

**Narragansett Bay National Estuarine Research Reserve (NAR NERR)**

**Nutrient Metadata**

**January 2022 – December 2022**

**Latest Update: Sunday, June 11, 2023**

Note: This is a provisional metadata document; it has not been authenticated as of its download date. Contents of this document are subject to change throughout the QAQC process, and it should not be considered a final record of data documentation until that process is complete. Contact the CDMO ([cdmosupport@baruch.sc.edu](mailto:cdmosupport@baruch.sc.edu)) or reserve with any additional questions.

# I. Data Set and Research Descriptors

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**2021 - present**

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## Research objectives

Nutrient and chlorophyll samples are being collected off Prudence Island in Narragansett Bay as part of the Narragansett Bay National Estuarine Research Reserve's (NAR NERR or Reserve in this document) System-Wide Monitoring Program (SWMP) (Figure 1). The goal is to develop long-term datasets for representative estuarine systems to track changes in water quality over time. Being Prudence Island located in the geographic center of Narragansett Bay, it is an ideal location for monitoring the status and trends in water quality in the Bay over time. One NAR NERR monitoring site has been established at Potter Cove (PC), on the Island's northeastern shore. This area is impacted by boat traffic and storm runoff from mainland urban and residential areas. Two NAR NERR monitoring sites are located at T-Wharf, on the southeastern shore of the island facing the open waters of Rhode Island Sound. The two T-Wharf stations (T-Wharf Surface and T-Wharf Bottom, TS and TB, respectively) measure conditions in the upper (~1.0 m from the surface) and bottom (~1 m from the bottom) layers of the water column, respectively. These stations are approximately 10 km south of the Potter Cove site. Boat traffic is sparse at T-Wharf and storm runoff is less likely to have a significant impact on water quality. A fourth monitoring site is located in Nag Creek (NC), a salt marsh tidal creek which flows into the West Passage of Narragansett Bay. The addition of this site completes our representation of dominant habitat types occurring in Narragansett Bay, i.e., salt marsh (Nag Creek), shallow cove (Potter Cove), and open Bay water (T-Wharf Surface and T-Wharf Bottom).

Diagram, map

Description automatically generated

**Figure 1.** Map or Prudence Island showing the location of the four water quality long-term monitoring sites where nutrients and chlorophyll samples are collected and EXO2 sondes are deployed: Potter Cove (PC), Nag Creek (NC), and T-Wharf Bottom (TB) and T-Wharf Surface (TS) stations represented by TW.

### Monthly grab sampling program

Monthly grab samples are collected once per month from each of the four sites to quantify seasonal patterns of selected nutrient species and chlorophyll *a* in different estuarine habitats (marsh creek, cove, open water surface, open water bottom).

### Diel sampling program

Once per month, samples are collected at approximately 2-hour 15-minute intervals over a full tidal cycle (lunar day) to document changes in nutrients and chlorophyll *a* in response to tidal forcing. Previously (from 2002 to 2010), the diel sample collection was done at T-Wharf. However, after analyzing the historic data from the site, no significant trend or patterns were found over time. Thus, it was moved and has been at Potter Cove since January of 2011, to characterize nutrients and chlorophyll from this site.

## Research methods

### Monthly grab sampling program

Monthly grab samples were taken at the four long-term water quality monitoring sites (Nag Creek, Potter Cove, T-Wharf Surface, and T-Wharf Bottom) throughout 2022, except in January due to a strong nor’easter passing through the New England region. Other exceptions this year where: no samples collected at Nag Creek in February because the creek was frozen, in April due to staff injury, and in May due to high winds.

Collection of samples happened at all sites on the same day between ± 2 hrs. before or at slack low-water. No distinction was made between neap and spring tide conditions. Replicate (N=2) samples were collected by hand at Nag Creek, and with a horizontal opaque Van-Dorn sampling bottle at the other three sites. All grab samples were collected at the same depth and in very close proximity to the data loggers that are deployed and collecting water quality parameters every 15 minutes; that is, at Nag Creek, grab samples were collected at approximately 0.30 m from the bottom, at Potter Cove and T-Wharf Bottom at 1 m off the bottom, and at T-Wharf Surface at 1 m below the surface.

In the field, all samples were transferred to Nalgene amber wide-mouth HDPE 500 ml sample bottles. All sampling bottles were previously rinsed (3x) with hot tap water, then washed with a phosphate-free, biodegradable detergent (Liquinox®), rinsed (3x) with hot tap water and let dry. Subsequently, they were acid washed in a solution of 10 % Hydrochloric acid, rinsed (3x) with distilled-deionized water, and let dry. In the field, the bottles were rinsed (3x) with ambient water prior to collection of the sample. Samples were immediately placed on ice and in the dark and returned to the Reserve’s laboratory for initial filtering the same day of collection.

Water quality field data (water temperature, salinity, dissolved oxygen, and pH) have been collected on every grab sampling field trip and when picking up the automated water sampler (ISCO) with a YSI 556 handheld data logger unit from 2008 to April 2019. Values for watertemperature, specific conductance (and salinity), dissolved oxygen (% saturation and mg/L), and pH were recorded real-time at either 0.5- or 1.0-meter intervals between the surface and bottom at each site. In May 2019, the handheld datalogger and probes were replaced by a new ProSolo Digital Water Quality data logger; the YSI 556 has been discontinued by the manufacturer. With this new data logger, values for water temperature, specific conductance (and salinity), and dissolved oxygen (% saturation and mg/L) are recorded real-time at the same depth intervals mentioned above. This new equipment does not have a pH probe and, even though recording pH sea-truthing data is informative, it is not mandatory in terms of sea-truthing by the established CDMO SOP. The calibration procedure, for both the YSI 556 and the ProSolo data loggers, used in sea-truthing, follows the same general procedure as that for the sonde data loggers used for extended deployments. Calibration of the sensors is done the day before a planned sonde deployment and checked for drift the day of grab sampling field trips. Data and calibrating logs for the YSI 556 and the ProSolo data loggers are kept at the Reserve and available upon request. Field parameter data (water temperature and salinity) included in the dataset are data collected with the handheld at the site during grab sampling.

Since the implementation of the program in 2002, the Reserve has contracted the University of RI, Marine Ecosystems Research Lab (MERL) for pigment analyses (chlorophyll-*a* and pheophytin-*a*). However, in 2020, the Reserve had the capacity to analyze chlorophyll samples and started running parallel samples with the contractor lab (MERL) for five months (August to December 2020) to verify ability and proficiency on performing the task. Sample collection, filtration, and storage remain the same (see below) and MERLs chlorophyll analytical procedures were followed closely. Comparison of the data showed that the procedures to analyze chlorophyll, and chlorophyll results at NAR NERR, were comparable to those used and obtained by MERL for the same samples (results available upon request). After initial demonstration of performance described in the NAR NERR SOP (available upon request), Reserve staff started analyzing chlorophyll samples in January 2021 with the continued check on laboratory performance to assure the generation of high-quality data.

For pigment analyses (chlorophyll-*a* and pheophytin-*a*), 20 ml of sample were filtered onto a glass microfiber filter Type GF/F (Whatman 1825-025), added 2 drops of magnesium carbonate (MgCO3) solution to the filter to preserve the sample, and the filter then folded in half, wrapped in aluminum foil, labeled, and stored at –20 oC in a Nalgene amber wide-mouth HDPE bottle until analysis. Samples were analyzed at NAR NERR, and efforts are made to analyze, approximately, a week after collection.

For nutrient analyses (ammonia, nitrate-nitrite, nitrite, phosphate, and silicate), 60 ml of sample were filtered through a nucleopore polycarbonate Track-Etch membrane 0.4 µm pore size (Whatman 111107) into a small sampling bottle which was acid washed, rinsed, and dried as described above for the Nalgene amber bottles. After filtering, all water samples were stored at –20 oC for one to two days. Subsequently, all samples were placed in a cooler with ice gel packs and shipped overnight to the Virginia Institute of Marine Science (VIMS) analytical laboratory for nutrient analyses.

### Monthly diel sampling program

The diel sampling program was conducted once per month throughout most of 2022, using an ISCO 6712 portable automated water sampler. January was the only month no samples were collected due to a strong nor’easter passing through the New England region and damaging the floating dock where the automated sampler is deployed.

The ISCO 6712 was programed to automatically rinse the tubing twice with ambient water before collecting each sample. The ISCO automatically samples 500 ml of water at 2-hr 15-min intervals, covering a complete semidiurnal tidal cycle that includes, at minimum, two low tides and two high tides. A total of 12 samples were collected each month. All samples were pumped into polyethylene sample bottles that were previously cleaned and acid washed as described in Section *a* above for Nalgene amber bottles. During the warm months (usually April to November), ice gel packs are used inside the sampler to keep the samples cool during the sampling period. At the end of the 24-hr. period, the ISCO was retrieved, making sure all samples were kept cool and in the dark when returning to the Reserve for filtering the same day.

For pigment and nutrient analyses, samples were filtered, frozen, stored, analyzed at the Reserve (pigment samples) and transported (nutrient samples) to the analytical laboratory as described in Section *a* of the Research Methods above. Field data (water temperature and salinity) included in the dataset are the closest 15-minute readings collected by the EXO2 sonde associated with the SWMP monitoring site.

## Site location and character

The NAR NERR consists of approximately 1802 ha (4453 acres) of diverse estuarine and terrestrial habitats ranging from deep water to salt marshes to forested uplands. The land holdings include approximately 65% of Prudence Island, most of nearby Patience Island, and all of Hope and Dyer Islands (see map below). The Reserve is located close to the geographic center of Narragansett Bay in Rhode Island.

The Narragansett Bay watershed consists of nine subwatersheds draining an area of approximately 4,836square km *[[1]](#footnote-1)*(Pilson, 1985) and numerous and substantial freshwater inputs to the Bay. Approximately 39% of the watershed lies in Rhode Island and 61% in Massachusetts. It is referred to as a shallow estuary; however, its water depth varies considerably. Depth averages approximately 9.0 m throughout the Bay, but it is deeper in the East Passage (approximately 15.2 m) and shallower in the West Passage (approximately 7.5 m). More information and a detailed description of the Narragansett Bay NERR and the Narragansett Bay watershed can be found in *[[2]](#footnote-2)*Raposa and Schwartz, available at [*http://nbnerr.org/research-and-monitoring/publications/*](http://nbnerr.org/research-and-monitoring/publications/).

Specific characteristics of the Narragansett Bay National Estuarine Research Reserve.

Location: 41°38’30” N, 71°20’30” W

Tidal range: -0.2 to 1.7 meters MLW

Salinity range: 15 to 32 psu

Temperature: -1.0 to 26 C

Province: North temperate, Virginian bioregion

Specific characteristics of the Potter Cove site are:

Location: 41o 38' 25.984" N, 71o 20' 27.165" W

Depth range: 0.9 to 3.9 meters

Salinity range: 20 to 32 psu

Bottom habitat: Sand, silt, some organic mud

Pollutants: Boaters’ wastes, storm runoff from

mainland urban areas

Watershed: Narragansett Bay, North Prudence (4801 km2)

Specific characteristics of the Nag Creek site are:

Location: 41o 37' 29.458" N, 71o 19' 27.421" W

Depth range: 0.1 to 1.4 meters

Salinity range: 2 to 31 psu

Bottom habitat: Organic mud

Pollutants: Negligible

Watershed: Narragansett Bay, West Passage

Specific characteristics of the T-Wharf Surface site are:

Location: 41o 34' 42.099" N, 71o 19' 16.049" W

Depth range: 0.2 to 0.9 meters

Salinity range: 25 to 32 psu

Bottom habitat: Sand, silt, some organic mud

Pollutants: Negligible

Watershed: Narragansett Bay, South Prudence

Specific characteristics of the T-Wharf Bottom site are:

Location: 41o 34' 42.099" N, 71o 19' 16.049" W

Depth range: 4.6 to 6.9 meters

Salinity range: 27 to 32 psu

Bottom habitat: Sand, silt, some organic mud

Pollutants: Negligible

Watershed: Narragansett Bay, South Prudence

**Table 1.** Details of NAR NERR SWMP Stations Timeline.

SWMP Status column: P = primary SWMP Station, Reason Decommissioned and Notes columns: NA = Not applicable.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Station Code** | **SWMP Status** | **Station Name** | **Location** | **Active Dates** | **Reason Decommissioned** | **Notes** |
| narncwq | P | Nag Creek | 41° 37' 29.46 N  71° 19' 27.42 W | 03/01/2002 00:00 - present | NA | NA |
| narpcwq | P | Potter Cove | 41° 38' 25.98 N  71° 20' 27.17 W | 12/01/1995 00:00 - present | NA | NA |
| nartbwq | P | T-Wharf Bottom | 41° 34' 42.10 N  71° 19' 16.05 W | 07/01/2002 00:00 - present | NA | NA |
| nartswq | P | T-Wharf Surface | 41° 34' 42.10 N  71° 19' 16.05 W | 07/01/2002 00:00 - present | NA | NA |

## Coded variable definitions

Station Code Names

narncnut = Narraganset Bay Nag Creek nutrients

narpcnut = Narragansett Bay Potter Cove nutrients

nartbnut = Narragansett Bay T-Wharf Bottom nutrients

nartsnut = Narragansett Bay T-Wharf Surface nutrients

Monthly grab sample program = 1

Monthly diel sample program = 2

## Data collection period

The NAR NERR started the monthly grab sampling program at each of the four sites in the spring of 2002. The diel sampling program started in 2002 at T-Wharf Bottom until 2010; it has been at Potter Cove since 2011.

The following tables list the date and time each grab replicate (R) was collected at each site (Table 2), and the date and time of the first and last diel sample collected each month (Table 3). For both grab and diel sampling, time is coded based on a 24-hour format and is referenced to Eastern Standard Time (EST).

**Table 2.** Date and time of monthly grab sample replicates (R1 and R2) at each of the four water quality long-term monitoring sites during the year 2022. Time is coded based on a 24-hr. format and is referenced to Eastern Standard Time.

| **Date** | **Nag Creek**  **R1 R2** | | **Potter Cove**  **R1 R2** | | **T-Wharf Bottom**  **R1 R2** | | **T-Wharf Surface**  **R1 R2** | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 01/11/22 | 10:18 | 10:20 | 09:43 | 09:45 | 11:23 | 11:25 | 11:13 | 11:15 |
| 02/16/22 | 13:13 | 13:15 | 12:28 | 12:30 | 11:58 | 12:00 | 11:48 | 11:50 |
| 03/15/22 | 09:13 | 09:15 | 09:50 | 09:52 | 11:15 | 11:17 | 11:06 | 11:08 |
| 04/12/22 | 09:13 | 09:15 | 09:48 | 09:50 | 09:00 | 09:02 | 08:52 | 08:54 |
| 05/10/22 | 08:28 | 08:30 | 08:58 | 09:00 | 10:04 | 10:06 | 09:58 | 10:00 |
| 06/14/22 | 11:13 | 11:15 | 10:46 | 10:48 | 11:53 | 11:55 | 11:43 | 11:45 |
| 07/12/22 | 09:58 | 10:00 | 08:58 | 09:00 | 10:23 | 10:25 | 10:13 | 10:15 |
| 08/08/22 | 08:58 | 09:00 | 08:43 | 08:45 | 09:43 | 09:45 | 09:33 | 09:35 |
| 09/08/22 | 09:23 | 09:25 | 08:55 | 08:57 | 10:02 | 10:04 | 09:55 | 09:57 |
| 10/03/22 | 06:47 | 06:49 | 06:18 | 06:20 | 07:31 | 07:33 | 07:26 | 07:28 |
| 11/07/22 | 10:48 | 10:50 | 10:08 | 10:10 | 11:28 | 11:30 | 11:23 | 11:25 |
| 12/05/22 | 10:16 | 10:18 | 09:36 | 09:38 | 11:16 | 11:18 | 11:10 | 11:12 |

**Table 3.** Start and end date and time of monthly diel sampling at Potter Cove long-term water quality monitoring sites during the year 2022. Time is coded based on a 24-hr. format and is referenced to Eastern Standard Time (EST).

| **Start Date** | **Start Time (EST)** | **End Date** | **End Time (EST)** |
| --- | --- | --- | --- |
| 01/11/22 | 09:30 | 01/12/22 | 10:15 |
| 02/21/22 | 09:30 | 02/22/22 | 10:15 |
| 03/15/22 | 09:30 | 03/16/22 | 10:15 |
| 04/12/22 | 10:00 | 04/13/22 | 10:45 |
| 05/10/22 | 08:45 | 05/11/22 | 09:30 |
| 06/14/22 | 10:15 | 06/15/22 | 11:00 |
| 07/12/22 | 09:15 | 07/13/22 | 10:00 |
| 08/08/22 | 08:30 | 08/09/22 | 09:15 |
| 09/08/22 | 09:00 | 09/09/22 | 09:45 |
| 10/03/22 | 06:00 | 10/04/22 | 06:45 |
| 11/07/22 | 10:25 | 11/08/22 | 11:10 |
| 12/05/22 | 09:35 | 12/06/22 | 10:20 |

## Associated researchers and projects

In 2004, the NAR NERR became involved in the Bay Window Monitoring Program (BWMP). The BWMP housed several programs under different state and federal agencies to study Narragansett Bay’s fish and fisheries, sediment pollution, currents, and hydrography. Even though Bay Window ended in 2010, some programs where able to keep their monitoring with other funding sources. Currently, NAR NERR continues to be an essential part of the original network of fixed-sites recording water quality data in the Bay (the Bay Assessment and Response Team -BART, <http://www.dem.ri.gov/programs/emergencyresponse/bart/>) under the Rhode Island Department of Environmental Management (RIDEM). NAR NERRs’ unique contribution consists of collecting year-around high frequency water quality data since it is the only fix site within the network deploying sondes during the winter months.

A close up of a device

Description generated with very high confidenceThe NAR NERR System-Wide Monitoring Program (SWMP) has four long-term water quality monitoring sites around Prudence Island. The principal objective of the SWMP program is to record short-term variability and long-term changes in water quality data to observe trends or patterns in water quality over time. Water quality parameters have been collected since 1995 with the establishment of the first water quality monitoring site at Potter Cove. The other three water quality sites (Nag Creek, T-Wharf Surface, and T-Wharf Bottom) were brought online in 2002. These sites were selected to represent a gradient in habitat types that range from salt marsh (Nag Creek) to shallow cove (Potter Cove) to open Bay water (T-Wharf Surface and T-Wharf Bottom). Water temperature, salinity, dissolved oxygen (% saturation, and mg L-1), pH, turbidity, and chlorophyll fluorescence data are collected at each site every 15 minutes using YSI 6600 V2 and EXO2 data loggers that are calibrated and swapped out at each site approximately every two to four weeks. In July 2018, the Reserve completed upgrading all the data loggers from YSI 6600 V2 to EXO2 at all sites.

Since 2001, meteorological data has been collected as part of the SWMP at the weather station (see image below) located on Prudence Island, approximately 389 m south of Potter Cove (41o 38’ 13.703” N, 71o 20’ 21.790” W, Trimble Geo XT, GeoExplorer 2008 Series; see map on section 5, Site Location and Character). Data on air temperature, relative humidity, barometric pressure, wind speed and direction, photosynthetic active radiation, and precipitation are collected by the CR1000 data logger every 15 minutes. In December 2019, the data logger was replaced with a newer model, CR1000X. Meteorological data is continually used to complement the water quality, biological monitoring, and scientific research efforts at NAR NERR and at Narragansett Bay, and to assist educational and stewardship activities around the Bay.

All this information is available through the CDMO www.nerrsdata.org, NAR NERR <http://nbnerr.org/>, or directly contacting the SWMP Coordinator or the Research Coordinator.

Courtney E. Schmidt, Ph.D., staff scientist at the Narragansett Bay Estuary Program in RI analyzed the chlorophyll *a* data from our long-term nutrient program to include in the Narragansett Bay Water Quality Status and Trends, RI of 2016, and plans to include the data in future reports.

## 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](http://www.nerrsdata.org); *accessed* 12 October 2022.

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

# II. Physical Structure Descriptors

## 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.

The Virginia Institute of Marine Science (VIMS) entered the nutrient data into Microsoft Excel spreadsheets, calculated and reported results in mg L-1, and sent the files electronically to the NAR NERR. For purposes of consistency in the NERR System, concentrations are calculated as mg L-1 based on atomic weights of 14.010, 30.97, and 28.09, and 12.01 for N, P, Si, and C, respectively.

The Marine Ecosystem Research Laboratory (MERL) entered the chlorophyll and pheophytin data into Microsoft Excel spreadsheets, calculated and reported the results in µg L-1 and sent the files electronically to the NAR NERR from 2002-2020.

The Reserve has been processing chlorophyll samples since January 2021. Data is entered into Microsoft Excel spreadsheets where results are calculated in µg L-1 and proofed by a different staff member. A monthly report file is created. Files are saved locally on a computer and backed up onto cloud folders.

Data entry verification is completed by Dr. Daisy Durant. Final verification and this metadata documentation were checked by Dr. Kenneth Raposa (Research Coordinator), before being sent to the CDMO permanent database.

## Parameter titles and variable names by category

**Table 4.** Required NOAA/NERRS System-wide Monitoring Program nutrient parameters are denoted by an asterisks “\*”.

| Data Category | Parameter | Variable Name | Units of Measure |
| --- | --- | --- | --- |
| Phosphorus | \*Orthophosphate | PO4F | mg L-1 as P |
| Nitrogen: | \*Ammonium, Filtered | NH4F | mg L-1 as N |
|  | \*Nitrite, Filtered | NO2F | mg L-1 as N |
|  | \*Nitrate, Filtered | NO3F | mg L-1 as N |
|  | \*Nitrite + Nitrate, Filtered | NO23F | mg L-1 as N |
|  | Dissolved Inorganic Nitrogen | DIN | mg L-1 as N |
| Plant Pigments: | \*Chlorophyll *a* | CHLA\_N | µg L-1 |
|  | Phaeophytin | PHEA | µg L-1 |
| Other Lab Parameters: | Silicate, Filtered | SiO4F | mg/L as Si |
| Field Parameters: | Water Temperature | WTEM\_N | oC |
|  | Salinity | SALT\_N | psu |

Notes:

* Time is coded based on a 2400 clock and is referenced to Eastern Standard Time format.
* Reserves have the option of measuring either NO2 or NO3 or they may substitute NO23 for individual analyses if they can show that NO2 is a minor component relative to NO3.

## Measured and Calculated Laboratory Parameters

### Parameters Measured Directly

* Nitrogen species: NH4F, NO2F, NO23F
* Phosphorus species: PO4F
* Other: CHLA\_N, PHEA, SiO4F

### Calculated Parameters

* NO3F: NO23F-NO2F
* DIN: NO23F+NH4F

## Limits of detection

Method Detection Limits (MDL), the lowest concentration of a parameter that an analytical procedure can reliably detect, have been established by VIMS Analytical Service Center (2010 – present) for nutrients, and by MERL (from 2002-2020) and NAR NERR (since 2021) for pigments. 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.

**Table 5.** Method Detection Limits.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Parameter | Start Date  (mm/dd/yyyy) | End Date  (mm/dd/yyyy) | MDL | Last date revisited (mm/dd/yyyy) |
| PO4F | 01/01/2022 | 09/30/2022 | 0.0016 mg L-1 | 01/05/2022 |
| PO4F | 10/01/2022 | 12/31/2022 | 0.0029 mg L-1 | 10/01/2022 |
| NH4F | 01/01/2022 | 12/31/2022 | 0.0062 mg L-1 | 01/05/2022 |
| NO2F | 01/01/2022 | 12/31/2022 | 0.0016 mg L-1 | 01/05/2022 |
| NO23F | 01/01/2022 | 12/31/2022 | 0.0055 mg L-1 | 01/05/2022 |
| SiO4F | 01/01/2022 | 12/31/2022 | 0.0620 mg L-1 | 01/05/2022 |
| CHLA\_N | 01/01/2022 | 12/31/2022 | 0.017 µg L-1 | 12/20/2021 |
| PHEA | 01/01/2022 | 12/31/2022 | 0.020 µg L-1 | 12/20/2021 |

## Laboratory methods

### Parameter: Chlorophyll *a* (CHLA\_N), Phaeophytin *a* (PHEA)

* + Marine Ecosystems Research Laboratory Method
    - Used by our contractor lab (MERL 2002-2020)
    - Currently used by NAR NERR since 2021
  + Method References: Oviatt, C. A., and K. M. Hindle. 1994. Manual of biological and geochemical techniques in coastal areas. MERL Series, Report No. 1, pp. 3-7.
* Method Descriptor: Chlorophyll *a* is extracted in 10 ml 90% acetone and fluorescence is measured and recorded (Fo). Two drops of 10% hydrochloric acid are added to convert the chlorophyll to pheophytin. The fluorescence is again measured and recorded (Fa). The concentration (μg L-1) of Chl*a* and Phe*a* are calculated using the Fo/Fa ratio.
* Preservation Method: 20 ml of sample is filtered onto a Whatman® Glass Microfiber Filter: Type GF/F (25 mm), treated with 2 drops of MgCO3 solution, folded in half, wrapped in foil, labeled, and stored at –20oC until analysis (at NAR NERR this is done approximately a week after sampling).

### Parameter: NH4F

* + VIMS Laboratory Method: SA156-350.1 - NH3
  + Method Reference:
* U.S. EPA. 1974. Methods for Chemical Analysis of Water and Wastes, pp. 168-174.
* Standard Methods for the Examination of Water and Wastewater, 14th edition. p 410. Method 418A and 418B (1975).
* Annual Book of ASTM Standards, Part 31. "Water", Standard 1426-74, Method A, p 237 (1976).
* EPA 600/R-97/072 Method 349.0. Determination of Ammonia in Estuarine and Coastal Waters by Gas Segmented Continuous Flow Colorimetric Analysis. IN: Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices -2nd Edition. National Exposure Research Laboratory, Office of Research and Development U.S. EPA, Cincinnati, Ohio 45268.
  + Method Descriptor: Ammonia reacts with alkaline phenol and hypochlorite to form indophenol blue in an amount that is proportional to the ammonia concentration. The blue color is intensified with sodium nitroprusside. The reaction is catalyzed by heat at 37oC. The range is 0.01 – 2.0 mg L-1.
  + Preservation Method: 60 ml of sample is filtered through a Whatman® Nuclepore Track-Etched Membrane, 0.4 µm disposable disk filter (47mm), and stored at –20oC until analyzed.

### Parameter: NO2F, and NO2F + NO3F

* + VIMS Laboratory Method: SA461-353.2 - NO2+3, NO2, TDN
  + Method Reference:
* U.S. EPA. 1974. Methods for Chemical Analysis of Water and Wastes, pp. 207 -212.
* Wood, E.D., F.A.G. Armstrong, and F.A. Richards. 1967. Determination of nitrate in seawater by cadmium-copper reduction to nitrite. J. Mar. Biol. Assoc. U.K. 47: 23
* Grasshoff, K., M. Ehrhardt and K. Kremling. 1983. Methods of Seawater Analysis. Verlag Chemie, Federal Republic of Germany. 419 pp.
* EPA 600/R-97/072 Method 353.4. Determination of Nitrate and Nitrite in Estuarine and Coastal Waters by Gas Segmented Flow Colorimetric Analysis. IN: Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices -2nd Edition. National Exposure Research Laboratory, Office of Research and Development U.S. EPA, Cincinnati, Ohio 45268.
* Method Descriptor: Nitrate is reduced quantitatively to nitrite by cadmium metal in the form of an open tubular reactor. The nitrite thus formed plus any originally present in the sample is colorimetrically detected at 540 nm, following its diazotization with sulfanilamide, and subsequent coupling with N-1-naphthylethylenediamine dihydrochloride. The dissolved nitrate concentrations of the samples are calculated as NO3-N.
  + Preservation Method: 60 ml of sample is filtered through a Whatman® Nuclepore Track-Etched Membrane, 0.4 µm disposable disk filter (47mm), and stored at –20oC until analyzed.

### Parameter: SiO4F

* + VIMS Laboratory Method: Skalar Method Silicates, Catnr. 563-052 issue 101899/MH/99208255
  + Method Reference:
* U.S. EPA. 1974. Methods for Chemical Analysis of Water and Wastes, Method 370.1
* Grasshoff, K., M. Ehrhardt and K. Kremling. 1983. Methods of Seawater Analysis. Verlag Chemie, Federal Republic of Germany. Pp 374-376.
* EPA 600/R-97/072 Method 366.0 Determination of Dissolved Silicate in Estuarine and Coastal Waters by Gas Segmented Flow Colorimetric Analysis. IN: Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices -2nd Edition. National Exposure Research Laboratory, Office of Research and Development U.S. EPA, Cincinnati, Ohio 45268.
  + Method Descriptor: Based on the reduction of silicomolybdate in acidic solution to “molybedenum blue” by ascorbic acid. Oxalic acid is introduced to the sample stream before the addition of ascorbic acid to eliminate interference from phosphates. The range is 0-1.1 mg Si L-1.
  + Preservation Method: Preservation Method: 60 ml of sample is filtered through a Whatman® Nuclepore Track-Etched Membrane, 0.4 µm disposable disk filter (47mm), and stored at –4oC until analyzed.

### Parameter: PO4F

* VIMS Laboratory Method SKALAR Method: O-Phosphate / Total Phosphate, Catnr. 503-365.1, issue 042993/MH/93-Demo1
* Method Reference:
  + - Murphy, J. and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Analytica Chim. Acta 27: 31-36
    - EPA 600/R-97/072 Method 365.5 Determination of Orthophosphate in Estuarine and Coastal Waters by Automated Colorimetric Analysis. IN: Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices -2nd Edition. National Exposure Research Laboratory, Office of Research and Development. U.S. EPA, Cincinnati, Ohio 45268
  + Method Descriptor: Ammonium molybdate and antimony potassium tartrate react in a sulfuric acid environment to form an antimony-phospho-molybdo complex, which is reduced to a blue colored complex by ascorbic acid. Reaction is heat catalyzed at 40oC.
  + Range is 1 - 50 ppb.
  + Preservation Method: Preservation Method: 60 ml of sample is filtered through a Whatman® Nuclepore Track-Etched Membrane, 0.4 µm disposable disk filter (47 mm), and stored at –20oC until analyzed.

## Field and laboratory QA/QC programs

### Precision

* 1. **Field Variability** - For the monthly grab sampling program, NAR NERR used an opaque Van-Dorn horizontal bottle to collect two successive grab samples for the determination of water mass variability.
  2. **Laboratory Variability** – For pigment analysis, laboratory variability is determine monthly for grab, and diel samples (for a total of two lab replicates/month). For nutrient analysis, one sample is done monthly (alternating grab and diel) for laboratory variability.
  3. **Inter-organizational Splits** – none

### Accuracy

1. **Sample Spikes** – blanks
2. **Standard Reference Material Analysis** – none
3. **Cross Calibration Exercises** – none

## 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.

**Table 6.** QAQC flag definitions.

|  |  |
| --- | --- |
| **Flag** | **Description** |
| -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 |

## 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 Value calculated with a value that is below the MDL

SCC Calculation with this component resulted in a negative value

SNV Calculated value is negative

SRD Replicate values differ substantially

SUL Value above upper limit of method detection

Parameter Comments

CAB Algal Bloom

CDR Sample diluted and rerun

CHB Sample held beyond specified holding time

CIP Ice present in sample vicinity

CIF Flotsam present in sample vicinity

CLE Sample collected later/earlier than scheduled

CRE Significant rain event

CSM See metadata

CUS Lab analysis from unpreserved sample

Record comments

CAB Algal bloom

CHB Sample held beyond specified holding time

CIP Ice present in sample vicinity

CIF Flotsam present in sample vicinity

CLE Sample collected later/earlier than scheduled

CRE Significant rain event

CSM See metadata

CUS Lab analysis from unpreserved sample

*Cloud cover*

CCL clear (0-10%)

CSP scattered to partly cloudy (10-50%)

CPB partly to broken (50-90%)

COC overcast (>90%)

CFY foggy

CHY hazy

CCC cloud (no percentage)

*Precipitation*

PNP none

PDR drizzle

PLR light rain

PHR heavy rain

PSQ squally

PFQ frozen precipitation (sleet/snow/freezing rain)

PSR mixed rain and snow

*Tide stage*

TSE ebb tide

TSF flood tide

TSH high tide

TSL low tide

*Wave height*

WH0 0 to <0.1 meters

WH1 0.1 to 0.3 meters

WH2 0.3 to 0.6 meters

WH3 0.6 to > 1.0 meters

WH4 1.0 to 1.3 meters

WH5 1.3 or greater meters

*Wind direction*

N from the north

NNE from the north northeast

NE from the northeast

ENE from the east northeast

E from the east

ESE from the east southeast

SE from the southeast

SSE from the south southeast

S from the south

SSW from the south southwest

SW from the southwest

WSW from the west southwest

W from the west

WNW from the west northwest

NW from the northwest

NNW from the north northwest

*Wind speed*

WS0 0 to 1 knot

WS1 > 1 to 10 knots

WS2 > 10 to 20 knots

WS3 > 20 to 30 knots

WS4 > 30 to 40 knots

WS5 > 40 knots

## Other remarks

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.

The following are descriptions of different events that happened during the grab and diel sampling in the field, and during the filtering processes at the Reserve for 2022.

**Grab Samples**

February 16. No samples were collected at Nag Creek due to the creek being frozen. Missing data were flagged and coded -2 GDM CSM. Calculated values that could not be determined due to missing data were flagged and coded -2 GCM CSM. Water quality parameters (water temperature and salinity) were not collected and could not be obtained from the EXO2 sonde due to ice; thus, were flagged and coded -2 GSM.

March 15. Water quality parameters were not collected due to handheld battery failure. Data could not be obtained from the EXO2 sonde associated to this SWMP monitoring site since it was not deployed at the time. Missing data were flagged and coded -2 GSM.

April 12. No samples were collected at Nag Creek due to staff injury not allowing to physically get to the site. Missing data were flagged and coded -2 GDM CSM. Calculated values that could not be determined due to missing data, were flagged and coded -2 GCM CSM. Water quality parameters (water temperature and salinity) were included in the dataset and are the closest 15-minute readings collected by the EXO2 sonde associated with this SWMP monitoring site.

May 10. No samples were collected at Nag Creek due to high winds of around 25-30 mph (verified with the weather station data collected on Prudence Island), making it very challenging to reach the site by kayak due, also, to the direction of the wind. Missing data were flagged and coded -2 GDM CSM. Calculated values that could not be determined due to missing data, were flagged and coded -2 GCM CSM. Water quality parameters (water temperature and salinity) were included in the dataset and are the closest 15-minute readings collected by the EXO2 sonde associated with this SWMP monitoring site.

October 03. Nag Creek chlorophyll and phaeophytin results were considered suspect of contamination in the field when the field blank (FB) taken at the site and analyzed at the Reserve, was higher than five time the MDL value for of our lab (following chlorophyll and phaeophytin SOP for the Reserve). Data was considered suspect and flagged and coded 1 GQS CSM.

**Diel Samples**

February 22 05:45. Diel sample lost by accident before performing chlorophyll sampling, as a result, phaeophytin *a* data is also missing. Missing data were flagged and coded -2 GDM CSM.

May 10. At Potter Cove, no water quality data (water temperature and salinity) were available from the EXO2 sonde at the site due to sonde malfunction. Missing data were flagged and coded -2 GSM.

**Grab and diel samples**

January 11 09:30 to January 12 10:15. Samples were not collected during this month, even when rescheduling a few times, due to many winter weather related issues. Missing data were flagged and coded -2 GDM CSM. Calculated values that could not be determined due to missing data, were flagged and coded -2 GCM CSM. Water quality parameters (water temperature and salinity) were included in the dataset anyway and are the closest 15-minute readings collected by the EXO2 sonde associated with this SWMP monitoring site.

July – December.

At the Reserve, a methods blank (MB) is prepared each month and submitted to the same nutrients analysis than the nutrient samples sent to VIMS analytical laboratory.

A MB is an analyte-free matrix such as deionized (DI) water that is processed in exactly the same manner as the samples. The main function of the MB is to document contamination resulting from the analytical process. At the Reserve, for an MB to be acceptable, it must be no higher than VIMS method detection limit (MDL: minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results). The MB provides confidence in assuring the reported values found in the nutrient samples are “real” and not the result of laboratory contamination.

After analyzing the MB results for the Reserve (see table below), it was found that the MB values from Jul-Dec for silicates (SiO4) and nitrates (NO23) were higher than VIMS MDL. It was also higher for ortho-phosphate (O-PO4) in August, September, and November; for ammonium (NH4) in September and November; and for nitrites (NO2) in November, implying that the DI water used at the lab from July to December was not ultrapure water, which is critical to all analytical procedures done at the Reserve.



**Highlighted cells + bold font** = MB values are higher than VIMS MDL.

Units: mg/L

At the Reserve, ultrapure water was generated by a Barnstead E-Pure DI H2O system. By the end of June 2022, the resistivity meter malfunctioned and broke. Paperwork was prepared to purchase a new system. However, due to supply chain issues, the purchase didn’t happen immediately. Since, the DI H2O system had new cartridges and the pump was working, following Barnstead technical advice, we continued to use the system without a resistivity meter from July to December, assuming the resistivity was higher than 17.9 MΩ/cm @ 25 C with new cartridges.

Due to the problem with the ultrapure water at the Reserve, the nutrient data from July – December were flagged and coded as follows:

* MB value higher than VIMS MDL: data were rejected and flagged and coded -3 GQD CSM.
* MB value lower than VIMS MDL: data were suspect and flagged and coded 1 GQS CSM
* Calculated parameters (nitrate = NO3, dissolved inorganic nitrogen = DIN) were flagged and coded -3 GCR CSM

**Holding times**

NERRS SOP allows nutrient samples to be held for up to 28 days and chlorophyll samples for 30 days at -20oC, plus allows for up to 5 days for collecting, processing, and shipping samples (see section ‘Preservation and Analysis of Samples’ below). Samples held beyond that time period are considered suspect and 1 GSM CHB flag and code are used in the dataset. Table 7 shows the calculated holding time for all samples in 2022 where none of the samples were held beyond the maximum holding time recommended.

**Table 7.** Holding times (number of days) for year 2022 were calculated for grab and diel sample analyses of nutrient or pigment species based on collection date and time at NAR NERR and the date of the analysis provided by the processing lab. None of the samples were held beyond the maximum holding time.

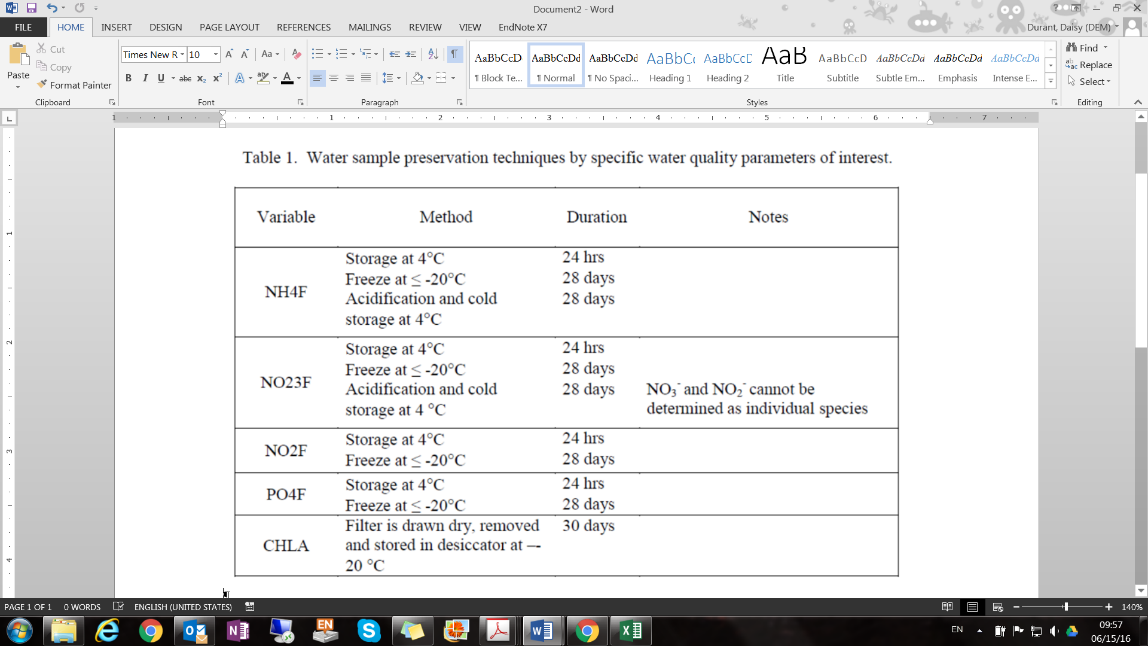


**Preservation and Analysis of Samples According to CDMO SOP.**

Nutrient and pigment preservation and analysis are time sensitive. To assure proper quality control, the CDMO SOP establishes the following in the ‘Nutrient and Chlorophyll Monitoring Program and Database Design SOP v1.8 available at [*http://cdmo.baruch.sc.edu/request-manuals/*](http://cdmo.baruch.sc.edu/request-manuals/).

**3.3 Sample Preservation**

If samples are kept in long-term storage, appropriate preservation techniques must be utilized to reduce the effects of volatilization, absorption, and biodegradation. Preservation techniques vary depending on analytes of interest; examples of preservation techniques are presented in Table 1 below taken from CDMO manual. It is recognized that adequate time, about 5 days, must be allowed for reserves to collect, filter, preserve and ship samples to analytical laboratories. Furthermore, it is recognized that whenever possible samples should be analyzed by the laboratory within 24 hours rather than deep freezing and storing.

**

**Precipitation**

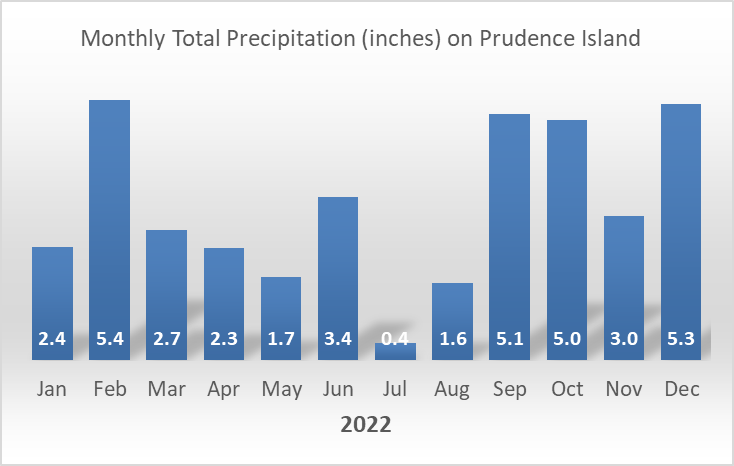
At the NAR NERR we make every effort possible to collect samples during periods that are not or are minimally impacted by previous storm/precipitation events (snow, rain). CDMO SOP recommends an antecedent dry period of 72 hours (3 days) but might not be practical and sometimes the weather is difficult to predict. Table 8 shows the total daily precipitation recorded at the weather station. Data that might have been impacted by precipitation was coded as CSM in the F\_Record column in the dataset file.

**Table 8.** Total daily precipitation (inches) recorded at the weather station on Prudence Island 72 hours prior sampling.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Jan-Mar | Total Precipitation | Apr-Jun | Total Precipitation | Jul-Sep | Total Precipitation | Oct-Dec | Total Precipitation |
| 01/08/22 | 0.0 | 04/09/22 | 0.0 | 07/09/22 | 0.0 | 09/30/22 | 0.0 |
| 01/09/22 | 0.1 | 04/10/22 | 0.0 | 07/10/22 | 0.0 | 10/01/22 | 0.9 |
| 01/10/22 | 0.0 | 04/11/22 | 0.0 | 07/11/22 | 0.0 | 10/02/22 | 0.0 |
| 01/11/22 | 0.0 | 04/12/22 | 0.0 | 07/12/22 | 0.0 | 10/03/22 | 0.0 |
| 02/18/22 | 0.8 | 05/07/22 | 0.2 | 08/05/22 | 0.0 | 11/07/22 | 0.0 |
| 02/19/22 | 0.0 | 05/08/22 | 0.0 | 08/06/22 | 0.0 | 11/08/22 | 0.0 |
| 02/20/22 | 0.0 | 05/09/22 | 0.0 | 08/07/22 | 0.0 | 11/09/22 | 0.0 |
| 02/21/22 | 0.0 | 05/10/22 | 0.0 | 08/08/22 | 0.0 | 11/10/22 | 0.0 |
| 03/12/22 | 0.4 | 06/11/22 | 0.0 | 09/05/22 | 1.6 | 12/02/22 | 0.0 |
| 03/13/22 | 0.0 | 06/12/22 | 0.0 | 09/06/22 | 0.6 | 12/03/22 | 0.7 |
| 03/14/22 | 0.0 | 06/13/22 | 0.3 | 09/07/22 | 0.0 | 12/04/22 | 0.0 |
| 03/15/22 | 0.0 | 06/14/22 | 0.0 | 09/08/22 | 0.0 | 12/05/22 | 0.0 |

Total Precipitation (inches of melted snow and/or rain) per month on Prudence Island for 2022.

Data from NAR NERR Weather Station.



1. Pilson, M.E.Q. 1985. On the residence time of water in Narragansett Bay. *Estuaries* 8:2–14. [↑](#footnote-ref-1)
2. Narragansett Bay National Estuarine Research Reserve. 2007. An Ecological Profile of the Narragansett Bay National Estuarine Research Reserve. K.B. Raposa and M.L. Schwartz (eds.), *Rhode Island Sea Grant, Narragansett, R.I*. 176pp. [↑](#footnote-ref-2)