

**North Carolina National Estuarine Research Reserve (NOC) NERR Nutrient Metadata**  
**Months and year the documentation covers**  
**Latest Update:** June 6<sup>th</sup>, 2022

**I. Data Set and Research Descriptors**

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**2) Research objectives –**

The objective of this research is to provide baseline information on inorganic nutrient and chlorophyll *a* water quality status within the North Carolina (NOC) NERR. Water samples are collected, processed, and analyzed for the following parameters: ammonium (NH<sub>4</sub><sup>+</sup>), nitrite + nitrate (NO<sub>3</sub><sup>-</sup>), nitrite (NO<sub>2</sub><sup>-</sup>), ortho-phosphate (PO<sub>4</sub><sup>-</sup>), and chlorophyll *a* concentrations. Data collected will assist in understanding the impacts of anthropogenic impacts on the watersheds.

**a) Monthly grab**

Monthly grab samples are collected to quantify the spatial and temporal variability of selected nutrients and chlorophyll *a* concentrations in the water column at sites representative of the local estuarine system.

**b) Diel sampling program**

Once per month, 13 samples are collected at Research Creek every two hours and four minutes through a complete tidal cycle to quantify the short-term temporal variability of selected nutrients and chlorophyll *a* in the water column.

**3) Research methods –**

**a) Monthly grab sampling program:**

Monthly grab samples were taken at four stations within the Masonboro Island and Zeke's Island components of the NOCNERR. Samples are taken at each of the principal NOCNERR datasonde stations, which are Research Creek, Loosin Creek, Zeke's Basin and East Cribbings. Efforts are made to collect all samples within a 24-hour time period during an ebb tide. No distinctions are made between neap and spring tide conditions. Single samples are collected by hand at an approximate depth of 10 cm

at each site monthly, and triplicate (N=3) samples are collected at one site selected randomly, every other month. All samples are collected in amber, wide-mouth, Nalgene sample bottles that are previously acid washed (10% HCl), rinsed (3x) with distilled-deionized water, dried and followed by rinsing (3x) of ambient water prior to collection of the sample. Samples are immediately placed on ice, in a dark cooler and returned to the laboratory.

Once in the NOCNERR laboratory, samples are inverted and processed for chlorophyll *a* and nutrient analyses. Sample processing includes the filtration of samples, then either shipment to the Virginia Institute for Marine Science (VIMS) or in-house analysis (chlorophyll *a*). For chlorophyll *a*, volumes of 100 ml are filtered through a 25 mm Millipore glass microfiber filter using a vacuum pump and filtering apparatus. Filters are folded in half, placed in aluminum foil, and stored in a freezer at -20°C with a desiccant until time of sample analysis. For nutrient processing, samples are filtered through a 47mm Millipore MF membrane filter (mixed cellulose ester, pore size 0.45µm). The membrane filter is discarded and the liquid filtrate poured into a 125 ml acid washed Nalgene bottle and placed in the freezer until shipment time. Sample collection bottles are acid washed (10% HCl) and rinsed (3x) using distilled-deionized water between sampling events to avoid any contamination.

#### **b) Diel sampling program:**

Diel samples are taken at the Research Creek datasonde station, located in the Masonboro Island reserve. Diel Sample protocol was changed after January 2009. 13 samples are now collected over a complete tidal cycle at intervals of two hours and four minutes (from 12 samples every 2:11) using an ISCO 6700 auto-sampler. Samples are collected at a fixed depth (0.5 m) from the bottom, representing the water mass sampled by the datasonde. No distinction is made between neap and spring tide conditions. Sampling events are staggered approximately 30 days apart to the best of the research staff's ability. All samples are collected in 1000 ml polyethylene bottles that are acid washed (10% HCL), rinsed (3x) with distilled-deionized water and dried. Samples are stored inside the ISCO sampler and kept cool with ice. Once in the laboratory, samples are inverted and processed for nutrient and chlorophyll *a*, in the same manner as described in previous section; "monthly grab sampling program".

#### **4) Site location and character –**

The components of North Carolina's National Estuarine Research Reserve (from north to south) are: Currituck Banks, Rachel Carson, Masonboro Island, and Zeke's Island. They are located along the southeast Atlantic coast of the United States. Currently, only data from Masonboro Island and Zeke's Island components are transferred to the CDMO. The four monitoring sites are:

##### **a) Research Creek, Masonboro Island**

The first Masonboro Island site (formerly called Masonboro Island (MS)) is 0.72 km north east from the mouth of Whiskey Creek, and east of the Intracoastal Waterway (ICW), in a small navigable channel called Research Creek at 34°09'21.7" latitude and 77°50'59.9" longitude. The site typically has a salinity range of 20-35 ppt and a tidal range that averages around 1.2 meters. The sole source of freshwater is rain and salinity values as little as 10 ppt have been recorded during periods of heavy rain. The creek bottom is characterized by sand and detritus based sediment with areas of soft mud with a depth ranging from 0.2 to 2.6 m. *Spartina* spp. marsh and dunes surround the site, which is relatively unimpacted by manmade perturbations and it is not accessible to road traffic. The site does experience minimal boat traffic.

##### **b) Loosin Creek, Masonboro Island**

The second Masonboro Island site (added in 2002) is 1.2 km east of the ICW, and 2.5 km south west of Masonboro Inlet, in a small navigable channel called Loosin Creek at 34°10'20.0" latitude and 77°49'58.1" longitude. The site generally has a salinity range of 22-35 ppt and a tidal range that averages 1.2 meters. The sole source of freshwater is rain and salinity values as little as 15 ppt have been recorded during periods of heavy rain. The creek bottom is characterized by sand and detritus based sediment with areas of soft mud with a depth ranging from 0.1 to 2.5 m. *Spartina* spp. marsh and dunes surround the site,

which is relatively unimpacted by manmade perturbations and it is not accessible to road traffic. The site experiences minimal boat traffic.

**c) East Cribbings, Zeke's Island**

The first Zeke's Island site (formerly called Zeke's Island (ZI)) is located 1.8 km south of Federal Point boat launch in a tidal basin estuary at 33°56'23.5" latitude and 77°56'28.1" longitude. This site receives minimal freshwater input from leakage of the Cape Fear River through the 5.6 km rock jetty that separates the two bodies of water. The site typically has a salinity range of 15-33 ppt, although values as little as 10 ppt have been recorded. Tidal range averages 1.2 meters. Depth varies, but usually can be found to range from 0.5 to 2.7 meters. Bottom type substratum consists of large rocks (the cribbings) with sand and detritus based sediment. Marsh and dunes surround the site. It is not accessible to road traffic but experiences minimal boat traffic.

**d) Zeke's Basin, Zeke's Island**

The second Zeke's Island site (added in 2002) is located 0.8 km south east of the Federal Point boat launch in a tidal basin estuary at 33°57'17.0" latitude and 77°56'6.0" longitude. This site receives estuarine exchange from the Cape Fear River through the 5.6 km rock jetty that separates the river and shallow lagoonal basin. The site has a characteristic salinity range of 12-30 ppt, but values below 10 ppt have been observed and are often associated with periods of heavy rainfall. Tidal range averages 1.2 meters. Depth varies, but typically it can be found to range from 0.1 to 1.8 meters. Bottom type substratum consists of sand and detritus based sediment with a layer of soft anoxic mud. Marsh and dunes surround the site. It is not accessible to road traffic but experiences minimal boat traffic.

All NOC NERR historical nutrient/pigment monitoring stations:

| Station Code | SWMP Status | Station Name   | Location                            | Active Dates          | Reason Decommissioned | Notes |
|--------------|-------------|----------------|-------------------------------------|-----------------------|-----------------------|-------|
| NOCECNUT     | P           | East Cribbing  | 33° 56' 23.64 N,<br>77° 56' 27.96 W | 01/01/2002<br>00:00 - | NA                    | NA    |
| NOCLCNUT     | P           | Loosin Creek   | 34° 10' 19.92 N,<br>77° 49' 58.08 W | 02/01/2002<br>00:00 - | NA                    | NA    |
| NOCRCNUT     | P           | Research Creek | 34° 9' 21.60 N,<br>77° 50' 59.64 W  | 01/01/2002<br>00:00 - | NA                    | NA    |
| NOCZBNUT     | P           | Zeke's Basin   | 33° 57' 16.92 N,<br>77° 56' 6.00 W  | 03/01/2002<br>00:00 - | NA                    | NA    |

**5) Coded variable definitions –**

Station codes:

|          |                                                     |
|----------|-----------------------------------------------------|
| nocrcnut | North Carolina Reserve Research Creek Nutrient data |
| nocecnut | North Carolina Reserve East Cribbing Nutrient data  |
| noclcnut | North Carolina Reserve Loosin Creek Nutrient data   |
| noczbnut | North Carolina Reserve Zeke's Basin Nutrient data   |

Program Codes:

Monthly Grab Sampling = 1  
Monthly Diel Sampling = 2

See Section 15 for QAQC flag definitions

6) Data collection period –

a) Diel Sampling (all times in EST):

| <u>Station Code</u> | <u>Start Date</u> | <u>End Date</u> |
|---------------------|-------------------|-----------------|
| nocrcnut            | 1/19/21 12:40     | 1/20/21 13:28   |
| nocrcnut            | 2/16/21 12:15     | 2/17/21 13:03   |
| nocrcnut            | 3/23/21 14:45     | 3/24/21 15:33   |
| nocrcnut            | 4/19/21 14:13     | 4/20/21 15:01   |
| nocrcnut            | 5/26/21 11:53     | 5/27/21 12:41   |
| nocrcnut            | 6/23/21 9:55      | 6/24/21 12:07   |
| nocrcnut            | 7/26/21 9:39      | 7/27/21 10:27   |
| nocrcnut            | na                | na              |
| nocrcnut            | 9/23/21 10:55     | 9/24/21 11:43   |
| nocrcnut            | 10/25/21 11:40    | 10/26/21 12:28  |
| nocrcnut            | 11/22/21 12:07    | 11/23/21 12:55  |
| nocrcnut            | na                | na              |

b) Grab Sampling (all times in EST):

**East Cribbings**

| <u>Station Code</u> | <u>DateTimeStamp</u> | <u>Rep</u> |
|---------------------|----------------------|------------|
| nocecnut            | 1/19/21 15:19        | 1          |
| nocecnut            | 2/16/21 14:15        | 1          |
| nocecnut            | 4/19/21 16:00        | 1          |
| nocecnut            | 5/19/21 15:00        | 1          |
| nocecnut            | 6/24/21 10:50        | 1          |
| nocecnut            | 7/27/21 13:13        | 1          |
| nocecnut            | 8/24/21 16:20        | 1          |
| nocecnut            | 9/23/21 13:05        | 1          |
| nocecnut            | 10/25/21 13:15       | 1          |
| nocecnut            | 11/22/21 13:45       | 1          |
| nocecnut            | 11/22/21 13:46       | 2          |
| nocecnut            | 11/22/21 13:47       | 3          |
| nocecnut            | 12/6/21 12:10        | 1          |

**Loosin Creek**

| <u>Station Code</u> | <u>DateTimeStamp</u> | <u>Rep</u> |
|---------------------|----------------------|------------|
| noclcnut            | 1/19/21 14:00        | 1          |
| noclcnut            | 2/16/21 12:40        | 1          |
| noclcnut            | 3/24/21 14:05        | 1          |
| noclcnut            | 4/19/21 15:00        | 1          |
| noclcnut            | 5/19/21 14:33        | 1          |
| noclcnut            | 5/19/21 14:34        | 2          |
| noclcnut            | 5/19/21 14:35        | 3          |
| noclcnut            | 6/23/21 10:25        | 1          |
| noclcnut            | 7/27/21 11:06        | 1          |

|         |                |   |
|---------|----------------|---|
| noclnut | 8/24/21 10:42  | 1 |
| noclnut | 9/23/21 11:15  | 1 |
| noclnut | 9/23/21 11:16  | 2 |
| noclnut | 9/23/21 11:17  | 3 |
| noclnut | 10/25/21 12:10 | 1 |
| noclnut | 11/22/21 11:45 | 1 |
| noclnut | 12/6/21 10:50  | 1 |

#### **Research Creek**

| Station Code | DateTimeStamp  | Rep |
|--------------|----------------|-----|
| nocrcnut     | 1/19/21 14:45  | 1   |
| nocrcnut     | 2/16/21 12:49  | 1   |
| nocrcnut     | 3/24/21 13:45  | 1   |
| nocrcnut     | 3/24/21 13:46  | 2   |
| nocrcnut     | 3/24/21 13:47  | 3   |
| nocrcnut     | 4/19/21 14:15  | 1   |
| nocrcnut     | 5/19/21 14:23  | 1   |
| nocrcnut     | 6/23/21 9:50   | 1   |
| nocrcnut     | 7/27/21 11:30  | 1   |
| nocrcnut     | 8/24/21 10:31  | 1   |
| nocrcnut     | 9/23/21 11:01  | 1   |
| nocrcnut     | 10/25/21 11:45 | 1   |
| nocrcnut     | 11/22/21 13:06 | 1   |
| nocrcnut     | 12/6/21 11:00  | 1   |

#### **Zekes Basin**

| Station Code | DateTimeStamp  | Rep |
|--------------|----------------|-----|
| noczbnut     | 1/19/21 15:45  | 1   |
| noczbnut     | 1/19/21 15:46  | 2   |
| noczbnut     | 1/19/21 15:47  | 3   |
| noczbnut     | 2/16/21 14:20  | 1   |
| noczbnut     | 4/19/21 16:15  | 1   |
| noczbnut     | 5/19/21 15:26  | 1   |
| noczbnut     | 6/23/21 11:45  | 1   |
| noczbnut     | 7/27/21 13:23  | 1   |
| noczbnut     | 7/27/21 13:24  | 2   |
| noczbnut     | 7/27/21 13:25  | 3   |
| noczbnut     | 8/24/21 16:40  | 1   |
| noczbnut     | 9/23/21 13:23  | 1   |
| noczbnut     | 10/25/21 13:40 | 1   |
| noczbnut     | 11/22/21 13:55 | 1   |
| noczbnut     | 12/6/21 11:57  | 1   |

7) Associated researchers and projects--

As part of the SWMP long-term monitoring program, NOC 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](http://www.nerrsdata.org). Additional projects are ongoing and continually changing. Check with the Research Coordinator for an updated list of research (see section I.1.)

#### **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](http://www.nerrsdata.org); *accessed* 12 October 2016.

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](http://www.nerrsdata.org). Data are available in comma separated version format

## **II. Physical Structure Descriptors**

#### **9) Entry verification –**

Nutrient data are entered into a Microsoft Excel worksheet and processed using the NutrientQAQC Excel macro. The NutrientQAQC macro sets up the data worksheet, metadata worksheets, and MDL worksheet; adds chosen parameters and facilitates data entry; allows the user to set the number of significant figures to be reported for each parameter and rounds using banker's rounding rules; allows the user to input MDL values and then automatically flags/codes measured values below MDL and inserts the MDL; calculates parameters chosen by the user and automatically flags/codes for component values below MDL, negative calculated values, and missing data; allows the user to apply QAQC flags and codes to the data; produces summary statistics; graphs selected parameters for review; and exports the resulting data file to the CDMO for tertiary QAQC and assimilation into the CDMO's authoritative online database. Byron Toothman and Heather Wells were responsible for data management during 2021.

## 10) Parameter titles and variable names by category –

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 |
| *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 |
|----------------|--------|------|

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.

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            |

### b) Calculated parameters

|      |            |
|------|------------|
| NO3F | NO23F-NO2F |
| DIN  | NO23F+NH4F |

## 12) Limits of detection –

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    | Date Revisited |
|-----------|------------|----------|--------|----------------|
| CHLA_N    | 01/01/21   | 12/31/21 | 0.4    | 12/16/2019     |
| NH4F      | 01/01/21   | 12/31/21 | 0.0062 | *              |
| NO23F     | 01/01/21   | 12/31/21 | 0.0055 | *              |
| NO2F      | 01/01/21   | 12/31/21 | 0.0016 | *              |
| PO4F      | 01/01/21   | 12/31/21 | 0.0016 | *              |

## 13) Laboratory methods –

### a) Parameter: Ammonia (NH4F)

Method References: Virginia Institute of Marine Science Analytical Service Center. U.S. EPA. 1974. Methods for Chemical Analysis of Water and Wastes, pp. 168-174.

Standard Methods for the Examination of Water and Wastewater, 14th edition. p 410. Method 418A and 418B (1975). Annual Book of ASTM Standards, Part 31. "Water", Standard 1426-74, Method A, p 237 (1976). EPA 600/R-97/072 Method 349.0. Determination of Ammonia in Estuarine and Coastal Waters by Gas Segmented Continuous Flow Colorimetric Analysis. IN: Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices - 2nd Edition. National Exposure Research Laboratory, Office of Research and Development U.S. EPA, Cincinnati, Ohio 45268.

Method Descriptor: Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The blue color formed is intensified with sodium nitroprusside. Reaction is heat catalyzed at 37°C and is measured colorimetrically at 660 nm. The range is 0.01 - 2.0 mg/L.

Preservation Method: A 100 ml volume of sample is filtered through a Whatman glass fiber filter (0.45 µm pore size, 47 mm diameter) using a vacuum pump. The pooled filtrate is then filtered through a Millipore membrane filter (0.45 µm pore size, 47 mm diameter). The liquid volume is then poured into a Nalgene bottle and stored at -20°C until sent for analysis.

**b) Parameter: Nitrate + Nitrite (NO<sub>2</sub>3F), Nitrate (NO<sub>3</sub>F), and Nitrite (NO<sub>2</sub>F)**

Method References: Virginia Institute of Marine Science Analytical Service Center.

SKALAR Method: Nitrate + Nitrite/ Total Dissolved Nitrogen Catnr. 461-353.2 issue 120293/MH/93128060. SKALAR Method 467. U.S. EPA. 1974 Methods for Chemical Analysis of Water and Wastes, pp. 207 -212. Wood, E.D., F.A.G. Armstrong and F.A. Richards. 1967.

Determination of nitrate in seawater by cadmium-copper reduction to nitrite. J. Mar. Biol. Assoc. U.K. 47: 23. Grasshoff, K., M. Ehrhardt and K. Kremling. 1983. Methods of Seawater Analysis. Verlag Chemie, Federal Republic of Germany. 419 pp. EPA 600/R-97/072 Method 353.4

Determination of Nitrate and Nitrite in Estuarine and Coastal Waters by Gas Segmented Flow Colorimetric Analysis. IN: Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices - 2nd Edition. National Exposure Research Laboratory, Office of Research and Development U.S. EPA, Cincinnati, Ohio 45268.

Method Descriptor: Nitrate is reduced to nitrite by a copper/cadmium reductor column. The nitrite ion then reacts with sulfanilimide to form a diazo compound. This compound then couples with n-1-naphthylenediamine dihydrochloride to form a reddish/purple azo dye and is read colorimetrically at 540 nm. Nitrate concentration is obtained by subtracting the corresponding nitrite value from the NO<sub>3</sub><sup>-</sup> + NO<sub>2</sub><sup>-</sup> concentration. The color development chemistry is the same as that used in Nitrite. Range is 0-1.2 mg/L.

Preservation Method: A 100 ml volume of sample is filtered through a Whatman glass fiber filter (0.45 µm pore size, 47 mm diameter) using a vacuum pump. The pooled filtrate is then filtered through a Millipore membrane filter (0.45 µm pore size, 47 mm diameter). The liquid volume is then poured into a Nalgene bottle and stored at -20°C until sent for analysis.

**c) Parameter: Orthophosphate (PO<sub>4</sub>)**

Method References: Virginia Institute of Marine Science Analytical Service Center.

SKALAR Method: O-Phosphate / Total Phosphate Catnr. 503-365.1, issue 042993/MH/93-Demo1. Murphy, J. and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chim. Acta* 27: 31-36. EPA 600/R-97/072 Method 365.5 Determination of Orthophosphate in Estuarine and Coastal Waters by Automated Colorimetric Analysis. IN: Methods for the Determination of Chemical Substances in Marine and Estuarine

Environmental Matrices - 2nd Edition. National Exposure Research Laboratory, Office of Research and Development. U.S. EPA, Cincinnati, Ohio 45268.

Method Descriptor: Ammonium molybdate and antimony potassium tartrate react in a sulfuric acid environment to form an antimony-phospho-molybdo complex, which is reduced to a blue colored complex by ascorbic acid. Reaction is heat catalyzed at 40°C and measured colorimetrically at 880 nm. The range is 1-50 ppb.

Preservation Method: A 100 ml volume of sample is filtered through a Whatman glass fiber filter (0.45 µm pore size, 47 mm diameter) using a vacuum pump. The pooled filtrate is then filtered through a Millipore membrane filter (0.45 µm pore size, 47 mm diameter). The liquid volume is then poured into a Nalgene bottle and stored at -20°C until sent for analysis.

**d) Parameter: Chlorophyll *a* (CHLA\_N)**

Method References: Virginia Institute of Marine Science Analytical Service Center.

Strickland, J.D.H., and Parson, T.R. 1972. A Practical Handbook of Seawater Analysis. Fish. Res. Bd. Canada 167:310.

TD-700 Laboratory Fluorometer Operating Manual. Version 1.8. July 7, 1999. Turner Designs, 845 West Maude Avenue, Sunnyvale, CA 94086.

EPA /600/ R-97/072 - Method 445.0. *In Vitro* Determination of Chlorophyll *a* and Pheophytin *a* in Marine and Freshwater Algae by Fluorescence. Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices Revision 1.2. September 1997.

Using the Turner Designs Model 10 Analog, The 10AU Digital, Or the TD-700 Fluorometer with EPA Method 445.0. January 19, 1999. Turner Designs, 845 West Maude Avenue, Sunnyvale, CA 94086.

Method Descriptor: Turner Design fluorometer method requires filtering a known quantity of water through a glass fiber filter (4.7 cm GF/F). This filter is later ground with a tissue grinder made of teflon/glass. Approximately 1-3 ml of 90% acetone are added to the filter before grinding. Acetone is also used to wash the filter into 17 x 150 test tube with tight fitting cap. The sample is steeped at least 2 hours and not exceeding 24 hours at 4°C, in the dark. The samples are centrifuged and read on a spectrophotometer or fluorometer. If the samples cannot be read within that time period, storage in the freezer at -20°C for a few days is acceptable.

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

**a) Precision**

- i) **Field variability** – All diel samples are taken as single samples and monthly grab are replicated with field triplicates from randomly selected sites at least every other month (20.7%). Replicates are collected as duplicates or triplicates and efforts are made to collect these one minute later than initial sample.
- ii) **Laboratory variability** – laboratory replication is 10% for nutrient samples, chlorophyll samples are not replicated
- iii) **Inter-organizational splits** – no samples are split between different laboratories for analyses

**b) Accuracy**

- i) **Sample spikes** – accepting data at 100 % +/- 20 %, samples are typically in the 90-110 % range
- ii) **Standard reference material analysis** – no NOCNERR samples are sent to EPA for analyses

**Cross calibration exercises** – NOCNERR is not participating in any cross calibration exercises

**15) QAQC flag definitions –**

QAQC flags provide documentation of the data and are applied to individual data points by insertion into the parameter's associated flag column (header preceded by an F\_). QAQC flags are applied to the nutrient data during secondary QAQC to indicate data that are out of sensor range low (-4), rejected due to QAQC checks (-3), missing (-2), optional and were not collected (-1), suspect (1), and that have been corrected (5). All remaining data are flagged as having passed initial QAQC checks (0) when the data are uploaded and assimilated into the CDMO ODIS as provisional plus data. The historical data flag (4) is used to indicate data that were submitted to the CDMO prior to the initiation of secondary QAQC flags and codes (and the use of the automated primary QAQC system for WQ and MET data). This flag is only present in historical data that are exported from the CDMO ODIS.

- 4 Outside Low Sensor Range
- 3 Data Rejected due to QAQC
- 2 Missing Data
- 1 Optional SWMP Supported Parameter
- 0 Data Passed Initial QAQC Checks
- 1 Suspect Data
- 4 Historical Data: Pre-Auto QAQC
- 5 Corrected Data

#### 16) QAQC code definitions –

QAQC codes are used in conjunction with QAQC flags to provide further documentation of the data and are also applied by insertion into the associated flag column. There are three (3) different code categories, general, sensor, and comment. General errors document general problems with the sample or sample collection, sensor errors document common sensor or parameter specific problems, and comment codes are used to further document conditions or a problem with the data. Only one general or sensor error and one comment code can be applied to a particular data point. However, a record flag column (F\_Record) in the nutrient data allows multiple comment codes to be applied to the entire data record.

##### General errors

|     |                                                               |
|-----|---------------------------------------------------------------|
| GCM | Calculated value could not be determined due to missing data  |
| GCR | Calculated value could not be determined due to rejected data |
| GDM | Data missing or sample never collected                        |
| GQD | Data rejected due to QA/QC checks                             |
| GQS | Data suspect due to QA/QC checks                              |
| GSM | See metadata                                                  |

##### Sensor errors

|     |                                                                       |
|-----|-----------------------------------------------------------------------|
| SBL | Value below minimum limit of method detection                         |
| SCB | Calculated value could not be determined due to a below MDL component |
| SCC | Calculation with this component resulted in a negative value          |
| SNV | Calculated value is negative                                          |
| SRD | Replicate values differ substantially                                 |
| SUL | Value above upper limit of method detection                           |

##### Parameter Comments

|     |                                               |
|-----|-----------------------------------------------|
| CAB | Algal bloom                                   |
| CDR | Sample diluted and rerun                      |
| CHB | Sample held beyond specified holding time     |
| CIP | Ice present in sample vicinity                |
| CIF | Flotsam present in sample vicinity            |
| CLE | Sample collected later/earlier than scheduled |

|     |                                      |
|-----|--------------------------------------|
| CRE | Significant rain event               |
| CSM | See metadata                         |
| CUS | Lab analysis from unpreserved sample |

#### Record comments

|     |                                               |
|-----|-----------------------------------------------|
| CAB | Algal bloom                                   |
| CHB | Sample held beyond specified holding time     |
| CIP | Ice present in sample vicinity                |
| CIF | Flotsam present in sample vicinity            |
| CLE | Sample collected later/earlier than scheduled |
| CRE | Significant rain event                        |
| CSM | See metadata                                  |
| CUS | Lab analysis from unpreserved sample          |

#### *Cloud cover*

|     |                                     |
|-----|-------------------------------------|
| CCL | clear (0-10%)                       |
| CSP | scattered to partly cloudy (10-50%) |
| CPB | partly to broken (50-90%)           |
| COC | overcast (>90%)                     |
| CFY | foggy                               |
| CHY | hazy                                |
| CCC | cloud (no percentage)               |

#### *Precipitation*

|     |                                                 |
|-----|-------------------------------------------------|
| PNP | none                                            |
| PDR | drizzle                                         |
| PLR | light rain                                      |
| PHR | heavy rain                                      |
| PSQ | squally                                         |
| PFQ | frozen precipitation (sleet/snow/freezing rain) |
| PSR | mixed rain and snow                             |

#### *Tide stage*

|     |            |
|-----|------------|
| TSE | ebb tide   |
| TSF | flood tide |
| TSH | high tide  |
| TSL | low tide   |

#### *Wave height*

|     |                       |
|-----|-----------------------|
| WH0 | 0 to <0.1 meters      |
| WH1 | 0.1 to 0.3 meters     |
| WH2 | 0.3 to 0.6 meters     |
| WH3 | 0.6 to > 1.0 meters   |
| WH4 | 1.0 to 1.3 meters     |
| WH5 | 1.3 or greater meters |

#### *Wind direction*

|     |                          |
|-----|--------------------------|
| N   | from the north           |
| NNE | from the north northeast |
| NE  | from the northeast       |
| ENE | from the east northeast  |
| E   | from the east            |
| ESE | from the east southeast  |
| SE  | from the southeast       |
| SSE | from the south southeast |
| S   | from the south           |
| SSW | from the south southwest |
| SW  | from the southwest       |
| WSW | from the west southwest  |

|                   |                          |
|-------------------|--------------------------|
| W                 | from the west            |
| WNW               | from the west northwest  |
| NW                | from the northwest       |
| NNW               | from the north northwest |
| <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 NO<sub>3</sub>F 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 -20°C. NERRS SOP allows nutrient samples to be held for up to 28 days (CHLA for 30) at -20°C, plus allows for up to 5 days for collecting, processing, and shipping samples. Samples held beyond that time period are flagged suspect <1> and coded (CHB). If measured values were below MDL, this resulted in <-4> [SBL] (CHB) flagging/coding.

| Sample Descriptor          | Date Analyzed    |                  |                  |                  |                   |
|----------------------------|------------------|------------------|------------------|------------------|-------------------|
|                            | PO4F             | NH4F             | NO2F             | NO3F             | CHLA_N            |
| 1/19/2021 grab samples     | 2/17/2021        | 2/17/2021        | 2/17/2021        | 2/17/2021        | 2/2/2021          |
| 1/19-20/2021 diel samples  | 2/17/2021        | 2/17/2021        | 2/17/2021        | 2/17/2021        | 2/2/2021          |
| 2/16/2021 grab samples     | 3/16/2021        | 3/16/2021        | 3/16/2021        | 3/16/2021        | 2/23/2021         |
| 2/16-17/2021 diel samples  | 3/16/2021        | 3/16/2021        | 3/16/2021        | 3/16/2021        | 2/23/2021         |
| 3/24/2021 grab samples     | 4/14/2021        | 4/14/2021        | 4/14/2021        | 4/14/2021        | 3/30/2021         |
| 3/23-24/2021 diel samples  | 4/14/2021        | 4/14/2021        | 4/14/2021        | 4/14/2021        | 3/30/2021         |
| 4/19/2021 grab samples     | 4/29/2021        | 4/29/2021        | 4/29/2021        | 4/29/2021        | 5/5/2021          |
| 4/19-21/2021 diel samples  | 4/29/2021        | 4/29/2021        | 4/29/2021        | 4/29/2021        | 5/5/2021          |
| 5/19/2021 grab samples     | 6/15/2021        | 6/15/2021        | 6/15/2021        | 6/15/2021        | 6/1/2021          |
| 5/26-27/2021 diel samples  | 6/15/2021        | 6/15/2021        | 6/15/2021        | 6/15/2021        | 6/1/2021          |
| 6/23/2021 grab samples     | <b>8/16/2021</b> | <b>8/16/2021</b> | <b>8/16/2021</b> | <b>8/16/2021</b> | <b>7/20/2021</b>  |
| 6/23-24/2021 diel samples  | <b>8/16/2021</b> | <b>8/16/2021</b> | <b>8/16/2021</b> | <b>8/16/2021</b> | <b>7/20/2021</b>  |
| 7/27/2021 grab samples     | 8/27/2021        | 8/27/2021        | 8/27/2021        | 8/27/2021        | 8/16/2021         |
| 7/26-27/2021 diel samples  | 8/27/2021        | 8/27/2021        | 8/27/2021        | 8/27/2021        | 8/16/2021         |
| 8/24/2021 grab samples     | 10/5/2021        | 10/5/2021        | 10/5/2021        | 10/5/2021        | 8/31/2021         |
| 9/23/2021 samples          | 10/5/2021        | 10/5/2021        | 10/5/2021        | 10/5/2021        | 9/28/2021         |
| 9/23-24/2021 diel samples  | 10/5/2021        | 10/5/2021        | 10/5/2021        | 10/5/2021        | 9/28/2021         |
| 10/25/2021 grab samples    | 11/19/2021       | 11/19/2021       | 11/19/2021       | 11/19/2021       | 11/4/2021         |
| 10/25-26/2021 diel samples | 11/19/2021       | 11/19/2021       | 11/19/2021       | 11/19/2021       | 11/4/2021         |
| 11/22/2021 grab samples    | <b>1/13/2022</b> | <b>1/13/2022</b> | <b>1/13/2022</b> | <b>1/13/2022</b> | <b>12/13/2021</b> |
| 11/22-23/2021 diel samples | <b>1/13/2022</b> | <b>1/13/2022</b> | <b>1/13/2022</b> | <b>1/13/2022</b> | <b>12/13/2021</b> |
| 12/6/2021 grab samples     | <b>1/13/2022</b> | <b>1/13/2022</b> | <b>1/13/2022</b> | <b>1/13/2022</b> | <b>12/13/2021</b> |

\* Samples held beyond protocol hold time indicated in bold.

#### Missing Samples

Diel samples not collected due to ISCO Auto-sampler malfunction:

2/16/21 20:31

2/16/21 22:35

2/17/21 0:39

2/17/21 2:43

2/17/21 4:47

2/17/21 6:51

2/17/21 8:55

2/17/21 10:59

3/24/21 15:33

August and January deployments.