

Chesapeake Bay Maryland (CBM) NERR Nutrient Metadata
January – December 2009
Latest Update: May 24, 2013

I. Data Set and Research Descriptors

1) Principal investigator(s) and contact persons –

a) Reserve Contacts

Patricia Delgado, Research Coordinator
Chesapeake Bay National Estuarine Research Reserve Maryland
Maryland Department of Natural Resources
580 Taylor Avenue, E-2
Annapolis, MD 21401
Phone: 410-260-8983
e-mail: pdelgado@dnr.state.md.us

Elizabeth Ebersole, Manager
Chesapeake Bay National Estuarine Research Reserve Maryland
Maryland Department of Natural Resources
580 Taylor Avenue, E-2
Annapolis, MD 21401
Phone: 410-260-8720
e-mail: bebersole@dnr.state.ms.us

John Zimmerelli, Research Technician
Lauren Cunningham, Research Technician
Maryland Department of Natural Resources
1919 Lincoln Drive
Annapolis, Maryland 21401
Phone: (410) 263-3369
Fax: (410) 263-2468
e-mail: jzimmerelli@dnr.state.md.us
e-mail: lcunningham@dnr.state.md.us

b) Laboratory Contact

Carl Zimmermann
Chesapeake Biological Laboratory
PO Box 38
1 Williams St.
Solomons, Maryland 20688
Phone: 410-326-7252
e-mail: carlz@cbl.umces.edu

2) Research objectives

The principal objectives of this effort are to provide baseline nutrient concentration data at fixed sites throughout the Chesapeake Bay National Estuarine Research Reserve in Maryland's (CBM NERR) tidal waters. This information supports the National Estuarine Research Reserve's (NERR) System Wide Monitoring Program (SWMP) and supplements water quality information taken at the same fixed sites.

Specific goals of this effort include: 1) tracking and recording nutrient conditions to better understand and explain current conditions with the aid of additional data (water quality and meteorological) collected concurrently 2) creating a database capable of detecting long-term changes in nutrient conditions of these systems 3) recording and identifying temporal and spatial differences in nutrient conditions to include changes on a diel time frame and to collect ancillary data in support of other research efforts.

At CBM NERR, water quality and nutrient data were collected at four sites during 2009. Three sites are at the Jug Bay Component of the Reserve and one site is at the Otter Point Creek Component. The three sites at Jug Bay were selected in an effort to examine water quality and nutrient information across different spatial scales and at sites demonstrating different levels of anthropogenic activities. The site at Otter Point Creek was selected to provide baseline information for the Otter Point Creek site and to use for comparison to one or more of the Jug Bay sites.

a) Monthly Grab Sampling Program

The goals of the monthly grab samples are to create a long-term database of nutrient information at each site for the purpose of detecting temporal and spatial changes. This nutrient information supplements water chemistry data to provide a complete picture of water quality at the NERR sites.

b) Diel Sampling Program

The goal of the diel sampling is to catalog short-term variability in nutrient concentrations across different tidal cycles at the Iron Pot Landing site. This site was moved from the Jug Bay Railroad site to the Iron Pot Landing location in September 2007. This temporal nutrient data provides a comprehensive look at the variation in water quality over a 24- hour period.

3) Research methods

a) Monthly Grab Sampling Program

Monthly nutrient grab samples were taken at the four principal water quality monitoring stations: Mataponi Creek, Railroad Bridge, Iron Pot Landing, and Otter Point Creek. NERR protocol calls for duplicate monthly nutrient grab samples taken at all four sites on the same day within 3 hours of slack tide. Due to the location of the Jug Bay sites being 2 to 3 hours away from the Otter Point Creek site and because they are completely different systems, Otter Point Creek was not sampled on the same day as the other three sites. Instead all three Jug Bay sites were sampled on the same day, while the Otter Point Creek was sampled separately. In accordance to NERR protocol, duplicate samples were taken once monthly at each of the four sites and analyzed for chlorophyll a concentrations, nitrate, nitrite, ammonium, and ortho-phosphate. Single grab samples were also taken mid-month (biweekly). Additional parameters to include total suspended solids, total volatile solids and total nitrogen, particulate organic nitrogen, particulate organic carbon and total and dissolved organic phosphorus were also sampled at the same time.

Duplicate whole water samples were collected using a horizontal Alpha Bottle lowered to the depth of the YSI instrument. A sample was captured in the Alpha Bottle at the same time the YSI 6600V2 logged a water quality reading. This sample was decanted from the Alpha Bottle to a one liter Nalgene bottle for filtering. After decanting the first sample the Alpha Bottle was lowered a second time to capture the duplicate sample. Nalgene bottles are only washed with Liquinox laboratory soap, rinsed three to five times with tap water and then rinsed three to five times with DI water. Acid washing is not used due to Chlorophyll sampling from the same bottle, to reduce the licing of cells from residual acid. The filter units are acid washed, barring the chlorophyll filter frit, with liquinox soap, rinsed three times with tap water, rinsed three times with 10% HCl solution, rinsed three times with tap again, and finally a rinse of DI water three times. Samples are placed on ice and stored in a freezer at the office until transport on ice to the analytical lab.

b) Diel Sampling Program

In addition to discrete grab samples taken at each of the four sites, additional diel data was collected once monthly beginning on February 25, 2009 at the Iron Pot Landing station located at the Jug Bay Component. Particulate organic nitrogen and carbon were not reported for these samples. Using an ISCO automated sampler field teams conducted diel sampling as per NERR protocol. The unattended sampler, set at a depth of approximately 0.3 meters off the bottom, was programmed to sample every two and one half hours, over a twenty-four hour period, starting at a scheduled YSI 6600V2 data collection interval. The ISCO sampler uses 1000mL plastic ISCO bottles. The bottles were only washed with Liquinox laboratory soap, rinsed three to five times with tap water and then rinsed three to five times with DI water. Acid washing is not used due to Chlorophyll sampling from the same bottle, to reduce the leaching of cells from residual acid. The filter units are acid washed, barring the chlorophyll filter frit, with liquinox soap, rinsed three times with tap water, rinsed three times with 10% HCl solution, rinsed three times with tap again, and finally a rinse of DI water three times. Samples are placed on ice and stored in a freezer at the office until courier transports them on ice to the lab. A two-liter bottle of frozen water was placed in the sample compartment of these samplers to preserve collected samples over the 24hr deployment period. During each 24hr deployment, 11 whole water samples were collected and stored in the automated sampler until retrieved and taken back to the lab for processing.

All whole water samples (biweekly, monthly duplicate, and monthly diel) were collected in the field and either filtered at the site or preserved on ice and taken back to the field office for filtering and sample preparation later that same day.

See the following filtration Standard Operating Procedure:

A. Particulate sample filtration, processing and storage

1. **Chlorophyll**

Chlorophyll samples are filtered in the same manner for all programs.

- a) For every depth sampled, clean a 47mm bell with deionized (DI) water. Set up unit for filtering. Be sure that there is a trap in line between the manifold and the vacuum source.
- b) Place a Whatman 47mm GF/F glass fiber filter pad (pore size = 0.7 μm) on the filter frit. Always use clean forceps when handling the filter pads.
- c) Mix sample thoroughly by agitating and shaking the sample bottle vigorously, then rinse graduated cylinder three times with sample.
- d) Agitate the sample again before measuring in the graduated cylinder. Fill graduated cylinder with sample and filter desired volume through filtration unit. Be sure to use a graduate that is close to the volume being filtered (ex: if you are only filtering 80 ml of sample use a 100 ml graduate). **Keep the vacuum pressure below 10 inches of Hg** (around 8" Hg is good).
- e) Filter sufficient volume of sample (50 - 1500 ml) to solidly color the filter pad.
- f) Record the total volume filtered on the foil square.
- g) Agitate the squirt bottle of MgCO_3 , as it settles rapidly. Add approximately 1 ml of MgCO_3 suspension (1.0 g MgCO_3 in 100 ml of DI water) to the last 25 ml of sample in the filtration bell.

NOTE: Samples for dissolved parameters are not to be collected from this filtrate.

- h) Using forceps (1 or 2 pair), fold filter in half with sample inside and remove filter pad.

- i) Place pad in pre-marked foil square, and carefully fold foil square in thirds, horizontally. Then fold the ends in to seal the filter inside. Be sure forceps do not touch sample residue on the filter pads, because the sample will adhere to the forceps.
- j) Be sure that the foil square is marked with date, station, depth of sample, volume of sample filtered, and sample number. Place foil packet into zip-lock plastic bag and place in an ice chest.
- k) Place the foils in the appropriately labeled bag in the Field Office freezer when you return to the office.
- l) Record sample station number, date, volume filtered (L), depth (m), layer, start time, end time and field scientist sign-off on the volume sheet. This sheet is submitted to the laboratory with the samples

NOTE: The filter pads for chlorophyll samples should be exposed to as little direct sunlight as possible. Store as soon as possible.

2. **Particulate Carbon/ Particulate Nitrogen (PC/PN)**

PC/PN samples are filtered in the same manner for all programs.

- a) Follow steps A.1.a. through A.1.d. above setting up two 25 mm filter bells using two pre-combusted 25 mm GF/F filters (pore size = 0.7 μ m). The PC/PN pads come from CBL.
- b) Filter 10-200 ml through each filter. Filter enough sample to leave noticeable color on the filter pad.
- c) Make sure filter is sucked dry and the **same volume is filtered for both pads.**
- d) Record the volume filtered (total volume through one pad - do not add the volumes for the 2 pads together) on the foil square.

NOTE: Samples for dissolved parameters are not to be collected from this filtrate.

- e) Using forceps, fold each filter in half.
- f) Place both filters in a foil square labeled with date, CBL sample number, station, sample layer, PC/PN, and volume filtered. Be sure that the pads are not overlapping in the foil square to keep them from freezing together.
- g) Fold the foil square as described in step A.1.i. above and then place folded foil in zip-lock bag and put in an ice chest.
- h) Place the foils in the appropriately labeled bag in the Field Office freezer when you return to the office.
- i) Record sample station number, date, volume filtered (L), depth (m), layer, start time, end time and field scientist sign-off on the volume sheet. This sheet is submitted to the laboratory with the samples

3. **Particulate Phosphorus/ Particulate Inorganic Phosphorus (PP/PIP)**

- a) Follow steps A.1.a. through A.1.d. above setting up and rinsing two 47 mm filter bells and flasks. The filters used are two pre-combusted Whatman 47 mm GF/F filters.
- b) Filter 50 ml of sample through each filter pad.
- c) Use the filtrate as an equipment rinse and discard.
- d) Then filter enough additional (another 50 - 450 ml) to leave a noticeable color on the filter pad.

- e) Record the **total** volume filtered through each pad being sure to add the 50 ml rinse water (total volume through one pad – do not add the volumes for the 2 pads together) on the foil square.
- f) **Use this filtrate to fill up the tubes for the dissolved parameter analysis. See section C (Filtered dissolved nutrient sample collection) below.**
- g) After collecting filtrate, make sure filter is sucked dry.
- h) Rinse the filter pad using at least three - 10 ml rinses of DI water, sucking the pad dry after each rinse.
- i) Using forceps, fold each filter in half.
- j) Place both filters in a foil square labeled with date, PP/PIP, CBL sample number, station, sample layer, and volume filtered (this is the total volume of sample through each pad, including the initial 50 ml rinse). Be sure that the pads are not overlapping in the foil square to keep them from freezing together.
- k) Fold the foil square as described in step A.1.i. above. Place foil square in zip-lock bag and place in an ice chest.
- l) Place the foils in the appropriately labeled bag in the Field Office freezer when you return to the office.
- m) Record sample station number, date, volume filtered (L), depth (m), layer, start time, end time and field scientist sign-off on the volume sheet. This sheet is submitted to the laboratory with the samples.

4. **Total Suspended Solids/ Volatile Suspended Solids (TSS/VSS)**

- a) Follow steps A.1.a. through A.1.d. above, setting up and rinsing one 47 mm filter bell and flask. The filter used is a pre-combusted and pre-weighed 47 mm GF/F filters (pore size = 0.7 μ m). The VSS pads come in individually numbered petri dishes from CBL. Remove one pad from its individual petri dish and place on the filter screen. Record the pad number from the petri dish on the TSS/VSS foil label in the space marked "Pad #".
- b) Filter 50 - 500 ml and filter through the filter pad leaving a noticeable color on the pad.
- c) Make sure filter is sucked dry and rinse the filter pad using at least three - 10 ml rinses of DI water, sucking the pad dry after each rinse.
- d) Using forceps, fold the filter in half. Place the filter in a foil square labeled with date, TSS/VSS, CBL sample number, station, sample layer, and volume filtered, and VSS pad number.
- e) Fold the foil square as described in step A.1.i. above. Place foil square in zip-lock bag and place in an ice chest.
- f) Place the foils in the appropriately labeled bag in the Field Office freezer when you return to the office.
- g) Record sample station number, date, volume filtered (L), depth (m), layer, start time, end time and field scientist sign-off on the volume sheet. This sheet is submitted to the laboratory with the samples.

B. Dissolved nutrient sample filtration & collection

NOTE: The filtrate collected for this sample must come from either the TSS/VSS or PP/PIP filtration set-up. If you cannot get enough water through these pads to fill all tubes, then use plain GF/F filters to get enough filtrate. The filtrate may not come from pads or units that are in contact with MgCO_3 (CHLA).

1. The following steps are to be completed for collection of all filtrate for the samples below:
 - a) Run 50 ml of sample water through the filter.

- b) Use this 50 ml of filtrate to rinse the flask and then discard.
 - c) Run more sample water through the filter and collect in the flask.
- 2. Total Dissolved Nitrogen & Phosphorus (TDN/TDP)**
- a) Rinse the TDN/P tube (30 ml borosilicate glass) and cap three times with filtrate.
 - b) Flick all remaining water droplets out of the test tube and cap.
 - c) Rinse the 10 ml graduated cylinder three times with filtrate.
 - d) Fill the graduated cylinder with 10 ml of filtrate.
 - e) Carefully, pour the 10 ml of filtrate into the test tube and cap tightly.
 - f) Store the test tube in the freezer.
- 3. Nitrate, Nitrite, Ammonia, Orthophosphate**
- a) Rinse the 3 like-numbered AA vials (4 ml polystyrene cups) and 3 caps three times with filtrate.
 - b) Fill the AA vials with filtrate up to ridge where the caps are seated.
 - c) Snap the caps on the vials. You should hear them snap twice to be fully seated.
 - d) Store 3 AA vials in the freezer.

4) Site location and character

The Chesapeake Bay National Estuarine Research Reserve in Maryland consists of three components: Otter Point Creek on the Bush River along the upper western shore of the Chesapeake Bay, Jug Bay along the Patuxent River in the middle of the Chesapeake Bay and Monie Bay on the lower eastern shore of the Chesapeake Bay. At CBM NERR, water quality and nutrient data are collected at four sites. Three sites are at the Jug Bay Component of the Reserve and one site is at the Otter Point Creek Component. The Jug Bay Component of the Reserve is located in the tidal headwaters of the Patuxent River. The watershed for this portion of the river includes portions of the DC Metropolitan area but has dense tracks of protected riparian areas surrounding this portion of the river. Jug Bay is a 722-acre tidal estuary providing a narrow transition zone between brackish marshes and upland freshwater wetlands. The broad, shallow waters of Jug Bay support a profusion of freshwater plants and animals. Vegetation crowds the river channel and forms an interlaced pattern of tidal and non-tidal marshes, swamps and forested wetlands surrounded by upland woods and fields. The Otter Point Creek Component of the Reserve is located along the tidal headwaters of the Bush River, which drains much of Harford County, including the rapidly growing town of Bel Air, Maryland. Otter Point Creek is a tributary of the Bush River in the upper Chesapeake Bay and consists of 672 acres of open water, tidal marshes, forested wetlands and upland hardwood forests, surrounded by major highways, large residential communities, and heavy commercial and industrial development.

The following is a list of sites with a detailed description of site characteristics and other relevant information.

Mataponi Creek (MC) 38° 44.599'N, 76° 42.446'W (NAD83) or 38.74331667, -76.70743333 (GIS format)

Site MC is located at the Jug Bay Component of the Reserve, in a small tributary (Mataponi Creek) off the upper tidal headwaters of the Patuxent River, Maryland. MC is 2.4 km upstream from the mouth and located in the midchannel of the creek, which is approximately 7m wide at that point. The southern bank is steep and covered mainly with hardwood trees while the Northern bank is tidal marsh. The YSI water quality sonde was deployed vertically in a perforated PVC pipe. Average depth at this site is roughly 0.7 meters with a mean tidal fluctuation of approximately 0.6 m. The YSI is deployed 0.25 m off of the creek bottom. Salinities at this site rarely exceed 0.1 ppt. The bottom habitat is soft sediment, and submerged macrophytes are abundant and dense during the summer months. Because this site is located along the main channel of the Mataponi Creek, water quality is reflective of the general quality of water flowing along the main portion of the creek. The submerged macrophyte community at this site is seasonally very dense and thus water quality is thought to be strongly influenced by the presence of SAV during the summer months. Because of

the dense submerged macrophyte community and limited degree of anthropogenic activities occurring within the watershed of this site, MC is thought to be a “reference” water quality site for the Reserve.

Railroad Bridge (RR) 38° 46.877'N, 76° 42.822'W (NAD 83) or 38.78128333, -76.7137 (GIS format)

Site RR is located in the mainstem of the upper tidal headwaters of the Patuxent River, Maryland. The site is slightly upstream (roughly 0.3km) from Jackson's Landing at the Patuxent River Park (previous PR site). This section of the Patuxent River is approximately 70m wide and average depth at the site is 1.4m. The YSI sonde is deployed 0.25 m off of the river bottom. Bottom habitat is soft sediment, and submerged macrophytes are evident in the shallow areas (<0.5m MLW) during summer months. Mean tidal fluctuation is approximately 0.6 m. The salinity at this site rarely exceeds 0.1 ppt. The site location (RR) is at the end of the old railroad bed and is deployed vertically in a perforated PVC pipe near midchannel of the Patuxent River. Because this site is located along the main channel of the Patuxent River, water quality is reflective of the general quality of water flowing along the main portion of the river. The site is roughly 1km downstream of the confluence of the Western Branch tributary and the Patuxent River Mainstem. Thus water quality is influenced by Western Branch tributary which receives tertiary treated effluent from a large wastewater treatment plant (averaging 10-20 mgd) which discharges directly into the Western Branch tributary of the Patuxent River just upstream of site IP. There are no other known pollutants at this site. Because of the location of this site along the main portion of the Patuxent River, this site is thought to be characteristic of this portion of the Patuxent River and thus similar to the historic (1995-2002) site (Jug Bay) located at 38° 46' 50.6" N, 76° 42' 29.1" W.

Iron Pot Landing (IP) 38° 47.760'N, 76° 43.248' W (NAD 83) or 38.796, -76.7208 (GIS Format)

Site IP is located 2.09km from the mouth of Western Branch. The YSI sonde at IP is deployed vertically in a perforated PVC pipe and attached to a small pier near midchannel of the river and has an average depth of 1.6m. The YSI is deployed 0.25 m off of the river bottom. The site is roughly 1km downstream of a large (10-20 mgd) wastewater treatment plant effluent discharge site. The river is approximately 15m wide and flows through extensive riparian buffers. Both banks of the river are flanked by hardwood flora. Tides are semi-diurnal and mean tidal fluctuation is approximately 0.6 m. Salinity at this site is generally 0.1 ppt. Bottom habitat is soft sediment, and narrow submerged macrophyte grassbeds are occasionally evident in the shallow areas downstream during the summer months. Because of the proximity of this site to the discharge location for a large WWTP, this site is considered an “impacted” site for the reserve. There are no other known pollutants at this location.

Otter Point Creek (OC) 39° 27.047'N, 76° 16.474'W (NAD 83) or 39.45078333, -76.27456667 (GIS Format)

Site OC is located within the Otter Point Creek Component of the Reserve, in the tidal headwaters of the Bush River. The Otter Point Creek component is a large but shallow tidally flooded marsh with average depths less than 1m on low tide. The site is approximately 0.3km from the Anita C. Leight Estuary Center. Site OC is deployed vertically in a perforated PVC pipe and has an average depth of 0.7m. The YSI is deployed 0.25 m off of the creek bottom. Bottom habitat is extremely soft sediment, and submerged macrophyte communities inundate the site during summer months, creating a dense and almost impenetrable ground cover. Salinity at this station rarely rises above 0.1 ppt. Tides in Otter Point Creek are semi-diurnal and have a mean range of about 0.3 m. The average water levels are generally lower in the winter due to north and northwest winds that increase the egress from Chesapeake Bay. The sonde is periodically exposed to air at some low tides, and sediments at the site are extremely fine and flocculent. Because of the shallowness of the tidal marsh, coupled with the dramatic daily changes in the depth, deployments at the site present many problems. These problems include periodic exposure of the sonde, and very high turbidity and sedimentation rates associated with tidal infiltration and wind and wave generated resuspension, which cause severe fouling of the probes. Water quality at the site represents extreme shallow water habitats. Thus it is not uncommon to see very large fluctuations in temperature and dissolved oxygen at this site ranging from complete anoxia to

full saturation, due in part to the shallow nature of the site, presence of dense macrophyte communities, and the effects of marsh processes on water quality. This site is thought to be representative of water quality within the Otter Point Creek component throughout most of the year, with the exception of the summer months (June – October) when dense submerged macrophyte communities greatly influence the site. There are no known pollutants at this location.

5) Coded variable definitions

cbmrrnut = Chesapeake Bay Maryland Reserve nutrient data for Railroad Bridge
 cbmmcnut = Chesapeake Bay Maryland Reserve nutrient data for Mataponi Creek
 cbmipnut = Chesapeake Bay Maryland Reserve nutrient data for Iron Pot Landing
 cbmocnut = Chesapeake Bay Maryland Reserve nutrient data for Otter Point Creek

Monitoring Program Codes:

- 1 = Monthly (biweekly) grab sample
- 2 = Diel sampling

Rep Codes:

- 1 = Routine sampling
- 2 = Duplicate sampling
- S = Routine monthly duplicate when there is a conflict with the Diel sample in the database.

6) Data collection period

SWMP nutrient monitoring first began at Railroad Bridge (Jug Bay Wetlands Sanctuary) (RR) on April 4, 2003; Mataponi Creek (MC) on April 22, 2003; Iron Pot Landing (IP) on April 4, 2003; and Otter Point Creek (OC) on April 15, 2003.

Nutrient samples were collected using an Alpha Bottle or ISCO sampler. At Railroad Bridge (Jug Bay Wetlands Sanctuary) (RR) sampling began on January 22, 2009 and continued through November 19, 2009; Mataponi Creek (MC) sampling began on March 26, 2009 and continued through November 19, 2009; Iron Pot Landing (IPL) sampling began on January 22, 2009 and continued through November 19, 2009; Otter Point Creek (OC) sampling began on March 31, 2009 and continued through December 1, 2009.

2009 data collection dates and times are as follows. All times are in Eastern Standard Time (EST).

(RR) Railroad Bridge Monthly Grab Sample

Station Code	DateTimeStamp	Monitoring Program	Rep
cbmrrnut	01/22/2009 07:45:00	1	1
cbmrrnut	01/22/2009 07:46:00	1	2
cbmrrnut	02/25/2009 08:15:00	1	1
cbmrrnut	02/25/2009 08:16:00	1	2
cbmrrnut	03/11/2009 08:15:00	1	1
cbmrrnut	03/26/2009 09:00:00	1	1
cbmrrnut	03/26/2009 09:01:00	1	2
cbmrrnut	04/09/2009 08:00:00	1	1
cbmrrnut	04/23/2009 07:15:00	1	1
cbmrrnut	04/23/2009 07:16:00	1	2
cbmrrnut	05/07/2009 08:15:00	1	1
cbmrrnut	05/21/2009 06:45:00	1	1

cbmrrnut	05/21/2009 06:46:00	1	2
cbmrrnut	06/08/2009 07:30:00	1	1
cbmrrnut	06/23/2009 09:15:00	1	1
cbmrrnut	06/23/2009 09:16:00	1	2
cbmrrnut	07/07/2009 08:00:00	1	1
cbmrrnut	07/23/2009 08:00:00	1	1
cbmrrnut	07/23/2009 08:01:00	1	2
cbmrrnut	08/10/2009 10:00:00	1	1
cbmrrnut	08/25/2009 11:00:00	1	1
cbmrrnut	08/25/2009 11:01:00	1	2
cbmrrnut	09/09/2009 10:00:00	1	1
cbmrrnut	09/24/2009 10:45:00	1	1
cbmrrnut	09/24/2009 10:46:00	1	2
cbmrrnut	10/08/2009 10:00:00	1	1
cbmrrnut	10/22/2009 08:15:00	1	1
cbmrrnut	10/22/2009 08:16:00	1	2
cbmrrnut	11/19/2009 09:15:00	1	1
cbmrrnut	11/19/2009 09:16:00	1	2

(MC) Mataponi Creek Monthly Grab Sample

Station Code	DateTimeStamp	Monitoring Program	Rep
cbmmcnut	03/26/2009 11:15:00	1	1
cbmmcnut	03/26/2009 11:16:00	1	2
cbmmcnut	04/09/2009 10:15:00	1	1
cbmmcnut	04/23/2009 10:00:00	1	1
cbmmcnut	04/23/2009 10:01:00	1	2
cbmmcnut	05/07/2009 11:00:00	1	1
cbmmcnut	05/21/2009 08:45:00	1	1
cbmmcnut	05/21/2009 08:46:00	1	2
cbmmcnut	06/08/2009 10:00:00	1	1
cbmmcnut	06/23/2009 11:30:00	1	1
cbmmcnut	06/23/2009 11:31:00	1	2
cbmmcnut	07/07/2009 11:45:00	1	1
cbmmcnut	07/23/2009 10:30:00	1	1
cbmmcnut	07/23/2009 10:31:00	1	2
cbmmcnut	08/11/2009 12:30:00	1	1
cbmmcnut	08/25/2009 13:30:00	1	1
cbmmcnut	08/25/2009 13:31:00	1	2
cbmmcnut	09/09/2009 12:15:00	1	1
cbmmcnut	09/24/2009 13:00:00	1	1
cbmmcnut	09/24/2009 13:01:00	1	2
cbmmcnut	10/08/2009 12:00:00	1	1
cbmmcnut	10/22/2009 10:45:00	1	1
cbmmcnut	10/22/2009 10:46:00	1	2
cbmmcnut	11/19/2009 11:30:00	1	1
cbmmcnut	11/19/2009 11:31:00	1	2

(IP) Iron Pot Landing Monthly Grab Sample

Station Code	DateTimeStamp	Monitoring Program	Rep
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cbmipnut	01/22/2009 09:15:00	1	1
cbmipnut	01/22/2009 09:16:00	1	2
cbmipnut	02/25/2009 09:28:00	1	1
cbmipnut	02/25/2009 09:29:00	1	2
cbmipnut	03/11/2009 09:45:00	1	1
cbmipnut	03/26/2009 10:15:00	1	1
cbmipnut	03/26/2009 10:16:00	1	2
cbmipnut	04/09/2009 09:15:00	1	1
cbmipnut	04/23/2009 08:30:00	1	1
cbmipnut	04/23/2009 08:31:00	1	2
cbmipnut	05/07/2009 09:44:00	1	1
cbmipnut	05/21/2009 07:45:00	1	1
cbmipnut	05/21/2009 07:46:00	1	2
cbmipnut	06/08/2009 08:45:00	1	1
cbmipnut	06/23/2009 10:30:00	1	1
cbmipnut	06/23/2009 10:31:00	1	2
cbmipnut	07/07/2009 09:30:00	1	1
cbmipnut	07/23/2009 09:30:00	1	1
cbmipnut	07/23/2009 09:31:00	1	2
cbmipnut	08/10/2009 11:29:00	1	1
cbmipnut	08/25/2009 12:15:00	1	1
cbmipnut	08/25/2009 12:16:00	1	2
cbmipnut	09/09/2009 11:15:00	1	1
cbmipnut	09/24/2009 11:45:00	1	1
cbmipnut	09/24/2009 11:46:00	1	2
cbmipnut	10/08/2009 11:01:00	1	1
cbmipnut	10/22/2009 09:30:00	1	1
cbmipnut	10/22/2009 09:31:00	1	2
cbmipnut	11/19/2009 10:30:00	1	1
cbmipnut	11/19/2009 10:31:00	1	2

(IP) Iron Pot Landing DIEL Sampling

Station Code	DateTimeStamp	Monitoring Program	Rep
cbmipnut	02/25/2009 09:30:00	2	1
cbmipnut	02/25/2009 12:00:00	2	1
cbmipnut	02/25/2009 14:30:00	2	1
cbmipnut	02/25/2009 17:00:00	2	1
cbmipnut	02/25/2009 19:30:00	2	1
cbmipnut	02/25/2009 22:00:00	2	1
cbmipnut	02/26/2009 00:30:00	2	1
cbmipnut	02/26/2009 03:00:00	2	1
cbmipnut	02/26/2009 05:30:00	2	1
cbmipnut	02/26/2009 08:00:00	2	1
cbmipnut	02/26/2009 10:30:00	2	1
cbmipnut	03/11/2009 10:00:00	2	1
cbmipnut	03/11/2009 12:30:00	2	1
cbmipnut	03/11/2009 15:00:00	2	1
cbmipnut	03/11/2009 17:30:00	2	1
cbmipnut	03/11/2009 20:00:00	2	1
cbmipnut	03/11/2009 22:30:00	2	1

cbmipnut	03/12/2009 01:00:00	2	1
cbmipnut	03/12/2009 03:30:00	2	1
cbmipnut	03/12/2009 06:00:00	2	1
cbmipnut	03/12/2009 08:30:00	2	1
cbmipnut	03/12/2009 11:00:00	2	1
cbmipnut	04/23/2009 10:00:00	2	1
cbmipnut	04/23/2009 12:30:00	2	1
cbmipnut	04/23/2009 15:00:00	2	1
cbmipnut	04/23/2009 17:30:00	2	1
cbmipnut	04/23/2009 20:00:00	2	1
cbmipnut	04/23/2009 22:30:00	2	1
cbmipnut	04/24/2009 01:00:00	2	1
cbmipnut	04/24/2009 03:30:00	2	1
cbmipnut	05/07/2009 09:45:00	2	1
cbmipnut	05/07/2009 12:15:00	2	1
cbmipnut	05/07/2009 14:45:00	2	1
cbmipnut	05/07/2009 17:15:00	2	1
cbmipnut	05/07/2009 19:45:00	2	1
cbmipnut	05/07/2009 22:15:00	2	1
cbmipnut	05/08/2009 00:45:00	2	1
cbmipnut	05/08/2009 03:15:00	2	1
cbmipnut	05/08/2009 05:45:00	2	1
cbmipnut	05/08/2009 08:15:00	2	1
cbmipnut	05/08/2009 10:45:00	2	1
cbmipnut	06/08/2009 09:15:00	2	1
cbmipnut	06/08/2009 11:45:00	2	1
cbmipnut	06/08/2009 14:15:00	2	1
cbmipnut	06/08/2009 16:45:00	2	1
cbmipnut	06/08/2009 19:15:00	2	1
cbmipnut	06/08/2009 21:45:00	2	1
cbmipnut	06/09/2009 00:15:00	2	1
cbmipnut	06/09/2009 02:45:00	2	1
cbmipnut	06/09/2009 05:15:00	2	1
cbmipnut	06/09/2009 07:45:00	2	1
cbmipnut	06/09/2009 10:15:00	2	1
cbmipnut	07/06/2009 08:00:00	2	1
cbmipnut	07/06/2009 10:30:00	2	1
cbmipnut	07/06/2009 13:00:00	2	1
cbmipnut	07/06/2009 15:30:00	2	1
cbmipnut	07/06/2009 18:00:00	2	1
cbmipnut	07/06/2009 20:30:00	2	1
cbmipnut	07/06/2009 23:00:00	2	1
cbmipnut	07/07/2009 01:30:00	2	1
cbmipnut	07/07/2009 04:00:00	2	1
cbmipnut	07/07/2009 06:30:00	2	1
cbmipnut	07/07/2009 09:00:00	2	1
cbmipnut	08/10/2009 11:30:00	2	1
cbmipnut	08/10/2009 14:00:00	2	1
cbmipnut	08/10/2009 16:30:00	2	1
cbmipnut	08/10/2009 19:00:00	2	1

cbmipnut	08/10/2009 21:30:00	2	1
cbmipnut	08/11/2009 00:00:00	2	1
cbmipnut	08/11/2009 02:30:00	2	1
cbmipnut	08/11/2009 05:00:00	2	1
cbmipnut	08/11/2009 07:30:00	2	1
cbmipnut	08/11/2009 10:00:00	2	1
cbmipnut	08/11/2009 12:30:00	2	1
cbmipnut	09/09/2009 11:30:00	2	1
cbmipnut	09/09/2009 14:00:00	2	1
cbmipnut	09/09/2009 16:30:00	2	1
cbmipnut	09/09/2009 19:00:00	2	1
cbmipnut	09/09/2009 21:30:00	2	1
cbmipnut	09/10/2009 00:00:00	2	1
cbmipnut	09/10/2009 02:30:00	2	1
cbmipnut	09/10/2009 05:00:00	2	1
cbmipnut	09/10/2009 07:30:00	2	1
cbmipnut	09/10/2009 10:00:00	2	1
cbmipnut	09/10/2009 12:30:00	2	1
cbmipnut	10/07/2009 10:00:00	2	1
cbmipnut	10/07/2009 12:30:00	2	1
cbmipnut	10/07/2009 15:00:00	2	1
cbmipnut	10/07/2009 17:30:00	2	1
cbmipnut	10/07/2009 20:00:00	2	1
cbmipnut	10/07/2009 22:30:00	2	1
cbmipnut	10/08/2009 01:00:00	2	1
cbmipnut	10/08/2009 03:30:00	2	1
cbmipnut	10/08/2009 06:00:00	2	1
cbmipnut	10/08/2009 08:30:00	2	1
cbmipnut	10/08/2009 11:00:00	2	1
cbmipnut	11/18/2009 09:00:00	2	1
cbmipnut	11/18/2009 11:30:00	2	1
cbmipnut	11/18/2009 14:00:00	2	1
cbmipnut	11/18/2009 16:30:00	2	1
cbmipnut	11/18/2009 19:00:00	2	1
cbmipnut	11/18/2009 21:30:00	2	1
cbmipnut	11/19/2009 00:00:00	2	1
cbmipnut	11/19/2009 02:30:00	2	1
cbmipnut	11/19/2009 05:00:00	2	1
cbmipnut	11/19/2009 07:30:00	2	1
cbmipnut	11/19/2009 10:00:00	2	1

(OC) Otter Point Creek Monthly Grab Sample

Station Code	DateTimeStamp	Monitoring Program	Rep
cbmocrnut	03/31/2009 13:45:00	1	1
cbmocrnut	03/31/2009 13:46:00	1	2
cbmocrnut	04/08/2009 10:45:00	1	1
cbmocrnut	04/21/2009 08:30:00	1	1
cbmocrnut	04/21/2009 08:31:00	1	2
cbmocrnut	05/05/2009 08:30:00	1	1
cbmocrnut	05/19/2009 08:00:00	1	1

cbmocnut	05/19/2009 08:01:00	1	2
cbmocnut	06/02/2009 07:30:00	1	1
cbmocnut	06/16/2009 07:15:00	1	1
cbmocnut	06/16/2009 07:16:00	1	2
cbmocnut	06/30/2009 07:15:00	1	1
cbmocnut	07/16/2009 07:45:00	1	1
cbmocnut	07/30/2009 10:30:00	1	1
cbmocnut	07/30/2009 10:31:00	1	2
cbmocnut	08/18/2009 10:00:00	1	1
cbmocnut	08/18/2009 10:01:00	1	2
cbmocnut	08/31/2009 09:00:00	1	1
cbmocnut	09/15/2009 10:00:00	1	1
cbmocnut	09/29/2009 09:00:00	1	1
cbmocnut	09/29/2009 09:01:00	1	2
cbmocnut	10/13/2009 07:30:00	1	1
cbmocnut	10/28/2009 07:30:00	1	1
cbmocnut	10/28/2009 07:31:00	1	2
cbmocnut	12/01/2009 10:30:00	1	1
cbmocnut	12/01/2009 10:31:00	1	2

7) Associated researchers and projects

The Jug Bay Wetlands Sanctuary staff has been collecting weekly to monthly temperature, salinity, dissolved oxygen, and nutrient samples at various tidal and non-tidal sites throughout the Jug Bay marsh since 1989. One of their historic sites includes the current (RR) site as well as the historic (1995-2002) (JB) site. Sampling for their sites is done monthly throughout the year (when ice is not present) and includes parameters such as nitrate/nitrite, ammonium and chlorophyll a. Additionally, the staff samples at other sites throughout the Jug Bay marsh, which provide additional similar data at a larger spatial scale.

Staff at the Anita C. Leight Estuary Center at Otter Point Creek, in conjunction with CBNERR/MD staff, have also been collecting bi-weekly to monthly temperature, salinity, dissolved oxygen, total suspended solids, chlorophyll a, and nutrient samples (to include nitrate/nitrite, ammonium, ortho-phosphate, total nitrogen and total phosphorus) at the same location as datalogger OC and 5 other sites in the Otter Point Creek marsh since 2002. For more information on either the Jug Bay Wetlands Sanctuary or Otter Point Creek monitoring, contact Patricia Delgado, the Reserve's Research Coordinator.

Additional discrete nutrient data and semi-continuous water quality data is also available through the Department of Natural Resources Continuous Monitoring Program (see www.eyesonthebay.net) that provides increased spatial coverage of many of the same parameters around both RR and OC sites for 2009. This monitoring program included as many as 40 additional continuous monitoring sites (similar to the CBM NERR effort) throughout Maryland tidal waters sampled semi-continuously (every 15 minutes) from April-October 2009. In addition to the high temporal resolution of water quality at these sites, Maryland Department of Natural Resources also conducts water quality cruises between and amongst many of these same sites which are used to create interpolated water quality maps, providing a high degree of spatial resolution around their permanent continuous monitoring (YSI sonde) sites. Interpolated water quality maps are available for both the Jug Bay and Otter Point Creek sites through the Maryland Department of Natural Resources or CBM NERR. The Maryland Department of Natural Resources Continuous Monitoring Program began in 1999. For more information on this program and the water quality monitoring cruises see www.eyesonthebay.net.

The NERR system-wide monitoring program also collects meteorological data from a weather station located at the Jug Bay Component of the Reserve, specifically at the Jug Bay Wetlands Sanctuary. The weather station is maintained by the Maryland Department of Natural Resources Continuous Monitoring Program. The principal objectives are to record meteorological information for the Chesapeake Bay National Estuarine Research Reserve in Maryland. This information is available for the following: 1) to track and record atmospheric and meteorological conditions useful to help understand and explain additional data collected concurrently 2) to create a database capable of detecting long-term changes in weather patterns 3) to record and identify the impact of storms, hurricanes, heavy rain and other episodic weather events capable of influencing other environmental conditions such as water quality (as monitored by the SWMP effort) and to collect ancillary data in support of other research efforts. The weather station records temperature, relative humidity, barometric pressure, wind speed, wind direction, light as measured by a LI-COR Quantum Sensor, and precipitation.

8) Distribution

NOAA/ERD retains the right to analyze, synthesize and publish summaries of the NERRS System-wide Monitoring Program data. The PI retains the right to be fully credited for having collected and processed the data. Following academic courtesy standards, the PI and NERR site where the data were collected will be contacted and fully acknowledged in any subsequent publications in which any part of the data are used. Manuscripts resulting from this NOAA/OCRM supported research that are produced for publication in open literature, including refereed scientific journals, will acknowledge that the research was conducted under an award from the Estuarine Reserves Division, Office of Ocean and Coastal Resource Management, National Ocean Service, National Oceanic and Atmospheric Administration. 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.

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 <http://cdmo.baruch.sc.edu/>. Data are available in text tab-delimited format.

II. Physical Structure Descriptors

9) Entry verification

Nutrient samples are sent to Nutrient Analytical Services Laboratory (NASL) at the University of Maryland's Chesapeake Biological Laboratory. The samples are analyzed and problems in sample quality are indicated with an Analytical Problem Code (APC). Additionally, quality assurance/quality control (QA/QC) samples are analyzed and reviewed by NASL to ensure their instrumentation and analytical procedures are not producing erroneous results. The APC codes in use have been regionally accepted by all partners participating in water quality monitoring of the Chesapeake Bay under guidance of the Environmental Protection Agency's Chesapeake Bay Program Office (CBP). The nutrient data is sent from NASL to the Maryland Department of Natural Resources' Tidewater Ecosystem Assessment division where it is entered into our main water quality database and is merged with the time and date matched field and chlorophyll data. Any APC codes associated with nutrient or chlorophyll data that indicate the data should be rejected are hidden and made unavailable. Data values that fall below CBP accepted Minimum Detection Limits (MDL) are hidden and a new value is set at the MDL and is flagged to indicate the value has been set to MDL. Once the data has been entered into the data management system, a series of reports and plots are generated for

review by an analyst (Matt Hall). Automatic range checks flag and report any data values that exceed the ranges. The analyst reviews the data and the range check reports to determine if the data are acceptable based on conditions at adjacent stations, weather at the time of sampling, and historic data. Data that are rejected during this QA/QC process are hidden. Once the data has undergone a QA/QC check by the analyst it is made final and available to the scientific community for use. This data is then sent to the DNR field office where a CBM NERR technician (Lauren Cunningham) conforms the data into the correct NERR format and variable comment codes.

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 asterisks “*”.

Data Category	Parameter	Variable Name	Units of Measure
Phosphorus and Nitrogen:			
	*Orthophosphate	PO4F	mg/L as P
	Total Dissolved Phosphorus	TDP	mg/L as P
	Dissolved Organic Phosphorus	DOP	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
	Total Dissolved Nitrogen	TDN	mg/L as N
	Particulate Organic Nitrogen	PON	mg/L as N
Other:			
	Particulate Organic Carbon	POC	mg/L as C
	Total Suspended Solids	TSS	mg/L
	Total Volatile Solids	TVS	mg/L
Plant Pigments:			
	*Chlorophyll a	CHLA_N	µg/L
	Phaeophytin	PHEA	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.

11) Measured or calculated laboratory parameters

- a) **Parameters measured directly**
- | | |
|---------------------|--|
| Nitrogen species: | NH ₄ , NO ₂ , NO ₃ , TDN, PON |
| Phosphorus species: | PO ₄ F, TDP |
| Other: | CHLA, PHEA, POC, TSS, TVS |
- b) **Calculated parameters**
- | | |
|-----------------|----------------------------------|
| NO ₃ | NO ₃ -NO ₂ |
| DIN | NO ₃ +NH ₄ |
| DOP | TDP-PO ₄ F |

12) Limits of detection

Parameter	Start Date	End Date	MDL
CHLA_N	01/01/09	12/31/09	0.62
PHEA	01/01/09	12/31/09	0.74
NH ₄ F	01/07/09	12/31/09	0.006
NO ₃ F	01/01/09	12/31/09	0.0007
NO ₂ F	01/07/09	12/31/09	0.0001
PO ₄ F	01/01/09	12/31/09	0.0006
POC	01/01/09	12/31/09	0.0633
PON	01/01/09	12/31/09	0.0105
TDN	01/01/09	12/31/09	0.05
TDP	01/01/09	12/31/09	0.0015
TSS	01/01/09	12/31/09	2.4
TVS	01/01/09	12/31/09	2.4

The MDL is determined as 3 times the standard deviation of a minimum of 7 replicates of a single low concentration sample.

13) Laboratory methods

a) Parameter: PO₄

i) **Method Summary:** Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex which is reduced to an intensely blue-colored complex by ascorbic acid. Color is proportional to phosphorus concentration.

ii) **Method References:** Technicon Industrial Method No. 155-71W/Tentative. 1973. Technicon Industrial Systems. Tarrytown, New York, 10591.

USEPA. 1979. Method No. 365.1 in Methods for chemical analysis of water and wastes. United States Environmental Protection Agency, Office of Research and Development. Cincinnati, Ohio. Report No. EPA-600/4-79-020 March 1979. 460pp.

Froelich, P.N. and M.E.Q. Pilson. 1978. Systematic absorbance error with Technicon AutoAnalyzer II colorimeter. Water Res. 12:599-603.

iii) **Preservation Method:** Samples are immediately filtered through 47mm glass fiber filter pads, decanted into an Auto Analyzer vial, and placed on ice. Upon returning to the lab Auto Analyzer vial is placed in freezer at -20°C until analysis. Maximum holding time is 28 days.

b) **Parameter: NH₄**

i) **Method Summary:** Determination of ammonium is by the Berthelot Reaction in which a blue-colored compound similar to indophenol forms when a solution of ammonium salt is added to sodium phenoxide, followed by the addition of sodium hypochlorite. The addition of a potassium sodium tartrate and sodium citrate solution prevents precipitation of hydroxides of calcium and magnesium.

ii) **Method References:** Technicon Industrial Method No. 804-86T. August 1986. Technicon Industrial Systems. Tarrytown, New York, 10591.

Kerouel, R. and A. Aminot. 1987. Procédure optimisée hors-contaminations pour l'analyse des éléments nutritifs dissous dans l'eau de mer. *Mar. Environ. Res.* 22:19-32.

iii) **Preservation Method:** Samples are immediately filtered through 47mm glass fiber filter pads, decanted into an Auto Analyzer vial, and placed on ice. Upon returning to the lab Auto Analyzer vial is placed in freezer at –20°C until analysis. Maximum holding time is 28 days.

c) **Parameter: NO₂**

i) **Method Summary:** Nitrite reacts under acidic conditions with sulfanilamide to form a diazo compound that couples with N-1-naphthylethylenediamine dihydrochloride to form a reddish-purple azo dye measured at 520 nm..

ii) **Method References:** Technicon Industrial Method No. 818-87T. February 1987. Technicon Industrial Systems. Tarrytown, New York, 10591.

iii) **Preservation Method:** Samples are immediately filtered through 47mm glass fiber filter pads, decanted into an Auto Analyzer vial, and placed on ice. Upon returning to the lab Auto Analyzer vial is placed in freezer at –20°C until analysis. Maximum holding time is 28 days.

d) **Parameter: NO₂3**

i) **Method Summary:** Filtered samples are mixed with Nitrate Reductase (an enzyme isolated from the plant *Arabidopsis thaliana*) and NADH (β -Nicotinamide adenine dinucleotide reduced form disodium salt). The nitrite, both that which was reduced from nitrate and nitrite that was originally present, is then determined by diazotizing with sulfanilamide and coupling with N-1-naphthylethylenediamine dihydrochloride to form a colored azo dye. Filtered samples with concentrations found to be below the method detection limit at analyzed via cadmium reduction with a Technicon Bran & Luebbe AutoAnalyzer II.

ii) **Method References:** Campbell, et al. (2006). Nitrate reductase for nitrate analysis in water. *Environ Chem Letters* 4:69. <http://www.nitrate.com/ECL2006.pdf>

Frank, J. M., C.F. Zimmermann and C. W. Keefe (2006). Comparison of results from Konelab Aquakem 250 and existing nutrient analyzers. UMCES CBL Nutrient Analytical Services Laboratory, Dec. 2006.

Patton, et al. (2002). Corn leaf nitrate reductase – a nontoxic alternative to cadmium for photometric nitrate determinations in water samples by airsegmented continuous-flow analysis, *Environ. Sci Tech.* 2002, 36, 729-735. <http://www.nitrate.com/pattonetal2002>.

iii) **Preservation Method:** Samples are immediately filtered through 47mm glass fiber filter pads with a nominal pore size of 0.7µm, decanted into an Auto Analyzer vial, and placed on ice. Upon returning to the lab Auto Analyzer vial is placed in freezer at -20°C until analysis. Maximum holding time is 28 days.

e) **Parameter: Chlorophyll**

i) **Method Summary:** The chlorophyll and related compounds are extracted from the filtered algae with aqueous buffered 90% acetone solution. The concentration of the pigments is determined by measuring the light absorption of the extract.

The chlorophyll *a* content in every sample is calculated as follows:

Calculating Chlorophyll

AMT_FILT = SAMVOL_L in database.

Divide the following by 1000:

OD630B
OD645B
OD647B
OD663B
OD664B
OD665A
OD750A
OD750B

Divide the Amount Filtered (AMT_FILT) by 100

$$PHEO = 26.7 * ((1.7 * (OD665A - OD750A)) - (OD664B - OD750B)) * (EXVOL_ML / (AMT_FILT * LIPAT_CM))$$

$$CHAA = 26.7 * ((OD664B - OD750B) - (OD665A - OD750A)) * (EXVOL_ML / (AMT_FILT * LIPAT_CM))$$

If:

ABS(OD664B - OD750B) < 0.00001 or
ABS(OD665A - OD750A) < 0.00001 or
(OD664B - OD750B) < (OD665A - OD750A) or
(OD664B - OD750B) > 2 * (OD665A - OD750A) or
(LIPAT_CM * AMT_FILT) < 0.00001

Then: Set PHEO = Null and Set CHAA = Null

If CHAA < 0.0 and is not Null, then set CHAA = 0.0

ii) **Method References:** 1002 G. Chlorophyll “1. Spectrophotometric Determination of Chlorophyll *a*, *b*, and *c* (Trichromatic method)” Standard Methods for the Examination of Water and Waste Water, 14th Ed., American Public Health Association, 1976, 1029-1031.

10200 H. Chlorophyll “2. Spectrophotometric Determination of Standard Methods for the Examination of Water and Waste Water, 17th Ed., American Public Health Association, 1989, 10-31 - 10-34.

Chlorophyll- Spectrophotometric U.S. Environment Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, Revised 3/91.

Standard Practices for Measurement of Chlorophyll Content of Algae in Surface Waters ASTM, D 3731 - 87, 15 - 18.

iii) **Preservation Method:** Samples are immediately filtered through a 47mm glass fiber filter pad, placed in a foil square, and then placed on ice. Upon returning the foil square is placed in freezer at -20°C until analysis. Maximum holding time is not to exceed 30 days.

f) **Parameter: PC/PN**

i) **Method Summary:** Samples are combusted in pure oxygen (O_2) under static conditions. Products of combustion are passed over suitable reagents in the combustion tube where complete oxidation occurs. In the reduction tube, oxides of nitrogen (N) are converted to molecular N. The carbon dioxide (CO_2), water vapor and N are mixed and released into the thermal conductivity detector where the concentrations of the sample gases are measured.

ii) **Method References:** U.S. Environmental Protection Agency, 1997. Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Samples. Method 440.0. U.S. Environmental Protection Agency. Washington, D.C.

Holme, N.A. and A.D. McIntyre (eds). 1971. Methods for the Study of Marine Benthos. International Biome Program. IBP Handbook #16. F.A. Davis Co., Philadelphia, PA.

Hurd, D.C. and D.W. Spencer (eds). 1991. Marine Particles: Analysis and Characterization. Geophysical Monograph: 63, American Geophysical Union, Washington, D.C. 472p.

Hirota, J. and J.P. Szyper. 1975. Separation of total particulate carbon into inorganic and organic components. Limnol and Oceanogr. 20:896-900.

Grasshoff, K., M. Ehrhardt and K. Kremling (eds). 1983. Methods of Seawater Analysis. Verlag Chemie.

Keefe, Carolyn W., The Contribution of Inorganic Compounds to the Particulate Carbon, Nitrogen and Phosphorus in Suspended Matter and Surface Sediments of the Chesapeake Bay, Estuaries, Vol. 17, No 1B, pp 122-130, March 1994.

40 CFR, Part 136, Appendix B. Definition and Procedure for the Determination of the Method Detection Limit. Revision 1.11.

Zimmermann, C.F., Keefe, C.W., and Bashe, J. 1997. Method 440.0. Determination of Carbon and Nitrogen in Sediments and Particulates of Estuarine/Coastal Waters Using Elemental Analysis. USEPA.

iii) **Preservation Method:** Samples are immediately filtered through a 25mm glass fiber filter pad (0.7um pore size), placed in a foil square, and then placed on ice. Upon returning the foil square is placed in freezer at -20°C until analysis. Maximum holding time is 28 days.

g) **Parameter: TSS/TVS**

i) **Method Summary:** Total suspended solids (TSS) is the retained material on a standard glass filter pad after filtration of a well-mixed sample of water. Total volatile solids (TVS) is the volatilized material that is lost on ignition from TSS. It is calculated from the measurement of a TSS sample minus the measurement of the quantity remaining after combustion. Both results are expressed in mg/L.

ii) **Method References:** APHA. 1975. Method 208D. Total Nonfilterable Residue Dried at 103 – 105 C (Total Suspended Matter) in Standard Methods for the Examination of Water and Wastewater, 14th Edition. American Public Health Association. Washington, DC. 1193pp.

UEPA. 1979. Method No. 160.2 (with slight modification) in Methods for chemical analysis of water and wastes. United States Environmental Protection Agency, Office of Research and Development. Cincinnati, Ohio. Report No. EPA-600/4-79-020 March 1979. 460pp.

APHA. 1975. Method 208 E (with modification). Total volatile and fixed residue at 550 C in Standard Methods for the Examination of Water and Wastewater, 14th Edition. American Public Health Association. Washington, DC. 1193pp.

iii) **Preservation Method:** Samples are immediately filtered through a 47mm glass fiber filter pad (0.7µm pore size), placed in a foil square, and then placed on ice. Upon returning the foil square is placed in freezer at –20°C until analysis. Maximum holding time is 28 days.

h) **Parameter: TDN/TDP**

i) **Method Summary:** This method is a persulfate oxidation technique for nitrogen and phosphorus where, under initially alkaline conditions, nitrate is the sole nitrogen product. Phosphate is the sole phosphorus product after acidic conditions are achieved following further autodecomposition of the persulfate in the heated oxidation tubes.

Digested samples are passed through a granulated copper-cadmium column to reduce nitrate to nitrite. The nitrite then is determined by diazotizing with sulfanilamide and coupling with N-1-naphthylethylenediamine dihydrochloride to form a colored azo dye. Color is proportional to nitrogen concentration.

Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex which is reduced to an intensely blue-colored complex by the ascorbic acid. Color is proportional to phosphorus concentration.

ii) **Method References:** D'Elia, C.F., P.A. Steudler and N. Corwin. 1977. Determination of total nitrogen in aqueous samples using persulfate digestion. Limnol. Oceanogr. 22:760-764.

Valderrama, J.C. 1981. The simultaneous analysis of total nitrogen and total phosphorus in natural waters. Mar. Chem. 10:109-122.

iii) **Preservation Method:** Samples are immediately placed in a 30mL screw cap test tube and frozen. Upon delivery to the lab, the test tube is placed in freezer at –20°C until analysis. Maximum holding time is 28 days. Digested samples may be stored for up to a year.

14) **Field and Laboratory QAQC programs**

a) **Precision**

i) **Field variability** – The Maryland Department of Natural Resources (MDNR) maintains CBMNERR sites in conjunction with their Continuous Monitoring Program, which maintains over 40 sites where water quality and nutrient data are collected. As such, field variability is checked with 10% of all samples being taken as duplicates. These duplicate samples are field duplicates taken as a replicate, or additional sample, taken concurrently at the time of sampling.

ii) **Laboratory variability** – The Chesapeake Biological Laboratory (CBL) is responsible for analyzing CBM NERR nutrient samples as well as other nutrient samples taken through MDNR's Continuous Monitoring Program. CBL verifies the quality of their analytical process by running 10% of all samples through an additional test to duplicate procedures and check the accuracy of their reporting.

iii) **Inter-organizational splits** – All nutrient parameters for CBM NERR were analyzed by CBL.

b) **Accuracy**

i) **Sample spikes** – Sample outliers range from 85 to 115 percent. CBL typically gets 90 to 110 percent recovery.

ii) **Standard reference material analysis** – none

iii) **Cross calibration exercises** - Nutrient Analytical Services has participated in many cross calibration exercises. Participation in such programs is an excellent means of determining accuracy of results. Examples of such cross calibration exercises include the Chesapeake Bay Program Quarterly Split Samples, Chesapeake Bay Program Blind Audits, USGS Standard Reference Sample Project, US EPA Method Validation Studies and International Council for the Exploration of the Sea Inter-comparison Exercise for Nutrients in Sea Water.

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

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
WS1	> 1 to 10 knots
WS2	> 10 to 20 knots
WS3	> 20 to 30 knots
WS4	> 30 to 40 knots
WS5	> 40 knots

17) Other remarks/notes

Data may be missing due to problems with sample collection or processing. Laboratories in the NERRS System submit data that are censored at a lower detection rate limit, called the Method Detection Limit or MDL. MDLs for specific parameters are listed in the Laboratory Methods and Detection Limits Section (Section II, Part 12) of this document. Concentrations that are less than this limit are censored with the use of a QAQC flag and code, and the reported value is the method detection limit itself rather than a measured

value. For example, if the measured concentration of NO₃F was 0.0005 mg/l as N (MDL=0.0008), the reported value would be 0.0008 and would be flagged as out of sensor range low (-4) and coded SBL. In addition, if any of the components used to calculate a variable are below the MDL, the calculated variable is removed and flagged/coded -4 SCB. If a calculated value is negative, it is rejected and all measured components are marked suspect. If additional information on MDL's or missing, suspect, or rejected data is needed, contact the Research Coordinator at the Reserve submitting the data.

Note: The way below MDL values are handled in the NERRS SWMP dataset was changed in November of 2011. Previously, below MDL data from 2007-2010 were also flagged/coded, but either reported as the measured value or a blank cell. Any 2007-2011 nutrient/pigment data downloaded from the CDMO prior to November of 2011 will reflect this difference.

There is no DIEL sampling program data for January and December 2009 due to hazardous weather conditions including snow and freezing rains. Nighttime temperatures consistently dropped below freezing during these months, which would have resulted in a frozen sampling hose. In addition, the Jug Bay Reserve experienced a large snowfall of approximately 20 inches on December 18-19 (see NOAA weather history). Due to the fact that the technicians must drive on off-road terrain to reach the Iron Pot Landing station where the ISCO sampler is deployed, the snow made the station inaccessible for the remainder of December.

There were only eight samples collected by the ISCO sampler for the DIEL program in the month of April. The battery in the ISCO sampler died after the eighth sample was collected and, therefore, did not collect the last three samples.

Western Branch Wastewater Treatment Plant, the treatment plant located just upstream of the Iron Pot Landing (IP) site, experienced an overflow during the month of May, around the time of the May 7th monthly grab sample and DIEL sampling. Large amounts of rainfall in the area at the beginning of May caused the overflow at the wastewater treatment plant. The nutrient data from that time shows elevated values for some parameters.

QA/QC “Check metadata for further details” (CSM) comments

The following TDN/TDP sample data are missing due to the test tubes being broken either in transit to the analytical lab or by the lab technicians during sample analysis:

Station Code	DateTimeStamp	Monitoring Program	Rep	TDN	F_TDN	TDP	F_TDP
cbmmcnut	03/26/2009 11:15:00	1	1		<-2> (CSM)		<-2> (CSM)
cbmmcnut	07/07/2009 11:45:00	1	1		<-2> (CSM)		<-2> (CSM)
cbmipnut	02/25/2009 19:30:00	2	1		<-2> (CSM)		<-2> (CSM)
cbmipnut	06/08/2009 16:45:00	2	1		<-2> (CSM)		<-2> (CSM)
cbmocrnut	08/31/2009 09:00:00	1	1		<-2> (CSM)		<-2> (CSM)

The following Chlorophyll A and Phaeophytin sample data are missing due to quality control standards. In the raw data received from the analytical lab, a problem code was associated with these samples indicating that the sample results were rejected by the lab due to quality control criteria:

Station Code	DateTimeStamp	Monitoring Program	Rep	CHLA_N	F_CHLA_N
cbmipnut	01/22/2009 09:15:00	1	1		<-2> [GQD] (CSM)
cbmipnut	01/22/2009 09:15:00	1	2		<-2> [GQD] (CSM)
cbmipnut	05/21/2009 07:45:00	1	1		<-2> [GQD] (CSM)
cbmipnut	07/07/2009 09:30:00	1	1		<-2> [GQD] (CSM)

cbmipnut	10/08/2009 11:00:00	1	1	<-2> [GQD] (CSM)
cbmipnut	10/22/2009 09:30:00	1	1	<-2> [GQD] (CSM)