

Tijuana River (TJR) NERR Nutrient Metadata
January – December 2017
Latest Update: August 4, 2021

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) was set up on the northern end of Oneonta Slough, which is still in place. 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.

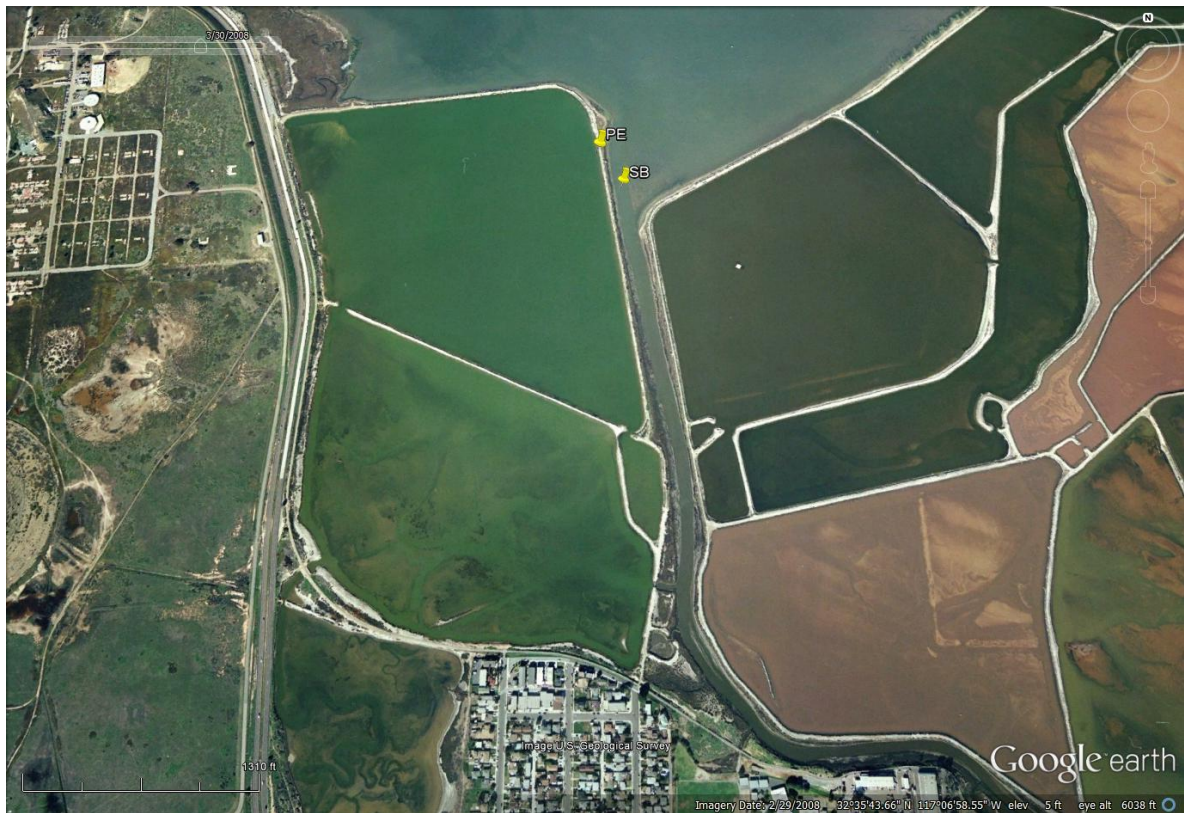
Another station was located at the inlet to the Model Marsh (MM), a constructed 20-acre restoration site in the southern arm of the estuary. The Model Marsh was opened to tidal flushing in February 2000 and data logging at the station began in October 2000. The site was discontinued in January 2008 due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

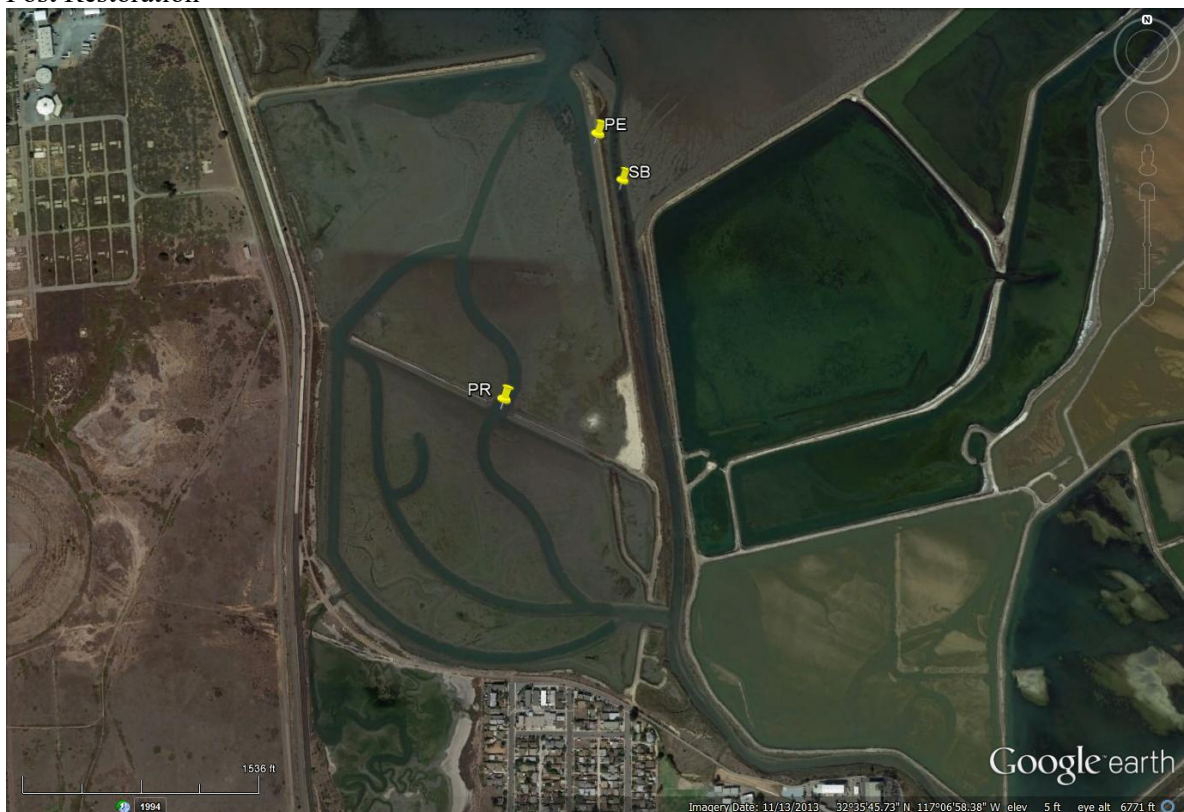
The South Bay (SB) station was established in January 2008 and is located at the mouth of Otay River, which flows into South San Diego Bay and is within the San Diego National Wildlife Refuge Complex.

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. Data sonde 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

Prior to sampling, 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. 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).

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). Duplicate samples were taken at each site, they were collected sequentially, within one minute of each other and adjacent to the datasondes deployed at each station in compliance with the NERRS Nutrient and Chlorophyll Monitoring SOP version 1.7.

At the time of nutrient grab sampling, in-situ measurements of temperature, specific conductivity, salinity and dissolved oxygen were taken using an 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

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 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, the sample bottles are capped and, typically, reach the reserve's lab within one hour for filtration.

After filtration, samples were delivered, generally, within 72 hours to the Chemistry Lab at the Oceanographic Data Facility, Scripps Institution of Oceanography (SIO), University of California, San Diego. All samples were frozen at -20°C and analyzed within 28 days (30 days for CHLA) unless indicated in red font in the “Samples collection and analysis date” table (see **Other Remarks**). The Oceanographic Data Facility’s nutrient analysis procedures can be found at <https://scripps.ucsd.edu/ships/shipboard-technical-support/odf/documentation/nutrient-analysis>.

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>.

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) Depth: approximately 0.2m to 2m
- 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 the area: Freshwater discharge with untreated sewage occurs year-round, although these have decreased with the construction of a binational water treatment plant.

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 a 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: -0.056m 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: 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 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: 0.295m NAVD88, approximately 0.5m above the channel bottom.

c) Depth: approximately 0.7m to 2.4m; directly below the datalogger

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: 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: approximately 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)

Specific Site Characteristics: 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° 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 -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° 07' 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.
tjrmnut	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
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	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
tjrrmnut	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) 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. 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	Rep 1	Rep 2
tjrbrnut	01/26/2017	14:58	14:59
tjrbrnut	02/23/2017	14:59	15:00
tjrbrnut	03/29/2017	15:36	15:37
tjrbrnut	04/21/2017	11:28	11:29
tjrbrnut	05/19/2017	09:58	09:59
tjrbrnut	06/20/2017	11:25	11:26
tjrbrnut	07/21/2017	12:48	12:49
tjrbrnut	08/15/2017	08:55	08:56
tjrbrnut	09/19/2017	14:13	14:14
tjrbrnut	10/18/2017	14:26	14:27
tjrbrnut	11/15/2017	13:28	13:29
tjrbrnut	12/14/2017	13:18	13:19

Oneonta Slough (OS)

Station	Date	Rep 1	Rep 2
tjrosnut	01/26/2017	14:26	14:27
tjrosnut	02/23/2017	14:12	14:13
tjrosnut	03/29/2017	14:51	14:52
tjrosnut	04/21/2017	08:55	08:56
tjrosnut	05/19/2017	09:18	09:19
tjrosnut	06/20/2017	11:01	11:02
tjrosnut	07/21/2017	11:39	11:40
tjrosnut	08/15/2017	08:26	08:27
tjrosnut	09/19/2017	13:43	13:44
tjrosnut	10/18/2017	13:47	13:48
tjrosnut	11/15/2017	12:54	12:55
tjrosnut	12/14/2017	12:39	12:40

Pond Eleven Restored (PR)

Station	Date	Rep 1	Rep 2
tjrprnut	01/26/2017	13:48	13:49
tjrprnut	02/23/2017	13:02	13:03
tjrprnut	03/29/2017	13:18	13:19

tjrprnut	04/21/2017	10:17	10:18
tjrprnut	05/19/2017	08:04	08:05
tjrprnut	06/20/2017	10:04	10:05
tjrprnut	07/21/2017	10:48	10:49
tjrprnut	08/15/2017	07:18	07:19
tjrprnut	09/19/2017	12:40	12:41
tjrprnut	10/18/2017	12:14	12:15
tjrprnut	11/15/2017	12:03	12:04
tjrprnut	12/14/2017	11:21	11:22

South Bay (SB)

Station	Date	Rep 1	Rep 2
tjrsbnut	01/26/2017	13:18	13:19
tjrsbnut	02/23/2017	12:34	12:35
tjrsbnut	03/29/2017	13:47	13:48
tjrsbnut	04/21/2017	09:51	09:52
tjrsbnut	05/19/2017	08:31	08:32
tjrsbnut	06/20/2017	09:34	09:35
tjrsbnut	07/21/2017	10:22	10:23
tjrsbnut	08/15/2017	06:55	06:56
tjrsbnut	09/19/2017	12:08	12:09
tjrsbnut	10/18/2017	12:52	12:53
tjrsbnut	11/15/2017	11:32	11:33
tjrsbnut	12/14/2017	11:47	11:48

Diel Samples

Boca Rio

Station	Start Date	Start Time	End Date	End Time
tjrbrnut	01/25/2017	14:15	01/26/2017	15:00
tjrbrnut	02/22/2017	13:15	02/23/2017	14:00
tjrbrnut	03/28/2017	16:15	03/29/2017	17:00
tjrbrnut	04/20/2017	12:00	04/21/2017	12:45
tjrbrnut	05/18/2017	10:00	05/19/2017	10:45
tjrbrnut	06/19/2017	10:00	06/20/2017	10:45
tjrbrnut	07/20/2017	12:15	07/21/2017	13:00
tjrbrnut	08/14/2017	08:15	08/15/2017	09:00
tjrbrnut	09/18/2017	13:45	09/19/2017	14:30
tjrbrnut	10/17/2017	13:45	10/18/2017	14:30
tjrbrnut	11/14/2017	13:00	11/15/2017	13:45
tjrbrnut	12/13/2017	12:45	12/14/2017	15:30

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.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.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.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 performed by Monica Almeida (please see **Principal investigators and contact persons**).

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	$\mu\text{g/L}$
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 NO₂ 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.

10) 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

11) Limits 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.”

MDLs were reported by the Chemistry Lab at the Oceanographic Data Facility, Scripps Institution of Oceanography, University of California, San Diego. The lab determines MDLs by running a minimum of seven samples prepared at low concentrations, and multiplying the calculated standard deviation by 3 (approximately, this factor depends on the number of measurements). The lab MDL SOP is based on the methodology described in the “**Definition and Procedure for the Determination of the Method Detection Limit, Revision 2**” by the U.S. Environmental Protection Agency, which can be found at:

https://www.epa.gov/sites/production/files/2016-12/documents/mdl-procedure_rev2_12-13-2016.pdf.

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

<u>Parameter</u>	<u>Start Date</u>	<u>End Date</u>	<u>MDL</u>	<u>Date Last Revisited</u>
NH ₄ F	01/01/2017	05/10/2017	0.0028mg/L as N	05/11/2017
NH ₄ F	05/11/2017	12/31/2017	0.0014mg/L as N	
NO ₂ 3F	01/01/2017	12/31/2017	0.00028mg/L as N	5/11/2017 (same MDL)
PO ₄ F	01/01/2017	12/31/2017	0.00062mg/L as N	5/11/2017 (same MDL)
SiO ₄ F	01/01/2017	05/10/2017	0.01405mg/L as N	05/11/2017
SiO ₄ F	05/11/2017	12/31/2017	0.00562mg/L as N	
CHLA_N	01/01/2017	08/13/2017	0.5µg/L	05/30/2018
CHLA_N	08/14/2017	12/31/2017	0.0013µg/L	

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, 1, 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 (.7µm pore size) and MF-Millipore (.45µm pore size) membrane filter, and stored at or below -20°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 glass fiber filter (.7µm pore size) and MF-Millipore (.45µm pore size) membrane filter, and stored at or below -20°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
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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 -20°C.

Instrumentation: AA3 Autoanalyzer made by SEAL Analytical.

d) Parameter: CHLA

January – June 2017

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 through Whatman .7µm particle retention glass fiber filters. Chlorophyll is extracted with aqueous acetone and concentrations are determined with a spectrophotometer.

Preservation Method: Filtered through a Whatman .7µm particle retention glass fiber filter and stored in a container with desiccant at or below -20°C.

Instrumentation: Thermo Spectronic Aquamate Spectrophotometer

August-December 2017

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 <i>a</i> 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 -20°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," <i>Deep-Sea Research</i> , 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 -20°C.
Instrumentation:	AA3 Autoanalyzer made by 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)
<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>		
	TSE	ebb tide
	TSF	flood tide
	TSH	high tide
	TSL	low tide
<i>Wave height</i>		
	WH0	0 to <0.1 meters
	WH1	0.1 to 0.3 meters
	WH2	0.3 to 0.6 meters
	WH3	0.6 to > 1.0 meters
	WH4	1.0 to 1.3 meters
	WH5	1.3 or greater meters
<i>Wind direction</i>		
	N	from the north
	NNE	from the north northeast
	NE	from the northeast
	ENE	from the east northeast
	E	from the east
	ESE	from the east southeast
	SE	from the southeast
	SSE	from the south southeast
	S	from the south
	SSW	from the south southwest
	SW	from the southwest
	WSW	from the west southwest
	W	from the west
	WNW	from the west northwest
	NW	from the northwest
	NNW	from the north northwest
<i>Wind speed</i>		
	WS0	0 to 1 knot
	WS1	> 1 to 10 knots
	WS2	> 10 to 20 knots
	WS3	> 20 to 30 knots
	WS4	> 30 to 40 knots
	WS5	> 40 knots

17) Other Remarks

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 NO₃F 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.

Sample Descriptor	Date Analyzed					
	PO ₄ F	NH ₄ F	NO ₂ F	NO ₃ F	CHLA_N	SiO ₄ F
1/25 - 1/26/2017, all diel samples	2/21//2017	2/21//2017	2/21//2017	2/21//2017	2/17/2017	2/21//2017
1/26/2017, all grab samples	2/21//2017	2/21//2017	2/21//2017	2/21//2017	2/17/2017	2/21//2017
2/22 - 2/23/2017, all diel samples	3/2/2017	3/2/2017	3/2/2017	3/2/2017	3/21/2017	3/2/2017
2/23/2017, all grab samples	3/2/2017	3/2/2017	3/2/2017	3/2/2017	3/21/2017	3/2/2017
3/28 - 3/29/2017, all diel samples	4/19/2017	4/19/2017	4/19/2017	4/19/2017	4/13/2017	4/19/2017
3/29/2017, PR OS SB grab samples	4/19/2017	4/19/2017	4/19/2017	4/19/2017	5/30/2017 (28 days)	4/19/2017
4/20 - 4/21/2017, all diel samples	5/12/2017	5/12/2017	5/12/2017	5/12/2017	5/12/2017	5/12/2017
4/21/2017, BR OS and PR grab samples	5/12/2017	5/12/2017	5/12/2017	5/12/2017	5/12/2017	5/12/2017
4/21/2017, SB grab samples	5/12/2017	5/12/2017	5/12/2017	5/12/2017	5/30/2017 (4 days)	5/12/2017
5/18 - 5/19/2017, all diel samples	6/1/2017	6/1/2017	6/1/2017	6/1/2017	5/30/2017	6/1/2017
5/19/2017, all grab samples	6/1/2017	6/1/2017	6/1/2017	6/1/2017	5/31/2017	6/1/2017
6/19 - 6/20/2017, all diel samples	6/29/2017	6/29/2017	6/29/2017	6/29/2017	7/14/2017	6/29/2017
6/20/2017, all grab samples	6/29/2017	6/29/2017	6/29/2017	6/29/2017	7/14/2017	6/29/2017
7/20 - 7/21/2017, all diel samples	8/9/2017	8/9/2017	8/9/2017	8/9/2017	N/A**	8/9/2017
7/21/2017, all grab samples	8/9/2017	8/9/2017	8/9/2017	8/9/2017	N/A**	8/9/2017
8/14 - 8/15/2017, all diel samples	8/24/2017	8/24/2017	8/24/2017	8/24/2017	12/6/2017 (79 days)	8/24/2017
8/15/2017, all grab samples	8/24/2017	8/24/2017	8/24/2017	8/24/2017	12/6/2017 (79 days)	8/24/2017
9/18 - 9/19/2017, all diel samples	10/17/2017	10/17/2017	10/17/2017	10/17/2017	12/15/2017 (53 days)	10/17/2017
9/19/2017, all grab samples	10/17/2017	10/17/2017	10/17/2017	10/17/2017	12/15/2017 (53 days)	10/17/2017

10/17 - 10/18/2017, all diel samples	11/21/2017 (2 days)	11/21/2017 (2 days)	11/21/2017 (2 days)	11/21/2017 (2 days)	11/21/2017	11/21/2017 (2 days)
10/18/2017, all grab samples	11/21/2017 (2 days)	11/21/2017 (2 days)	11/21/2017 (2 days)	11/21/2017 (2 days)	11/21/2017	11/21/2017 (2 days)
11/14 - 11/15/2017, all diel samples	11/21/2017	11/21/2017	11/21/2017	11/21/2017	12/21/2017 (2 days)	11/21/2017
11/15/2017, all grab samples	11/21/2017	11/21/2017	11/21/2017	11/21/2017	12/21/2017 (2 days)	11/21/2017
12/13 - 12/14/2017, all diel samples	12/19/2017	12/19/2017	12/19/2017	12/19/2017	1/25/2018 (8 days)	12/19/2017
12/14/2017, all grab samples	12/19/2017	12/19/2017	12/19/2017	12/19/2017	1/25/2018 (8 days)	12/19/2017

*Due to laboratory equipment issues, the following samples exceeded holding time:

**Due to laboratory equipment issues no chlorophyll samples were analyzed this month.

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):

1/18 - 1/24 52mm total precipitation

2/11 – 2/12 0.762mm total precipitation

2/17-2/18 33.53mm total precipitation

2/26-2/27 62.74mm total precipitation

4/18 flows into US from groundwater dewatering activities in Mexico that exceed the capacity of pump station

6/20 @ 1600 - sewage spill - flow is approximately 0.2 cfs (90 gpm) as of 1600 hours.

11/7 – 1.52mm total precipitation

11/7@1600 to 11/9 @1650 - flow in the Tijuana River into the US due to precipitation and runoff.

12/11@0245 to 0430 - flow in the Tijuana River into the US - approximately 220,000 gallons - due to windblown trash that clogged the pump station system in the Mexico side of the border.

The ISCO water sampler had some battery failure incidents that resulted in missing data with the following time stamps:

3/29/17 1:15

3/29/17 3:30

3/29/17 5:45
3/29/17 8:00
3/29/17 10:15
3/29/17 12:30
3/29/17 14:45
4/21/17 8:15
4/21/17 10:30

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

3/28/17 20:45
3/29/17 15:36
3/29/17 15:37
4/21/17 10:18
5/19/17 9:58

In July, our spectrophotometer stopped functioning and it resulted in the loss of that month's **chlorophyll** data. Chlorophyll samples from August to present have been analyzed by the UCSD-SIO laboratory.

The missing **chlorophyll** data are the following:

7/20/16 12:15
7/20/16 14:30
7/20/16 16:45
7/20/16 19:00
7/20/16 21:15
7/20/16 23:30
7/21/16 1:45
7/21/16 4:00
7/21/16 6:15
7/21/16 8:30
7/21/16 10:45
7/21/16 13:00
7/21/17 12:48
7/21/17 12:49
7/21/17 11:39
7/21/17 11:40
7/21/17 10:48
7/21/17 10:49
7/21/17 10:22
7/21/17 10:22

Additional Citations:

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Aoyama, M., Susan B., Minhan, D., Hideshi, D., Louis, I. G., Kasai, H., Roger, K., Nurit, K., Doug, M., Murata, A., Nagai, N., Ogawa, H., Ota, H., Saito, H., Saito, K., Shimizu, T., Takano, H., Tsuda, A., Yokouchi, K., and Agnes, Y. 2007. Recent Comparability of Oceanographic Nutrients Data: Results of a 2003 Intercomparison Exercise Using Reference Materials. *Analytical Sciences*, 23: 1151-1154.

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