Elkhorn Slough (ELK) NERR Nutrient Metadata January to December 2018

Latest Update: November 17, 2022

I. Data Set and Research Descriptors

1) Principal investigator(s) and contact persons –

a) Reserve Contact

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b) Laboratory 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* sample filters were extracted in 8 mL acetone, stored in the freezer for at least 24 hrs, and analyzed on a Turner 700 fluorometer.

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 2018, the tide ranged from 1.16 to 2.49 meters at this site and salinity ranged from 23.0 ppt during heavy run-off to 39.8 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 runoff. In 2018, the tide ranged from approximately 0.57 to 1.05 meters at this site. Salinity ranged between 21.7 and 45.3 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 2018, the tidal range was from -1.11 to 2.23 meters 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 2018, the tidal range was from -0.39 to 2.36 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 Elkhorn Slough 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	Р	Vierra Mouth	36°48'39.95"N, 121°46'45.22"W	March 2001 - current	NA	NA

5) Code 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

SWMP nutrient montoring first began in April 2002 for elkapnut, elknmnut, elkvmnut, and in August 2002 for elksmnut.

Sampling occurred between 06:00 January 9, 2018 and 06:48 December 5, 2018.

Diel Sampling

Site	Start Date	Start Time	End Date	End Time
Elksm	01/09/2018	06:00	01/10/2018	06:48
	, ,		, ,	
Elksm	02/06/2018	06:00	02/07/2018	06:48
Elksm	03/13/2018	06:00	03/14/2018	06:48
Elksm	04/10/2018	06:00	04/11/2018	06:48
Elksm	05/08/2018	06:00	05/09/2018	06:48

Elksm	06/05/2018	06:00	06/06/2018	06:48
Elksm	07/10/2018	06:00	07/11/2018	06:48
Elksm	08/07/2018	06:00	08/08/2018	06:48
Elksm	09/04/2018	06:00	09/05/2018	06:48
Elksm	10/02/2018	06:00	10/03/2018	06:48
Elksm	11/06/2018	06:00	11/07/2018	06:48
Elksm	12/04/2018	06:00	12/05/2018	06:48

Elksm	12/04/2018	8 06:00	12/05/2	2018 06:4
Grab S	ampling			
Site	Start date	Start time	End date	End time
elkap	1/9/2018	10:41	1/9/2018	10:42
elkap	2/6/2018	9:24	2/6/2018	9:25
elkap	3/13/2018	12:24	3/13/2018	12:25
elkap	4/10/2018	11:14	4/10/2018	11:16
elkap	5/8/2018	10:09	5/8/2018	10:10
elkap	6/5/2018	9:09	6/5/2018	9:10
elkap	7/10/2018	12:11	7/10/2018	12:12
elkap	8/7/2018	10:55	8/7/2018	10:57
elkap	9/4/2018	9:31	9/4/2018	9:32
elkap	10/2/2018	8:49	10/2/2018	8:50
elkap	11/6/2018	14:17	11/6/2018	14:18
elkap	12/4/2018	13:23	12/4/2018	13:25
Site	Start date	Start time	End date	End time
elknm	1/9/2018	9:21	1/9/2018	9:21
elknm	2/6/2018	7:59	2/6/2018	8:00
elknm	3/13/2018	11:46	3/13/2018	11:48
elknm	4/10/2018	9:50	4/10/2018	9:50
elknm	5/8/2018	8:51	5/8/2018	8:51
elknm	6/5/2018	7:36	6/5/2018	7:37
elknm	7/10/2018	10:47	7/10/2018	10:49
elknm	8/7/2018	9:38	8/7/2018	9:38
elknm	9/4/2018	9:02	9/4/2018	9:02
elknm	10/2/2018	7:49	10/2/2018	7:50
elknm	11/6/2018	13:35	11/6/2018	13:37
elknm	12/4/2018	12:14	12/4/2018	12:14
Site	Start date	Start time	End date	End time
elksm	1/9/2018	8:31	1/9/2018	8:32

Site	Start date	Start time	End date	End time
elksm	1/9/2018	8:31	1/9/2018	8:32
elksm	2/6/2018	7:04	2/6/2018	7:06
elksm	3/13/2018	10:55	3/13/2018	10:56
elksm	4/10/2018	9:04	4/10/2018	9:05
elksm	5/8/2018	7:58	5/8/2018	7:59
elksm	6/5/2018	6:32	6/5/2018	6:34
elksm	7/10/2018	9:52	7/10/2018	9:53
elksm	8/7/2018	8:48	8/7/2018	8:49

elksm	9/4/2018	7:56	9/4/2018	7:57
elksm	10/2/2018	6:55	10/2/2018	6:57
elksm	11/6/2018	12:38	11/6/2018	12:39
elksm	12/4/2018	11:24	12/4/2018	11:25
Site	Start date	Start time	End date	End time
elkvm	1/9/2018	12:14	1/9/2018	12:16
elkvm	2/6/2018	10:51	2/6/2018	10:51
elkvm	3/13/2018	14:07	3/13/2018	14:07
elkvm	4/10/2018	13:05	4/10/2018	13:06
elkvm	5/8/2018	11:42	5/8/2018	11:44
elkvm	6/5/2018	10:17	6/5/2018	10:17
elkvm	7/10/2018	13:53	7/10/2018	13:53
elkvm	8/7/2018	11:28	8/7/2018	11:29
elkvm	9/4/2018	10:38	9/4/2018	10:40
elkvm	10/2/2018	10:03	10/2/2018	10:03
elkvm	11/6/2018	14:20	11/6/2018	14:20
elkvm	12/4/2018	14:35	12/4/2018	14:36

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.

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

Appy, Ralph, Cabrillo Marine Aquarium: collects fish and shrimp to investigate parasites

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.

Espinosa, Sara; Staedler, Michelle, et al., UC Santa Cruz, USGS: observe otters from land-based sites in order to track sea otter movement and survival (radio-tagged animals) and patterns of distribution, abundance, and behavior (entire Slough population)

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

Gaskins, Lindsay, 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

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

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

Requested citation format:

NOAA National Estuarine Research Reserve System (NERRS). System-wide Monitoring Program. Data accessed from the NOAA NERRS Centralized Data Management Office website: www.nerrsdata.org; accessed 12 October 2018.

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 and Rikke Jeppesen are responsible for filtering all samples and for analyzing the samples to determine chlorophyll concentration. Kim Null, 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. Kim Null e-mails the nutrient results monthly, and Null's results are then entered into the same monthly nutrient Excel sheet by Rikke Jeppesen and 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*10-4 µg Chla/mL/RFU)*RFU_{measured}*dilution factor* (extraction volume/filtered volume)*1000mL/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 Data Category

Only list those parameters that are reported in the data. See Table 2 in the "Nutrient and Chlorophyll Monitoring Program and Database Design" SOP version 1.7 (March 2016) document for a full list of directly measured and computed variables.

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

Data Category Parameter Variable Name Units of Measure

Phosphorus and Nitrogen:

*Orthophosphate PO4F mg/L as P *Ammonium, Filtered NH4F mg/L as N

NO2F	mg/L as N
NO3F	mg/L as N
NO23F	mg/L as N
DIN	mg/L as N
	0,
CHLA_N	$\mu g/L$
	. 0
SiO4F	mg/L as SI
	NO3F NO23F DIN CHLA_N

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 and Calculated Laboratory Parameters –

a) Parameters measured directly

Nitrogen species: NH4F, NO2F, NO23F

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 five replicates of a single low concentration sample. The MDL is calculated each month and reported below. The MDLs for each individual month are also listed in the submitted dataset workbook within the MDL worksheet.

MDL TABLE

Parameter	Start Date	End Date	MDL
PO4F	01/01/2018	01/31/2018	0.0040
PO4F	02/01/2018	02/28/2018	0.0015
NO2F	01/01/2018	01/31/2018	0.0007
NO2F	02/01/2018	02/28/2018	0.0012
NO23F	01/01/2018	01/31/2018	0.0101
NO23F	02/01/2018	02/28/2018	0.0239
NH4F	01/01/2018	01/31/2018	0.0124
NH4F	02/01/2018	02/28/2018	0.0086
SiO4F	01/01/2018	01/31/2018	0.0538
SiO4F	02/01/2018	02/28/2018	0.1579
CHLA_N	01/01/2018	01/31/2018	0.1096
CHLA_N	02/01/2018	02/28/2018	0.0918
PO4F	03/01/2018	03/31/2018	0.0010
PO4F	04/01/2018	04/30/2018	0.0009
NO2F	03/01/2018	03/31/2018	0.0016

NO2F	04/01/2018	04/30/2018	0.0012
NO23F	03/01/2018	03/31/2018	0.0004
NO23F	04/01/2018	04/30/2018	0.0202
NH4F	03/01/2018	03/31/2018	0.0060
NH4F	04/01/2018	04/30/2018	0.0017
SiO4F	03/01/2018	03/31/2018	0.0344
SiO4F	04/01/2018	04/30/2018	0.0324
CHLA_N	03/01/2018	03/31/2018	0.0846
CHLA_N	04/01/2018	04/30/2018	0.1724
PO4F	05/01/2018	05/31/2018	0.0011
PO4F	06/01/2018	06/30/2018	0.0047
NO2F	05/01/2018	05/31/2018	0.0011
NO2F	06/01/2018	06/30/2018	0.0007
NO23F	05/01/2018	05/31/2018	0.0035
NO23F	06/01/2018	06/30/2018	0.0123
NH4F	05/01/2018	05/31/2018	0.0094
NH4F	06/01/2018	06/30/2018	0.0041
SiO4F	05/01/2018	05/31/2018	0.0198
SiO4F	06/01/2018	06/30/2018	0.0247
CHLA_N	05/01/2018	05/31/2018	0.0896
CHLA_N	06/01/2018	06/30/2018	0.0627
PO4F	07/01/2018	07/31/2018	0.0022
PO4F	08/01/2018	08/31/2018	0.0010
NO2F	07/01/2018	07/31/2018	0.0094
NO2F	08/01/2018	08/31/2018	0.0023
NO23F	07/01/2018	07/31/2018	0.0013
NO23F	08/01/2018	08/31/2018	0.0020
NH4F	07/01/2018	07/31/2018	0.0012
NH4F	08/01/2018	08/31/2018	0.0008
SiO4F	07/01/2018	07/31/2018	0.0238
SiO4F	08/01/2018	08/31/2018	0.0168
CHLA_N	07/01/2018	07/31/2018	0.1632
CHLA_N	08/01/2018	08/31/2018	0.1342
PO4F	09/01/2018	09/30/2018	0.0075
PO4F	10/01/2018	10/31/2018	0.0022
NO2F	09/01/2018	09/30/2018	0.0014
NO2F	10/01/2018	10/31/2018	0.0012
NO23F	09/01/2018	09/30/2018	0.0010
NO23F	10/01/2018	10/31/2018	0.0006
NH4F	09/01/2018	09/30/2018	0.0009
NH4F	10/01/2018	10/31/2018	0.0031
SiO4F	09/01/2018	09/30/2018	0.0299
SiO4F	10/01/2018	10/31/2018	0.0203
CHLA_N	09/01/2018	09/30/2018	0.3752
CHLA_N	10/01/2018	10/31/2018	0.1091

CHLA_N	11/01/2018	11/30/2018	0.1484
CHLA_N	12/01/2018	12/31/2018	0.0368
SiO4F	11/01/2018	11/30/2018	0.0652
SiO4F	12/01/2018	12/31/2018	0.0432
NH4F	11/01/2018	11/30/2018	0.0025
NH4F	12/01/2018	12/31/2018	0.0012
NO23F	11/01/2018	11/30/2018	0.0007
NO23F	12/01/2018	12/31/2018	0.0003
NO2F	11/01/2018	11/30/2018	0.0009
NO2F	12/01/2018	12/31/2018	0.0446
PO4F	11/01/2018	11/30/2018	0.0174
PO4F	12/01/2018	12/31/2018	0.0006

13) Laboratory Methods

- a) Parameter: NH4F
 - i) Method Reference: EPA 350.1 / Lachat Quickchem Method 31-107-06-1-B
 - ii) 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.
 - iii) Preservation Method: Samples filtered and stored at 4°C up to 48 hours.

b) Parameter: NO23F, NO3F

- i) Method Reference: EPA 353.2 / Lachat Quickchem Method 31-107-04-1-E
- ii) 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-napthyl)-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 N02F.
- iii) Preservation Method: Samples filtered and stored at 4°C up to 48 hours.

b) Parameter: NO2F

- i) Method Reference: EPA 353.2 / Lachat Quickchem Method 31-107-05-1-A
- ii) Method Descriptor: Nitrite is measured by diazotization with sulfanilamide under acidic conditions to form diazonium ion. The diazonium ion is coupled with N-(1-napthyl)-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.
- iii) Preservation Method: Samples filtered and stored at 4 °C up to 48 hours.

c) 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
- ii. 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.
- iii. <u>Preservation Method</u>: Samples filtered and stored at 4°C up to 48 hours.

d) Parameter: SiO4

- i) Method Reference: Lachat Quickchem Method 10-114-27-1-D
- ii) Method Descriptor: Soluble silica species react with molybdate at 37°C and a pH of 1.2 to form a yellow silicamolybdate 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.
- iii) Preservation Method: Samples filtered and stored at 4°C up to 48 hours.

e) Parameter: ChlA

- iv) Method Reference. EPA method 445.0*UNESCO* (1994) Protocols for the joint global ocean flux study (JGOFS) core measurements. pp. 97-100.
- v) Method Descriptor: CHLA is extracted in 8 ml 90% acetone for 24 hrs and then fluorescence is measured and recorded (Fo).
- vi) <u>Preservation Method</u>: 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 -4°C until analysis 24 hrs later.

14) Field and Laboratory QA/QC 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 are 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 2018 was found to be:

	PO4	NO2	NO3	NH4	SIO
Average	110%	94%	122%	100%	96%
Minimum	89%	80%	93%	28%	90%
Maximum	136%	109%	144%	134%	113%

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 2018 was found to be:

	PO4	NO2	NO3	NH4	SIO
Average	125%	126%	131%	123%	128%
Minimum	103%	107%	110%	86%	102%
Maximum	173%	165%	157%	158%	215%

iii. **Cross Calibration Exercises** – An inter-comparison study is conducted in some years of a known concentration of nutrients in seawater as part of the NOAA National Estuarine Research Reserve System-Wide Monitoring Program. Our analyses of all the nutrients have been within one standard

deviation of all nutrients analyzed among all labs in the program. There was no inter-comparison for 2018

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

00	
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
	7 1 1
Record comn	nents
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	eroud (no percentage)
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	mace rain and snow
TSE	ebb tide
TSF	flood tide
TSH	high tide
TSL	low tide
Wave height	low tide
WHO	$0 \text{ to } \le 0.1 \text{ meters}$
WH1	0.1 to 0.3 meters
WH2	0.3 to 0.5 meters
WH3	0.6 to > 1.0 meters
WH4	1.0 to 1.3 meters
WH5	
Wind direction	1.3 or greater meters
w ina airection N	
NNE	from the north from the north northeast
NE ENE	from the cost postboost
ENE E	from the east northeast from the east
ESE	from the east southeast
SE SSE	from the south couth cost
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 2018

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 24 hrs, before the nutrient analysis is conducted. If samples can not be processed within 24 hrs, samples are frozen at -20°C for up to one month 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 col	llection d	late S	Sampl	e ana	lysis	date

All	Chl_A	NO2, NO23, NH4, PO4, SiO4
1/9/2018	2/7/2018	1/12/2018
2/6/2018	3/14/2018*	2/9/2018

2/12/2019	4/11/2019	2/16/2019
3/13/2018 4/10/2018	4/11/2018 5/9/2018	3/16/2018 4/12/2018
5/8/2018	6/6/2018	5/10/2018
6/5/2018	7/11/2018*	6/9/2018
7/10/2018	8/8/2018	7/12/2018
8/7/2018	9/5/2018	8/9/2018
9/4/2018	10/3/2018	9/7/2018
10/2/2018		10/4/2018
	11/7/2018*	
11/6/2018	12/5/2018	11/7/2018
12/4/2018	1/16/2019*	1/15/2019*
Diel samples	0 1 1 1 1 .	
Sample collection date	Sample analysis date	NOO NOOO NIIIA DOA 6'OA
ISCO 1-9	Chl_A	NO2, NO23, NH4, PO4, SiO4
1/9/2018	2/7/2018	1/12/2018
2/6/2018	3/14/2018*	2/9/2018
3/13/2018	4/11/2018	3/16/2018
4/10/2018	5/9/2018	4/12/2018
5/8/2018	6/6/2018	5/10/2018
6/5/2018	7/11/2018*	6/9/2018
7/10/2018	8/8/2018	7/12/2018
8/7/2018	9/5/2018	8/9/2018
9/4/2018	10/3/2018	9/7/2018
10/2/2018	11/7/2018*	10/4/2018
11/6/2018	12/5/2018	11/7/2018
12/4/2018	1/16/2019*	1/15/2019*
ISCO 10-13	Chl_A	NO2, NO23, NH4, PO4, SiO4
1/10/2018	2/7/2018	1/12/2018
2/7/2018	3/14/2018	2/9/2018
3/14/2018	4/11/2018	3/16/2018
4/11/2018	5/9/2018	4/12/2018
5/9/2018	6/6/2018	5/10/2018
6/6/2018	7/11/2018	6/9/2018
7/11/2018	8/8/2018	7/12/2018
8/8/2018	9/5/2018	8/9/2018
9/5/2018	10/3/2018	9/7/2018
10/3/2018	11/7/2018	10/4/2018
11/7/2018	12/5/2018	11/7/2018
12/5/2018	1/16/2019*	1/15/2019*
12/5/2010	1/10/2017	1/15/2017

^{*}sample held longer than allowed by NERRS protocols

Missing data notes:

4/11/2018 04:44 & 06:48 – ISCO battery failure
7/10/2018 16:20 – 01/11/2018 06:48 - ISCO battery failure
09/04/2018 18:24 – 09/05/2018 06:48 – ISCO battery failure