Tijuana River (TJR) NERR Nutrient Metadata
January – December 2018
Latest Update: June 10, 2019

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@belle.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 impacted heavily 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. Two stations were originally set up: a treatment station (RC) was set up close to the river mouth on the southern end of the Oneonta Slough, while a control station (OS) was set up on the northern end of Oneonta Slough. The treatment station location was chosen because it would be the site most affected by sewage outflow. Deployment at the treatment station, 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, logging at this site was terminated in 2004.

Currently, there are two YSI datalogger stations installed at the TRNERR and two datalogger 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. The original control station (OS) in the northern end of Oneonta Slough is still in place. 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 second active datalogger site, Boca Rio (BR), was established in December 2004 and is located near the mouth of the Tijuana River. This station replaces the River Channel station (RC), which was established in August 2002 to monitor the Tijuana River, the largest source of freshwater to the reserve.

The South Bay (SB) datalogger was established in January 2008 and is located at the mouth of Otay River, which flows into South San Diego Bay. The fourth sonde location, Pond Eleven (PE), was 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 datalogger site was relocated. Sonde deployments 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 South Bay and Pond Restored sites are located within the San Diego National Wildlife Refuge Complex. The images below show pre- and post-restoration of the salt ponds and the datalogger sites. The post restoration photo includes the PE datalogger site as a reference to the new PR datalogger site. No sampling occurs at the PE site.

a) Monthly Grab Sampling Program:

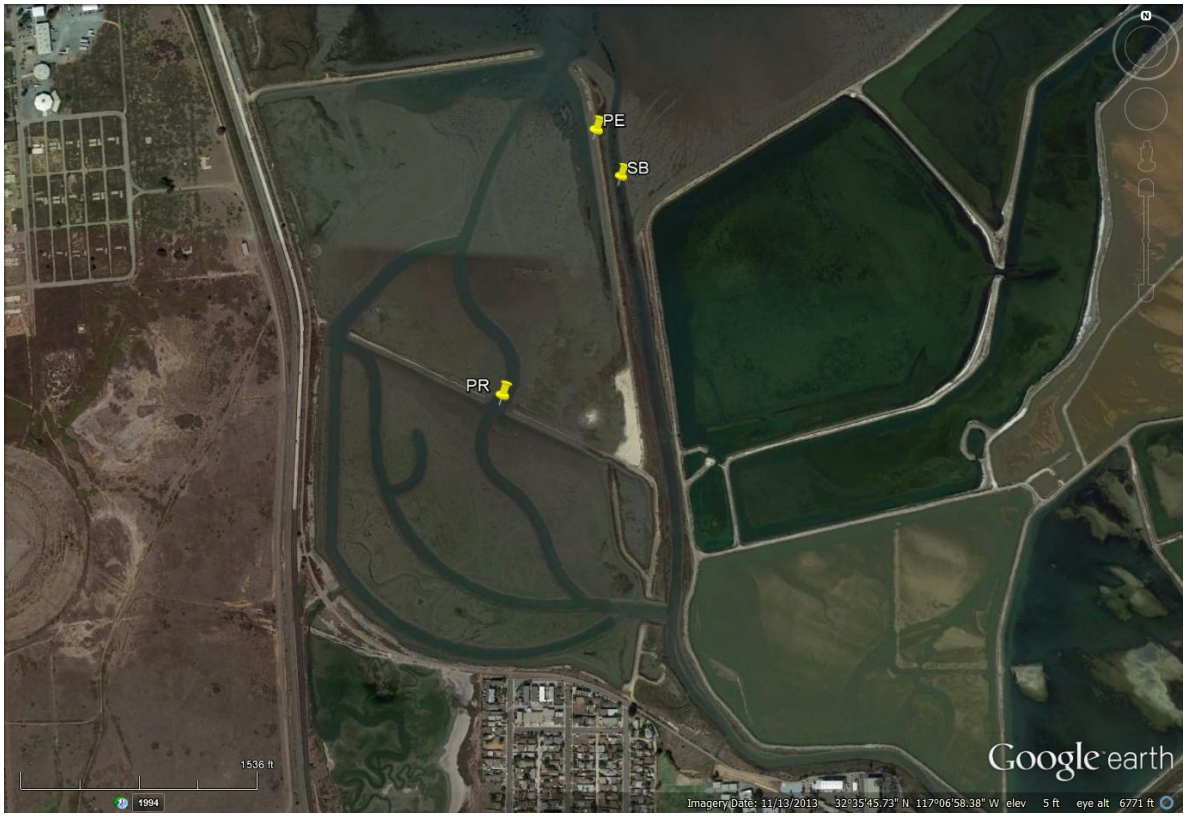
Grab samples were collected monthly at all SWMP water quality sonde sites. Monthly grab sampling provides information as to the spatial differences in nutrient levels within the system. The placement of these sites also offers the opportunity to better isolate the possible origin of nutrient inputs as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

Pre Restoration

Post Restoration



3) Research Methods

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 section **17) Other Remarks** at the end of this document). Samples were taken sequentially, within one minute of each other and adjacent to the sonde probes 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. At this time the TRNERR also began reporting silicate. All samples were immediately stored on ice and frozen within four hours. Samples were delivered to the lab typically within 48 hours. 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 an YSI Pro Plus water quality handheld instrument. Measurements are included in the datasheet.

b) Diel Sampling

Diel samples were collected at the Boca Rio site. Samples were taken at intervals of 2hrs 15mins for a total of either 11 or 12 samples over one full tidal cycle. 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 sonde. The sampler was located approximately 1.5m above the strainer on the channel's bank. The sampler was programmed to collect 1 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 twenty minutes in 10% HCl, and, lastly, six rinses with Type 1 reagent water (18MΩ-cm or greater).

4) Site Location and Character

General site Characteristics (TRNERR)

a) Latitude and Longitude: 32º 34' N, 117º 7' W
b) Tidal range: approximately -2 to + 7ft MLLW
c) Depth: approximately 0.2 to 2m
d) The dominant freshwater source to the estuary is the Tijuana River, which drains a 4,483km^2 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 0.82m^3/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 Mm^3), 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. Freshwater discharge with untreated sewage occurs year round, although these have decreased with the construction of a binational water treatment plant. Vegetation in the area is dominated by common pickleweed (*Salicornia pacifica*) and Pacific cordgrass *(Spartina foliosa*).

Specific Site characteristics: Boca Rio (BR)

a) Location of site: the datalogger station is located approximately 400m north of the Tijuana River in the middle of a channel which runs north-south; 32º 33' 33.7'' N, 117º 7' 44.4" W.
b) Elevation of sonde:
January 27, 2015 - December 11, 2017 0.053m NAVD88, approximately .5m above the channel bottom.
December 12, 2017 - present -0.056m NAVD88, approximately .5m above the channel bottom.
c) Channel width: approximately 30 m.
d) Bottom type: sand, some silt and clay.
e) Salinity: 1 ppt (extreme rain events) to 36 ppt (average of 33ppt)

Specific Site characteristics: Oneonta Slough (OS)

a) Location of site: the datalogger 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 in the middle of the same channel as the Boca Rio site; 32º 34' 6.0" N, 117º 7' 52.7" W.
b) Elevation of sonde:
January 23, 2015 - December 4, 2017 0.332m NAVD88, approximately .5m above the channel bottom.
December 5, 2017 - present 0.295m NAVD88, approximately .5m above the channel bottom.
c) Depth: approximately 0 to 1.8m; directly below the datalogger, is approx. 0.55m below Mean Sea Level
d) Channel width: approximately 23 meters.
e) Bottom type: silty clay.
f) Salinity: 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.
h) Direct impacts may be runoff from streets into channel during rain events.

Specific Site Characteristics: Pond Restored (PR)
a) Location of site: The datalogger 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 ; 32º 35' 46.0", 117º 7' 5.5" W.
b) Elevation of sonde: -.310m NAVD88, approximately .5m above the channel bottom.
c) Depth: approximately 0 to 2.7m
d) Channel width: approximately 40m.
e) Bottom type: silt and clay.
f) Tidal Exchange (extremes): approximately -2 to +7ft MLLW.
g) Salinity: 4ppt (extreme rain event) to 39 ppt (average of 35ppt)

Specific Site Characteristics: South Bay (SB)
a) Location of site: The datalogger is located at the mouth of Otay River where it flows into San Diego Bay; 32º 36' 3.6" N, 117º 06 min 56.9" W.
b) Elevation of sonde: -.379m NAVD88, approximately .5m above the channel bottom.
c) Depth: approximately 0 to 2.7m
d) Channel width: approximately 25m
e) Bottom type: silt and clay.
f) Tidal Exchange (extremes): approximately -2 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	12/11/2004 12:48 -	NA	Grab sample until present; Diel sample from1/18/2007 to 12/6/2012 and from1/20/2016 to present
tjrosnut	P	Oneonta Slough	32° 34' 6.00 N, 117° 7' 52.60 W	09/01/2002 10:51 -	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° 07' 5.59 W	01/04/2012 10:36	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	01/03/2008 14:30 -	NA	Grab sample

tjrmmnut	P	Model Marsh	32° 32' 52.08 N, 117° 7' 22.80 W	9/02/2002 10:50 - 07/15/2008 10:17	Heavy sedimentation compromised the datalogger station	Grab sample
tjrpenut	P	Pond Eleven	32° 36' 3.54 N, 117° 06' 58.46 W	07/15/2008 11:14 – 09/23/2010 13:03	Sampling at this site was temporarily 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.
tjrrcnut	P	River Channel	32° 33' 28.08 N, 117° 6' 21.96 W	08/01/2002 00:00 - 11/30/2004 15:30	Heavy sedimentation compromised the datalogger station	Grab sample; replaced by Boca Rio site
tjrtlnut	P	Tidal Linkage	32° 34' 27.84 N, 117° 7' 37.92 W	08/01/2002 00:00 - 12/06/2007 00:00	Site too shallow for diel samples; heavy sedimentation compromised the datalogger station	Grab sample; diel sample on 7/27/2006

5) Code Variable Definitions

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
tjrprnut = 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. Start and end times for the diel sampling are listed in the last table of this section. All other (grab) samples were collected 3 hours prior to the low tide corresponding to the end of the ISCO sampling period. Grab samples date and time are recorded below.

Grab Samples (PST)

Boca Rio (BR)

Station	Date	Rep 1	Rep 2
tjrbrnut	1/17/2018	15:45	15:46
tjrbrnut	2/15/2018	14:45	14:46
tjrbrnut	3/23/2018	8:40	8:41
tjrbrnut	4/24/2018	11:31	11:32

tjrbrnut	5/22/2018	10:45	10:46
tjrbrnut	6/20/2018	10:09	10:10
tjrbrnut	7/11/2018	13:07	13:08
tjrbrnut	8/24/2018	14:29	14:30
tjrbrnut	9/11/2018	15:53	15:54
tjrbrnut	10/25/2018	14:34	14:35
tjrbrnut	11/21/2018	13:56	13:57
tjrbrnut	12/17/2018	11:44	11:45

Oneonta Slough (OS)

Station	**Date**	**Rep 1**	**Rep 2**
tjrosnut	1/17/2018	14:30	14:31
tjrosnut	2/15/2018	14:15	14:16
tjrosnut	3/23/2018	7:54	7:55
tjrosnut	4/24/2018	10:45	10:46
tjrosnut	5/22/2018	10:14	10:15
tjrosnut	6/20/2018	9:26	9:27
tjrosnut	7/11/2018	12:36	12:37
tjrosnut	8/24/2018	12:46	12:47
tjrosnut	9/11/2018	15:10	15:11
tjrosnut	10/25/2018	14:05	14:06
tjrosnut	11/21/2018	13:22	13:23
tjrosnut	12/17/2018	10:48	10:49

Pond Eleven Restored (PR)

Station	**Date**	**Rep 1**	**Rep 2**
tjrprnut	1/17/2018	13:45	13:46
tjrprnut	2/15/2018	13:30	13:31
tjrprnut	3/23/2018	6:23	6:24
tjrprnut	4/24/2018	9:23	9:24
tjrprnut	5/22/2018	8:21	8:22
tjrprnut	6/20/2018	8:08	8:09
tjrprnut	7/11/2018	11:05	11:06
tjrprnut	8/24/2018	11:22	11:23
tjrprnut	9/11/2018	13:48	13:49
tjrprnut	10/25/2018	13:14	13:15
tjrprnut	11/21/2018	12:22	12:23
tjrprnut	12/17/2018	9:33	9:34

South Bay (SB)

Station	Date	Rep 1	Rep 2
tjrsbnut	1/17/2018	13:15	13:16
tjrsbnut	2/15/2018	13:00	13:01
tjrsbnut	3/23/2018	6:48	6:49
tjrsbnut	4/24/2018	9:50	9:51
tjrsbnut	5/22/2018	8:48	8:49
tjrsbnut	6/20/2018	8:31	8:32
tjrsbnut	7/11/2018	11:32	11:33
tjrsbnut	8/24/2018	11:46	11:47
tjrsbnut	9/11/2018	14:16	14:17
tjrsbnut	10/25/2018	12:49	12:50
tjrsbnut	11/21/2018	11:52	11:53
tjrsbnut	12/17/2018	10:01	10:02

Diel Samples

Boca Rio

Station	Start Date	Start Time	End Date	End Time
tjrbrnut	1/16/2018	15:15	1/17/2018	16:00
tjrbrnut	2/14/2018	15:00	2/15/2018	13:30
tjrbrnut	3/22/2018	6:30	3/23/2018	7:15
tjrbrnut	4/23/2018	10:30	4/24/2018	11:15
tjrbrnut	5/21/2018	8:45	5/21/2018	15:30
tjrbrnut	6/19/2018	8:00	6/20/2018	8:45
tjrbrnut	7/10/2018	12:30	7/11/2018	11:00
tjrbrnut	8/23/2018	13:15	8/24/2018	14:00
tjrbrnut	9/10/2018	15:15	9/11/2018	13:45
tjrbrnut	10/24/2018	14:45	10/25/2018	13:15
tjrbrnut	11/20/2018	12:00	11/21/2018	10:30
tjrbrnut	12/16/2018	10:00	12/17/2018	10:45

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 Professional Plus water quality instrument 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.nerrsdata.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 2012.

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

II. Physical Structure Descriptors

9) Entry Verification

TRNERR staff collected and filtered the samples and were responsible for data entry and QAQC. After filtration, the samples were delivered 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 Tijuana River 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, TRNERR staff 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.

Parameter Titles and Variable Names by Data Category

Required NOAA/NERRS System-wide Monitoring Program water quality parameters are denoted by an asterisks "*".

Data Category	Parameter	Variable Name	Units of Measure
a) Phosphorus	*Orthophosphate	PO4F	mg/L as P
b) Nitrogen	*Nirite+Nitrate, filtered	NO23F	mg/L as N
	*Ammonium, filtered	NH4F	mg/L as N
	*Dissolved Inorganic Nitrogen	DIN	mg/L as N
c) Plant Pigments	*Chlorophyll a,	CHLA_N	µg/L
d) Other	Silicate, Filtered	SiO4F	mg/L as SI

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.

10) Measured and Calculated Laboratory Parameter

a) **Parameters Measured Directly**

Nitrogen species:	NO2F, NO23F, NH4F
Phosphorus species:	PO4F
Other	CHLA, SiO4F

b) **Calculated Variables**

DIN:	NO23F + NH4F
NO3:	NO23F - NO2

11) Limit of Detection

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."

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

Parameter	Start Date	End Date	MDL
NH4F	01/01/2018	05/22/2018	0.0014 mg/L as N
NH4F	05/23/2018	12/31/2018	0.0010 mg/L as N
NO23F	01/01/2018	05/22/2018	0.00028 mg/L as N
NO23F	05/23/2018	12/31/2018	0.0003 mg/L as N
NO2F	01/01/2018	05/22/2018	0.00028 mg/L as N
NO2F	05/23/2018	12/31/2018	0.00003 mg/L as N
NO3F	01/01/2018	05/22/2018	0.00028 mg/L as N
NO3F	05/23/2018	12/31/2018	0.0003 mg/L as N
PO4F	01/01/2018	05/22/2018	0.00062 mg/L as N
PO4F	05/23/2018	12/31/2018	0.0006 mg/L as N
SiO4F	01/01/2018	05/22/2018	0.00562 mg/L as N
SiO4F	05/23/2018	12/31/2018	0.0017 mg/L as N
CHLA_N	01/01/2018	05/22/18	0.07 µg/L
CHLA_N	05/23/2018	12/31/18	0.00134 µg/L

MDLs were determined by the Chemistry Lab at the Oceanographic Data Facility, Scripps Institution of Oceanography, University of California, San Diego.

12) Laboratory Methods

a) **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 absorbanceis measured at 820nm. The absorbance is proportional to the concentration of orthophosphate in the sample.
Preservation Method:	Filtered through both Whatman glass fiber filter (.7µm pore size) and MF-Millipore (.45µm pore size) membrane filter, and stored at or below -10°C.
Instrumentation:	AA3 Autoanalyzer made my SEAL Analytical.

b) **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 75ºC. Fluorescence proportional to the ammonia concentration is emitted at 460nm following excitation at 370nm.
Preservation Method:	Filtered through both Whatman glass fiber filter (.7µm pore size) and MF-Millipore (.45µm pore size) membrane filter, and stored at or below -10°C.
Instrumentation:	AA3 Autoanalyzer made my SEAL Analytical.

c) **Parameters: NO2F, NO3F**

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 (.7µm pore size) and MF-Millipore (.45µm pore size) membrane filter, and stored at or below -10°C.

Instrumentation: AA3 Autoanalyzer made my SEAL Analytical.

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 .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.

Preservation Method: Filtered through a Whatman .7µm particle retention glass fiber filter and stored in a container with desiccant at or below -10°C.

Instrumentation: Turner 10-005R fluorometer

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 (.7µm pore size) and MF-Millipore (.45µm pore size) membrane filter, and stored at or below -10°C.

Instrumentation: AA3 Autoanalyzer made my SEAL Analytical.

13) Field and Laboratory QAQC programs

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 Exercise**: 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

Wind direction

N	from the north
NNE	from the north northeast
NE	from the northeast
ENE	from the east northeast
E	from the east
ESE	from the east southeast
SE	from the southeast
SSE	from the south southeast
S	from the south
SSW	from the south southwest
SW	from the southwest
WSW	from the west southwest
W	from the west
WNW	from the west northwest
NW	from the northwest
NNW	from the north northwest

Wind speed

WS0	0 to 1 knot
WS1	> 1 to 10 knots
WS2	> 10 to 20 knots
WS3	> 20 to 30 knots
WS4	> 30 to 40 knots
WS5	> 40 knots

17) Other Remarks

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 table below details nutrient sample collection dates and those dates on which the analyses of the samples occurred. Dates in red highlight those samples that were analyzed after the 28 days holding period - 30 days for Chlorophyll - including the number of days by which that holding period was exceeded.

	Date Analyzed					
Sample Descriptor	PO4F	NH4F	NO2F	NO23F	CHLA_N,PHEA	SiO4F
1/16 - 1/17/2018, all diel samples	1/24/2018	1/24/2018	1/24/2018	1/24/2018	1/26/2018	1/24/2018
1/17/2018, all grab samples	1/24/2018	1/24/2018	1/24/2018	1/24/2018	1/26/2018	1/24/2018
2/14 - 2/15/2018, all diel samples	2/21/2018	2/21/2018	2/21/2018	2/21/2018	2/23/2018	2/21/2018
2/15/2018, all grab samples	2/21/2018	2/21/2018	2/21/2018	2/21/2018	2/23/2018	2/21/2018
3/22 -3/23/2018, all diel samples	4/4/2018	4/4/2018	4/4/2018	4/4/2018	4/2/2018	4/4/2018
3/23/2018, all grab samples	4/4/2018	4/4/2018	4/4/2018	4/4/2018	4/2/2018	4/4/2018
4/23 - 4/24/2018, all diel samples	4/27/2018	4/27/2018	4/27/2018	4/27/2018	5/15/2018	4/27/2018
4/24/2018, all grab samples	4/27/2018	4/27/2018	4/27/2018	4/27/2018	5/15/2018	4/27/2018
5/21 - 5/22/2018, all diel samples	5/23/2018	5/23/2018	5/23/2018	5/23/2018	5/30/2018	5/23/2018
5/22/2018, all grab samples	5/23/2018	5/23/2018	5/23/2018	5/23/2018	5/30/2018	5/23/2018
6/19 - 6/20/2018, all diel samples	6/22/2018	6/22/2018	6/22/2018	6/22/2018	7/11/2018	6/29/2017
6/20/2018, all grab samples	6/22/2018	6/22/2018	6/22/2018	6/22/2018	7/11/2018	6/29/2017
7/10 - 7/11/2018, all diel samples	7/30/2018	7/30/2018	7/30/2018	7/30/2018	7/26/2018	7/30/2018
7/11/2018, all grab samples	7/30/2018	7/30/2018	7/30/2018	7/30/2018	7/26/2018	7/30/2018
8/23 - 8/24/2018, all diel samples	8/30/2018	8/30/2018	8/30/2018	8/30/2018	8/29/2018	8/30/2018
8/24/2018, all grab samples	8/30/2018	8/30/2018	8/30/2018	8/30/2018	8/29/2018	8/30/2018
9/10 - 9/11/2018, all diel samples	10/9/2018	10/9/2018	10/9/2018	10/9/2018	10/12/2018 (1 day)	10/9/2018
9/11/2018, all grab samples	10/9/2018	10/9/2018	10/9/2018	10/9/2018	10/12/2018 (1 day)	10/9/2018
10/24 - 10/25/2018, all diel samples	11/16/2018	11/16/2018	11/16/2018	11/16/2018	11/20/2018	11/16/2018
10/25/2018, all grab samples	11/16/2018	11/16/2018	11/16/2018	11/16/2018	11/20/2018	11/16/2018
11/20 - 11/21/2018, all diel samples	12/6/2018	12/6/2018	12/6/2018	12/6/2018	12/18/2018	12/6/2018
11/21/2018, all grab samples	12/6/2018	12/6/2018	12/6/2018	12/6/2018	12/18/2018	12/6/2018
12/16 - 12/17/2018, all diel samples	1/16/2019 (2 days)	1/16/2019 (2 days)	1/16/2019 (2 days)	1/16/2019 (2 days)	1/11/2019	1/16/2019 (2 days)
12/17/2018, all grab samples	1/16/2019 (2 days)	1/16/2019 (2 days)	1/16/2019 (2 days)	1/16/2019 (2 days)	1/11/2019	1/16/2019 (2 days)

During storm events (when flow in the Tijuana River exceeds 1300 liters per second) and occasionally during maintenance and/or infrastructure failure, the International Boundary and Water Commission's CILA pump station is shut off, resulting in rainwater, urban runoff and raw sewage flowing over the United States – Mexico border and into the Tijuana River Estuary. Note that this will affect the nutrient data, resulting in higher than normal values. 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):

Precipitation and other events

1/9 - 1/20 flow in the Tijuana River into the US

1/13 - 1/17 0.254mm total precipitation

2/9 @ 6:00 to 8:00 flow in the Tijuana River into the US – approximately 560,000 gallons

2/10 – 2/11 flow in the Tijuana River into the US – approximately 665,000 gallons

2/12 - 2/15 1.27mm total precipitation

2/15 @ 21:00 TJ River Pump Station suspended operation because of increased flows in the River due to rainfall event

3/14 - 3/17 18.288mm total precipitation

3/22 - 3/23 0.508mm total precipitation

4/19 - 4/20 1.524mm total precipitation

11/21 - flow in the Tijuana River into the US – approximately 2.24 million gallons

Sample specific notes

1/16/2018 15:15	BR - Diel	1	NH4 1:10 dilution
1/16/2018 17:30	BR - Diel	2	NH4 1:10 dilution
1/16/2018 19:45	BR - Diel	3	NH4 1:30 dilution
1/16/2018 22:00	BR - Diel	4	NH4 1:10 dilution
1/17/2018 02:30	BR - Diel	6	NH4 1:10 dilution
1/17/2018 04:45	BR - Diel	7	NH4 1:10 dilution
1/17/2018 13:45	BR - Diel	11	NH4 1:10 dilution
1/17/2018 16:00	BR - Diel	12	NH4 1:10 dilution
1/17/2018 15:45	BR - Grab	BR	NH4 1:10 dilution
1/17/2018 15:46	BR - Grab	BR	NH4 1:10 dilution
1/17/2018 14:30	OS - Grab	OS	NH4 1:10 dilution
1/17/2018 14:31	OS - Grab	OS	NH4 1:10 dilution
3/22/2018 06:30	BR - Diel	1	NH4 1:30 dilution
3/22/2018 08:45	BR - Diel	2	NH4 1:30 dilution
3/22/2018 11:00	BR - Diel	3	NH4 1:30 dilution
3/22/2018 13:15	BR - Diel	4	NH4 1:30 dilution
3/22/2018 15:30	BR - Diel	5	NH4 1:30 dilution

3/22/2018 17:45	BR - Diel	6	NH4 1:30 dilution
3/22/2018 20:00	BR - Diel	7	NH4 1:30 dilution
3/22/2018 22:15	BR - Diel	8	NH4 1:30 dilution
3/23/2018 02:45	BR - Diel	10	NH4 1:30 dilution
3/23/2018 05:00	BR - Diel	11	NH4 1:30 dilution
3/23/2018 07:15	BR - Diel	12	NH4 1:30 dilution
3/23/2018 08:40	BR - Grab	BR	NH4 1:30 dilution
3/23/2018 08:41	BR - Grab	BR	NH4 1:30 dilution
3/23/2018 07:54	OS - Grab	OS	NH4 1:30 dilution
3/23/2018 07:55	OS - Grab	OS	NH4 1:30 dilution
5/21/2018 17:45	BR - Diel	5	missing - vandalism
5/21/2018 20:00	BR - Diel	6	missing - vandalism
5/21/2018 22:15	BR - Diel	7	missing - vandalism
5/22/2018 00:30	BR - Diel	8	missing - vandalism
5/22/2018 02:45	BR - Diel	9	missing – vandalism
5/22/2018 05:00	BR - Diel	10	missing – vandalism
5/22/2018 07:15	BR - Diel	11	missing - vandalism
5/22/2018 09:30	BR - Diel	12	missing - vandalism
12/16/2018 10:00	BR - Diel	1	NH4 value from 1:30 dilution
12/16/2018 12:15	BR - Diel	2	NH4 value from 1:30 dilution
12/16/2018 14:30	BR - Diel	3	NH4 value from 1:30 dilution
12/16/2018 16:45	BR - Diel	4	NH4 value from 1:30 dilution
12/16/2018 19:00	BR - Diel	5	NH4 value from 1:30 dilution
12/16/2018 21:15	BR - Diel	6	NH4 value from 1:30 dilution
12/16/2018 23:30	BR - Diel	7	NH4 value from 1:30 dilution
12/17/2018 01:45	BR - Diel	8	NH4 value from 1:30 dilution

12/17/2018 11:44	BR - Grab	BR	NH4 value from 1:30 dilution
12/17/2018 11:45	BR - Grab	BR	NH4 value from 1:30 dilution
12/17/2018 10:48	OS - Grab	OS	NH4 value from 1:30 dilution
12/17/2018 10:49	OS - Grab	OS	NH4 value from 1:30 dilution

Additional Citations:

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