

Jobos Bay (JOB) NERR Nutrient Metadata
January-July 2019
Latest Update: September 24, 2024

I. Data Set and Research Descriptors

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2) Research objectives –

The main objective of this monitoring program is to understand the nutrients dynamics within Jobos Bay that may come from the watershed affecting the health of the estuary. Inorganic nutrients, particularly nitrogen and phosphorus are naturally found in mangrove and estuarine habitats. They can be significantly increased by human activities reaching the system through non-point source run-off or direct discharge. Eutrophication is defined as gradual accumulation of nutrients and organic biomass accompanied with an increase in photosynthesis and a decrease in the average depth of the water column caused by the accumulation of sediment.

a) Monthly grab sampling program

The objective of this study is to provide baseline information on inorganic nutrients and chlorophyll levels in the Jobos Bay estuary. It will also assess nutrients and chlorophyll levels in areas within the Reserve that may be receiving impact from human activities from surrounding areas or may act as a habitat gradient in the Bay. In order to compare these with physical (abiotic) water quality parameters, monitoring sites were established at the four SWMP datasonde stations.

Station number nine (9), was chosen as the impacted site, and collects water quality data in a site associated with runoff from littoral and basin mangrove areas. This lagoon has an average depth of 1.5 meters and its water regime is subject to high concentrations of tannin pigments associated with red mangroves. This station is characterized by a low water exchange due to a low circulation pattern. This sampling station is located in the most inland lagoon northeast of Mar Negro, closest to the thermoelectric power plant. It is subjected to runoff, which may include potential oil spill contamination from this industrial facility and agrochemicals from agricultural activities within the northern boundary of the reserve. Information compiled from historical environmental documents, indicate that station nine (9) was used as a disposal site for residues of the previously operating sugar mill operation, and therefore might have high organic input into the sediments. Of the four water quality monitoring stations, this has the lowest dissolved oxygen values during the year. Benthic vegetation is scarce.

Station number ten (10), located in a mangrove lagoon area towards the southwestern section of Mar Negro is considered the reference or non-impacted site. This station is characterized by a low water exchange due to a low circulation pattern. This lagoon has an average depth of 2 meters and the water regime is subject to high concentrations of tannin pigments associated with red mangroves. Benthic vegetation is scarce.

Station number nineteen (19) is located in Jobos Bay surrounded by sea grass beds composed of *Thalassia testudinum*. This station is close to the power plant navigation channel, used by barges to bring oil and gas into the power plant pier. This area is exposed to barge standings and sediment re-suspension, and oil spills are always a threat.

Station number twenty (20) is located adjacent to the Cayos Caribe reef system. Water currents coming from the reef platform may bring to this station an indication of water conditions behind the coral reef. These water currents are part of the main marine current coming from the eastern side of Jobos Bay that runs along the coast, coming in contact with sensitive areas like agricultural fields, a coal power plant, an oil refinery (Phillips Core - shut down in 2005) and other industries.

See the Site location and character section for more information on the chosen sample sites.

b) Diel sampling program

The diel sampling program objective is to quantify the temporal variability of important nutrients and sediment loading in the water column as a function of tidal forcing.

3) Research methods –

a) Monthly grab sampling program

Monthly grab samples are taken at the four datasonde stations. Grab samples are taken on the same day, at or as near as possible to slack low-tide conditions. Efforts are made to collect samples at approximately monthly intervals. Samples are not influenced by previous storm events. Grab samples are representative of the water mass sampled by the datasonde. Because we have shallow and well-mixed water at our stations, two surface grab samples are collected that are representative of the datasonde sampling area. Replicate (N=2) sample were collected by hand at an approximate depth of 30 cm.

Grab samples are taken in duplicate (two separate samples collected in different bottles); resulting in a total of eight samples. All samples were collected in amber, Nalgene™ sample bottles that were previously acid washed (10%) rinsed (3x) with distilled-deionized water, dried and followed by rinsing (3x) with ambient water prior to collection of the sample. Samples were immediately placed on ice, in the dark and returned to the laboratory. Samples from January to July were immediately placed on ice in dark bottles for chlorophyll and clear bottles for nutrients, and sent to the Laboratorio Central Analitico at UPR for filtering and analysis.

b) Diel sampling program

Diel samples are taken at long-term datasonde station 9. Samples are collected over a full lunar cycle (24 hr:48 min) time period at 2 hours 11 minute intervals using an ISCO auto-sampler model 6712. The suction line is set to sample at 0.5 meters from the bottom, and is covered with a mesh to avoid clogging with organic debris. Efforts are made to collect samples at approximately monthly (30 days) intervals. Samples are not influenced by previous storm events; an antecedent dry period of 72 hours is desirable but may not be practical at all locations throughout the year. Sampling depth follows the following design; samples are collected at a fixed depth from the bottom, generally 0.5 meter, and reflect the water mass sampled by the datasonde. The ISCO automatically samples 1000 ml of water every 2 hrs 11 min. A field blank consisting of DI water is placed in the bottle rack and left open during the diel sampling. All samples are pumped into polyethylene sample bottles that were previously acid washed (10%), rinsed (3x) with distilled-deionized water and dried. At the end of the 24 hr period, the 12 samples are kept in the dark and returned to the laboratory for immediate processing. Samples from January to July were immediately placed on ice in the dark bottles for Chlorophyll and clear bottles for nutrients and sent to the Laboratorio Central Analitico at UPR for filtering and analysis.

4) Site location and character –

The Jobos Bay National Estuarine Research Reserve (JOB NERR) is located on the southern coastal plain of the island of Puerto Rico, a reserve within the West Indies geographical area. JOB NERR is composed of two major areas: (1) Mar Negro, located on the western margin of the Bay, and (2) Cayos Caribe (a chain of 17 tear-shaped islets located to the southeast) and Cayos Barca (a chain of 7 tear-shaped islets located to the southwest boundaries), both with a back-reef system. The Mar Negro area comprises the bulk of the reserve, and consists of mangrove forests and a complex system of lagoons and channels interspersed with salt and mud flats. Coral reefs and sea grass beds, with small beach deposits and upland areas fringe the Cayos Caribe and Cayos Barca mangrove islands. Few areas in the watershed drain directly to the bay. Rio Seco to the north-east of the bay is active only during heavy rain events during the wet season. A small creek, Quebrada Coqui, near JOB NERR's pier to the north of the bay, drains into an extensive mangrove fringe forest in a laminar flow. During heavy rain events, Station 09 receives runoff water from the upland, and finally, a diffuse flow of water reaches the bay from the local aquifer.

Station 9 is an impacted site and is located on the northeastern section of the Mar Negro component. This sampling station is associated with mangrove lagoon areas and receives runoff from mudflats, the thermoelectric power plant, and adjacent areas. The tidal range varies from 0.3 to 0.36 meters near the monitoring station. The salinity at the vicinity of the monitoring station varies from 30.9 to 37.5 psu. The average depth and total depth at station 09 is 0.72 and 1.22 meters respectively. The bottom is covered by a thick layer of thin sediments with a high content of organic material. *Microcoleus* sp. (blue-green algae), brown and green algae (*Caulerpa* sp.) are also present at this site, but a better assessment is needed. The station was located at 17°56'34.87" N and 66°14'18.64" W until 09/02/2010 12:00PM, then it was relocated to 17°56'35.0" N and 66°14'18.9" W approximately 65.0 meters from its original position. The relocation was due to sedimentation issues and the construction of a new telemetry station. Fresh water input to the station comes only from runoff and rain. This station has been the subject of several studies indicating the presence of relatively high levels of copper and pesticides compared to other stations. Since 2015 an invasive seagrass, *Halophila stipulacea* was reported at Jobos Bay, and it was after the passage of Hurricane Maria on September 21, 2017 that it was more evident and widely distributed. Although it is not present at Station 9, it is present in the channels toward the station and we expect it will colonize the area in the near future.

Statistics for station 9 during 2019

	Temp	SpCond	Sal	DO_pct	DO_mgl	Depth	pH	Turb
Min	25.0	47.48	30.9	1.5	0.1	0.39	6.9	0
Max	32.9	56.50	37.5	108.5	9.8	0.90	8.2	32
Average	29.2	53.29	35.0	56.1	3.8	0.66	7.5	2
Std Dev	1.4	1.02	0.7	18.9	1.4	0.09	0.2	1

Station 10 is located in a mangrove lagoon not impacted directly by any upland or marine activities. It provides a reference for comparison of data obtained in other stations, especially to the station in Mar Negro lagoon. The tidal range varies from 0.3 to 0.36 meters. The salinity at the vicinity of the monitoring station varies from 20.7 to 36.7 psu. The average depth and total depth at station 10 is 0.66 and 1.00 meters respectively. The bottom is covered with a layer of fine sediments with organic material, followed by a layer of calcareous material mainly from shells and oysters. At this site, we can find sea grass (*Thalassia testudinum*), calcareous algae (*Halimeda* sp.), green algae (*Caulerpa* sp.) and brown algae (*Dictyota* sp.) among others. The station is located at 17°56'19.00 N, 66°15'27.85 W. Fresh water input to the station comes only from runoff and rain. There is no direct source of fresh water. Since 2015 an invasive seagrass, *Halophila stipulacea* was reported at Jobos Bay, and it was after the passage of Hurricane Maria on September 21, 2017 that it was more evident and widely distributed, and has been observed in the perimeter of the station.

Statistics for station 10 during 2019

	Temp	SpCond	Sal	DO_pct	DO_mgl	Depth	pH	Turb
Min	25.1	33.30	20.7	3.0	0.2	0.34	7.2	0
Max	32.9	55.68	36.7	101.8	7.7	0.97	8.0	17
Average	29.4	51.10	33.4	68.5	4.5	0.68	7.7	2
Std Dev	1.4	4.26	3.1	17.7	1.3	0.14	0.1	2

Station 19 is located on the western inner section of the bay at a distance of 233 meters from Cayo Colchones Mangroves over sea grass beds (*Thalassia testudinum*). Tidal ranges in this area vary from 0.3 to 0.36 meters. The salinity at the vicinity of the monitoring station varies from 32.0 to 35.4 psu. The average depth and total depth at this station is 0.77 and 2.00 meters respectively. The datasonde is deployed at about 0.5 meter from the bottom. The bottom is of sandy composition, and sea grass, algae, echinoderms and other related organisms can be found in the area. The station is located at 17°56'34.49" N, 66°13'43.77" W. There is no freshwater input to this area. Since 2015 an invasive seagrass, *Halophila stipulacea* was reported at Jobos Bay, and it was after the passage of Hurricane Maria in September 21, 2017 that it was more evident and widely distributed, and has been observed in the perimeter of the station.

Statistics for station 19 during 2019

	Temp	SpCond	Sal	DO_pct	DO_mgl	Depth	pH	Turb
Min	25.3	49.14	32.0	56.6	3.5	0.60	7.7	0
Max	31.8	53.77	35.4	147.4	9.1	1.07	8.3	77
Average	28.8	52.32	34.3	99.1	6.3	0.84	8.0	1
Std Dev	1.4	0.84	0.6	14.9	0.9	0.09	0.1	2

Station 20 is located in the inner eastern section at about 190 meters from the Cayos Caribe mangrove islets and at about 688 meters from the coral reef barrier. This station is the closest to Mar

Caribe. It has a sandy bottom, with calcareous and coral fragments, sea grass (*Thalassia testudinum*) communities, echinoderms and other associated organisms. Tidal range in this area varies from 0.3 to 0.36 meters. The salinity at the vicinity of the monitoring station varies from 31.1 to 37.4 psu. The average depth and total depth at this station is 0.48 and 2.00 meters respectively. There is no surface freshwater input to this area. These waters are part of the main marine current coming from the eastern side of Jobos Bay that runs along the coast, getting in contact with sensitive areas like agricultural fields, a coal power plant, an oil refinery Phillips Core (shut down in 2005) and other industries. The station is located at 17°55'49.14" N, 66°12'41.30". Since 2015 an invasive seagrass, *Halophila stipulacea* was reported at Jobos Bay, and it was after the passage of Hurricane Maria in September 21, 2017 that it was more evident and widely distributed. It has been observed in the perimeter of the station.

Statistics for station 20 during 2019

	Temp	SpCond	Sal	DO_pct	DO_mgl	Depth	pH	Turb
Min	25.5	47.87	31.1	48.3	3.2	0.02	7.5	0
Max	31.8	56.35	37.4	157.2	10.9	0.84	9.7	9
Average	28.6	52.61	34.6	96.5	6.6	0.60	8.1	2
Std Dev	1.3	1.06	0.8	19.0	1.4	0.09	0.1	1

Nutrient data from stations 9, 10, 19 and 20 is being submitted to the CDMO. In addition, eight datasondes are permanently devoted to taking water quality readings from these four sites, to assure continuous readings while datasondes are taken out of the water for data upload and maintenance. This will avoid data gaps for the stations between datasonde maintenance procedures. Due to errors in calibration, turbidity data in these files is considered inadequate. All monitoring is considered long term.

All Jobos Bay NERR historical nutrient/pigment monitoring stations:

Station Code	SWMP Status	Station Name	Location	Active Dates	Reason Decommissioned	Notes
JOB09NUT	P	STATION 9	17° 56' 35.0" N 66° 14' 18.9" W	07/2002 - current	NA	NA
JOB10NUT	P	STATION 10	17° 56' 19.00 N, 66° 15' 27.85 W	07/2002 - current	NA	NA
JOB19NUT	P	STATION 19	17° 56' 34.49"N, 66° 13' 43.77"W	07/2002 - current	NA	NA
JOB20NUT	P	STATION 20	17° 55' 49.14"N, 66° 12' 41.30"W	07/2002 - current	NA	NA

5) Coded variable definitions –

Station Code Names:

job09nut – Station 9

job10nut – Station 10

job19nut – Station 19

job20nut – Station 20

Monitoring Programs:
 Monthly grab sample program (1)
 Diel grab sample program (2)

6) Data collection period –

Sampling did not occur from August to December 2019 due to administrative issues related to laboratory contract.

Diel:

Site	Start Date/ Time	Stop Date/ Time
9	01/16/2019 09:00	01/17/2019 09:01
9	02/26/2019 09:00	02/27/2019 09:01
9	03/19/2019 10:10	03/20/2019 10:11
9	04/10/2019 09:00	04/11/2019 09:01
9	05/07/2019 09:00	05/08/2019 09:01
9	07/01/2019 09:00*	07/02/2019 09:01*
9	07/15/2019 10:00	07/16/2019 10:01

Grab:

Site	Start Date/ Time	Stop Date/ Time
9	01/17/2019 10:31	01/17/2019 10:33
9	02/27/2019 09:21	02/27/2019 09:22
9	03/20/2019 10:50	03/20/2019 10:51
9	04/11/2019 09:20	04/11/2019 09:21
9	05/08/2019 09:20	05/08/2019 09:21
9	07/02/2019 10:20*	07/02/2019 10:21*
9	07/16/2019 11:18	07/16/2019 11:19

Site	Start Date/ Time	Stop Date/ Time
19	01/17/2019 09:45	01/17/2019 09:46
19	02/27/2019 08:55	02/27/2019 08:56
19	03/20/2019 09:05	03/20/2019 09:06
19	04/11/2019 08:30	04/11/2019 08:31
19	05/08/2019 10:53	05/08/2019 10:54
19	07/02/2019 08:52*	07/02/2019 08:53*
19	07/16/2019 09:05	07/16/2019 09:06

Grab (CONT):

Site	Start Date/ Time	Stop Date/ Time
10	01/17/2019 10:10	01/17/2019 10:11
10	02/27/2019 09:50	02/27/2019 09:51
10	03/20/2019 10:15	03/20/2019 10:16
10	04/11/2019 08:55	04/11/2019 08:56
10	05/08/2019 10:16	05/08/2019 10:17
10	07/02/2019 10:00*	07/02/2019 10:01*
10	07/16/2019 10:07	07/16/2019 10:08

Site	Start Date/ Time	Stop Date/ Time
20	01/17/2019 09:25	01/17/2019 09:26
20	02/27/2019 08:33	02/27/2019 08:34
20	03/20/2019 09:35	03/20/2019 09:36
20	04/11/2019 09:57	04/11/2019 09:58
20	05/08/2019 09:00	05/08/2019 09:01
20	07/02/2019 08:33*	07/02/2019 08:34*
20	07/16/2019 08:35	07/16/2019 08:36

*June grab and diel samples were collected in early July due to boat failure.

7) Associated researchers and projects–

As part of the SWMP long-term monitoring program, JOB NERR also monitors 15-minute meteorological and water quality data which may be correlated with this nutrient/pigment dataset. These data are available at www.nerrsdata.org.

The JOB NERR water quality monitoring data has been incorporated into the Puerto Rico Environmental Quality Board (EQB) Integrated Report 303(d)/305(b) of the Federal Clean Water Act. This document consists of a water quality inventory and list of impaired waters and is used by the Environmental Protection Agency (EPA) to inform Congress of the progress made at the national level towards the achievement of the statutory water quality goals and purposes established by the Federal Clean Water Act.

8) Distribution –

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

Requested citation format:

NOAA National Estuarine Research Reserve System (NERRS). System-wide Monitoring Program. Data accessed from the NOAA NERRS Centralized Data Management Office website: www.nerrsdata.org; accessed 12 October 2020.

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 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
	*Ammonium, Filtered	NH4F	mg/L as N
	*Nitrite, Filtered	NO2F	mg/L as N
	*Nitrate, Filtered	NO3F	mg/L as N
	*Nitrite + Nitrate, Filtered	NO23F	mg/L as N
	Dissolved Inorganic Nitrogen	DIN	mg/L as N
Plant Pigments:			
	*Chlorophyll-a	CHLA_N	µg/L
	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 –

- Parameters measured directly**
 - Nitrogen species: NH4F, NO2F, NO23F
 - Phosphorus species: PO4F
 - Other: CHLA_N, PHEA
- Calculated parameters**
 - NO3F NO23F-NO2F
 - DIN NO23F+NH4F

12) Limits of detection –

Method Detection Limits (MDL), the lowest concentration of a parameter that an analytical procedure can reliably detect, have been established by the Laboratorio Central Analitico at UPR. The MDL is determined as 3 times the standard deviation of a minimum of 7 replicates of a single low concentration sample. These values are reviewed and revised periodically.

Parameter	Start Date	End Date	MDL	Revisited
PO4F	01/01/19	07/31/19	0.015mg/L	06/12/20
NH4F	01/01/19	07/31/19	0.010 mg/L	06/12/20
NO2F	01/01/19	07/31/19	0.016mg/L	06/12/20
NO23F	01/01/19	07/31/19	0.022mg/L	06/12/20
CHLA_N	01/01/19	07/31/19	0.10 ug/L	06/12/20
PHEA	01/01/19	07/31/19	0.10 ug/L	06/12/20

13) **Laboratory methods** – all samples were held at -20°C until analysis.

a) **Parameter: NH₄F**

Laboratorio Central Analitico (UPR) Method:

Method No. G-171-96 Rev. 17 (Multitest MT19)

Ammonia in Water and Seawater

Ranges: 0 - 3 to 0 - 27 $\mu\text{mol/L}$ (0 - 42 to 0 - 380 $\mu\text{g/L}$ as N)

and 0- 25 to 0- 300 $\mu\text{mol/L}$ (0-0.35 to 4.2 mg/L as N)

Description

This method uses the Berthelot reaction, in which a blue-green colored complex is formed which is measured at 660 nm. A complexing agent is used to prevent the precipitation of calcium and magnesium hydroxides. Sodium nitroprusside is used to enhance the sensitivity. Alternative reagents are given for reaction with salicylate and phenate.

Hardware: 37°C heating bath (5.37 mL)

Pump tubes: 6 + 2 air + sampler wash

Multitest: aluminum, ammonia, color, copper, chloride, iron, manganese, nitrate, total N in persulphate digests, nitrogen (total Kjeldahl), phosphate, total phosphorus (Kjeldahl), silicate, sulfide and zinc.

Performance data using synthetic seawater standards and AA3 colorimeter

Test conditions: range: 0 - 10 $\mu\text{mol/L}$ $\Rightarrow$ yel/yel sample tube, AA3 colorimeter, 10 mm flowcell and lamp

Reagents: **Salicylate**

	Sample A 0-10 μmol	Sample B 0-300 μmol
Sample tube	yel/yel	orn/grn
Sampling rate	60/h	60/h
Sample : wash ratio	4:1	4:1
Sensitivity at 10 / 300 $\mu\text{mol/L}$	0.04-0.07	0.15-0.19
Reagent absorbance	0.02-0.04	0.02-0.04
Coefficient of Variation	0.3%	
Pooled standard deviation		
25 at 5 levels	0.05 $\mu\text{mol/L}$	
Correlation Coefficient (5 points, linear)	0.999	
Detection limit	0.040 $\mu\text{mol/L}$	
(determined according to EPA procedure (0.56 $\mu\text{g/L}$ as N) pt. 136, app. B)		
Detection Limit (EPA pt. 136, app B)	0.034 $\mu\text{mol/L}$	
Range 0-3 $\mu\text{mol/L}$ (0-40 $\mu\text{g/L}$ N)	(0.48 $\mu\text{g/L}$ as N)	

b) Parameter: NO₂F

Laboratorio Central Analitico (UPR) Method:

Method No. G-172-96 Rev. 19 (Multitest MT 19)

Nitrate and Nitrite in Water and Seawater Total Nitrogen in persulfate digests

**Ranges: 0 – 4.0 to 0 – 50 $\mu\text{mol/L}$ (0 - 56 to 0 - 700 $\mu\text{g/L}$ as N)
and 0 - 50 to 0 - 714 $\mu\text{mol/L}$ (0 - 700 to 0 - 10000 $\mu\text{g/L}$ as N)**

Description

This automated procedure for the determination of nitrate and nitrite uses the procedure whereby nitrate is reduced to nitrite by a copper-cadmium reductor column (1,2). The nitrite then reacts with sulfanilamide under acidic conditions to form a diazo compound. This compound then couples with N-1-naphthylethylene diamine dihydrochloride to form a purple azo dye. In most normal water and seawater samples the concentration of oxidizing or reducing agents and interfering metal ions is well below the limits causing interferences. When present in sufficient concentration, metal ions may produce a positive error, i.e. divalent mercury and divalent copper may form colored complex ions having adsorption bands in the region of the color measurement (3). Significant amounts of sulfate, sulfide or organic material, especially oil, interfere with the performance of the copper-cadmium reductor column. Such samples should be pre-treated before analysis. The method is also suitable for persulfate digested samples (see operating note 15) (4). The method is based on the nitrate determination in Standard Methods and in the DIN / ISO Standards for automatic nitrate measurements.

Hardware: 37°C heating bath (5.4 mL), Cd column **Pump tubes:** 6 + 2 air + sampler wash
Multitest: aluminum, ammonia, color, copper, chloride, iron, manganese, nitrate, total N in persulfate digests, nitrogen (total Kjeldahl), phosphate, total phosphorus (Kjeldahl), silicate, sulfide and zinc.

Typical performance using aqueous standards and AA3 colorimeter

Test conditions: range: 0 - 50 $\mu\text{mol/L}$ and 0 – 714 $\mu\text{mol/L}$ with AA3 colorimeter (10 mm flowcell and lamp)

	Sample A 0 - 50 $\mu\text{mol/L}$	Sample B 0 - 714 $\mu\text{mol/L}$
Pump tube	yell/yel	orn/grn
Sampling rate	60/hr	60/hr
Sample: wash ratio	4:1	4:1
Sensitivity: Extinction at 50 / 714 $\mu\text{mol/L}$	0.91	1.03
Reagent Absorbance	0.01-0.03	0.01-0.03
Coefficient of Variation (10 replicates at 50 %)	0.13%	3.66%
Pooled Standard Deviation (25 randomized at 5 levels)	0.143 $\mu\text{mol/L}$	0.143 $\mu\text{mol/L}$
Correlation Coefficient (5 points, linear)	0.9999	1.000
Detection Limit (determined according to EPA procedure pt. 136, app. B)	0.007 $\mu\text{mol/L}$	0.118 $\mu\text{mol/L}$
Detection Limit in lowest range (lowest range 0- 4.0 $\mu\text{mol/L}$)	0.006 $\mu\text{mol/L}$	

Note: the above performance specifications were developed with the exclusive use of genuine SEAL Analytical parts and consumables.

c) Parameter: NO23F

Laboratorio Central Analitico (UPR) Method:

Method No. G-172-96 Rev. 19 (Multitest MT 19)

Nitrate and Nitrite in Water and Seawater Total Nitrogen in persulfate digests

**Ranges: 0 – 4.0 to 0 – 50 $\mu\text{mol/L}$ (0 - 56 to 0 - 700 $\mu\text{g/L}$ as N)
and 0 - 50 to 0 - 714 $\mu\text{mol/L}$ (0 - 700 to 0 - 10000 $\mu\text{g/L}$ as N)**

Description

This automated procedure for the determination of nitrate and nitrite uses the procedure whereby nitrate is reduced to nitrite by a copper-cadmium reductor column (1,2). The nitrite then reacts with sulfanilamide under acidic conditions to form a diazo compound. This compound then couples with N-1-naphthylethylene diamine dihydrochloride to form a purple azo dye. In most normal water and seawater samples the concentration of oxidizing or reducing agents and interfering metal ions is well below the limits causing interferences. When present in sufficient concentration, metal ions may produce a positive error, i.e. divalent mercury and divalent copper may form colored complex ions having adsorption bands in the region of the color measurement (3). Significant amounts of sulfate, sulfide or organic material, especially oil, interfere with the performance of the copper-cadmium reductor column. Such samples should be pre-treated before analysis. The method is also suitable for persulfate digested samples (see operating note 15) (4). The method is based on the nitrate determination in Standard Methods and in the DIN / ISO Standards for automatic nitrate measurements.

Hardware: 37°C heating bath (5.4 mL), Cd column **Pump tubes:** 6 + 2 air + sampler wash
Multitest: aluminum, ammonia, color, copper, chloride, iron, manganese, nitrate, total N in persulfate digests, nitrogen (total Kjeldahl), phosphate, total phosphorus (Kjeldahl), silicate, sulfide and zinc.

Typical performance using aqueous standards and AA3 colorimeter

Test conditions: range: 0 - 50 $\mu\text{mol/L}$ and 0 – 714 $\mu\text{mol/L}$ with AA3 colorimeter (10 mm flowcell and lamp)

	Sample A 0 - 50 $\mu\text{mol/L}$	Sample B 0 - 714 $\mu\text{mol/L}$
Pump tube	yel/yel	orn/grn
Sampling rate	60/hr	60/hr
Sample: wash ratio	4:1	4:1
Sensitivity: Extinction at 50 / 714 $\mu\text{mol/L}$	0.91	1.03
Reagent Absorbance	0.01-0.03	0.01-0.03
Coefficient of Variation (10 replicates at 50 %)	0.13%	3.66%
Pooled Standard Deviation (25 randomized at 5 levels)	0.143 $\mu\text{mol/L}$	0.143 $\mu\text{mol/L}$
Correlation Coefficient (5 points, linear)	0.9999	1.000
Detection Limit (determined according to EPA procedure pt. 136, app. B)	0.007 $\mu\text{mol/L}$	0.118 $\mu\text{mol/L}$
Detection Limit in lowest range (lowest range 0- 4.0 $\mu\text{mol/L}$)	0.006 $\mu\text{mol/L}$	

Note: the above performance specifications were developed with the exclusive use of genuine SEAL Analytical parts and consumables.

d) Parameter: PO4F

Laboratorio Central Analitico (UPR) Method:

Method-No. G-297-03 Rev. 7 (Multitest MT 19)

Phosphate in water or Bray soil extracts

Range: 0 – 50 to 0 - 500 µg/L as P
Range: 1 – 200 µg/L as P (for Bray extracts)

Description

Following the method of Murphy and Riley, this automated procedure for the determination of ortho-phosphate is based on the colorimetric method in which a blue color is formed by the reaction of ortho-phosphate, molybdate ion and antimony ion followed by reduction with ascorbic acid at an pH<1. The reduced blue phospho-molybdenum complex is colorimetrically read at 880 nm.

Hardware: 37°C heating bath (5.37 mL)

Pump tubes: 6 + 2 air + sampler wash

Multitest: aluminium, ammonia, color, copper, chloride, iron, manganese, nitrate, total N in persulfate digests, nitrogen (total Kjeldahl), phosphate, total phosphorus (Kjeldahl), silicate, sulfide and zinc.

Typical performance data using aqueous standards and AA3 colorimeter

Test conditions: range: 0 - 50 µg/L as P and AA3 colorimeter with 10 mm flowcell

Sampling rate	60/h
Sample : wash ratio	3:1
Sensitivity: Extinction at 50 µg/L	0.016-0.020
Reagent absorbance	0.009-0.011
Coefficient of variation (10 replicates at 50%)	0.4%
Pooled standard deviation (25 randomized at 5 levels)	0.18 µg/L
Correlation Coefficient (linear, 5 points)	0.999
Detection limit (determined according to EPA procedure pt. 136, app. B)	0.29 µg/L

e) Parameter: CHLA_N and PHA

Laboratorio Central Analitico Method:

EPA or other Reference Method: EPA 445 REV 1.2

Method Reference: US.EPA 1997. USEPA 600/R-97/072. Method 445.0

Method Descriptor: Samples were filtered with a 0.47 µm membrane filter, placed dry in an amber vial and stored with ice packs. They were kept in the dark and extracted using 90% acetone.

Preservation Method: Samples are stored at 4°C up to 24 hours, followed by freezing @ -20°C.

Summary of Method:

The method for determining Chlorophyll-a is using fluorometry with a Turner Designs fluorometer. The method used requires filtering a known quantity of water through a glass fiber filter. This filter is later ground with a tissue grinder made of Teflon/glass. Approximately 2-3 mls of 90% acetone are added to the filter before grinding. Acetone is also used to wash the filter in to 17 x 150 test tube with tight fitting cap. The sample is steeped at least 2 hours and not exceeding 24 hours at 4°C, in the dark. The samples are centrifuged and read on the Turner fluorometer. If pheophytin measurements are desired, the sample is acidified and read again.

14) Field and Laboratory QAQC programs –

a) Precision

- i) **Field variability** – Two successive true replicate grab samples are collected for the monthly grab samples at each of the four stations ensuring that replicate samples are collected at the same depth. They are collected successively by hand within the same minute.
- ii) **Laboratory variability** – n/a
- iii) **Inter-organizational splits** – n/a

b) Accuracy

- i) **Sample spikes** – n/a
- ii) **Standard reference material analysis** – n/a
- iii) **Cross calibration exercises** – *None*.

15) QAQC flag definitions –

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

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

16) QAQC code definitions –

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

flag column (F_Record) in the nutrient data allows multiple comment codes to be applied to the entire data record.

General errors

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

Sensor errors

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

Parameter Comments

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

Record comments

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

Cloud cover

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

Precipitation

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

PSR	mixed rain and snow
<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 NO₂3F was 0.0005 mg/l as N (MDL=0.0008), the reported value would be 0.0008 and would be flagged as out of sensor range low (-4) and coded SBL. In addition, if any of the components used to calculate a variable are below the MDL, the calculated variable is removed and flagged/coded -4 SCB. If a calculated value is negative, it is rejected and all measured components are marked suspect. If additional information on MDL's or missing, suspect, or rejected data is needed, contact the Research Coordinator at the reserve submitting the data.

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

Sample hold times for 2019: Samples are held at -20°C. NERRS SOP allows nutrient samples to be held for up to 28 days (CHLA for 30) at -20°C, plus allows for up to 5 days for collecting, processing, and shipping samples. Samples held beyond that time period are flagged suspect and coded CHB.

Collection_ Date	Date of lab analysis					
	CHLA	PHEO	NH3	NOx	NO2	O-PO4
01/16/2019- 01/17/2019	1/30/2019	1/30/2019	4/3/2019*	4/10/2019*	4/4/2019*	4/23/2019*
02/26/2019- 02/27/2019	6/24/2019*	6/24/2019*	4/3/2019*	4/10/2019*	4/4/2019*	4/23/2019*
03/19/2019- 03/20/2019	6/24/2019*	6/24/2019*	4/3/2019	4/10/2019	4/4/2019	4/25/2019*
04/10/2019- 04/11/2019	NA	NA	5/15/2019*	5/17/2019*	5/8/2019	4/25/2019
05/07/2019- 05/08/2019	NA	NA	5/15/2019	5/17/2019	5/20/2019	5/22/2019
07/01/2019- 07/02/2019	NA	NA	7/11/2019	7/11/2019	7/12/2019	7/16/2019
07/15/2019- 07/16/2019	NA	NA	7/19/2019	7/22/2019	8/7/2019	8/15/2019

*sample held longer than allowed by NERRS protocols. NA means sample not analyzed.

Missing data:

From 04/10/2019 to 04/11/2019 collected samples for CHLA/PHEO Lab# A-19-0382 to A-19-0401. The water was filtered in the laboratory on April 12, 2019, but was not analyzed.

From 05/07/2019 to 05/08/2019 collected samples for CHLA/PHEO Lab# A-19-0448 to A-19-0467. The water was filtered in the laboratory on May 9, 2019 but was not analyzed.

From 07/01/2019 to 07/02/2019 collected samples for CHLA/PHEO Lab# A-19-0596 to A-19-0607. The water was filtered in the laboratory on July 3, 2019 but was not analyzed.

From 07/15/2019 to 07/16/2019 collected samples for CHLA/PHEO Lab# A-19-0622 to A-19-0641. The water was filtered in the laboratory on July 17, 2019 but was not analyzed.

07/01/2019 Diel Sample Station 09 data (5,6,7,8,9,10,11,12) from 17:44 to 22:06 and 07/02/2019 from 00:17 to 09:01. Sample empty. Flagged <-2> [GDM]

Lab# 5 at 17:44
Lab# 6 at 19:55
Lab# 7 at 22:06
Lab# 8 at 00:17

Lab# 9 at 02:26
Lab# 10 at 04:39
Lab# 11 at 06:50
Lab# 12 at 09:01

Rain event:

Date	Precipitation (mm)	Event associated with
03/29/2019	25.4	
04/28/2019	23.4	
05/24/2019	42.9	
05/27/2019	18.54	
08/22/2019	30.5	
09/24/2019	64.0	Tropical Storm Karen
09/26/2019	30.7	
11/30/2019	51.1	

Remarks:

Sampling did not occur from August to December 2019 due to administrative issues related to laboratory contract.

The high minimum detection limits (MDLs) provided by the UPR laboratory resulted in much of the data registering below the MDL and therefore being replaced by the MDL value itself. Users should be aware that this difference in methodology can significantly impact the dataset for the time period that UPR analyzed samples and should consider this when looking for trends or performing data syntheses.