

Tijuana River (TJR) NERR Nutrient Metadata
January – December 2020

Latest Update: June 15, 2021

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) or reserve with any additional questions.

I. Data Set and Research Descriptors

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2) Research objectives –

The Tijuana River National Estuarine Research Reserve (TRNERR) is heavily impacted by periodic raw sewage outflows and urban development. About a quarter of the reserve's 2,531 acres are tidally influenced and few channels are deep enough for datalogger deployment. Currently, there are two SWMP stations installed at the TRNERR and two SWMP stations are located off the reserve. Station locations are designed to investigate spatial gradients of water quality parameters across the reserve, as well as to document the water quality changes over time to areas in the reserve that have been restored to increase tidal flushing.

Two stations were originally set up: a control station (OS), which is still in place, was set up on the northern end of Oneonta Slough. A treatment station (RC) was set up in the site most affected by sewage outflow. Datalogger deployment, however, was continually halted by both shifting sediment and massive wracks of kelp (*Macrocystis pyrifera*), which would often bury the deployment set-up on incoming tides. After a number of different deployment equipment designs were implemented without success, data collection at the RC site was terminated in 2004.

Another station was located at the inlet to the Model Marsh (MM), a constructed 20-acre restoration site in the southern arm of the estuary. The Model Marsh was opened to tidal flushing in February 2000 and data logging at the station began in October 2000. The site was discontinued in January 2008 due to heavy sedimentation.

The Boca Rio (BR) site is located near the mouth of the Tijuana River, which is the largest source of freshwater to the reserve. The BR station was established in December 2004 to replace the RC station and remains active.

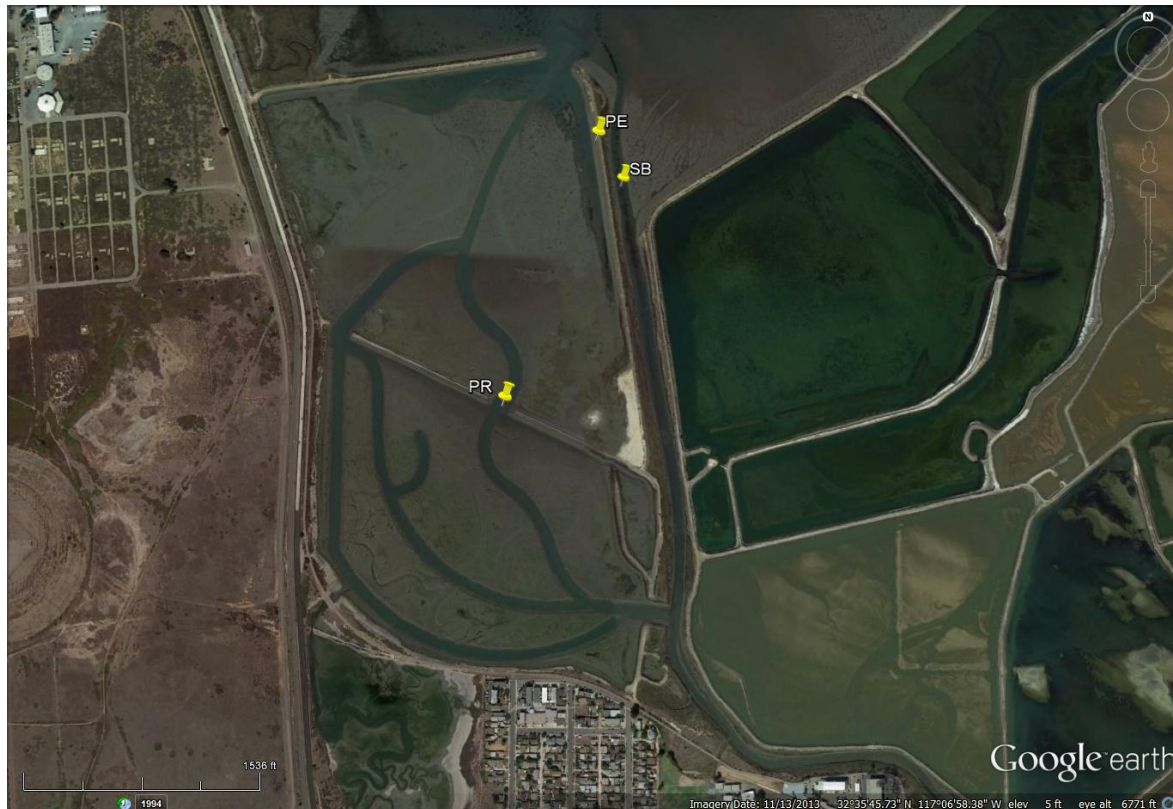
The South Bay (SB) station was established in January 2008 and is located at the mouth of Otay River, which flows into South San Diego Bay and is within the San Diego National Wildlife Refuge Complex.

The Pond Eleven (PE) station, was located in a non-tidal salt pond adjacent to the South Bay logger. A flood gate was the only source of water into the pond. The Pond Eleven sonde was deployed from July 2008 to September 2010. The US Fish and Wildlife Service began restoration of this area, including Pond Eleven, from September 2010 to its completion in October 2011. Channels were dredged near the Pond Eleven site, the surrounding ponds and the adjacent Otay River. A levee was breached to open Pond Eleven to the bay, which made the area tidal. Due to extensive restoration, the site was relocated. Datasonde deployments and nutrient data collection began in January 2012 at a new location site named Pond Restored (PR). The Pond Restored datalogger is located approximately 560 meters southwest from where the Pond Eleven datalogger was originally. The Pond Restored site is also located within the San Diego National Wildlife Refuge Complex. The images below show pre- and post-restoration of the salt ponds and the station locations. The post restoration photo includes the PE site as a reference to the new PR site. No sampling currently occurs at the PE site.

Pre Restoration



Post Restoration



a) Monthly grab sampling program

Grab samples were collected monthly at all SWMP water quality sonde sites. Monthly grab sampling provides information as to the spatial differences in nutrient levels within the system. The placement of these sites also offers the opportunity to better isolate the possible origin of nutrient inputs as well as the degree of tidal flushing.

b) Diel sampling program

Diel samples were collected monthly at one site. This sampling method provides a temporal perspective of nutrient flux over one tidal cycle at this particular site. Given the location of the site, the diel sampling also provides valuable information as to the degree of tidal flushing of nutrients from the estuary.

3) Research methods –

[Instructions/Remove: Detail the specifics of sample collection, collection intervals, sample processing, how samples are held, and QAQC of the equipment and analyzers for each program.]

a) Monthly grab sampling program:

Monthly grab samples were taken at the SWMP sites (Boca Rio, Oneonta Slough, Pond Restored, and South Bay). All samples were collected less than three hours prior to the projected slack low tide ending a diel sampling cycle. Samples were collected vertically, by hand, in amber wide mouth 1 L acid washed (10% HCl) Nalgene bottles. Sample bottles were rinsed three times with ambient water before sampling. Sampling typically followed a dry period of 72 hours or greater, unless otherwise noted (see **Other Remarks** at the end of this document). Samples were taken sequentially, within one minute of each other and adjacent to the

datasonde deployed at each station in compliance with the NERRS Nutrient and Chlorophyll Monitoring SOP version 1.7.

Duplicate samples were taken at each site and, after filtration, processed by the Chemistry Lab at the Oceanographic Data Facility, Scripps Institution of Oceanography (SIO), University of California, San Diego. The Oceanographic Data Facility's nutrient analysis procedures can be found at <https://scripps.ucsd.edu/ships/shipboard-technical-support/odf/documentation/nutrient-analysis>. All samples were immediately stored on ice and frozen within four hours. Samples were delivered to the lab typically within 72 hours.

In addition to required parameters, the TRNERR also began reporting silicate in 2015. Chlorophyll analyses were performed in house at the TRNERR until June 2017. Starting in August 2017, the frozen chlorophyll samples were also delivered to the SIO lab. The chlorophyll analysis method used by SIO lab can be found at <http://calcofi.org/ccpublications/calcofi-methods/8-chlorophyll-methods.html>.

At the time of nutrient sampling, in-situ measurements of temperature, specific conductivity, salinity and dissolved oxygen were taken using a YSI Pro Plus water quality handheld instrument. When handheld instrument was not available, nutrient samples were taken as close as possible to a 15-minute mark, when a water quality measurement is taken by the adjacent datasonde. These measurements are included in the datasheet.

b) Diel sampling program:

Diel samples were collected at the Boca Rio site. Samples were taken at intervals of 2hrs 15mins for a total of, at least, 11 samples over one lunar day. Samples were collected using an ISCO model 6712 autosampler with a sixty-foot sample tube and polypropylene strainer. The strainer was suspended in a minnow trap (approximately 25 cm above the channel bottom) within 20m of the associated datasonde. The sampler was located approximately 1.5m above the strainer on the channel's bank. The sampler was programmed to collect 0.5 liter per sample utilizing ISCO's 24-bottle kit in a standard tub stocked with ice. At the time of retrieval, the sampling program is suspended and the sample bottles are capped. Samples typically reached the lab within one hour of retrieval for filtration.

All sample containers (ISCO 1L Polyethylene bottles for diel samples and Nalgene 1L wide mouth amber opaque HDPE bottles for grab samples) were acid washed prior to sampling. The washing procedure consisted of four rinses with DI water, a gentle squirt of Liquinox phosphate free detergent, six rinses with DI water, a soak of at least ten minutes in 10% HCl, and, lastly, six rinses with Type 1 reagent water (18M Ω -cm).

4) Site location and character –

General site Characteristics (TRNERR)

- a) Latitude and longitude: 32° 34' N, 117° 7' W
- b) Tidal range: approximately -2ft to + 7ft MLLW
- c) Water depth: approximately 0.2m to 2.7m
- d) Type and amount of freshwater input: the dominant freshwater source to the estuary is the Tijuana River, which drains a 4,483km² watershed, approximately 2/3 of which resides in Mexico. Stream flows in the river vary considerably from season to season and year to year, with no flow during many months and a mean annual discharge of 0.82m³/s. Additional freshwater sources are storm drains located mostly in the northern arm of the estuary from the adjacent military airfield and residential area. The entire estuary is shallow and has a relatively small tidal prism (0.36 Mm³), so even low freshwater flows result in reduced salinity throughout the reserve. Estimated residence times for freshwater entering the estuary vary from 7 hours to a few days, depending on the tide and mouth conditions. Rainfall within the watershed accounts for most of the freshwater entering the reserve, with 90% of the mean annual rainfall occurring between November and

April. Vegetation in the area is dominated by common pickleweed (*Salicornia pacifica*) and Pacific cordgrass (*Spartina foliosa*).

e) Pollutants in area: Freshwater discharge with untreated sewage occurs year-round. Although these have decreased with the construction of a binational water treatment plant, repeated infrastructure failures have increased the frequency of raw sewage discharged throughout the year affecting the water quality.

Specific Site characteristics:

Boca Rio (BR)

a) Location of site: this station is located approximately 400m north of the Tijuana River, in the middle of channel which runs north-south; 32° 33' 33.7" N, 117° 7' 44.3" W

b) Elevation of sonde's depth port:

January 27, 2015 - December 11, 2017: 0.053m NAVD88, approximately 0.5m above the channel bottom.

December 12, 2017 - present: -0.056m NAVD88, approximately 0.5m above the channel bottom.

c) Water depth: approximately 0.5m to 2.7m

d) Channel width: approximately 30m

e) Bottom type: sand, some silt and clay

f) Salinity range: 1 ppt (extreme rain events) to 36 ppt (average of 33ppt)

Oneonta Slough (OS)

a) Location of site: this station is located on the upper portion of the Oneonta Slough in the northwest corner of the reserve, approximately 1.4km north of the Tijuana River. OS station is established in the middle of the same channel as the Boca Rio site; 32° 34' 6.0" N, 117° 7' 52.6" W

b) Elevation of sonde's depth port:

January 23, 2015 - December 4, 2017: 0.332m NAVD88, approximately 0.5m above the channel bottom.

December 5, 2017 – present: 0.295m NAVD88, approximately 0.5m above the channel bottom

c) Water depth: approximately 0.7m to 2.4m

d) Channel width: approximately 23m

e) Bottom type: silty clay

f) Salinity range: 1 ppt (extreme rain events) to 39 ppt (average of 32ppt)

g) The area adjacent to the west side of the channel is developed. There is a 50+ meter buffer of natural vegetation between development and the channel. The area adjacent to the east side of the channel is relatively undisturbed. Direct impacts on this site may be runoff from streets into channel during rain events.

Pond Restored (PR)

a) Location of site: this station is located at the middle levee breach between Pond Eleven and Pond Ten, which is part of the South San Diego Bay Coastal Wetland Restoration and Enhancement Project; 32° 35' 45.9", 117° 7' 5.5" W.

b) Elevation of sonde's depth port: -0.310m NAVD88, approximately 0.5m above the channel bottom.

c) Depth: 0.5m to 3.2m.

d) Channel width: approximately 40m.

e) Bottom type: silt and clay.

f) Tidal Exchange (extremes): approximately -2ft to +7ft MLLW.

g) Salinity: 4ppt (extreme rain event) to 39 ppt (average of 35ppt)

South Bay (SB)

a) Location of site: this station is located at the mouth of Otay River where it flows into San Diego Bay; 32° 36' 3.6" N, 117° 6' 57.0" W.

b) Elevation of sonde's depth port: -0.379m NAVD88, approximately 0.5m above the channel bottom.

c) Depth: approximately 0.7 to 3.2m

d) Channel width: approximately 25m

e) Bottom type: silt and clay.

f) Tidal Exchange (extremes): approximately -2ft to +7ft MLLW.

g) Salinity: 4ppt (extreme rain event) to 39 ppt (average of 35ppt)

All Tijuana River NERR historical nutrient/pigment monitoring stations:

Station Code	SWMP Status	Station Name	Location	Active Dates	Reason Decommissioned	Notes
tjrbrnut	P	Boca Rio	32° 33' 33.70 N, 117° 7' 44.30 W	12/01/2004 - current	NA	Grab sample until present; Diel sample from 1/18/2007 to 12/6/2012 and from 1/20/2016 to present
tjrosnut	P	Oneonta Slough	32° 34' 6.00 N, 117° 7' 52.60 W	09/01/2002 - current	NA	Grab sample until present; diel sample from 9/1/2002 until 12/06/2006
tjrprnut	P	Pond Eleven Restored	32° 35' 45.90 N, 117° 7' 5.50 W	01/01/2012 - current	NA	Grab sample until present; diel sample from 1/8/2013 to 12/18/2015
tjrsbnut	P	South Bay	32° 36' 3.60 N, 117° 6' 57.00 W	01/01/2008 - current	NA	Grab sample
tjrpenut	P	Pond Eleven	32° 36' 3.54 N, 117° 6' 58.46 W	07/01/2008 – 12/31/2011	Sampling at this site was interrupted due to an extensive Restoration project	Grab sample; restoration project was concluded in October 2011. Pond Eleven site was relocated and renamed to Pond Eleven Restored. Sampling resumed in January 2013.
tjrmmnut	P	Model Marsh	32° 32' 52.08 N, 117° 7' 22.80 W	09/01/2002 – 07/30/2008	Heavy sedimentation compromised the datalogger station	Grab sample
tjrtlnut	P	Tidal Linkage	32° 34' 27.84 N, 117° 7' 37.92 W	09/01/2002 – 12/06/2007	Site too shallow for diel samples; heavy sedimentation compromised the datalogger station	Grab sample; diel sample on 7/27/2006
tjrrcnut	P	River Channel	32° 33' 28.08 N, 117° 6' 21.96 W	09/01/2002 – 11/30/2004	Heavy sedimentation compromised the datalogger station	Grab sample; replaced by Boca Rio site
tjrhpnut	NA	Helicopter Pad	32° 33' 31.46 N, 117° 7' 9.34 W	09/01/2002 - 09/30/2002	Grab sample collected to test site suitability	Data only available by contacting the reserve directly
tjrmmnut	NA	River Mouth	32° 33' 13.32 N, 117° 7' 34.32 W	09/01/2002 – 12/01/2002	Grab samples collected to test site feasibility	Data only available by contacting the reserve directly

5) Coded variable definitions –

[Instructions/Remove: Explain the station code names and monitoring program codes. Use the following format:]

Station code names:

tjrbrnut = Tijuana River Reserve Boca Rio nutrient data
tjrosnut = Tijuana River Reserve Oneonta Slough nutrient data
tjrsbnut = Tijuana River Reserve South Bay nutrient data
tjrpenut = Tijuana River Reserve Pond Restored nutrient data

Monitoring program codes:

monthly grab sample program = 1
diel grab sample program = 2

6) Data collection period

Sampling was performed on a monthly basis, attempting to sample at approximately 1 month intervals. Diel sampling at Boca Rio began with the first of the ISCO samples at the projected low tide. All other (grab) samples were collected 3 hours prior to the low tide corresponding to the end of the ISCO sampling period. Date and time for both Grab and Diel samples are recorded below

Grab Samples

Boca Rio (BR)

Station	Date	Rep1	Rep 2
tjrbrnut	1/23/2020	15:16	15:17
tjrbrnut	2/20/2020	14:06	14:07
tjrbrnut	3/17/2020	11:41	11:42
tjrbrnut	9/4/2020	16:06	16:07
tjrbrnut	10/14/2020	13:20	13:21
tjrbrnut	11/23/2020	11:45	11:46
tjrbrnut	12/14/2020	14:30	14:31

Oneonta Slough (OS)

Station	Date	Rep1	Rep 2
tjrosnut	1/23/2020	14:33	14:34
tjrosnut	2/20/2020	13:17	13:18
tjrosnut	3/17/2020	10:47	10:48
tjrosnut	9/4/2020	15:20	15:21
tjrosnut	10/14/2020	12:30	12:31
tjrosnut	11/23/2020	11:15	11:16
tjrosnut	12/14/2020	13:30	13:31

Pond Restored (PR)

Station	Date	Rep1	Rep 2
tjrprnut	1/23/2020	13:00	13:01
tjrprnut	2/20/2020	12:04	12:05
tjrprnut	3/17/2020	09:48	09:49
tjrprnut	7/16/2020	09:50	09:51
tjrprnut	8/31/2020	14:47	14:48
tjrprnut	10/13/2020	12:47	12:48
tjrprnut	11/24/2020	11:01	11:02
tjrprnut	12/14/2020	15:15	15:16

South Bay (SB)

Station	Date	Rep1	Rep 2
tjrsbnut	1/23/2020	13:34	13:35
tjrsbnut	2/20/2020	12:32	12:33
tjrsbnut	3/17/2020	09:20	09:21
tjrsbnut	7/16/2020	09:30	09:31
tjrsbnut	8/31/2020	15:20	15:21
tjrsbnut	10/13/2020	12:30	12:31
tjrsbnut	11/24/2020	11:33	11:34
tjrsbnut	12/14/2020	15:30	15:31

Diel Samples

Boca Rio

Station	Start Date	Start Time	End Date	End Time
tjrbrnut	1/22/2020	14:15	1/23/2020	15:00
tjrbrnut	2/19/2020	13:30	2/20/2020	14:15
tjrbrnut	3/16/2020	10:15	3/17/2020	11:00
tjrbrnut	10/13/2020	12:30	10/14/2020	13:15
tjrbrnut	11/23/2020	11:15	11/24/2020	12:00
tjrbrnut	12/13/2020	14:30	12/14/2020	13:00

Note that the time stamps are based on a 24-hour clock and refer to Pacific Standard Time. The date format is mm/dd/yyyy. Water quality parameters such as Specific Conductivity, Salinity, Dissolved Oxygen Saturation and Temperature are measured by YSI handheld water quality multiparameter meter or by YSI multiparameter datasonde upon samples collection. These measurements are included in the nutrient datasheet.

7) Associated researchers and projects–

The research program at the TRNERR focuses on adaptive approaches to wetlands management, which involves coupling scientific investigation with management action. One focal area of research continues to be adaptive restoration, and the TRNERR has a long history of science-based restoration efforts. These programs incorporate descriptive and experimental approaches to investigate biotic and abiotic responses to marsh restoration, including ways to better achieve desired ecosystem responses. Two SWMP sites, based in South San Diego Bay, are associated with a marsh restoration in that area. Another active area of research is invasive species ecology and management. Although estuaries are typically invaded by a broad suite of species from many habitat types, current research is focusing on terrestrial and riparian invaders able to cross ecotones and invade salt marsh habitats. Researchers at the TRNERR are investigating mechanisms of invasions, impacts of invaders, and ecosystem recovery after exotic species control.

NERR SWMP water quality and weather data are used in a variety of reserve-based and external research and education programs. Water quality data from the Tijuana River, which rarely experiences mouth closures, provides an interesting contrast to data from other regional systems that experience frequent closure events. Also, SWMP water quality data are incorporated into a high school curriculum developed at the reserve. Tier 1 nutrient sampling is being conducted at all water quality datalogger stations. NERR SWMP meteorological sampling is being conducted at 1 station which is located near the former Tidal Linkage water quality station. In addition, much of the reserve is used as a test bed for research related to adaptive marsh restoration, with recent attention on the Model Marsh. NERR SWMP WQ and MET data are available at www.nerrdata.org.

8) Distribution –

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

Requested citation format:

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

TJR NERR staff collected, filtered and delivered the samples to the chemistry lab at the Oceanographic Data Facility, Scripps Institution of Oceanography, University of California, San Diego, where lab analyses were performed. The results are reported in μM . For purposes of consistency in the NERR System, the TJR NERR calculates the concentrations as mg/l based on atomic weights of 14.01, 30.97, and 28.09 for N, P, and Si, respectively. Therefore, TJR NERR multiplies the concentrations reported by 0.01401, 0.03097, and 0.02809 to yield concentrations in mg/L as N, P, and Si, respectively.

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. Data entry and verification was done by Monica Almeida (please see **Principal investigators and contact persons**).

10) Parameter titles and variable names by category –

Required NOAA NERRS System-wide Monitoring Program nutrient parameters are denoted by an asterisk “*”.

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 + Nitrate, Filtered	NO23F	mg/L as N
	Dissolved Inorganic Nitrogen	DIN	mg/L as N
Plant Pigments:			
	*Chlorophyll a	CHLA_N	µg/L
Carbon:			
Other Lab Parameters:			
	Silicate, Filtered	SiO4F	mg/L as SI
Microbial:			
Field Parameters:			
	Water Temperature	WTEM_N	°C

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. NO₂ levels are predominately low at TJR Reserve and analysis was discontinued as a result.

11) Measured or calculated laboratory parameters –

[Instructions/Remove: This section lists all measured and calculated variables. Only list those parameters that are collected and reported, do not list field parameters. See Table 2 in the “Nutrient and Chlorophyll Monitoring Program and Database Design” SOP version 1.8 (March 2017) document for a full list of directly measured and computed variables. Do not include field parameters in this section.]

a) Parameters measured directly

Nitrogen species:	NH4F, NO23F
Phosphorus species:	PO4F
Other:	CHLA_N, SiO4F

b) Calculated parameters

DIN	NO23F+NH4F
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12) Limits of detection –

[Instructions/Remove: This section explains how the laboratory determines the minimum detection limit (MDL). List the method detection limits used and dates they were in use. You may copy this data from the MDL sheet created in the NutrientQAQC macro. ***You must also include the date that each MDL was revisited by the lab for appropriateness (this should be done at least annually).***]

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

Method detection limit as defined in the Code of Federal Regulations, 40 CFR 136, Appendix B, as: “the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.”

MDLs are determined, reviewed and revised annually by the Chemistry Lab at the Oceanographic Data Facility, Scripps Institution of Oceanography, University of California, San Diego.

MDLs were determined as ≈ 3 times the standard deviation of a minimum of 7 replicates. Laboratory follows the “**The Method Detection Limit Procedure of The U.S. Environmental Protection Agency**” described by U.S. Geological Survey at https://water.usgs.gov/owq/OFR_99-193/detection.html#detection1

Method Detection Limits (MDL) for measured water quality parameters:

Parameter	Start Date	End Date	MDL	Revisited
PO4F	01/01/20	07/20/20	0.0003	
PO4F	07/21/20	12/31/20	0.0004	07/21/20
NH4F	01/01/20	07/20/20	0.0003	
NH4F	07/21/20	12/31/20	0.0004	07/21/20
NO23F	01/01/20	07/20/20	0.0003	
NO23F	07/21/20	12/31/20	0.00035	07/21/20
CHLA_N	01/01/20	08/12/20	0.00077	
CHLA_N	08/13/20	12/31/20	0.00155	08/13/20
SiO4F	1/1/2020	7/20/2020	0.0014	
SiO4F	7/21/2020	12/31/2020	0.0035	7/21/2020

13) Laboratory methods –

a) **Parameter: NH4F**

Method Reference:

Ammonia is analyzed using the method described by Kerouel and Aminot. Kerouel, R. and Aminot, A., 1997. “Fluorometric determination of ammonia in sea and estuarine waters by direct segmented flow analysis.” Marine Chemistry, vol 57, no. 3-4, pp. 265-275.

Method Descriptor:

The sample is combined with a working reagent made up of ortho-phthalaldehyde, sodium sulfite and borate buffer and heated to 75°C. Fluorescence proportional to the ammonia concentration is emitted at 460nm following excitation at 370nm.

Preservation Method:

Filtered through both Whatman glass fiber filter (0.7 μ m pore size) and MF-Millipore (0.45 μ m pore size) membrane filter, and stored at or below -20°C.

b) **Parameter: NO23F**

Method Reference:

A modification of the Armstrong et al. procedure is used for the analysis of nitrate and nitrite. Armstrong, F.A.J., Stearns, C.A., and Strickland, J.D.H., 1967. "The measurement of upwelling and subsequent biological processes by means of the Technicon Autoanalyzer and associated equipment," Deep-Sea Research, 14, pp.381-389.

Method Descriptor:

For the nitrate analysis, a water sample is passed through a cadmium column where the nitrate is reduced to nitrite. This nitrite is then diazotized with sulfanilamide and coupled with N-(1-naphthyl)-ethylenediamine to form a red dye. The sample is then passed through a 10mm flowcell and the absorbance is measured at 540nm. The procedure is the same for the nitrite analysis but without the cadmium column.

Preservation Method:

Filtered through both Whatman glass fiber filter (0.7µm pore size) and MF-Millipore (0.45µm pore size) membrane filter, and stored at or below -20°C.

c) **Parameter: PO4F**

Method Reference:

Orthophosphate is analyzed using a modification of the Bernhardt and Wilhelms method. Bernhardt, H., and Wilhelms, A., 1967. "The continuous determination of low-level iron, soluble phosphate and total phosphate with the AutoAnalyzer," Technicon Symposia, I, pp.385-389.

Method Descriptor:

Acidified ammonium molybdate is added to a water sample to produce phosphomolybdic acid, which is then reduced to phosphomolybdous acid (a blue compound) following the addition of dihydrazine sulfate. The sample is passed through a 10mm flowcell and absorbance is measured at 820nm. The absorbance is proportional to the concentration of orthophosphate in the sample.

Preservation Method:

Filtered through both Whatman glass fiber filter (0.7µm pore size) and MF-Millipore (0.45µm pore size) membrane filter, and stored at or below -20°C.

d) **Parameter: CHLA**

Method Reference:

Chlorophyll was analyzed using the California Cooperative Oceanic Fisheries Investigations (CalCOFI) methods, which is based on several references such as:

Holm_Hansen, O., Lorenzen, C.J., Holms, R.W., Strickland, J.D.H. (1965). Fluorometric Determination of Chlorophyll. J. Cons.perm.int Explor. Mer. 30: 3-15.

Lorenzen, C. J. (1967) Determination of chlorophylls and phaeopigments: spectrophotometric equations. Limnol. Oceanogr. 12: 343-346.

Yentsch, C.S., Menzel, D.W. (1963). A method for the determination of phytoplankton chlorophyll and phaeophytin by fluorescence. Deep-Sea Res. 10: 221-231.

Method Descriptor:

Samples are filtered through Whatman 0.7µm particle retention glass fiber filters. Chlorophyll *a* is extracted in an acetone solution. Chlorophyll and phaeopigments are then measured fluorometrically using an acidification technique.

Detailed method can be found at

<https://scripps.ucsd.edu/ships/shipboard-technical-support/odf/chemistry-services/chlorophyll>

Preservation Method:

Filtered through a Whatman glass fiber filter (0.7µm pore size), stored in foil packets at or below -20°C.

e) **Parameter: SiO₄F**

Method Reference:

Silicate is analyzed using the basic method of Armstrong et al. Armstrong, F.A.J., Stearns, C.A., and Strickland, J.D.H., 1967. "The measurement of upwelling and subsequent biological processes by means of the Technicon Autoanalyzer and associated equipment," Deep-Sea Research, 14, pp.381-389.

Method Descriptor:

Acidified ammonium molybdate is added to a water sample to produce silicomolybdic acid which is then reduced to silicomolybdous acid (a blue compound) following the addition of stannous chloride. The sample is passed through a 10mm flowcell and measured at 660nm.

Preservation Method:

Filtered through both Whatman glass fiber filter (0.7µm pore size) and MF-Millipore (0.45µm pore size) membrane filter, and stored at or below -20°C.

14) Field and Laboratory QAQC programs –

[Instructions/Remove: This section describes field variability, laboratory variability, the use of inter-organizational splits, sample spikes, standards, and cross calibration exercises. Include any information on QAQC checks performed by your lab.]

a) **Precision**

i) **Field variability** – Duplicate samples (i.e., two successive samples in different bottles) were collected at all sites.

ii) **Laboratory variability** – NONE.

iii) **Inter-organizational splits** – NONE.

b) **Accuracy**

i) **Sample spikes** – NONE.

- ii) **Standard reference material analysis** – Accuracy is based on the quality of the following standards, supplied from Johnson Matthey Chemical Co. and Fisher Scientific. Primary standards for silicate (Na_2SiF_6), nitrate (KNO_3), nitrite (NaNO_2), phosphate (KH_2PO_4), and ammonia (NH_3) have purities of >99%, 99.999%, 98%, 99.999% and > 99.0%, respectively, as reported by the supplier.

Reference materials for nutrients in seawater (RMNS) are also used as a check sample and run periodically (approximately once a month). The RMNS preparation, verification, and suggested protocol for use of the material are described by (Aoyama et al., 2006, 2007, 2008) and Sato (2010). See the end of this document for these citations.

Results of these analyses are within the stated accuracy for the reference materials.

- 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

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
<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 NO₂F 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.

A shelter in place order was issued on March 17th because of the COVID – 19 pandemic. Office and field work were affected and sampling was paused from April to June, resulting in missing samples for these months. In addition to the pandemic, several issues with the infrastructure of the water treatment plants have prevented the treatment of the Tijuana River water before entering the estuary. A mixture of run-off, treated wastewater and sewage was constantly flowing in the Tijuana River into the reserve, posing a healthy risk to the reserve staff and the community. Since then, there were numerous episodes of sewage contamination, and those added to the COVID-19 pandemic resulted

in stricter rules to limit staff contact with water. This resulted in the several missing nutrient samples listed below:

April – all diel and grab samples

May – all diel and grab samples

June - all diel and grab samples

July – all diel samples and grab samples affected by bad water quality (BR, OS stations)

August - all diel samples and grab samples affected by bad water quality (BR, OS stations)

September - all diel samples and grab samples PR, SB stations (these were collected 3 days before September sampling)

Flows and rain events that occurred 72 hours, or sooner, prior to nutrient sampling are listed below (total precipitation values are measured by the tipping bucket that is part of our SWMP Tidal Linkage meteorological station):

1/21 - 11.176mm

15-16/3 – 6.3mm

12/14 – 0.9mm

Samples are held at -20°C. NERRS SOP allows nutrient samples to be held for up to 28 days (CHLA for 30), 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, however no samples exceeded the holding time in 2020.

Sample Descriptor	Date Analyzed					
	PO4F	NH4F	NO2F	NO23F	CHLA_N	SiO4F
1/22 - 1/23/2020, all diel samples	2/13/2020	2/13/2020	2/13/2020	2/13/2020	2/20/2020	2/13/2020
1/23/2020, all grab samples	2/13/2020	2/13/2020	2/13/2020	2/13/2020	2/20/2020	2/13/2020
2/19 - 2/20/2020, all diel samples	3/11/2020	3/11/2020	3/11/2020	3/11/2020	3/10/2020	3/11/2020
2/20/2020, all grab samples	3/11/2020	3/11/2020	3/11/2020	3/11/2020	3/10/2020	3/11/2020
3/16 -3/17/2020, all diel samples	3/19/2020	3/19/2020	3/19/2020	3/19/2020	3/20/2020	3/19/2020
3/17/2020, all grab samples	3/19/2020	3/19/2020	3/19/2020	3/19/2020	3/20/2020	3/19/2020
7/16/2020, 09:30, 09:50 grab samples	8/3/2020	8/3/2020	8/3/2020	8/3/2020	8/13/2020	8/3/2020
8/31/2020,14:47, 15:20 grab samples	9/24/2020	9/24/2020	9/24/2020	9/24/2020	9/17/2020	9/24/2020
9/4/2020, 15:20, 16:06 grab samples	9/24/2020	9/24/2020	9/24/2020	9/24/2020	9/17/2020	9/24/2020
10/13 - 10/14/2020, all diel samples	11/4/2020	11/4/2020	11/4/2020	11/4/2020	11/5/2020	11/4/2020
10/14/2020, all grab samples	11/4/2020	11/4/2020	11/4/2020	11/4/2020	11/5/2020	11/4/2020
11/23 - 11/24/2020, all diel samples	12/1/2020	12/1/2020	12/1/2020	12/1/2020	12/2/2020	12/1/2020
11/24/2020, all grab samples	12/1/2020	12/1/2020	12/1/2020	12/1/2020	12/2/2020	12/1/2020
12/13 - 12/14/2020, all diel samples	12/18/2020	12/18/2020	12/18/2020	12/18/2020	12/22/2020	12/18/2020
12/14/2020, all grab samples	12/18/2020	12/18/2020	12/18/2020	12/18/2020	12/22/2020	12/18/2020

During lab analysis, samples with high values are diluted. Samples and dilution ratios are detailed below:

1/22/2020 14:15 BR - Diel PO4, NO2, NH4 based on 1:30 dilution

1/22/2020 16:30	BR - Diel	PO4, NO2, NH4 based on 1:30 dilution
1/22/2020 18:45	BR - Diel	PO4, Sil, based on 1:30 dilution, NH4 1:100 dilution
1/22/2020 21:00	BR - Diel	PO4, NH4 based on 1:30 dilution
1/22/2020 23:15	BR - Diel	NH4 based on 1:30 dilution
1/23/2020 01:30	BR - Diel	NH4 based on 1:30 dilution
1/23/2020 03:45	BR - Diel	NH4 based on 1:30 dilution
1/23/2020 06:00	BR - Diel	NH4 based on 1:30 dilution
1/23/2020 08:15	BR - Diel	NH4 based on 1:30 dilution
1/23/2020 10:30	BR - Diel	NH4 based on 1:30 dilution
1/23/2020 12:45	BR - Diel	PO4 NH4 based on 1:30 dilution
1/23/2020 15:00	BR - Diel	PO4 NH4 based on 1:100 dilution
1/23/2020 15:16	BR - Grab	PO4 based on 1:30 dilution
1/23/2020 15:17	BR - Grab	PO4 based on 1:30 dilution
1/23/2020 14:33	OS - Grab	PO4 based on 1:30 dilution
1/23/2020 14:34	OS - Grab	PO4 based on 1:30 dilution
2/19/2020 13:30	BR - Diel	PO4 derived from 1:30 dilution of sample, NH4 derived from 1:60 dilution of sample
2/19/2020 15:45	BR - Diel	PO4 derived from 1:30 dilution of sample, NH4 derived from 1:60 dilution of sample
2/19/2020 18:00	BR - Diel	PO4 derived from 1:30 dilution of sample, NH4 derived from 1:60 dilution of sample
2/19/2020 20:15	BR - Diel	NH4 derived from 1:30 dilution of sample
2/19/2020 22:30	BR - Diel	NH4 derived from 1:30 dilution of sample
2/20/2020 00:45	BR - Diel	NH4 derived from 1:30 dilution of sample
2/20/2020 03:00	BR - Diel	NH4 derived from 1:30 dilution of sample
2/20/2020 05:15	BR - Diel	NH4 derived from 1:30 dilution of sample
2/20/2020 12:00	BR - Diel	PO4 derived from 1:30 dilution of sample, NH4 derived from 1:30 dilution of sample
2/20/2020 14:15	BR - Diel	PO4 derived from 1:30 dilution of sample, NH4 derived from 1:30 dilution of sample
2/20/2020 14:06	BR - Grab	PO4 derived from 1:30 dilution of sample, NH4 derived from 1:30 dilution of sample
2/20/2020 14:07	BR - Grab	PO4 derived from 1:30 dilution of sample, NH4 derived from 1:30 dilution of sample
2/20/2020 13:17	OS - Grab	PO4 derived from 1:30 dilution of sample, NH4 derived from 1:60 dilution of sample
2/20/2020 13:08	OS - Grab	PO4 derived from 1:30 dilution of sample, NH4 derived from 1:60 dilution of sample
3/16/2020 10:15	BR - Diel	NH4 derived from 1:30 dilution of sample
3/16/2020 12:30	BR - Diel	NH4 derived from 1:30 dilution of sample
3/16/2020 14:45	BR - Diel	NH4 derived from 1:30 dilution of sample
3/16/2020 17:00	BR - Diel	NH4 derived from 1:30 dilution of sample
3/16/2020 19:15	BR - Diel	NH4 derived from 1:30 dilution of sample
3/16/2020 21:30	BR - Diel	NH4 derived from 1:30 dilution of sample
3/16/2020 23:45	BR - Diel	NH4 derived from 1:30 dilution of sample
3/17/2020 02:00	BR - Diel	NH4 derived from 1:30 dilution of sample

3/17/2020 04:15	BR - Diel	NH4 derived from 1:30 dilution of sample
3/17/2020 06:30	BR - Diel	NH4 derived from 1:30 dilution of sample
3/17/2020 08:45	BR - Diel	NH4 derived from 1:30 dilution of sample
3/17/2020 11:00	BR - Diel	NH4 derived from 1:30 dilution of sample
3/17/2020 11:41	BR - Grab	PO4 derived from 1:30 dilution of sample, NH4 derived from 1:100 dilution of sample
3/17/2020 11:42	BR - Grab	PO4 derived from 1:30 dilution of sample, NH4 derived from 1:100 dilution of sample
3/17/2020 10:47	OS - Grab	PO4 derived from 1:30 dilution of sample, NH4 derived from 1:100 dilution of sample
3/17/2020 10:48	OS - Grab	PO4 derived from 1:30 dilution of sample, NH4 derived from 1:100 dilution of sample
9/4/2020 14:45	OS - Grab	PO4 determined by 1:3 dilution
9/4/2020 14:46	OS - Grab	PO4 determined by 1:3 dilution
10/13/2020 14:45	BR - Diel	NH4 determined by 1:30 dilution
11/23/2020 20:15	BR - Diel	NH4 determined by 1:30 dilution
11/23/2020 22:30	BR - Diel	NH4 determined by 1:30 dilution
11/24/2020 09:45	BR - Diel	NH4 determined by 1:30 dilution
11/24/2020 12:00	BR - Diel	NH4 determined by 1:30 dilution
11/23/2020 11:15	OS - Grab	NH4 determined by 1:30 dilution
11/23/2020 11:16	OS - Grab	NH4 determined by 1:30 dilution
12/13/2020 19:00	BR - Diel	NH4 based on 1:30 dilution
12/14/2020 04:00	BR - Diel	NH4 based on 1:30 dilution

Additional Citations:

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