, nitrite, ammonia, and silica analyses.

4) Site location and character

Azevedo Pond (AP)(36°50'44.64"N, 121°45'13.24"W) is in a pond that receives fertilizer and pesticide run-off from a strawberry field in year-round production. The sample station is located about 10m from a tidal control structure in front of a culvert connecting the pond to the slough. In 2023, the tide ranged from 1.26 m to 2.51 meters at this site and salinity ranged from 1.3 ppt during heavy run-off to 38.5 ppt during strong evaporation. The YSI sonde associated with this site (collecting readings for the water quality dataset) is located approximately 30 cm off the bottom, which is composed of silty mud. An EXO2 sonde is deployed at this site.

North Marsh (NM)(36°50'04.75"N, 121°44'18. 33"W) is located in-between South Marsh and Azevedo Pond. This site is impacted by both agricultural and urban run-off. In 2023, the tide ranged from approximately 0.84 m to 1.34 meters at this site. Salinity ranged between 2.4 and 38.9 ppt and is affected by freshwater run-off from agriculture and upland run-off. The YSI sonde associated with this site (WQ dataset) is approximately 30 cm off the bottom, which is composed of silty mud. An EXO2 sonde is deployed at this site.

South Marsh (SM)(36°49'05.00"N, 121°44'21.83"W) which is located approximately 3 km south of NM and is surrounded by mostly reserve land, is in a side channel of the slough and is relatively free from impact by anthropogenic influence. This site receives run-off mostly from uplands with some run-off coming from cattle ranches. This site receives the least amount of pollution. In 2023, the tidal range was from -0.81 to 2.16 meters at this site and the salinity range was from 10.7 to 33.9 ppt. The YSI sonde associated with this site (collecting readings for the water quality dataset) is approximately 30 cm off the bottom, which is composed of compacted silty mud. An EXO2 sonde is deployed at this site.

The fourth site Vierra Mouth (VM) (36°48'39.95"N, 121°46'45.22"W) is located at the mouth of the slough and is used to identify oceanic influence. In 2023, the tidal range was from -0.47 m to 2.25 meters at this site and salinity ranged from 8.5 to 33.3 ppt. The YSI sonde associated with this site (collecting readings for the water quality dataset) is located approximately 30 cm off the bottom which is composed of compacted mud and sand due to strong tidal currents. This site receives drainage from the entire watershed due to its location at the mouth. There are several auto wrecking yards located approximately 2 km east of this site. An EXO2 sonde is deployed at this site.

Site name	Azevedo Pond, AP
Latitude and longitude	36°50'44.64"N, 121°45'13.24"W
Tidal range (<i>meters</i>)	1.26-2.51 m
Salinity range (<i>psu</i>)	1.3-38.5 psu
Type and amount of freshwater input	heavy run-off and fresh water input during rainy season (Oct-Mar) and strong evaporation during summer (June-Sept).
Water depth (<i>meters, MLW</i>)	1.358 m, calculated average of the daily lowest tide level

Sonde distance from bottom (<i>meters</i>)	0.30 m
Bottom habitat or type	Soft sediment, silty mud
Pollutants in area	fertilizer and pesticide run-off from a strawberry field in year-round production.
Description of watershed	The sample station is located about 10m from a tidal control structure in front of a culvert connecting the pond to the main channel of the slough.

Site name	North Marsh, NM
Latitude and longitude	36°50'04.75"N, 121°44'18.33"W
Tidal range (<i>meters</i>)	0.84-1.34 m
Salinity range (<i>psu</i>)	2.4-38.9 psu
Type and amount of freshwater input	heavy run-off and fresh water input during rainy season (Oct-Mar) and strong evaporation during summer (June-Sept).
Water depth (<i>meters, MLW</i>)	0.917 m, calculated average of the daily lowest tide level
Sonde distance from bottom (<i>meters</i>)	0.30 m
Bottom habitat or type	Soft sediment, silty mud
Pollutants in area	freshwater run-off from agriculture and upland run-off
Description of watershed	located in-between South Marsh and Azevedo Pond. This site is impacted by both agricultural and urban run-off.

Site name	South Marsh, SM
Latitude and longitude	36°49'05.00"N, 121°44'21.83"W
Tidal range (<i>meters</i>)	-0.81-2.16 m
Salinity range (<i>psu</i>)	10.7-33.9 psu
Type and amount of freshwater input	Some run-off and fresh water input during rainy season (Oct-Mar) and very low evaporation during summer (June-Sept).
Water depth (<i>meters, MLW</i>)	-0.272 m, calculated average of the daily lowest tide level
Sonde distance from bottom (<i>meters</i>)	0.30 m
Bottom habitat or type	Soft sediment, compacted silty mud

Pollutants in area	This site receives run-off mostly from uplands with some run-off coming from cattle ranches.
Description of watershed	surrounded by mostly reserve land, is in a side channel of the slough and is relatively free from impact by anthropogenic influence. This site receives the least amount of pollution.

Site name	Vierra Mouth, VM
Latitude and longitude	36°48'39.95"N, 121°46'45.22"W
Tidal range (<i>meters</i>)	-0.47-2.25 m
Salinity range (<i>psu</i>)	8.5-33.3 psu
Type and amount of freshwater input	Some run-off and fresh water input during rainy season (Oct-Mar) and minimal evaporation during summer (June-Sept).
Water depth (<i>meters, MLW</i>)	-0.218 m, calculated average of the daily lowest tide level
Sonde distance from bottom (<i>meters</i>)	0.30 m
Bottom habitat or type	compacted mud and sand
Pollutants in area	There are several auto wrecking yards located approximately 2 km east of this site.
Description of watershed	This site receives drainage from the entire watershed due to its location at the mouth.

All ELK NERR historical nutrient/pigment monitoring stations:

Station code	SWMP status	Station name	Location	Active dates	Reason decommissioned	Notes
AP	P	Azevedo Pond	36°50'44.64"N, 121°45'13.24"W	June 1995-current	NA	NA
NM	P	North Marsh	36°50'04.75"N, 121°44'18.33"W	April 1999 - current	NA	NA
SM	P	South Marsh	36°49'05.00"N, 121°44'21.83"W	June 1995-current	NA	NA
VM	P	Vierra Mouth	36°48'39.95"N, 121°46'45.22"W	March 2001 - current	NA	NA

5) Coded variable definitions

elkapnut = Elkhorn Slough Reserve Azevedo Pond Site nutrient data

elknmnut = Elkhorn Slough Reserve North Marsh Site nutrient data
 elksmnut = Elkhorn Slough Reserve South Marsh Site nutrient data
 elkvmnut = Elkhorn Slough Reserve Vierra Mouth Site nutrient data
 Monthly grab sample program= 1
 Diel grab sample program= 2

6) Data collection period

Diel sampling

Site	Start date	Start time	End date	End time
elksmnut	1/3/2023	6:00	1/4/2023	8:00
elksmnut	2/1/2023	6:00	2/2/2023	8:00
elksmnut	3/1/2023	6:00	3/2/2023	8:00
elksmnut	4/11/2023	6:00	4/12/2023	8:00
elksmnut	5/2/2023	6:00	5/3/2023	8:00
elksmnut	6/13/2023	6:00	6/14/2023	8:00
elksmnut	7/11/2023	6:00	7/12/2023	8:00
elksmnut	8/8/2023	6:00	8/9/2023	8:00
elksmnut	9/12/2023	6:00	9/13/2023	8:00
elksmnut	10/10/2023	6:00	10/11/2023	8:00
elksmnut	11/7/2023	6:00	11/8/2023	8:00
elksmnut	12/5/2023	6:00	12/6/2023	8:00

Grab sampling

Site	Start date	Start time	End date	End time	Replicates
elkapnut	1/3/2023	13:20	1/3/2023	13:21	2
elkapnut	2/1/2023	13:10	2/1/2023	13:11	2
elkapnut	3/1/2023	12:07	3/1/2023	12:08	2
elkapnut	4/11/2023	8:32	4/11/2023	8:34	3
elkapnut	5/2/2023	12:29	5/2/2023	12:30	2
elkapnut	6/13/2023	10:55	6/13/2023	10:56	2
elkapnut	7/11/2023	9:21	7/11/2023	9:22	2
elkapnut	8/8/2023	8:53	8/10/2023	8:55	3
elkapnut	9/12/2023	12:25	9/12/2023	12:26	2
elkapnut	10/10/2023	12:16	10/10/2023	12:17	2
elkapnut	11/7/2023	11:17	11/7/2023	11:18	2
elkapnut	12/5/2023	9:35	12/5/2023	9:37	3

Grab sampling

Site	Start date	Start time	End date	End time	Replicates
elknmnut	1/3/2023	12:06	1/3/2023	12:06	1
elknmnut	2/1/2023	12:06	2/1/2023	12:07	2
elknmnut	3/1/2023	10:47	3/1/2023	10:49	3
elknmnut	4/11/2023	7:04	4/11/2023	7:04	1
elknmnut	5/2/2023	11:15	5/2/2023	11:15	1
elknmnut	6/13/2023	9:37	6/13/2023	9:38	2

elknmnut	7/11/2023	8:20	7/11/2023	8:22	3
elknmnut	8/8/2023	7:21	8/8/2023	7:21	1
elknmnut	9/12/2023	11:09	9/12/2023	11:09	1
elknmnut	10/10/2023	10:19	10/10/2023	10:20	2
elknmnut	11/7/2023	10:14	11/7/2023	10:16	3
elknmnut	12/5/2023	8:30	12/5/2023	8:30	1

Grab sampling

Site	Start date	Start time	End date	End time	Replicates
elksmnut	1/3/2023	11:18	1/3/2023	11:19	2
elksmnut	2/1/2023	11:17	2/1/2023	11:19	3
elksmnut	3/1/2023	10:45	3/1/2023	10:46	2
elksmnut	4/11/2023	6:06	4/11/2023	6:07	2
elksmnut	5/2/2023	10:18	5/2/2023	10:19	2
elksmnut	6/13/2023	8:49	6/13/2023	8:51	3
elksmnut	7/11/2023	8:18	7/11/2023	8:19	2
elksmnut	8/8/2023	6:27	8/8/2023	6:28	2
elksmnut	9/12/2023	10:19	9/12/2023	10:20	2
elksmnut	10/10/2023	11:12	10/10/2023	11:14	3
elksmnut	11/7/2023	9:27	11/7/2023	9:28	2
elksmnut	12/5/2023	7:46	12/5/2023	7:47	2

Grab sampling

Site	Start date	Start time	End date	End time	Replicates
elkvmnut	1/3/2023	14:07	1/3/2023	14:09	3
elkvmnut	2/1/2023	13:53	2/1/2023	13:53	1
elkvmnut	3/1/2023	12:12	3/1/2023	12:12	1
elkvmnut	4/11/2023	9:06	4/11/2023	9:07	2
elkvmnut	5/2/2023	13:01	5/2/2023	13:03	3
elkvmnut	6/13/2023	11:40	6/13/2023	11:40	1
elkvmnut	7/11/2023	10:10	7/11/2023	10:10	1
elkvmnut	8/8/2023	6:29	8/8/2023	6:30	2
elkvmnut	9/12/2023	13:17	9/12/2023	13:19	3
elkvmnut	10/10/2023	13:11	10/10/2023	13:11	1
elkvmnut	11/7/2023	12:07	11/7/2023	12:07	1
elkvmnut	12/5/2023	10:19	12/5/2023	10:20	2

7) Associated researchers and projects

As part of the SWMP long-term monitoring program, ELK 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 our reserve staff, multiple researchers from multiple institutions conduct research that makes use of our long-term monitoring data. The researchers are listed below.

Research conducted by reserve staff

Susie Fork conducts field survey monitoring of shorebirds; egret and heron rookery, bird nest boxes, raptors, and invertebrate populations.

Rikke Jeppesen and Susie Fork conduct annual crab trapping in order to track crab populations, particularly invasions by non-native European crabs. Additionally, Susie Fork conducts annual invertebrate surveys on mudflats, in permanent transects. The surveys include various clam and shrimp species, in addition to fat innkeeper worms.

Charlie Endris works on remote-sensing using GIS to analyze habitat change and NERR bio-monitoring pilot studies for Tier 1, emergent vegetation.

Kerstin Wasson monitors oyster recruitment and conducts experiments to determine the status and trajectory of native oyster populations.

Rikke Jeppesen, John Haskins, and Melany Scannell conduct water quality research currently focusing on eutrophication in the slough and are managing the SWMP weather monitoring and the SWMP water quality programs, from which the data are used in conjunction with eutrophication research.

The following researchers are affiliated with other institutions.

Aiello, Ivano, Moss Landing Marine Laboratories: examines sediment characteristics relevant to Hester Marsh restoration by collecting sediment cores using a Vibrocore

Carswell, Lilian and Mayer, Karl, University of California Santa Cruz; capture/tag sea otters and track them to detect social network in sea otters and stress responses.

Fujii, Jessica; Monterey Bay Aquarium: supports otters rehabilitated and released by the aquarium.

Guillas, Kennan; Moss Landing Marine Laboratories: collects orange sponge to study rhythmic contracts and waste elimination in Hymeniacidon

Joergensen, Salvador, California State University Monterey Bay: catches & tags/releases sharks; retrieve tags when they pop off; install and maintain antenna on barn in order to track leopard shark movement and is looking at shark and water quality condition correlations

Meredith, Paul, ESNERR volunteer; Catch and release bumblebees to contribute to bumblebee diversity atlas

Monismith, Stephen, Stanford University; deploys and maintains ADCPs and CTPs in Hester and Yampah creeks to characterize hydrodynamics around Hester and Yampah, to complement Paytan's eddy covariance towers

Paytan, Adina; University of California, Santa Cruz: monitors greenhouse gas flux with eddy covariance towers

Searcy, Chris; Stemle, Leyna; Mosserman, Ariana: University of Miami: installs drift fences and checks pitfall traps to assess salamander metamorph success at Upper Cattail Pond.

Siegler, Katie, University of California, Davis: seines for topsmelt to study the levels of pesticide in indicator species

Frequent docent researchers: Ron Eby (marsh, bird, otter monitoring). Celeste Stanik, Margie Kay, Ken Pollak, (NUT monitoring field and lab work).

Frequent interns: John McClaran until December 2023

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

Monthly nutrient data are obtained by filtering grab and diel samples at Moss Landing Marine Laboratory, Moss Landing, CA. John Haskins, Rikke Jeppesen, Ken Pollak, and Celeste Stanik were responsible for filtering all samples and for analyzing the samples to determine chlorophyll concentration.

Steven Cunningham, Katie Graves, or Elizabeth Allen, Moss Landing Marine Laboratories was responsible for measuring nitrite, nitrite + nitrate, ammonia, orthophosphate, and silicate concentrations.

For nutrient analyses, 60 mL aliquots of grab sample water were filtered (0.45 micron) in the lab, and stored in dark and cool conditions (refrigerator) until analysis. Ammonia, nitrate, nitrite, silica, and soluble reactive phosphate were measured by colorimetric methods on a flow injection auto analyzer (FIA, Lachat Instruments Model QuickChem 8000).

Chlorophyll-*a* sample filters were extracted in 5mL acetone, stored in the freezer for at least 24 hrs, and analyzed on a Turner Trilogy fluorometer. The Trilogy was calibrated in May 2019, in December 2020, and in August 2023. All data were entered in an Excel spread sheet while processing the samples for chlorophyll-*a*. Steven Cunningham, Katie Graves, or Elizabeth Allen e-mailed the remaining results monthly, and these Moss Landing results were then entered into the same monthly nutrient Excel sheet by Rikke Jeppesen or Melany Scannell. The Excel file contains information of sampling station ID, date and time, and parameter values expressed in unit concentrations. Rikke Jeppesen verified all parameter values in the excel file by cross comparison with laboratory data sheets and by graphing the data and identifying anomalous data points or other problems. Monthly excel files were compiled into a yearly excel file. Missing data are verified through inspection of fields.

All parameter values at Moss Landing Marine Laboratories (MLML) are reported in mg/L. Chlorophyll-*a* was measured in RFU and ESNERR staff converts RFU to µg/L by using the following conversion:

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$$(1.45 \times 10^{-4} \mu\text{g Chla}/\text{mL}/\text{RFU}) * \text{RFU}_{\text{measured}} * \text{dilution factor} * (\text{extraction volume}/\text{filtered volume}) * 1000 \text{mL}/\text{L}$$

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	PO4F	mg/L as P
	*Ammonium, Filtered	NH4F	mg/L as N
	*Nitrite, Filtered	NO2F	mg/L as N
	*Nitrate, Filtered	NO3F	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
Carbon:			
Other Lab Parameters:			
	Silicate, Filtered	SiO4F	mg/L as SI

Notes:

1. Time is coded based on a 2400 clock and is referenced to Standard Time.
2. Reserves have the option of measuring either NO2 and NO3 or they may substitute NO23 for individual analyses if they can show that NO2 is a minor component relative to NO3.

11) Measured or calculated laboratory parameters

- Parameters measured directly**
 - Nitrogen species: NH4F, NO2F, NO23F
 - Phosphorus species: PO4F
 - Other: CHLA_N, SiO4F
- Calculated parameters**
 - NO3F: NO23F-NO2F
 - 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 ELK NERR for CHLA_N and by Moss Landing Marine

Laboratory for all other parameters. The MDL is determined as 3 times the standard deviation of a minimum of 7 replicates of a single low concentration sample. These values are reviewed and revised periodically.

Parameter	Start Date	End Date	Average MDL	Revisited
PO4F	1/1/2023	12/31/2023	0.00219	Monthly
NO2F	1/1/2023	12/31/2023	0.00198	Monthly
NO23F	1/1/2023	12/31/2023	0.00699	Monthly
NH4F	1/1/2023	12/31/2023	0.00502	Monthly
SiO4F	1/1/2023	12/31/2023	0.04708	Monthly
CHLA_N	1/1/2023	12/31/2023	0.00259	Monthly

13) Laboratory methods

a) **Parameter: NH4F**

Moss Landing Marine Laboratory

Method Reference: EPA 350.1 / Lachat Quickchem Method 31-107-06-1-B

Method Descriptor: The method is based on the Berthelot reaction. Ammonia reacts in alkaline solution with hypochlorite to form monochloramine, which in the presence of phenol, nitroprusside, and hypochlorite gives indophenol blue. EDTA is added to the buffer to prevent precipitation of calcium and magnesium in high pH seawater. The indophenol blue is measured at 630 nm and is proportional to the original ammonia concentration.

Preservation Method: Samples filtered and stored at 4 °C up to 24 hours.

b) **Parameter: NO23F**

Moss Landing Marine Laboratory

Method Reference: EPA 353.2 / Lachat Quickchem Method 31-107-04-1-E

Method Descriptor: The water sample is first filtered then is passed through a cadmium column where the nitrate is reduced to nitrite. The nitrite is determined by diazotizing nitrite with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored dye which is measured colorimetrically where the absorbance is measured at 540 nm through a 10 mm flow cell. Nitrate concentration equals the NO23F (nitrate + nitrite) concentration minus the nitrite concentration. Thus NO3 is calculated by subtracting NO23F - NO2F.

Preservation Method: Samples filtered and stored at 4 °C up to 24 hours.

c) **Parameter: NO2F**

Moss Landing Marine Laboratory

Method Reference: EPA 353.2 / Lachat Quickchem Method 31-107-05-1-A

Method Descriptor: Nitrite is measured by diazotization with sulfanilamide under acidic conditions to form diazonium ion. The diazonium ion is coupled with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored dye which is measured colorimetrically. The pink dye absorbance is measured at 520 nm through a 10 mm flow cell.

Preservation Method: Samples filtered and stored at 4 °C up to 24 hours.

d) **Parameter: PO4F**

Moss Landing Marine Laboratory

Method Reference: Gordon, Jennings, and Ross 2001. A Suggested Protocol for Continuous Flow Automated Analysis of Seawater Nutrients Using the Alpkem Flow Solution System

Method Descriptor: Ammonium molybdate is added to a water sample to produce phosphomolybdic acid, which is then reduced to phosphomolybdous acid (a blue compound) following the addition of dihydrazine (or hydrazine) sulfate. The sample is passed through a 10 mm flow cell and absorbance is measured at 820 nm.

Preservation Method: Samples filtered and stored at 4 °C up to 24 hours.

e) **Parameter: SiO₄**

Moss Landing Marine Laboratory

Method Reference: Lachat Quickchem Method 10-114-27-1-D

Method Descriptor: Soluble silica species react with molybdate at 37 °C and a pH of 1.2 to form a yellow silicomolybdate complex. The complex is subsequently reduced with stannous chloride to form a blue complex that has an absorbance at 820 nm. The absorbance is proportional to the concentration of "molybdate reactive" silica.

Preservation Method: Samples filtered and stored at 4 °C up to 24 hours.

f) **Parameter: ChlA**

ELK NERR

Method Reference: EPA method 445.0 UNESCO (1994) Protocols for the joint global ocean flux study (JGOFS) core measurements. pp. 97-100.

Method Descriptor: ChlA is extracted in 5 mL 90% acetone for 24 hrs and then fluorescence is measured and recorded (F₀).

Preservation Method: A known volume of sample is filtered onto a 25 mm GF/F filter, folded in half and placed in a known volume (5mL) of 90% acetone and then stored at -4°C until analysis, no more than 35 days.

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14) **Field and Laboratory QA/QC programs**

a) **Precision**

i) **Field variability**

Field replicates are successive grab samples, replicates split from a single field sample are considered laboratory replicates/splits.

**Field
replicates**

	AP	NM	SM	VM
Jan		1		3
Feb			3	1
Mar		3		1
Apr	3	1		
May		1		3
Jun			3	1
Jul		3		1
Aug	3	1		
Sep		1		3
Oct			3	1
Nov		3		1
Dec	3	1		

ii) **Laboratory variability.**

ELKNERR uses three of the ISCO samples to provide laboratory replicates each month (see table below, Lab Min, Max, Avg). Each month, we randomly select three numbers between 1 and 14. The three random numbers will be the ISCO sample numbers used as the laboratory replicates. An ISCO replicate is filtered twice. For example, if the replicate is ISCO 3, then we first filter ISCO 3 and label it ISCO 3. Then we filter

ISCO 3 again and label it replicate 1. In 2023 we had a total of 36 (3 each month) laboratory replicates and 36 field replicates.

			PO4 [%]	NO2 [%]	NO3 [%]	NH4 [%]	SiO4 [%]	Chl-a [%]
Annual	Field	Min	1	0	6	3	2	1
Annual	Field	Max	44	37	45	124	35	57
Annual	Field	Average	8	16	22	25	10	12
Annual	Lab	Min	1	3	1	4	0	3
Annual	Lab	Max	43	46	37	79	53	9
Annual	Lab	Average	11	12	11	23	11	5

iii) Inter-organizational splits

There we no inter-organizational split samples in 2022

b) Accuracy

i) Sample spikes

Sample spikes were split from a single diel sample. Sample spikes are done for orthophosphate, nitrite, nitrate+nitrite, ammonium and silicate on a monthly basis. Average percent recovery for the 12 months of 2023 was found to be:

	PO4	NO2	NO3	NH4	SIO
Average	89%	91%	99%	82%	103%
Minimum	4%	9%	30%	14%	95%
Maximum	113%	109%	118%	110%	109%

ii) Standard reference material analysis

Standard reference materials are diluted from a single concentrated stock sample. Standard reference analysis is conducted for orthophosphate, nitrite, nitrate+nitrite, ammonium and silicate on a monthly basis. Average percent recovery for the 12 months of 2023 was found to be:

	PO4	NO2	NO3	NH4	SIO
Average	107%	107%	103%	106%	108%
Minimum	94%	92%	95%	99%	104%
Maximum	157%	110%	109%	110%	111%

iii) Cross calibration exercises

ELK, NERR did not participate in any cross calibration exercises in 2023.

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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
<i>Cloud cover</i>	
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)
<i>Precipitation</i>	
PNP	none
PDR	drizzle
PLR	light rain
PHR	heavy rain
PSQ	squally
PFQ	frozen precipitation (sleet/snow/freezing rain)
PSR	mixed rain and snow
<i>Tide stage</i>	
TSE	ebb tide
TSF	flood tide
TSH	high tide
TSL	low tide
<i>Wave height</i>	
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
<i>Wind direction</i>	
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
<i>Wind speed</i>	
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 NERR 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 NO₂F 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: Once filtered, if not processed within 24 hrs, 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 hold times for 2023: NERRS SOP allows nutrient samples to be held for up to 24 hours if held at 4°C with no preservation, for NH₄F and NO₂F up to 28 days if acidified and held at 4°C, and up to 28 days (CHLA for 30 days) if held at -20°C. Tier II parameters, with a few exceptions, are subject to the same sample hold times. In all cases, up to an additional 5 days is allowed for collecting, processing, and shipping samples. Samples held beyond that time period are flagged suspect and coded CHB in the data set.

Grab samples

Sample collection date Sample analysis date

		NO ₂ , NO ₃ , NH ₄ , PO ₄ , SiO ₄	
All	Chl_A		
1/3/2023	1/19/2023	1/26/2023	
2/1/2023	2/28/2023	3/23/2023	*
3/1/2023	3/8/2023	3/30/2023	
4/11/2023	4/19/2023	5/12/2023	
5/2/2023	5/31/2023	6/8/2023	*
6/13/2023	6/26/2023	7/3/2023	
7/11/2023	7/28/2023	8/4/2023	
8/8/2023	8/29/2023	9/4/2023	
9/12/2023	10/3/2023	10/11/2023	
10/10/2023	11/1/2023	11/30/2023	*
11/7/2023	11/15/2023	11/29/2023	
12/5/2023	12/13/2023	1/4/2024	

ISCO samples

Sample collection date Sample analysis date

ISCO 1-9	Chl_A	NO2, NO3, NH4, PO4, SiO4	
1/3/2023	1/19/2023	1/26/2023	
2/1/2023	2/28/2023	3/23/2023	*
3/1/2023	3/8/2023	3/30/2023	
4/11/2023	4/19/2023	5/12/2023	
5/2/2023	5/31/2023	6/8/2023	*
6/13/2023	6/26/2023	7/3/2023	
7/11/2023	7/28/2023	8/4/2023	
8/8/2023	8/29/2023	9/4/2023	
9/12/2023	10/3/2023	10/11/2023	
10/10/2023	11/1/2023	11/30/2023	*
11/7/2023	11/15/2023	11/29/2023	
12/5/2023	12/13/2023	1/4/2024	

ISCO 10-13	Chl_A	NO2, NO3, NH4, PO4, SiO4	
1/4/2023	1/19/2023	1/26/2023	
2/2/2023	2/28/2023	3/23/2023	*
3/2/2023	3/8/2023	3/30/2023	
4/12/2023	4/19/2023	5/12/2023	
5/3/2023	5/31/2023	6/8/2023	*
6/14/2023	6/26/2023	7/3/2023	
7/12/2023	7/28/2023	8/4/2023	
8/9/2023	8/29/2023	9/4/2023	
9/13/2023	10/3/2023	10/11/2023	
10/11/2023	11/1/2023	11/30/2023	*
11/8/2023	11/15/2023	11/29/2023	
12/6/2023	12/13/2023	1/4/2024	

*sample held longer than allowed by NERRS protocols

04/11/2023

Elkapnut, and elkmnut PO4 values are both high in April 2023, so although they look suspect, we believe they are reliable values.

elkmnut NO23, NO3 and SIO4 values were also high in April 2023