Elkhorn Slough (ELK) ~~Reserve Name (include 3 letter code here)~~ **NERR Nutrient Metadata**
January to December 2021~~Months and year the documentation covers~~
~~Months and year the documentation covers~~
Latest Update: June 8, 2021~~Date that the last edits were made~~

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) Reserve Contact
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c) Laboratory Contact
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d) Research Coordinator
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Field Code Changed

~~[Instructions/Remove: List the reserve staff members responsible for the implementation and collection of the nutrient data. List the laboratory staff members responsible for processing of the samples and data output. Include name, title, mailing address, phone number, and email address for the Research Coordinator, SWMP technician(s), person(s) responsible for data management, and laboratory contact.]~~

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 13 water samples through a 24-hour tidal cycle once per month, at a permanent water quality station, South Marsh.

~~[Instructions/Remove: Describe briefly the nature of each monitoring program resulting in this data set (monitoring along land use, vertical, salinity or habitat gradients).]~~

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

3) Research methods –

During 2021 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 2021 samples were analyzed for phosphate, nitrate, nitrite, ammonia, and silicate at Moss Landing.

~~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. 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 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 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 shaken, filtered and processed for nutrient and Chl-a analysis. Rikke Jeppesen or Fuller Gerbl was responsible for the

chlorophyll analysis. Steven Cunningham was 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 kept in a dark cooler on ice and returned to the laboratory for immediate processing, unless there are problems with any equipment. If samples 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 Fuller Gerbl was responsible for the chlorophyll analysis. Steven Cunningham or Katie Graves was responsible for the phosphate, nitrate, nitrite, ammonia, and silica analyses.

~~[Instructions/Remove: Detail the specifics of sample collection, collection intervals, sample processing, how samples are held, and QAQC of the equipment and analyzers for each program.]~~

~~a) Monthly grab sampling program~~
~~b) Diel sampling program~~

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 2021, the tide ranged from 1.27 m to 2.53 meters at this site and salinity ranged from 2.9 ppt during heavy run-off to 38.7 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 2021, the tide ranged from approximately 0.59 m to 1.17 meters at this site. Salinity ranged between 19.9 and 42.5 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 2021, the tidal range was from -0.37 to 2.38 meters at this site and the salinity range was from 22.7 to 34.6 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 2021, the tidal range was from -0.49 m to 2.27 meters at this site and salinity ranged from 21.7 to 34.8 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.

~~[Instructions/Remove: Describe your NERR site in general and the sampling sites associated with each YSI data logger / nutrient collection in more detail. Include the following in your description for each sampling location. If certain characteristics apply to all sample sites or the entire reserve they may be discussed in an overview:]~~

~~a) latitude and longitude~~
~~b) tidal range~~
~~c) salinity range~~
~~d) type and amount of freshwater input~~
~~e) water depth (mean depth or depth range at site, NOT depth of sonde deployment)~~
~~f) bottom habitat or type (soft sediment, grassbed, oyster bar, etc)~~
~~g) pollutants in area~~
~~h) description of watershed draining 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 - curernt	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 –

SWMP nutrient montoring first began in April 2002 for elkap, elknm, elkvm, and in August 2002 for elksm.
Sampling occurred between 06:00 January 12, 2021 and 06:00 December 15, 2021.

Diel sampling

Site	Start date	Start time	End date	End time
elksmnut	1/12/2021	6:00	1/13/2021	6:00
elksmnut	2/9/2021	6:00	2/10/2021	6:00
elksmnut	3/16/2021	6:00	3/17/2021	6:00
elksmnut	4/6/2021	6:00	4/7/2021	6:00
elksmnut	5/4/2021	6:00	5/5/2021	6:00
elksmnut	6/8/2021	6:00	6/9/2021	6:00
elksmnut	7/7/2021	6:00	7/8/2021	6:00
elksmnut	8/3/2021	6:00	8/4/2021	6:00
elksmnut	9/14/2021	6:00	9/15/2021	6:00
elksmnut	10/5/2021	6:00	10/6/2021	6:00
elksmnut	11/2/2021	6:00	11/3/2021	6:00
elksmnut	12/14/2021	6:00	12/15/2021	6:00

Grab sampling

Site	Start date	Start time	End date	End time	reps
elkapnut	1/12/2021	14:16	1/12/2021	14:17	2
elkapnut	2/9/2021	13:37	2/9/2021	13:38	2
elkapnut	3/16/2021	14:31	3/16/2021	14:32	2
elkapnut	4/6/2021	11:59	4/6/2021	12:01	3
elkapnut	5/4/2021	10:12	5/4/2021	10:13	2
elkapnut	6/8/2021	12:35	6/8/2021	12:36	2
elkapnut	7/7/2021	12:11	7/7/2021	12:12	2
elkapnut	8/3/2021	10:22	8/4/2021	10:24	3
elkapnut	9/14/2021	7:59	9/14/2021	8:00	2
elkapnut	10/5/2021	13:28	10/5/2021	13:29	2
elkapnut	11/2/2021	12:47	11/2/2021	12:48	2
elkapnut	12/14/2021	12:33	12/14/2021	12:35	3

Grab sampling

Site	Start date	Start time	End date	End time	reps
elknmnut	1/12/2021	13:00	1/12/2021	13:00	1
elknmnut	2/9/2021	12:30	2/9/2021	12:31	2
elknmnut	3/16/2021	14:03	3/16/2021	14:05	3
elknmnut	4/6/2021	10:27	4/6/2021	10:27	1
elknmnut	5/4/2021	8:50	5/4/2021	8:50	1
elknmnut	6/8/2021	11:33	6/8/2021	11:34	2
elknmnut	7/7/2021	11:07	7/7/2021	11:09	3
elknmnut	8/3/2021	9:15	8/3/2021	9:15	1
elknmnut	9/14/2021	7:04	9/14/2021	7:04	1
elknmnut	10/5/2021	11:51	10/5/2021	11:52	2
elknmnut	11/2/2021	11:46	11/2/2021	11:48	3
elknmnut	12/14/2021	11:20	12/14/2021	11:20	1

Grab sampling

Site	Start date	Start time	End date	End time	reps
elksmnut	1/12/2021	12:33	1/12/2021	12:34	2
elksmnut	2/9/2021	11:43	2/9/2021	11:45	3
elksmnut	3/16/2021	14:01	3/16/2021	14:02	2
elksmnut	4/6/2021	9:33	4/6/2021	9:34	2
elksmnut	5/4/2021	7:55	5/4/2021	7:56	2
elksmnut	6/8/2021	10:50	6/8/2021	10:52	3
elksmnut	7/7/2021	11:05	7/7/2021	11:06	2
elksmnut	8/3/2021	8:21	8/3/2021	8:22	2
elksmnut	9/14/2021	6:18	9/14/2021	6:19	2
elksmnut	10/5/2021	12:32	10/5/2021	12:34	3

elksmnut	11/2/2021	10:49	11/2/2021	10:50	2
elksmnut	12/14/2021	10:31	12/14/2021	10:32	2

Grab sampling

Site	Start date	Start time	End date	End time	reps
elkvmnut	1/12/2021	14:52	1/12/2021	14:54	3
elkvmnut	2/9/2021	14:12	2/9/2021	14:12	1
elkvmnut	3/16/2021	14:02	3/16/2021	14:02	1
elkvmnut	4/6/2021	11:59	4/6/2021	12:00	2
elkvmnut	5/4/2021	10:16	5/4/2021	10:18	3
elkvmnut	6/8/2021	13:03	6/8/2021	13:03	1
elkvmnut	7/7/2021	12:55	7/7/2021	12:55	1
elkvmnut	8/3/2021	10:54	8/3/2021	10:55	2
elkvmnut	9/14/2021	8:31	9/14/2021	8:33	3
elkvmnut	10/5/2021	13:55	10/5/2021	13:55	1
elkvmnut	11/2/2021	13:11	11/2/2021	13:11	1
elkvmnut	12/14/2021	12:50	12/14/2021	12:51	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.

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 Vibrocore

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

Brennan, Colin; ICF.com: works on detecting new longfin smelt breeding sites.

Fullmer, Sierra; Moss Landing Marine Laboratories: characterizes effects of recreational users on otters

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

Hoeke, Jackson; Moss Landing Marine Laboratories: studies feeding and ecosystem effects of invasive orange sponge.

McGee, Matthew; California State University Monterey Bay: assess how wildlife diversity and abundance changes along transect from urban to rural

Nicholson, Emma. Moss Landing Marine Laboratories: tracks seasonal and spatial patterns of harbor seal haul out

Ralson, Mitch; Washington State University: tests efficacy of environmental DNA for detecting listed amphibian species in our region

Pausch, Rachel; University of California, Santa Cruz: investigates why some parts of Hester Marsh foster more marsh growth than others

Paytan, Adina; University of California, Santa Cruz: monitors greenhouse gas flux

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

Shanebeck, Kyle: University of Alberta, Canada: detects parasites of sea otters in their prey

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

Wasserman, Naomi; Lawrence Livermore Laboratories: tests new instrument, studies particulate flux, and trace metals

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

Frequent interns: none this year

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 2021.

Also include the following excerpt in the metadata to address how and where the data can be obtained.

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 are responsible for filtering all samples and for analyzing the samples to determine chlorophyll concentration.

Steven Cunningham or Katie Graves, Moss Landing Marine Laboratories is 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 Trilogi was calibrated in May 2019, and then again in December 2020.

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All data are entered in an Excel spread sheet while processing the samples for chlorophyll-*a*. Steven Cunningham e-mails the remaining 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.

All parameter values at Moss Landing Marine Laboratories (MLML) are calculated and reported in µM. For purposes of consistency in the NERR System, Elkhorn Slough NERR calculates the concentrations as mg/ l-1 based on atomic weights of 14.01, 30.97 for N and P respectively. Therefore, Elkhorn Slough NERR staff multiplies the concentrations reported by MLML by 0.01401, 0.03097 to yield concentrations in mg/L as N and P respectively.

Chlorophyll a is measured in RFU and ESNERR 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 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, NO23F
Phosphorus species:	PO4F
Other:	CHLA_N, SiO4F

b) **Calculated parameters**

NO3F	NO23F-NO2F
DIN	NO23F+NH4F

12) Limits of detection –
[Instructions/Remove: This section explains how the laboratory determines the minimum detection limit (MDL). List the method detection limits used and dates they were in use. You may copy this data from the MDL sheet created in the NutrientQAQC macro. ***You must also include the date that each MDL was revisited by the lab for appropriateness (this should be done at least annually).***]

Example: Method Detection Limits (MDL), the lowest concentration of a parameter that an analytical procedure can reliably detect, have been established by the VIMS Nutrient Analytical Laboratory. 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	MDL	Revisited
PO4F	1/1/2021	12/31/2021	0.00846	Monthly
NO2F	1/1/2021	12/31/2021	0.00577	Monthly
NO23F	1/1/2021	12/31/2021	0.03171	Monthly
NH4F	1/1/2021	12/31/2021	0.01577	Monthly

SiO4F	1/1/2021	12/31/2021	0.04440	Monthly
CHLA_N	1/1/2021	12/31/2021	0.01708	Monthly

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.

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-napthyl)-ehtylenediamine 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.
Preservation Method: Samples filtered and stored at 4 °C up to 48 hours.

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-napthyl)-ehtylenediamine 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.

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 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 48 hours.

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 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.
Preservation Method: Samples filtered and stored at 4 °C up to 48 hours.

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 5 mL 90% acetone 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 know volume of 90% acetone and then stored at -4°C until analysis 24 hrs later.

~~a) **Parameter: NH4F**~~

~~VIMS Laboratory Method: *126*~~
~~EPA or other Reference Method: *170.1*~~
~~Method Reference: *US.EPA 1983. USEPA 600/4-79-020. Method 170.1*~~
~~Method Descriptor: *Filtered sample subjected to hypochlorite phenol…*~~
~~Preservation Method: *Samples filtered and stored at 4 °C up to 24 hours.*~~

~~b) **Parameter: NO2F**~~

~~VIMS Laboratory Method: *142*~~
~~EPA or other Reference Method: *167.1*~~
~~Method Reference: *US.EPA 1983. USEPA 600/4-79-020. Method 167.1*~~
~~Method Descriptor: *Filtered sample subjected to cadmium reduction column…*~~
~~Preservation Method: *Samples filtered and stored frozen at –20 °C up to 14 days.*~~

14) Field and Laboratory QAQC 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		

% Difference in Field and Lab replicates

			PO4 [%]	NO2 [%]	NO3 [%]	NH4 [%]	SiO4 [%]	Chl-a [%]
Annual	Field	Min	2	2	2	4	4	3
Annual	Field	Max	64	125	175	52	109	47
Annual	Field	Average	16	31	34	19	24	20
Annual	Lab	Min	5	2	1	2	3	2

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Annual	Lab	Max	87	127	69	68	78	87
Annual	Lab	Average	23	27	19	21	19	14

ii) **Laboratory variability** –
ELKNERR uses three of the ISCO samples to provide laboratory replicates (see table above, Lab Min, Max, Avg). 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.~~List specific number (10%) of laboratory replicates.~~

iii) **Inter-organizational splits** – Specify if samples were split and analyzed by two different labs.
~~iv)~~ There we no inter-organizational split samples in 2021

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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 2021 was found to be:

	PO4	NO2	NO3	NH4	SiO4
Average	87%	101%	111%	91%	100%
Minimum	40%	91%	94%	49%	46%
Maximum	115%	120%	133%	123%	170%

i) **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 2021 was found to be:

	PO4	NO2	NO3	NH4	SiO4
Average	104%	105%	106%	105%	106%
Minimum	90%	95%	97%	94%	86%
Maximum	111%	121%	111%	110%	125%

ii) **Cross calibration exercises** - *CBNERRVA participates in cross calibration exercises. Cross calibration exercises include the Chesapeake Bay Quarterly Split Sample Program and the US EPA Method Validation Studies.*
ELKNERR did not participate in any cross calibration excercises in 2021

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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
Cloud cover	
CCL	clear (0-10%)
CSP	scattered to partly cloudy (10-50%)
CPB	partly to broken (50-90%)
COC	overcast (>90%)
CFY	foggy
CHY	hazy
CCC	cloud (no percentage)
Precipitation	
PNP	none
PDR	drizzle
PLR	light rain
PHR	heavy rain
PSQ	squally
PFQ	frozen precipitation (sleet/snow/freezing rain)
PSR	mixed rain and snow
Tide stage	
TSE	ebb tide
TSF	flood tide
TSH	high tide
TSL	low tide
Wave height	
WH0	0 to <0.1 meters
WH1	0.1 to 0.3 meters
WH2	0.3 to 0.6 meters
WH3	0.6 to > 1.0 meters
WH4	1.0 to 1.3 meters
WH5	1.3 or greater meters
Wind direction	
N	from the north
NNE	from the north northeast
NE	from the northeast
ENE	from the east northeast
E	from the east
ESE	from the east southeast
SE	from the southeast
SSE	from the south southeast
S	from the south
SSW	from the south southwest
SW	from the southwest
WSW	from the west southwest
W	from the west
WNW	from the west northwest
NW	from the northwest
NNW	from the north northwest
Wind speed	
WS0	0 to 1 knot

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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 –

[Instructions/Remove: Use this section for further documentation of the data set. Include any additional notes regarding the data set in general, circumstances not covered by the flags and comment codes, or specific data that were coded with the CSM "See Metadata" comment code. Any data coded CSM must have a corresponding statement in this section. You may include the metadata worksheets here if so desired. You may also include information on major storms or precipitation events that could have affected the data recorded. ***You must include a table (not an image of a table) detailing sample/parameter collection and processing dates.*** Include the following excerpt.]

> 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 2021:** Samples are held at -4°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.

Grab samples

Sample collection date	Sample analysis date	
All	Chl_A	NO2, NO23, NH4, PO4, SiO4
1/12/2021	1/14/2021	1/15/2021
2/9/2021	2/15/2021	2/19/2021
3/16/2021	3/22/2021	2/23/2021
4/6/2021	4/26/2021	5/6/2021
5/4/2021	5/27/2021	5/20/2021
6/8/2021	7/2/2021	7/3/2021

7/7/2021	7/30/2021	8/1/2021	
8/3/2021	8/9/2021	9/9/2021	*
9/14/2021	10/7/2021	10/8/2021	
10/5/2021	10/7/2021	10/22/2021	
11/2/2021	11/23/2021	12/3/2021	*
12/14/2021	1/3/2022	1/14/2022	*

ISCO samples

Sample collection date	Sample analysis date		
ISCO 1-9	Chl_A	NO2, NO23, NH4, PO4, SiO4	
1/12/2021	1/14/2021	1/15/2021	
2/9/2021	2/15/2021	2/19/2021	
3/16/2021	3/22/2021	2/23/2021	
4/6/2021	4/26/2021	5/6/2021	
5/4/2021	5/27/2021	5/20/2021	
6/8/2021	7/2/2021	7/3/2021	
7/7/2021	7/30/2021	8/1/2021	
8/3/2021	8/9/2021	9/9/2021	*
9/14/2021	10/7/2021	10/8/2021	
10/5/2021	10/7/2021	10/22/2021	
11/2/2021	11/23/2021	12/3/2021	*
12/14/2021	1/3/2022	1/14/2022	*
ISCO 10-13	Chl_A	NO2, NO23, NH4, PO4, SiO4	
1/13/2021	1/14/2021	1/15/2021	
2/10/2021	2/15/2021	2/19/2021	
3/17/2021	3/22/2021	2/23/2021	
4/7/2021	4/26/2021	5/6/2021	
5/5/2021	5/27/2021	5/20/2021	
6/9/2021	7/2/2021	7/3/2021	
7/8/2021	7/30/2021	8/1/2021	
8/4/2021	8/9/2021	9/9/2021	*
9/15/2021	10/7/2021	10/8/2021	
10/6/2021	10/7/2021	10/22/2021	
11/3/2021	11/23/2021	12/3/2021	
12/15/2021	1/3/2022	1/14/2022	

*sample held longer than allowed by NERRS protocols