

Chesapeake Bay Maryland (CBM) NERR Nutrient Metadata
January – December 2011
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I. Data Set and Research Descriptors

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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 2011. 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 concentration, nitrate, nitrite, ammonium, and ortho-phosphate. Single grab samples were also taken mid-month (biweekly), if possible, at the Otter Point Creek and Jug Bay sites. Additional parameters to include total suspended and volatile solids (replicate 1 samples only), total and dissolved nitrogen (replicate 1 samples only), and total and dissolved organic phosphorus (replicate 1 samples only) were also collected at the same time. These parameters are available by choosing the yearly files data export option from www.nerrsdata.org or by contacting the Reserve directly (see contacts).

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 into 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 lysing 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 Chesapeake Biological Laboratory.

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 January 4, 2011 at the Iron Pot Landing station located at the Jug Bay Component. 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 1000 ml plastic ISCO bottles. The bottles were washed only 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 lysing 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 transported on ice to the Chesapeake Biological Laboratory. Ice was placed in the sample compartment of these samplers to preserve collected samples over the 24-hr deployment period. During each 24-hr deployment, 11 whole water samples were collected and stored in the automated sampler until retrieved and filtered.

All whole water samples (weekly, 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 47 mm 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 47 mm 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.**
- 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 50 ml of sample in the filtration bell.

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

- h) Using forceps, 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, sample type, sample layer, 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, salinity, 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. 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 = $0.7 \mu\text{m}$). 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, 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, salinity, 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 the TSS/VSS filtration set-up. If you cannot get enough water through this pad 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. 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 the AA vials in the freezer.
- 3. Total Dissolved Nitrogen & Phosphorus (TDN/TDP)**
- a) Rinse the TDN/P tube (30 ml borosilicate glass) and cap three times with whole water.
 - b) Flick all remaining water droplets out of the test tube and cap.
 - c) Rinse the 10 ml graduated cylinder three times with whole water.
 - d) Fill the graduated cylinder with 10 ml of whole water.
 - e) Carefully, pour the 10 ml of whole water into the test tube and cap tightly.
 - f) Store the test tube 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 7 m 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, such that the YSI is 0.25 m off of the creek bottom. Average depth at this site is roughly 0.7 meters with a mean tidal fluctuation of approximately 0.6 m. 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 considered 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 0.3 km) from Jackson's Landing at the Patuxent River Park (previous PR site). This section of the Patuxent River is approximately 70 m wide and average depth at the site is 1.4 m. Bottom habitat is soft sediment, and submerged macrophytes are evident in the shallow areas (<0.5 m 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 such that the YSI sonde is 0.25 m off of the river bottom. 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 1 km 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. 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 2.09 km 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 1 km downstream of a large (10-20 mgd) wastewater treatment plant effluent discharge site. The river is approximately 15 m 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 grass beds 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 wastewater treatment plant, this site is considered an “impacted” site for the reserve.

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 1 m on low tide. The site is approximately 0.3 km from the Anita C. Leight Estuary Center. Site OC is deployed vertically in a perforated PVC pipe and has an average depth of 0.7 m, and 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 site.

5) Coded variable definitions

cbmrrnut = Chesapeake Bay Maryland Railroad Bridge nutrients
 cbmmcnut = Chesapeake Bay Maryland Mataponi Creek nutrients
 cbmipnut = Chesapeake Bay Maryland Iron Pot Landing nutrients
 cbmocnut = Chesapeake Bay Maryland Otter Point Creek nutrients

Monitoring Program Codes:

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

Rep Codes:

- 1 = Routine sampling
- 2 = Duplicate sampling

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.

Sampling dates for 2011: Railroad Bridge (Jug Bay Wetlands Sanctuary) (RR) sampling began on January 5, 2011 and continued through December 13, 2011; Mataponi Creek (MC) sampling began on March 23, 2011 and continued through December 13, 2011; Iron Pot Landing (IP) sampling began on January 5, 2011 and continued through December 13, 2011; Otter Point Creek (OC) sampling began on March 29, 2011 and continued through December 19, 2011; DIEL sampling at Iron Pot Landing began on January 4, 2011 and continued through December 20, 2011.

2011 data collection dates and times are as follows. All times are in Eastern Standard Time (EST).

Mataponi Creek (MC) Monthly Grab Sample

Station Code	DateTimeStamp	Monitoring Program	Rep
cbmmcnut	03/23/2011 11:45	1	1
cbmmcnut	03/23/2011 11:46	1	2
cbmmcnut	04/05/2011 11:15	1	1
cbmmcnut	04/19/2011 10:45	1	1
cbmmcnut	04/19/2011 10:46	1	2
cbmmcnut	05/03/2011 10:30	1	1
cbmmcnut	05/17/2011 09:30	1	1

cbmmcnut	05/17/2011 09:31	1	2
cbmmcnut	05/31/2011 09:30	1	1
cbmmcnut	06/14/2011 10:15	1	1
cbmmcnut	06/28/2011 10:45	1	1
cbmmcnut	06/28/2011 10:46	1	2
cbmmcnut	07/13/2011 10:00	1	1
cbmmcnut	07/28/2011 10:15	1	1
cbmmcnut	07/28/2011 10:16	1	2
cbmmcnut	08/11/2011 10:45	1	1
cbmmcnut	08/25/2011 11:15	1	1
cbmmcnut	08/25/2011 11:16	1	2
cbmmcnut	09/12/2011 10:15	1	1
cbmmcnut	09/26/2011 11:45	1	1
cbmmcnut	09/26/2011 11:46	1	2
cbmmcnut	10/11/2011 10:30	1	1
cbmmcnut	10/27/2011 08:45	1	1
cbmmcnut	10/27/2011 08:46	1	2
cbmmcnut	11/14/2011 12:15	1	1
cbmmcnut	11/14/2011 12:16	1	2
cbmmcnut	12/13/2011 11:15	1	1
cbmmcnut	12/13/2011 11:16	1	2

Railroad Bridge (RR) Monthly Grab Sample

Station Code	DateTimeStamp	Monitoring Program	Rep
cbmrrnut	01/05/2011 08:30	1	1
cbmrrnut	01/05/2011 08:31	1	2
cbmrrnut	02/23/2011 11:45	1	1
cbmrrnut	02/23/2011 11:46	1	2
cbmrrnut	03/23/2011 09:30	1	1
cbmrrnut	03/23/2011 09:31	1	2
cbmrrnut	04/05/2011 09:15	1	1
cbmrrnut	04/19/2011 08:15	1	1
cbmrrnut	04/19/2011 08:16	1	2
cbmrrnut	05/03/2011 08:15	1	1
cbmrrnut	05/17/2011 07:30	1	1
cbmrrnut	05/17/2011 07:31	1	2
cbmrrnut	05/31/2011 07:15	1	1
cbmrrnut	06/14/2011 07:15	1	1
cbmrrnut	06/28/2011 07:00	1	1
cbmrrnut	06/28/2011 07:01	1	2
cbmrrnut	07/13/2011 07:15	1	1
cbmrrnut	07/28/2011 07:15	1	1
cbmrrnut	07/28/2011 07:16	1	2
cbmrrnut	08/11/2011 07:30	1	1
cbmrrnut	08/25/2011 07:15	1	1
cbmrrnut	08/25/2011 07:16	1	2
cbmrrnut	09/12/2011 07:30	1	1
cbmrrnut	09/26/2011 07:45	1	1
cbmrrnut	09/26/2011 07:46	1	2
cbmrrnut	10/11/2011 07:45	1	1

cbmrrnut	10/26/2011 07:30	1	1
cbmrrnut	10/26/2011 07:31	1	2
cbmrrnut	11/14/2011 10:00	1	1
cbmrrnut	11/14/2011 10:01	1	2
cbmrrnut	12/13/2011 09:00	1	1
cbmrrnut	12/13/2011 09:01	1	2

Iron Pot Landing (IP) Monthly Grab Sample

Station Code	DateTimeStamp	Monitoring Program	Rep
cbmipnut	01/05/2011 09:45	1	1
cbmipnut	01/05/2011 09:46	1	2
cbmipnut	02/23/2011 13:15	1	1
cbmipnut	02/23/2011 13:16	1	2
cbmipnut	03/23/2011 10:30	1	1
cbmipnut	03/23/2011 10:31	1	2
cbmipnut	04/05/2011 10:15	1	1
cbmipnut	04/19/2011 09:30	1	1
cbmipnut	04/19/2011 09:31	1	2
cbmipnut	05/03/2011 09:30	1	1
cbmipnut	05/17/2011 08:30	1	1
cbmipnut	05/17/2011 08:31	1	2
cbmipnut	05/31/2011 08:30	1	1
cbmipnut	06/14/2011 08:30	1	1
cbmipnut	06/28/2011 09:00	1	1
cbmipnut	06/28/2011 09:01	1	2
cbmipnut	07/13/2011 08:15	1	1
cbmipnut	07/28/2011 09:00	1	1
cbmipnut	07/28/2011 09:01	1	2
cbmipnut	08/11/2011 09:15	1	1
cbmipnut	08/25/2011 09:45	1	1
cbmipnut	08/25/2011 09:46	1	2
cbmipnut	09/12/2011 09:00	1	1
cbmipnut	09/26/2011 10:15	1	1
cbmipnut	09/26/2011 10:16	1	2
cbmipnut	10/11/2011 09:15	1	1
cbmipnut	10/26/2011 08:45	1	1
cbmipnut	10/26/2011 08:46	1	2
cbmipnut	11/14/2011 11:00	1	1
cbmipnut	11/14/2011 11:01	1	2
cbmipnut	12/13/2011 10:15	1	1
cbmipnut	12/13/2011 10:16	1	2

Iron Pot Landing (IP) DIEL Sampling

Station Code	DateTimeStamp	Monitoring Program	Rep
cbmipnut	01/04/2011 08:30	2	1
cbmipnut	01/04/2011 11:00	2	1
cbmipnut	01/04/2011 13:30	2	1
cbmipnut	01/04/2011 16:00	2	1
cbmipnut	01/04/2011 18:30	2	1
cbmipnut	01/04/2011 21:00	2	1

cbmipnut	02/23/2011 13:15	2	1
cbmipnut	02/23/2011 15:45	2	1
cbmipnut	02/23/2011 18:15	2	1
cbmipnut	02/23/2011 20:45	2	1
cbmipnut	02/23/2011 23:15	2	1
cbmipnut	02/24/2011 01:45	2	1
cbmipnut	02/24/2011 11:45	2	1
cbmipnut	02/24/2011 14:15	2	1
cbmipnut	03/23/2011 10:30	2	1
cbmipnut	03/23/2011 13:00	2	1
cbmipnut	03/23/2011 15:30	2	1
cbmipnut	03/23/2011 18:00	2	1
cbmipnut	03/23/2011 20:30	2	1
cbmipnut	03/23/2011 23:00	2	1
cbmipnut	03/24/2011 01:30	2	1
cbmipnut	03/24/2011 04:00	2	1
cbmipnut	03/24/2011 06:30	2	1
cbmipnut	03/24/2011 09:00	2	1
cbmipnut	03/24/2011 11:30	2	1
cbmipnut	04/04/2011 07:30	2	1
cbmipnut	04/04/2011 10:00	2	1
cbmipnut	04/04/2011 12:30	2	1
cbmipnut	04/04/2011 15:00	2	1
cbmipnut	04/04/2011 17:30	2	1
cbmipnut	04/04/2011 20:00	2	1
cbmipnut	04/04/2011 22:30	2	1
cbmipnut	04/05/2011 01:00	2	1
cbmipnut	04/05/2011 03:30	2	1
cbmipnut	04/05/2011 06:00	2	1
cbmipnut	04/05/2011 08:30	2	1
cbmipnut	05/03/2011 09:45	2	1
cbmipnut	05/03/2011 12:15	2	1
cbmipnut	05/03/2011 14:45	2	1
cbmipnut	05/03/2011 17:15	2	1
cbmipnut	05/03/2011 19:45	2	1
cbmipnut	05/03/2011 22:15	2	1
cbmipnut	05/04/2011 00:45	2	1
cbmipnut	05/04/2011 03:15	2	1
cbmipnut	05/04/2011 05:45	2	1
cbmipnut	05/04/2011 08:15	2	1
cbmipnut	05/04/2011 10:45	2	1
cbmipnut	06/13/2011 07:00	2	1
cbmipnut	06/13/2011 09:30	2	1
cbmipnut	06/13/2011 12:00	2	1
cbmipnut	06/13/2011 14:30	2	1
cbmipnut	06/13/2011 17:00	2	1
cbmipnut	06/13/2011 19:30	2	1
cbmipnut	06/13/2011 22:00	2	1
cbmipnut	06/14/2011 00:30	2	1
cbmipnut	06/14/2011 03:00	2	1

cbmipnut	06/14/2011 05:30	2	1
cbmipnut	06/14/2011 08:00	2	1
cbmipnut	07/12/2011 07:30	2	1
cbmipnut	07/12/2011 10:00	2	1
cbmipnut	07/12/2011 12:30	2	1
cbmipnut	07/12/2011 15:00	2	1
cbmipnut	07/12/2011 17:30	2	1
cbmipnut	07/12/2011 20:00	2	1
cbmipnut	07/12/2011 22:30	2	1
cbmipnut	07/13/2011 01:00	2	1
cbmipnut	07/13/2011 03:30	2	1
cbmipnut	07/13/2011 06:00	2	1
cbmipnut	07/13/2011 08:30	2	1
cbmipnut	08/24/2011 07:15	2	1
cbmipnut	08/24/2011 09:45	2	1
cbmipnut	08/24/2011 12:15	2	1
cbmipnut	08/24/2011 14:45	2	1
cbmipnut	08/24/2011 17:15	2	1
cbmipnut	08/24/2011 19:45	2	1
cbmipnut	08/24/2011 22:15	2	1
cbmipnut	08/25/2011 00:45	2	1
cbmipnut	08/25/2011 03:15	2	1
cbmipnut	08/25/2011 05:45	2	1
cbmipnut	08/25/2011 08:15	2	1
cbmipnut	09/12/2011 09:15	2	1
cbmipnut	09/12/2011 11:45	2	1
cbmipnut	09/12/2011 14:15	2	1
cbmipnut	09/12/2011 16:45	2	1
cbmipnut	09/12/2011 19:15	2	1
cbmipnut	09/12/2011 21:45	2	1
cbmipnut	09/13/2011 00:15	2	1
cbmipnut	09/13/2011 02:45	2	1
cbmipnut	09/13/2011 05:15	2	1
cbmipnut	09/13/2011 07:45	2	1
cbmipnut	09/13/2011 10:15	2	1
cbmipnut	10/26/2011 08:45	2	1
cbmipnut	10/26/2011 11:15	2	1
cbmipnut	10/26/2011 13:45	2	1
cbmipnut	10/26/2011 16:15	2	1
cbmipnut	10/26/2011 18:45	2	1
cbmipnut	10/26/2011 21:15	2	1
cbmipnut	10/26/2011 23:45	2	1
cbmipnut	10/27/2011 02:15	2	1
cbmipnut	10/27/2011 04:45	2	1
cbmipnut	10/27/2011 07:15	2	1
cbmipnut	10/27/2011 09:45	2	1
cbmipnut	11/14/2011 11:30	2	1
cbmipnut	11/14/2011 14:00	2	1
cbmipnut	11/14/2011 16:30	2	1
cbmipnut	11/14/2011 19:00	2	1

cbmipnut	11/14/2011 21:30	2	1
cbmipnut	11/15/2011 00:00	2	1
cbmipnut	11/15/2011 02:30	2	1
cbmipnut	11/15/2011 05:00	2	1
cbmipnut	11/15/2011 07:30	2	1
cbmipnut	11/15/2011 10:00	2	1
cbmipnut	11/15/2011 12:30	2	1
cbmipnut	12/19/2011 09:15	2	1
cbmipnut	12/19/2011 11:45	2	1
cbmipnut	12/19/2011 14:15	2	1
cbmipnut	12/19/2011 16:45	2	1
cbmipnut	12/19/2011 19:15	2	1
cbmipnut	12/19/2011 21:45	2	1
cbmipnut	12/20/2011 00:15	2	1
cbmipnut	12/20/2011 02:45	2	1
cbmipnut	12/20/2011 05:15	2	1
cbmipnut	12/20/2011 07:45	2	1
cbmipnut	12/20/2011 10:15	2	1

Otter Point Creek (OC) Monthly Grab Sample

Station Code	DateTimeStamp	Monitoring Program	Rep
cbmocnut	03/29/2011 09:45	1	1
cbmocnut	03/29/2011 09:46	1	2
cbmocnut	04/12/2011 09:30	1	1
cbmocnut	04/26/2011 07:15	1	1
cbmocnut	04/26/2011 07:16	1	2
cbmocnut	05/10/2011 07:15	1	1
cbmocnut	05/24/2011 07:15	1	1
cbmocnut	05/24/2011 07:16	1	2
cbmocnut	06/08/2011 07:45	1	1
cbmocnut	06/23/2011 07:15	1	1
cbmocnut	06/23/2011 07:16	1	2
cbmocnut	07/07/2011 07:15	1	1
cbmocnut	07/26/2011 10:15	1	1
cbmocnut	07/26/2011 10:16	1	2
cbmocnut	08/09/2011 07:45	1	1
cbmocnut	08/23/2011 08:00	1	1
cbmocnut	08/23/2011 08:01	1	2
cbmocnut	09/06/2011 07:30	1	1
cbmocnut	09/20/2011 07:00	1	1
cbmocnut	09/20/2011 07:01	1	2
cbmocnut	10/06/2011 07:15	1	1
cbmocnut	10/20/2011 07:30	1	1
cbmocnut	10/20/2011 07:31	1	2
cbmocnut	11/03/2011 07:30	1	1
cbmocnut	11/21/2011 08:15	1	1
cbmocnut	11/21/2011 08:16	1	2
cbmocnut	12/06/2011 08:45	1	1
cbmocnut	12/06/2011 08:46	1	2
cbmocnut	12/19/2011 08:30	1	1

7) Associated researchers and projects

As part of the SWMP long-term monitoring program, CBM NERR also monitors meteorological and water quality data which may be correlated with this nutrient dataset. These data are available from the Research Coordinator or online at <http://cdmo.baruch.sc.edu>.

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 for 2010. 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 2011. 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

The National Estuarine Research Reserve retains the right to be fully credited for having collected and processed the data. Following academic courtesy standards, the reserve 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. These data sets are 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 or 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.

Suggested citation format:

National Estuarine Research Reserve System (NERRS). 2012. System-wide Monitoring Program. Data accessed from the NOAA NERRS Centralized Data Management Office website: www.nerrsdata.org; accessed 12 October 2012.

NERR nutrient data and metadata can be obtained from the Research Coordinator at the individual NERR site (please see Principal investigators and contact persons), from the Data Manager at the Centralized Data Management Office (please see personnel directory under the general information link on the CDMO home page) and online at the CDMO home page www.nerrsdata.org. Data are available in comma separated version format.

II. Physical Structure Descriptors

9) Entry verification

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. 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 Phosphorous	TDP	mg/L as P
	Dissolved Organic Phosphorous	DOP	mg/L as P
	Total Dissolved Nitrogen	TDN	mg/L as N
	*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
	Dissolved Organic Nitrogen	DON	mg/L as N
Plant Pigments:			
	*Chlorophyll a	CHLA_N	µg/L
	Phaeophytin	PHEA	µg/L
Other Lab parameters:			
	Total Suspended Solids	TSS	mg/L
	Total Volatile Solids	TVS	mg/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:	NH4F, NO2F, NO23F, TDN
Phosphorus species:	PO4F, TDP
Other:	CHLA_N, PHEA, TSS, TVS

b) Calculated parameters

NO3F	NO23F-NO2F
DIN	NO23F+NH4F
DON	TDN-NO23F+NH4F
DOP	TDP-PO4F

12) Limits of detection

The Method Detection Limit (MDL), the lowest concentration of a parameter than an analytical procedure can reliably detect, have been established by NASL at the UMCES CBL. 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
PHEA	01/01/11	12/31/11	0.74
CHLA_N	01/01/11	12/31/11	0.62
NH4F	01/01/11	12/31/11	0.001
NO23F	01/01/11	12/31/11	0.0007
NO2F	01/01/11	12/31/11	0.0002
PO4F	01/01/11	12/31/11	0.0006
TDN	01/01/11	12/31/11	0.05
TDP	01/01/11	12/31/11	0.0015
TSS	01/01/11	12/31/11	2.4
TVS	01/01/11	12/31/11	0.9

13) Laboratory methods

a) Parameter: PO4F

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 47 mm glass fiber filter pads, decanted into an Auto Analyzer vial, and placed on ice. Upon returning to the lab, the Auto Analyzer vial is placed in freezer at -20°C until analysis. Maximum holding time is 28 days.

b) Parameter: NH4F

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 47 mm glass fiber filter pads, decanted into an Auto Analyzer vial, and placed on ice. Upon returning to the lab, the Auto Analyzer vial is placed in freezer at -20°C until analysis. Maximum holding time is 28 days.

c) **Parameter: NO2F**

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 47 mm glass fiber filter pads, decanted into an Auto Analyzer vial, and placed on ice. Upon returning to the lab, the Auto Analyzer vial is placed in freezer at -20°C until analysis. Maximum holding time is 28 days.

d) **Parameter: NO23F**

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 are 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 air-segmented continuous-flow analysis, Environ. Sci Tech. 2002, 36, 729-735. <http://www.nitrate.com/pattonetal2002>.

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

e) **Parameter: Chlorophyll and Phaeophytin**

i) **Method Summary:** The chlorophyll and related compounds are extracted from the filtered algae with aqueous buffered 90% acetone solution. The sample is allowed to extract for a minimum of 2 and not to exceed 24 hours in the dark under refrigeration at 4 degrees C, plus or minus 2 degrees C. The samples are centrifuged to separate sample material from the extract. The sample extract is filtered through a 0.45 um PTFE or nylon syringe filter before analysis due to waters from the Maryland portion of the Chesapeake Bay being relatively turbid. The concentration of the pigments is determined by measuring the light absorption of the extract at 750nm. To determine phaeophytin and active ChlA, the extract is then acidified with enough 1N HCl to achieve a concentration of 0.003 N HCl within the sample and reread. The concentrations are then calculated using Lorenzen's modified monochromatic equation.

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 47 mm 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: 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 47 mm glass fiber filter pad (0.7 µm 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: 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 30 ml screw cap test tubes and frozen. Upon delivery to the lab, the test tubes are placed in the 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 up to 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
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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
<i>Cloud cover</i>	
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)
<i>Precipitation</i>	
PNP	none
PDR	drizzle
PLR	light rain
PHR	heavy rain
PSQ	squally
PFQ	frozen precipitation (sleet/snow/freezing rain)
PSR	mixed rain and snow
<i>Tide stage</i>	
TSE	ebb tide
TSF	flood tide
TSH	high tide
TSL	low tide
<i>Wave height</i>	
WH0	0 to <0.1 meters
WH1	0.1 to 0.3 meters
WH2	0.3 to 0.6 meters
WH3	0.6 to > 1.0 meters
WH4	1.0 to 1.3 meters
WH5	1.3 or greater meters
<i>Wind direction</i>	
N	from the north
NNE	from the north northeast
NE	from the northeast
ENE	from the east northeast
E	from the east
ESE	from the east southeast
SE	from the southeast
SSE	from the south southeast
S	from the south
SSW	from the south southwest

SW	from the southwest
WSW	from the west southwest
W	from the west
WNW	from the west northwest
NW	from the northwest
NNW	from the north northwest
<i>Wind speed</i>	
WS0	0 to 1 knot
WS1	> 1 to 10 knots
WS2	> 10 to 20 knots
WS3	> 20 to 30 knots
WS4	> 30 to 40 knots
WS5	> 40 knots

17) Other remarks/notes

Data may be missing due to problems with sample collection or processing. Laboratories in the NERRS System submit data that are censored at a lower detection rate limit, called the Method Detection Limit or MDL. MDLs for specific parameters are listed in the Laboratory Methods and Detection Limits Section (Section II, Part 12) of this document. Concentrations that are less than this limit are censored with the use of a QAQC flag and code, and the reported value is the method detection limit itself rather than a measured value. For example, if the measured concentration of NO₃F was 0.0005 mg/l as N (MDL=0.0008), the reported value would be 0.0008 and would be flagged as out of sensor range low (-4) and coded SBL. In addition, if any of the components used to calculate a variable are below the MDL, the calculated variable is removed and flagged/coded -4 SCB. If a calculated value is negative, it is rejected and all measured components are marked suspect. If additional information on MDL's or missing, suspect, or rejected data is needed, contact the Research Coordinator at the Reserve submitting the data.

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

The ISCO sampler for the DIEL program only collected six samples in January and eight samples in February. Nighttime temperatures dropped below freezing during these collection times, which resulted in a frozen sampling hose.

Water quality monitors were pulled from Otter Point Creek (OC) and Mataponi Creek (MC) during the months of January and February. Due to the shallow nature of these sites and freezing temperatures during the winter months, the creeks freeze over and the probes become exposed to the cold air, making it unsafe to leave the sondes deployed. Therefore, no nutrient sampling was performed at these sites during those months.

QAQC "Check metadata for further details" (CSM) comments

The following samples at IP had elevated NH4F concentrations. It is unclear what caused the elevated concentrations, but they do not appear to be due to sample contamination and there is a wastewater treatment plant upstream. The elevated March samples coincided with a rain event.

Station Code	DateTimeStamp	Monitoring Program	Rep	NH4F	F_NH4F
cbmipnut	02/24/2011 11:45	2	1	1.140	<0> (CSM)
cbmipnut	02/24/2011 14:15	2	1	2.120	<0> (CSM)
cbmipnut	03/23/2011 13:00	2	1	1.050	<0> (CSM)
cbmipnut	03/23/2011 15:30	2	1	1.120	<0> (CSM)
cbmipnut	03/23/2011 18:00	2	1	1.210	<0> (CSM)
cbmipnut	03/23/2011 20:30	2	1	1.160	<0> (CSM)
cbmipnut	03/23/2011 23:00	2	1	1.200	<0> (CSM)

The following November grab samples at IP and RR also show elevated nitrogen levels. The cause is unknown but does not appear to be sample contamination.

Station Code	DateTimeStamp	Monitoring Program	Rep	NH4F	F_NH4F	NO2F	F_NO2F	NO3F	F_NO3F	NO23F	F_NO23F
cbmrrnut	11/14/2011 10:00	1	1	0.242	<1> [SRD] (CSM)	0.1007	<0> (CSM)	1.309	<0> (CSM)	1.410	<0> (CSM)
cbmrrnut	11/14/2011 10:01	1	2	0.189	<1> [SRD] (CSM)	0.0997	<0> (CSM)	1.300	<0> (CSM)	1.400	<0> (CSM)
cbmipnut	11/14/2011 11:00	1	1	0.102	<0> (CSM)	0.0645	<0> (CSM)	1.286	<0> (CSM)	1.350	<0> (CSM)
cbmipnut	11/14/2011 11:01	1	2	0.094	<0> (CSM)	0.0617	<0> (CSM)	1.348	<0> (CSM)	1.410	<0> (CSM)

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	12/13/2011 11:15	1	1		<-2> [GDM] (CSM)		<-2> [GDM] (CSM)
cbmocrnut	05/24/2011 07:15	1	1		<-2> [GDM] (CSM)		<-2> [GDM] (CSM)
cbmocrnut	11/03/2011 07:30	1	1		<-2> [GDM] (CSM)		<-2> [GDM] (CSM)
cbmocrnut	12/06/2011 08:45	1	1		<-2> [GDM] (CSM)		<-2> [GDM] (CSM)

The following TDN/TDP sample data are missing with a problem code from the lab associated with them stating that no sample was received:

Station Code	DateTimeStamp	Monitoring Program	Rep	TDN	F_TDN	TDP	F_TDP
cbmipnut	04/04/2011 17:30	2	1		<-2> [GDM] (CSM)		<-2> [GDM] (CSM)
cbmipnut	09/26/2011 10:15	1	1		<-2> [GDM] (CSM)		<-2> [GDM] (CSM)

The following Chlorophyll A and Phaeophytin sample data are missing due to laboratory accidents:

Station Code	DateTimeStamp	Monitoring Program	Rep	CHLA_N	F_CHLA_N	PHEA	F_PHEA
cbmmcnut	12/13/2011 11:15	1	1		<-2> [GDM] (CSM)		<-2> [GDM] (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	PHEA	F_PHEA
cbmmcnut	09/12/2011 10:15	1	1		<-2> (CSM)		<-2> (CSM)
cbmrrnut	09/12/2011 07:30	1	1		<-2> (CSM)		<-2> (CSM)
cbmrrnut	12/13/2011 09:01	1	2		<-2> (CSM)		<-2> (CSM)
cbmipnut	05/03/2011 09:30	1	1		<-2> (CSM)		<-2> (CSM)
cbmipnut	09/12/2011 09:00	1	1		<-2> (CSM)		<-2> (CSM)
cbmipnut	10/11/2011 09:15	1	1		<-2> (CSM)		<-2> (CSM)
cbmipnut	10/26/2011 08:45	1	1		<-2> (CSM)		<-2> (CSM)
cbmipnut	10/26/2011 08:46	1	2		<-2> (CSM)		<-2> (CSM)
cbmipnut	11/14/2011 11:00	1	1		<-2> (CSM)		<-2> (CSM)
cbmipnut	11/14/2011 11:01	1	2		<-2> (CSM)		<-2> (CSM)
cbmipnut	12/13/2011 10:15	1	1		<-2> (CSM)		<-2> (CSM)
cbmipnut	12/13/2011 10:16	1	2		<-2> (CSM)		<-2> (CSM)

The following TVS sample data is missing due to laboratory accidents:

Station Code	DateTimeStamp	Monitoring Program	Rep	TVS	F_TV_S
cbmipnut	10/26/2011 08:45	1	1		<-2> [GDM] (CSM)

The following TVS sample data is missing due to quality control standards. In the raw data received from the analytical lab, a problem code was associated with the sample indicating that the sample result was rejected by the lab due to quality control criteria:

Station Code	DateTimeStamp	Monitoring Program	Rep	TVS	F_TV_S
cbmrrnut	07/13/2011 07:15	1	1		<-2> (CSM)

The following TVS sample data are missing for an unknown reason. There was no problem code associated with this sample in the raw data received from the analytical lab:

Station Code	DateTimeStamp	Monitoring Program	Rep	TVS	F_TV_S
cbmmcnut	11/14/2011 12:15	1	1		<-2> [GDM] (CSM)
cbmrrnut	11/14/2011 10:00	1	1		<-2> [GDM] (CSM)
cbmipnut	11/14/2011 11:00	1	1		<-2> [GDM] (CSM)
cbmocnut	11/03/2011 07:30	1	1		<-2> [GDM] (CSM)
cbmocnut	11/21/2011 08:15	1	1		<-2> [GDM] (CSM)

Significant weather events of note in 2011 (to possibly explain observed data):

01/26/2011 – Large winter storm consisting of snow (“thundersnow”), rain, and sleet

04/16-17/2011 – Large amounts of rain (flooding)

07/08/2011 – Flash flooding

08/27-29/2011 – Hurricane Irene – Large amounts of rain

09/05-09/2011 – Tropical Storm Lee – Massive amounts of rain causing historical flooding in the Chesapeake Bay and its watershed (upwards of 13 inches of rain in some areas).

12/07/2011 – Massive amounts of rain