

Tijuana River (TJR) NERR Nutrient Metadata
January – December 2016
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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. 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.

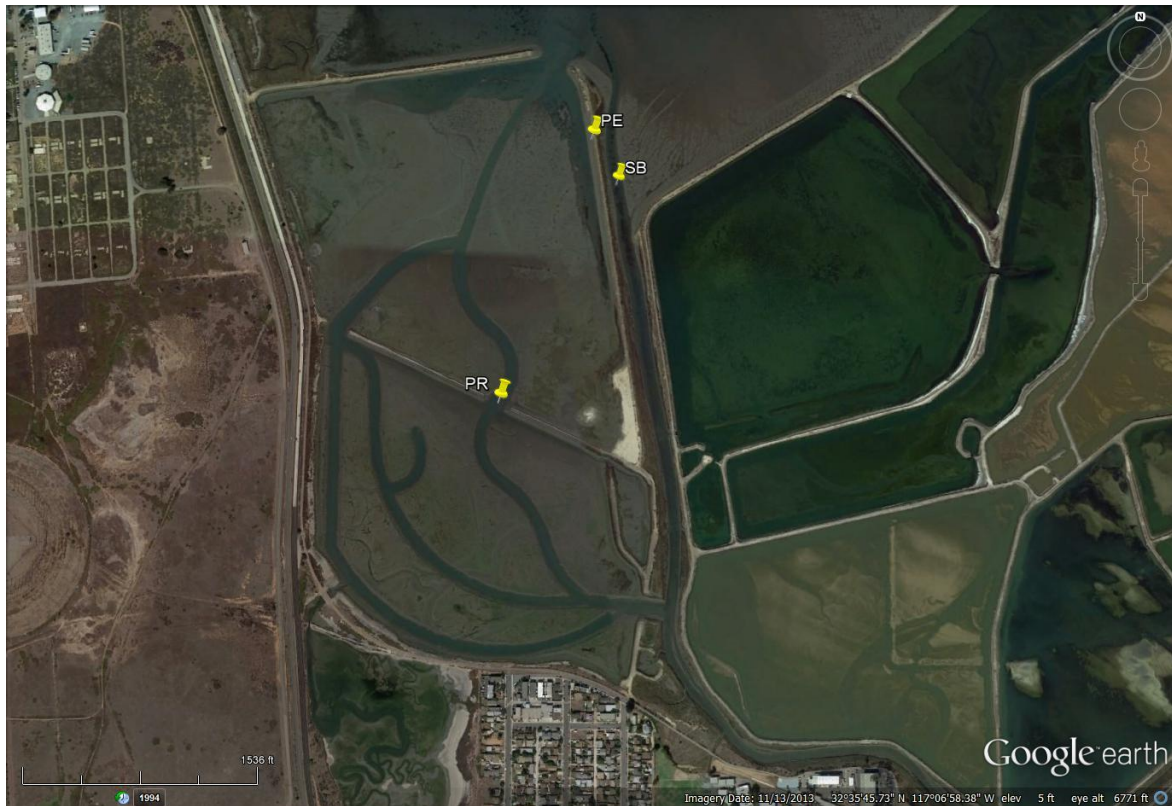
b) Diel Sampling Program:

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, 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 48 hours. Chlorophyll analyses are performed in house at the TRNERR.

At the time of nutrient sampling, in-situ measurements of temperature, salinity and dissolved oxygen were taken using a handheld YSI Pro Plus water quality instrument (see section 6) **Data Collection Period** below).

b) Diel Sampling

Diel samples were collected at the Boca Rio site. Samples were taken at intervals of 2hrs 15mins for a total of 12 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 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 (18M Ω -cm or greater).

4) Site Location and Character

General site Characteristics (TRNERR)

- a) Latitude and Longitude: 3° 34' N, 117° 7' W
- b) Tidal range: approximately -2ft to + 7ft MLLW
- d) 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. 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; 32° 33' 33.7" N, 117° 7' 44.3" W.
- b) Elevation of sonde's depth port: 0.053m NAVD88, approximately 0.5m above the channel bottom.
- c) Depth: approximately 0.5m to 2.7m.
- d) Channel width: approximately 30 m.
- e) Bottom type: sand, some silt and clay.
- f) 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; 32° 34' 6.0" N, 117° 7' 52.6" W.
- b) Elevation of sonde's depth port: 0.332m NAVD88, approximately 0.5m above the channel bottom.
- c) Depth: approximately 0.7m to 2.4m.
- d) Channel width: approximately 23m.
- 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 ; 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 -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; 32° 36' 3.6" N, 117° 06 min 57.0" W.
- b) Elevation of sonde's depth port: -0.379m NAVD88, approximately 0.5m above the channel bottom.
- c) Depth: approximately 0.7m to 3.2m
- 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 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° 07' 5.50 W	01/01/2002 - 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 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.
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	Grab sample; diel sample on 7/27/2006

					compromised the datalogger station	
tjrncnut	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	S	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
tjrrmnut	S	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) 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

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. Samples are collected every 2 hours and 15 minutes, the begin and end time of each sample session are included below. Grab samples were collected 3 hours prior to the low tide corresponding to the end of the ISCO sampling period. The water quality measurements at the time of retrieving the grab samples, as measured by the handheld YSI Professional Plus water quality instrument, are also included below. Note that the time stamps are based on a 24 hour clock and refer to Pacific Standard Time. The date format is mm/dd/yy.

Diel samples:

Station	Start date/time	End date/time
br	1/20/16 13:15	1/21/16 14:00
br	2/17/16 12:15	2/18/16 13:00
br	3/21/16 14:15	3/22/16 15:00
br	4/18/16 13:15	4/19/16 14:00
br	5/19/16 13:30	5/20/16 14:15
br	6/13/16 10:00	6/14/16 10:45
br	7/13/16 10:00	7/14/16 10:45
br	8/17/16 14:00	8/18/16 14:45
br	9/14/16 14:15	9/15/16 15:00
br	10/12/16 13:15	10/13/16 14:00

br	11/14/16 15:00	11/15/16 15:45
br	12/13/16 15:00	12/14/16 15:45

Grab Samples:

Station	Date/time	Rep 1	Rep 2	Temp (°C)	DO %	DO mg/l	Sp. Cond. (mS/cm)	Salinity (ppt)
br	1/21/16	13:37	13:38	17.5	122.0	9.57	50.334	33.04
br	2/18/16	12:54	12:55	18.4	93.3	7.18	50.86	33.43
br	3/22/16	14:34	14:35	18.5	139.6	10.74	50.518	33.18
br	4/19/16	12:55	12:56	21.5	123.2	9.05	48.451	31.66
br	5/20/16	13:45	13:46	20.7	132.0	9.7	50.86	33.4
br	6/14/16	10:43	10:44	20.5	43.5	3.24	49.71	35.59
br	7/14/16	10:38	10:39	24.7	50.7	3.47	51.202	33.62
br	8/18/16	14:05	14:06	23.3	71.8	5.04	51.635	33.97
br	9/15/16	13:37	13:38	23.6	119.0	8.31	51.399	33.79
br	10/13/16	12:36	12:37	20.2	119.1	8.91	49.697	32.58
br	11/15/16	15:24	15:25	19.2	94.2	7.11	51.578	33.96
br	12/14/16	12:08	12:09	16.3	118.6	9.49	51.306	33.74
os	1/21/16	13:12	13:13	18.5	122.1	9.36	51.195	33.68
os	2/18/16	12:29	12:30	19.0	109.3	8.31	51.028	33.56
os	3/22/16	12:55	12:56	20.7	155.6	11.52	49.946	32.76
os	4/19/16	12:22	12:23	23.1	169.1	12.05	48.706	31.82
os	5/20/16	12:45	12:46	21.8	117.5	8.4	52.50	34.6
os	6/14/16	10:15	10:16	21.5	56.5	4.05	53.815	35.61
os	7/14/16	10:03	10:04	25.5	79.9	5.32	54.817	36.29
os	8/18/16	13:28	13:29	26.7	103.3	6.73	55.518	36.78
os	9/15/16	13:13	13:14	24.7	203.7	13.72	55.513	36.83
os	10/13/16	12:05	12:06	22.3	157.6	11.22	52.266	34.45
os	11/15/16	14:53	14:55	19.2	85.8	6.47	51.94	34.23
os	12/14/16	11:46	11:47	16.2	114.0	9.13	51.271	33.71
pr	1/21/16	12:32	12:33	18.4	91.3	7.21	44.711	28.96
pr	2/18/16	11:34	11:35	20.0	94.3	7.06	50.148	32.91
pr	3/22/16	12:02	12:03	21.8	112	8.07	51.591	33.96
pr	4/19/16	11:25	11:26	24.2	105.6	7.29	51.915	34.16
pr	5/20/16	13:33	13:34	23.5	99.6	6.92	53.118	35.07
pr	6/14/16	9:36	9:37	21.4	71.8	5.13	55.077	36.55
pr	7/14/16	8:55	8:56	25.3	65.4	4.33	57.057	37.97
pr	8/18/16	12:49	12:50	28.8	115.3	7.25	56.014	37.09
pr	9/15/16	12:12	12:13	24.6	132.2	8.9	56.238	37.37

pr	10/13/16 11:22	11:23	22.3	99.9	6.99	56.299	37.46
pr	11/15/16 14:05	14:06	20.3	103.3	7.53	54.902	36.43
pr	12/14/16 13:34	13:35	18.4	115.3	8.77	53.458	35.35
sb	1/21/16 12:12	12:13	17.9	88.6	7.14	42.241	27.19
sb	2/18/16 12:02	12:03	20.3	88.9	6.68	48.174	31.46
sb	3/22/16 11:44	11:45	20.2	100.7	7.49	50.775	33.37
sb	4/19/16 11:49	11:50	22.7	92.6	6.59	50.895	33.43
sb	5/20/16 13:10	13:11	22.4	98.2	6.95	53.308	35.22
sb	6/14/16 9:18	9:19	21.6	76.0	5.45	53.697	35.52
sb	7/14/16 9:20	9:21	25.3	61.5	4.06	57.791	38.52
sb	8/18/16 12:11	12:12	26.8	95.9	6.23	55.891	37.06
sb	9/15/16 12:31	12:32	22.7	107.6	7.47	56.571	37.66
sb	10/13/16 10:55	10:56	21.0	85.3	6.12	55.612	36.96
sb	11/15/16 13:42	13:43	19.7	95.9	7.05	55.324	36.75
sb	12/14/16 13:11	13:12	17.3	100.9	7.81	54.076	35.8

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.nerrdata.org; *accessed* 12 October 2016.

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.nerrdata.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.

10) 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	Unit 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	$\mu\text{g/L}$

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

11) Measured and Calculated Laboratory Parameter

a) **Parameters Measured Directly**

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

b) **Calculated Variables**

DIN: NO23F + NH4F

12) 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.

<u>Parameter</u>	<u>Start Date</u>	<u>End Date</u>	<u>MDL</u>	<u>Data Last Revisited</u>
NH4F	1/1/2016	12/31/2016	0.0028mg/L as N	06/01/2015
NO23F	1/1/2016	12/31/2016	0.00028mg/L as N	06/01/2015
PO4F	1/1/2016	12/31/2016	0.00062mg/L as N	06/01/2015
CHLA_N	1/1/2016	12/31/2016	0.5 µg/L	Unknown
SiO4F	1/1/2016	12/31/2016	0.01405mg/L as Si	06/01/2015

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

13) 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 absorbance is measured at 820nm. The absorbance is proportional to the concentration of orthophosphate in the sample.

Preservation Method: Filtered through both Whatman GF/F (.7µm pore size) and MF-Millipore (.45µm pore size) membrane filters and stored at or below -10°C.

Instrumentation: AA3 Autoanalyzer made by 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 75°C. Fluorescence proportional to the ammonia concentration is emitted at 460nm following excitation at 370nm.

Preservation Method: Filtered through both Whatman GF/F (.7µm pore size) and MF-Millipore (.45µm pore size) membrane filters and stored at or below -10°C.

Instrumentation: AA3 Autoanalyzer made by SEAL Analytical.

c) Parameters: 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 GF/F (.7µm pore size) and MF-Millipore (.45µm pore size) membrane filters and stored at or below -10°C.

Instrumentation: AA3 Autoanalyzer made by SEAL Analytical.

d) Parameter: CHLA

Method Reference:	Chlorophyll was analyzed using EPA standard methods. Eaton, A. D., Clesceri, L. S., Rice, E.E., Greenberg, A. E., American Public Health Association., American Water Works Association., and Water Environment Federation. 2005. Standard Methods for the Examination of Water and Wastewater, 21st Edition. Part 10200 H: Chlorophyll, pp. 18-26.
Method Descriptor:	Samples are filtered at .7µm. Chlorophyll is extracted with aqueous acetone and concentrations are determined with a spectrophotometer.
Preservation Method:	Filtered through a Whatman GF/F (.7µm pore size) membrane filter and stored in a container with desiccant at or below -10°C.
Instrumentation:	Thermo Spectronic Aquamate Spectrophotometer
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 GF/F (.7µm pore size) and MF-Millipore (.45µm pore size) membrane filters and stored at or below -10°C.
Instrumentation:	AA3 Autoanalyzer made by SEAL Analytical.

14) 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
<i>Cloud cover</i>		
	CCL	clear (0-10%)
	CSP	scattered to partly cloudy (10-50%)
	CPB	partly to broken (50-90%)
	COC	overcast (>90%)
	CFY	foggy
	CHY	hazy
	CCC	cloud (no percentage)
<i>Precipitation</i>		
	PNP	none
	PDR	drizzle
	PLR	light rain
	PHR	heavy rain
	PSQ	squally
	PFQ	frozen precipitation (sleet/snow/freezing rain)
	PSR	mixed rain and snow
<i>Tide stage</i>		
	TSEebb	ebb tide
	TSF	flood tide
	TSH	high tide
	TSL	low tide
<i>Wave height</i>		
	WH0	0 to <0.1 meters
	WH1	0.1 to 0.3 meters
	WH2	0.3 to 0.6 meters

WH3	0.6 to > 1.0 meters
WH4	1.0 to 1.3 meters
WH5	1.3 or greater meters
<i>Wind direction</i>	
N	from the north
NNE	from the north northeast
NE	from the northeast
ENE	from the east northeast
E	from the east
ESE	from the east southeast
SE	from the southeast
SSE	from the south southeast
S	from the south
SSW	from the south southwest
SW	from the southwest
WSW	from the west southwest
W	from the west
WNW	from the west northwest
NW	from the northwest
NNW	from the north northwest
<i>Wind speed</i>	
WS0	0 to 1 knot
WS1	> 1 to 10 knots
WS2	> 10 to 20 knots
WS3	> 20 to 30 knots
WS4	> 30 to 40 knots
WS5	> 40 knots

17) Other Remarks

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. 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, and are indicated with red font below.

Start/End Times of Diel Nutrient Sampling	Date of Nutrient Analyses	Date of Chlorophyll Analyses
1/20 13:15 – 1/21 13:30	2/9/2016	2/18/2016
2/17 12:15 – 2/18 12:30	3/3/2016	3/18/2016
3/21 14:15 – 3/22 14:30	3/30/2016	4/20/2016
4/18 13:15 – 4/19 13:30	6/15/2016 (25 days)	5/17/2016
5/19 13:30 – 5/20 14:15	6/15/2016	6/21/2016
6/13 10:00 – 6/14 10:45	6/29/2016	7/14/2016
7/13 10:00 – 7/14 10:45	8/2/2016	8/19/2016 (4 days)
8/17 14:00 – 8/18 15:15	9/23/2016 (4 days)	9/16/2016
9/4 14:15 – 9/15 15:00	10/4/2016	10/14/2016
10/12 13:15 – 10/13 14:00	11/8/2016	11/9/2016
11/14 15:00 – 11/15 15:30	12/20/2016 (3 days)	12/7/2016
12/13 15:00 – 12/14 15:45	1/5/2017	1/19/2017 (4 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. Unfortunately, not always are we informed when the pump is shutoff, though, we are generally informed when operation resumes. In those cases, only the time and date of when the pump operation resumed is shown.

At **00:45** on **2/18/2016**, the tipping bucket at the SWMP meteorological station recorded .254mm. This occurred during February's sampling (**2/17/2016 – 2/18/2016**).

Approximately 10mm of rainfall occurred locally, as measured by the SWMP tipping bucket, between 4/6 and 4/8. This rain and that which occurred throughout the Tijuana River watershed resulted in flow exceeding the pump station's capacity. The pump station resumed operation on 4/15/2016 at 08:30, approximately 3 days before the monthly sampling (**4/18/2016 - 4/19/2016**).

Missing **chlorophyll** data with the following time stamps were due to lab processing errors resulting in the loss of the sample:

1/20/2016 20:00	1/21/2016 2:45	1/21/2016 5:00	1/21/2016 14:00
2/18/2016 8:30	2/18/2016 11:34	4/19/2016 2:45	4/19/2016 11:45
4/19/2016 14:00	5/19/2016 15:45	7/14/2016 8:56	7/14/2016 9:21
7/14/2016 10:39	8/17/2016 20:45	8/18/2016 12:11	9/15/2016 10:30

Samples from **1/21/2016 9:30 and 11:45** and those between **3/21/2016 16:30 and 3/22/2016 8:15** were not taken due to a battery failure.

The BR grab samples with the time stamps **9/15/2016 13:37** and **13:38** were not diluted and reanalyzed. So the values for NH₄ of 0.280mg/l as N are minimum values and flagged as suspect, <1> (CSM).

Additional Citations:

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