

Elkhorn Slough (ELK) NERR Nutrient Metadata
January to December 2019
Latest Update: August 24, 2022

I. Data Set and Research Descriptors

1) Principal investigator(s) and contact persons –

a) Reserve Contact

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c) Other Contacts and Programs

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2) Research objectives –

Elkhorn Slough (ELK NERR) is a unique estuary along the central Californian coast. ELK NERR 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

To quantify the temporal variability of important nutrients in the water column as a function of tidal forcing we collect 13 water samples through a 24-hour tidal cycle (lunar day) once per month, at a permanent water quality station, South Marsh.

3) Research methods –

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 ELK NERR 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 -3 to 0 hours before low tide. At each station either replicate samples were taken ($n = 2$) or at one of the four stations, triplicate samples were 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. If we arrived at a station after low tide, no sample was grabbed. 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 by contacting 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 distilled-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.

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* samples were processed slightly differently in the first two thirds of the year, compared to the last third of the year. From January to July, chlorophyll-*a* sample filters were extracted in 8 mL acetone, stored in the freezer for at least 24 hrs, and analyzed on a Turner 700 fluorometer. From August to December, chlorophyll-*a* sample filters were extracted in 5 mL acetone, stored in the freezer for at least 24 hrs, and analyzed on a Turner Trilogy fluorometer. During the months of July and August, we processed the samples on both fluorometers, to ensure consistency in data output from the two different instruments.

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 4 min (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 13 samples are kept in the dark and returned to the laboratory for immediate processing. From January to December, samples were collected every other hour through a 24-hour tidal cycle. Diel samples were processed in the same manner as described above.

4) Site location and character –

Elkhorn Slough is located on the West Coast of the United States in Central California. The estuarine water of Elkhorn Slough enters the Pacific Ocean in central Monterey Bay near Moss Landing, California. There are four NERR sampling sites in Elkhorn Slough:

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 10 m from a tidal control structure in front of a culvert connecting the pond to the slough. In 2019, the tide ranged from 1.19 m to 2.36 meters at this site and salinity ranged from 12.4 ppt during heavy run-off to 38.9 ppt during strong evaporation. Depth at mean low tide is approximately 1.5 meters. 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.

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 2019, the tide ranged from approximately 0.61 m to 1.20 meters at this site. Salinity ranged between 15.3 and 41.2 ppt and is affected by freshwater run-off from agriculture and upland run-off . Depth at mean low tide is approximately 1 meter. The YSI sonde associated with this site (WQ dataset) is approximately 30 cm off the bottom, which is composed of silty mud.

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 2019, the tidal range was from -0.97 m to 2.18 m at this site and the salinity range was from 28.3 to 36.2 ppt. Depth at mean low tide is approximately 3 meters. 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.

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 2019, the tidal range was from -0.97 m to 2.18 meters at this site and salinity ranged from 24.5 to 34.3 ppt. Depth at mean low water is approximately 4 meters. 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.

All 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
elknlmnt = Elkhorn Slough Reserve North Marsh Site nutrient data
elksmnt = Elkhorn Slough Reserve South Marsh Site nutrient data
elkvmnt = Elkhorn Slough Reserve Vierra Mouth Site nutrient data
Monthly grab sample program= 1
Diel grab sample program= 2

6) Data collection period –

SWMP nutrient monitoring first began in April 2002 for elkapnut, elknlmnt, elkvmnt, and in August 2002 for elksmnt.

Sampling occurred between 06:00 January 15, 2019 and 06:48 December 4, 2019.

Diel Sampling

Site	Start Date	Start Time	End Date	End Time
elksm	01/15/2019	06:00	01/16/2019	06:48
elksm	02/12/2019	06:00	02/13/2019	06:48
elksm	03/05/2019	06:00	03/06/2019	06:48
elksm	04/02/2019	06:00	04/03/2019	06:48
elksm	05/14/2019	06:00	05/15/2019	06:48
elksm	06/11/2019	06:00	06/12/2019	06:48
elksm	07/09/2019	06:00	07/10/2019	06:48
elksm	08/06/2019	06:00	08/07/2019	06:48
elksm	09/10/2019	06:00	09/11/2019	06:48
elksm	10/08/2019	06:00	10/09/2019	06:48
elksm	11/05/2019	06:00	11/06/2019	06:48
elksm	12/03/2019	06:00	12/04/2019	06:48

Grab sampling

Site	Start date	Start time	End date	End time
elkap	01/15/2019	10:52	01/15/2019	10:53
elkap	02/12/2019	10:05	02/12/2019	10:06
elkap	03/05/2019	13:55	03/05/2019	13:56
elkap	04/02/2019	13:19	04/02/2019	13:21
elkap	05/14/2019	11:26	05/14/2019	11:27
elkap	06/11/2019	10:05	06/11/2019	10:06
elkap	07/09/2019	08:09	07/09/2019	08:10
elkap	08/06/2019	09:00	08/06/2019	09:02
elkap	09/10/2019	12:28	09/10/2019	12:29
elkap	10/08/2019	11:42	10/08/2019	11:43
elkap	11/05/2019	10:00	11/05/2019	10:01
elkap	12/03/2019	09:36	12/03/2019	09:38

Grab sampling

Site	Start date	Start time	End date	End time
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elknm	01/15/2019	09:31	01/15/2019	09:31
elknm	02/12/2019	08:31	02/12/2019	08:32
elknm	03/05/2019	13:04	03/05/2019	13:06
elknm	04/02/2019	11:43	04/02/2019	11:43
elknm	05/14/2019	10:29	05/14/2019	10:29
elknm	06/11/2019	08:58	06/11/2019	08:59
elknm	07/09/2019	07:11	07/09/2019	07:13
elknm	08/06/2019	07:58	08/06/2019	07:58
elknm	09/10/2019	11:31	09/10/2019	11:31
elknm	10/08/2019	10:36	10/08/2019	10:37
elknm	11/05/2019	09:06	11/05/2019	09:08
elknm	12/03/2019	08:18	12/03/2019	08:18

Grab sampling

Site	Start date	Start time	End date	End time
elksm	01/15/2019	08:32	01/15/2019	08:33
elksm	02/12/2019	07:31	02/12/2019	07:33
elksm	03/05/2019	12:19	03/05/2019	12:20
elksm	04/02/2019	10:51	04/02/2019	10:52
elksm	05/14/2019	09:30	05/14/2019	09:31
elksm	06/11/2019	07:57	06/11/2019	07:59
elksm	07/09/2019	06:24	07/09/2019	06:25
elksm	08/06/2019	07:00	08/06/2019	07:01
elksm	09/10/2019	10:44	09/10/2019	10:45
elksm	10/08/2019	09:56	10/08/2019	09:58
elksm	11/05/2019	08:27	11/05/2019	08:28
elksm	12/03/2019	07:31	12/03/2019	07:32

Grab sampling

Site	Start date	Start time	End date	End time
elkvm	01/15/2019	11:21	01/15/2019	11:23
elkvm	02/12/2019	09:56	02/12/2019	09:56
elkvm	03/05/2019	13:37	03/05/2019	13:37
elkvm	04/02/2019	13:19	04/02/2019	13:20
elkvm	05/14/2019	12:16	05/14/2019	12:18
elkvm	06/11/2019	10:47	06/11/2019	10:47
elkvm	07/09/2019	08:46	07/09/2019	08:46
elkvm	08/06/2019	09:59	08/06/2019	10:00
elkvm	09/10/2019	13:34	09/10/2019	13:36
elkvm	10/08/2019	12:10	10/08/2019	12:10
elkvm	11/05/2019	10:32	11/05/2019	10:32
elkvm	12/03/2019	10:15	12/03/2019	10:16

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.

John Haskins and Rikke Jeppesen 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 Vibracore.

Apodaca, Alec, University of California Berkeley, uses instruments to assess topography, canoe surveys to examine banks, auger holes to examine sediment, in order to understand indigenous interactions with estuarine resources.

Behesti, Kat; University of California, Santa Cruz: monitors marsh, crabs, and otters with fencing experiments to examine the effects of otters and crabs on salt marsh health.

Francis, Chris, Stanford University: collects water samples and sediment cores to study the diversity and activity of (de)-nitrifying microbial communities.

Gaskins, Leo, Duke University: collects native crabs, *Pachygrapsus crassipes*, tether and video observe them to investigate predation on crabs by raccoons and Southern sea otters.

Hammerstrom, Kamille; Oliver, John; Moss Landing Marine Laboratories: assess effects of Parsons sill on benthic infauna, coffee-can cores and sieving of mud; from shore and boat.

Jue, Nathaniel, California State University Monterey Bay: collects soil and water samples at South Marsh and Whistlestop to examine microbial processes remediating pesticides.

Parkin, Jennifer; ELKNERR volunteer; monitors salt marsh restoration effects on water birds, and observes the tern colony.

Searcy, Chris, 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.

Tanner, Karen, Martin Genova; University of California Santa Cruz; transplants and monitors plants to explore the role of mycorrhizae in supporting marsh plants.

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

Frequent interns: Kathleen Hicks (water quality interns).

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.nerrsddata.org; accessed 12 October 2020.

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 and Rikke Jeppesen are responsible for filtering all samples and for analyzing the samples to determine chlorophyll concentration. Steven Cunningham, Moss Landing Marine Laboratories is responsible for measuring nitrite, nitrite + nitrate, ammonia, orthophosphate, and silicate concentrations.

All chlorophyll-*a* data are entered into a monthly Excel spread sheet while the chlorophyll samples are being processed. Steven Cunningham e-mails the nutrient results monthly, and Cunningham's results are then entered into the same monthly nutrient Excel sheet by Rikke Jeppesen and/or John Haskins. The Excel file contains information of sampling station ID, date and time, and parameter values expressed in unit concentrations. Rikke Jeppesen verifies

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 and then processed using the NutrientQAQC macro as detailed below.

All nutrient parameter values at Moss Landing Marine Laboratories (MLML) are calculated and reported in mg/L and therefore require no conversion.

Chlorophyll a is measured in RFU and ELK NERR staff converts RFU to µg/L by using the following conversion:

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

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 –

a) Parameters measured directly

Nitrogen species:	NH4F, NO2F, NO3F
Phosphorus species:	PO4F
Other:	CHLA_N, SiO4F

b) **Calculated parameters**

NO3F	NO23F-NO2F
DIN	NO23F+NH4F

12) Limits of detection –

The Moss Landing Marine Lab (MLML) Nutrient Analytical Laboratory has established Method Detection Limits (MDL), the lowest concentration of a parameter that an analytical procedure can reliably detect. The MDL is determined as 3 times the standard deviation of a minimum of seven replicates of a single low concentration sample. The overall annual MDL is calculated as the average of the monthly MDLs. The first table below presents the 2019 average MDL's; these values are reviewed and revised periodically. The MDLs for each individual month are listed in the submitted raw metadata dataset workbook within the MDL worksheet and in the second table below.

2019 Average MDLs

Parameter	Start Date	End Date	MDL	Revisited
PO4F	01/01/19	12/31/19	0.00418	Monthly
NH4F	01/01/19	12/31/19	0.00483	Monthly
NO2F	01/01/19	12/31/19	0.02449	Monthly
NO23F	01/01/19	12/31/19	0.00881	Monthly
SiO4F	01/01/19	12/31/19	0.02430	Monthly
CHLA_N	01/01/19	07/31/19	0.15747	Monthly
CHLA_N	08/01/19	12/31/19	0.00569	Monthly

2019 Monthly MDLs

Parameter	Start Date	End Date	MDL
PO4F	01/01/19	01/31/19	0.0019
PO4F	02/01/19	02/28/19	0.0041
PO4F	03/01/19	03/31/19	0.0044
PO4F	04/01/19	04/30/19	0.0006
PO4F	05/01/19	05/31/19	0.0011
PO4F	06/01/19	06/30/19	0.0013
PO4F	07/01/19	07/31/19	0.0099
PO4F	08/01/19	08/31/19	0.0096
PO4F	09/01/19	09/30/19	0.0039
PO4F	10/01/19	10/31/19	0.0060
PO4F	11/01/19	11/30/19	0.0064
PO4F	12/01/19	12/31/19	0.0011
NO2F	01/01/19	01/31/19	0.0016
NO2F	02/01/19	02/28/19	0.0016
NO2F	03/01/19	03/31/19	0.0012
NO2F	04/01/19	04/30/19	0.0030
NO2F	05/01/19	05/31/19	0.0145
NO2F	06/01/19	06/30/19	0.0005

NO2F	07/01/19	07/31/19	0.0051
NO2F	08/01/19	08/31/19	0.0028
NO2F	09/01/19	09/30/19	0.0092
NO2F	10/01/19	10/31/19	0.0054
NO2F	11/01/19	11/30/19	0.0024
NO2F	12/01/19	12/31/19	0.0009

NO23F	01/01/19	01/31/19	0.0005
NO23F	02/01/19	02/28/19	0.0750
NO23F	03/01/19	03/31/19	0.0014
NO23F	04/01/19	04/30/19	0.0019
NO23F	05/01/19	05/31/19	0.0038
NO23F	06/01/19	06/30/19	0.0009
NO23F	07/01/19	07/31/19	0.0062
NO23F	08/01/19	08/31/19	0.0047
NO23F	09/01/19	09/30/19	0.0074
NO23F	10/01/19	10/31/19	0.0012
NO23F	11/01/19	11/30/19	0.0009
NO23F	12/01/19	12/31/19	0.0020

NH4F	01/01/19	01/31/19	0.0014
NH4F	02/01/19	02/28/19	0.0018
NH4F	03/01/19	03/31/19	0.0020
NH4F	04/01/19	04/30/19	0.0021
NH4F	05/01/19	05/31/19	0.0056
NH4F	06/01/19	06/30/19	0.0013
NH4F	07/01/19	07/31/19	0.0044
NH4F	08/01/19	08/31/19	0.0132
NH4F	09/01/19	09/30/19	0.0021
NH4F	10/01/19	10/31/19	0.0023
NH4F	11/01/19	11/30/19	0.0084
NH4F	12/01/19	12/31/19	0.0133

SiO4F	01/01/19	01/31/19	0.0336
SiO4F	02/01/19	02/28/19	0.0226
SiO4F	03/01/19	03/31/19	0.0071
SiO4F	04/01/19	04/30/19	0.0071
SiO4F	05/01/19	05/31/19	0.0018
SiO4F	08/01/19	08/31/19	0.0358
SiO4F	09/01/19	09/30/19	0.0617
SiO4F	10/01/19	10/31/19	0.0188
SiO4F	11/01/19	11/30/19	0.0244
SiO4F	12/01/19	12/31/19	0.0139

CHLA_N	01/01/19	01/31/19	0.2875
CHLA_N	02/01/19	02/28/19	0.0413
CHLA_N	03/01/19	03/31/19	0.2175
CHLA_N	04/01/19	04/30/19	0.2476
CHLA_N	05/01/19	05/31/19	0.1144
CHLA_N	06/01/19	06/30/19	0.1373
CHLA_N	07/01/19	07/31/19	0.0567
CHLA_N	08/01/19	08/31/19	0.0009
CHLA_N	09/01/19	09/30/19	0.0009
CHLA_N	10/01/19	10/31/19	0.0073
CHLA_N	11/01/19	11/30/19	0.0038
CHLA_N	12/01/19	12/31/19	0.0107

13) Laboratory methods –

a) **Parameter: NH4F**

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 48 hours, or at -20°C up to 29 days, if they can't be analyzed within 48 hrs of filtration.

b) **Parameter: NO23F**

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 48 hours, or at -20°C up to 29 days, if they can't be analyzed within 48 hrs of filtration.

c) **Parameter: NO2F**

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 48 hours, or at -20°C up to 29 days, if they can't be analyzed within 48 hrs of filtration.

d) **Parameter: PO4F**

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 phosphomolybdic 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 48 hours, or at -20°C up to 29 days, if they can't be analyzed within 48 hrs of filtration.

e) **Parameter: SiO₄**

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 48 hours, or at -20°C up to 29 days, if they can't be analyzed within 48 hrs of filtration.

f) **Parameter: ChlA**

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 8 mL 90% acetone (Jan-Jul) and 5 mL 90% acetone (Aug-Dec) for 24 hrs and then fluorescence is measured and recorded (Fo).

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 of 90% acetone and then stored at -20°C until analysis 24 hrs later.

14) **Field and Laboratory QAQC programs –**

a) **Precision**

- i) **Field variability** ELK NERR collects two or three successive grab samples for the determination of water mass variability within each site. Each collection date, there are three true field replicates, which are successive grab samples.
- ii) **Laboratory variability** – ELK NERR uses three of the ISCO samples to provide laboratory replicates. Each month, we randomly select three numbers between 1 and 13. 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.
- iii) **Inter-organizational splits** – None. All split samples were analyzed by the same lab.

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 2019 was found to be:

	PO ₄	NO ₂	NO ₃	NH ₄	SiO ₄
Average	101%	100%	123%	104%	102%
Minimum	79%	85%	90%	85%	72%
Maximum	126%	129%	156%	125%	132%

- 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 2019 was found to be:

	PO4	NO2	NO3	NH4	SIO4
Average	103%	105%	108%	100%	97%
Minimum	90%	90%	98%	90%	42%
Maximum	115%	117%	119%	116%	114%

- iii) **Cross calibration exercises** – ELKNERR did not participate in any cross calibration exercises in 2019.

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
<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 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 NO₃F 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.

Chlorophyll instrumentation

In 2019, ELKNERR bought a new fluorometer. From January to July we used the old fluorometer (TD 700) and from August to December we used the new fluorometer (Trilogy).

In August we processed the Chlorophyll-*a* samples on both instruments. We found a strong correlation between the results from the two different instruments, and thus were confident that chlorophyll-*a* reporting is consistent across the two different pieces of equipment.

Incorrect NO23F concentrations posted 6/8/2020-8/23/2022

From 6/8/2020 when this dataset was first made available as provisional-plus data, until it was authenticated on 8/24/2022, reported NO23F concentrations were incorrect due to a calculation error. Correct NO23F data for the 2019 dataset were uploaded to the NERRS CDMO database on 8/24/22 and made available for distribution immediately.

Sample hold times for 2019

All sample collection dates and analysis dates are listed below. Grab samples are held up to five hours, from the time the first sample is collected until the samples are filtered. ISCO samples are filtered within 27 hrs of the first sample collection time. Once filtered, samples are held in a dark 4°C space for up to 48 hrs, before the nutrient analysis is conducted. If samples can not be processed within 48 hrs, samples are frozen at -20°C for up to 29 days before processing further. For Chl-*a*, samples are analyzed up to 35 days after extraction in acetone. Chl-*a* samples are stored in a freezer at all times.

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 and coded CHB.

Grab samples

Sample collection date	Sample analysis date	
<i>All</i>	NO2, NO23, NH4, PO4, SiO4	Chl_A
1/15/2019	1/16/2019	2/12/2019
2/12/2019	2/14/2019	3/6/2019
3/5/2019	3/6/2019	4/3/2019
4/2/2019	4/3/2019	5/15/2019 *
5/14/2019	5/15/2019	6/12/2019
6/11/2019	6/13/2019	7/10/2019
7/9/2019	7/12/2019	7/11/2019
8/6/2019	8/8/2019	9/11/2019 *
9/10/2019	9/11/2019	10/1/2019
10/8/2019	10/9/2019	10/17/2019
11/5/2019	11/6/2019	11/12/2019
12/3/2019	12/4/2019	12/17/2019

ISCO samples

Sample collection date	Sample analysis date	
<i>ISCO 1-9</i>	NO2, NO23, NH4, PO4, SiO4	Chl_A
1/15/2019	1/16/2019	2/12/2019
2/12/2019	2/14/2019	3/6/2019
3/5/2019	3/6/2019	4/3/2019
4/2/2019	4/3/2019	5/15/2019 *
5/14/2019	5/15/2019	6/12/2019
6/11/2019	6/13/2019	7/10/2019
7/9/2019	7/12/2019	7/11/2019

8/6/2019	8/8/2019	9/11/2019	*
9/10/2019	9/11/2019	10/1/2019	
10/8/2019	10/9/2019	10/17/2019	
11/5/2019	11/6/2019	11/12/2019	
12/3/2019	12/4/2019	12/17/2019	

ISCO 10-13	NO2, NO23, NH4, PO4, SiO4	Chl_A	
1/16/2019	1/16/2019	2/12/2019	
2/13/2019	2/14/2019	3/6/2019	
3/6/2019	3/6/2019	4/3/2019	
4/3/2019	4/3/2019	5/15/2019	*
5/15/2019	5/15/2019	6/12/2019	
6/12/2019	6/13/2019	7/10/2019	
7/10/2019	7/12/2019	7/11/2019	
8/7/2019	8/8/2019	9/11/2019	
9/11/2019	9/11/2019	10/1/2019	
10/9/2019	10/9/2019	10/17/2019	
11/6/2019	11/6/2019	11/12/2019	
12/4/2019	12/4/2019	12/17/2019	

*sample held longer than allowed by NERRS protocols