

Padilla Bay Reserve (PDB) NERR Nutrient Metadata
January to December 2013
Latest Update: 05/15/2014

I. Data Set and Research Descriptors

1) Principal investigator(s) and contact persons

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2) Research objectives –

a) Monthly Grab

Monthly grab samples are collected at each of five monitoring stations in Padilla Bay; Bayview Channel, Ploeg Channel, Gong Shallow, Gong Deep and Joe Leary Estuary. Two of the objectives of the monthly sampling series are to determine if there are onshore to offshore gradients in nutrient concentrations, and to determine whether these change seasonally.

Bayview Channel and Ploeg Channel are located about half way between the shore of Padilla Bay and the offshore channels and straits that are the source of water for Padilla Bay. Bayview Channel is in the southern half and Ploeg Channel is in the northern half of the bay. Gong Shallow and Gong Deep sites are located in the offshore channel on the north western edge of Padilla Bay. This is a deepwater sample station and samples are collected at the surface (1m) and at 20m in depth. Data from a preliminary study have indicated an offshore to onshore dissolved inorganic nitrogen gradient during the summer and an onshore to offshore gradient during the winter.

Historically, the Joe Leary Slough site was located on the freshwater side of the tide gates at the mouth of the largest freshwater drainage to Padilla Bay, Joe Leary Slough. This site had been set at the mouth of the slough to detect long-term changes in water quality in the slough associated with implementation of a non point source pollution watershed action plan. The current site, Joe Leary Estuary, was established in March of 2009 to improve data collection and replaced the Joe Leary Slough which was collecting inaccurate data due to burial from high sedimentation rates in the slough.

The Joe Leary Estuary site is on the marine side of the tide gates. It provides data on both the freshwater coming out of the tide gates at low tides when the tide gates are open as well as marine water when the tide gates are closed. Nutrient sampling is timed for low tides in order to collect freshwater samples coming from Joe Leary Slough. These samples are representative of the historic samples collected from the Joe Leary Slough site.

Due to budget reductions, semi- monthly sampling was reduced to monthly sampling in September of 2011. Monthly nutrient sample collection is the minimum required by CDMO and the standard collection frequency for the reserve system. Objectives of measuring seasonal gradients in nutrient concentrations remain the same with the reduction in sampling frequency.

b) Diel Sampling Program

Diel sampling is conducted at the Bayview Channel site in Padilla Bay. Bayview channel, the largest channel in Padilla Bay, floods the southern end of Padilla Bay with marine waters on incoming tides and drains inter-tidal flats that are mainly covered with dense eelgrass, *Zostera marina* and *Z. japonica*. Two of the objectives of the 26 hour (over 1 lunar day) sampling each month are to determine whether nutrient concentrations are higher in the water flowing off the eelgrass-covered tidal flats or onto the flats, and to determine whether this pattern changes seasonally.

3) Research methods –

At the Padilla Bay laboratory, samples were immediately placed in a refrigerator at 5 °C until processing. Within 4-6 hours of return to the Padilla Bay laboratory, samples were filtered and placed in sample bottles provided by the Chemical Oceanography Laboratory of the University of Washington (U of WA). Immediately after filtering, sample bottles were placed in a freezer and kept frozen at -20 °C.

a) Monthly Grab Sampling Program

Monthly grab samples were taken at the four principal PBNERR stations within Padilla Bay (Bayview Channel, Ploeg Channel, Gong, Joe Leary Slough and Joe Leary Estuary). No distinction was made between neap and spring tide conditions. Replicate (N=2) samples at Bayview and Ploeg Channel sites were taken at 0.5 meters from the bottom. At Gong samples were taken at two depths: one at 0.5 meters from the surface for Gong Surface and one near the bottom (about 20m) for Gong Deep. At Joe Leary Slough samples were taken at a depth of 0.7m and at Joe Leary Estuary samples were taken at 0.3m above the bottom.

Bayview and Ploeg Channels, Gong and Joe Leary Estuary are only accessible by boat; therefore, sampling sometimes occurred before or after inclement weather that may have included significant rainfall, and at times other than low tide. Samples obtained using a Kemmerer water sampler lowered to the sample depth. Two samples were taken, one immediately after the other and then transferred into bottles. At the time of sample collection, water temperature, salinity and dissolved oxygen were measured with a YSI Model 85 meter. All samples were transported in amber, wide-mouth, nalgene sample bottles that were previously acid washed (10% HCl) and rinsed (3x) with distilled-deionized water. Bottles were rinsed (2x) with ambient water and (1x) with sample water prior to collection of the sample. Samples were immediately placed in a cooler and returned to the laboratory, usually within 4 hours of collection.

Once in the Padilla Bay laboratory, samples were shaken and filtered for orthophosphate (PO₄), ammonium (NH₄), nitrite (NO₂) and nitrate (NO₃), chlorophyll *a*, phaeophytin, total nitrogen (TN), total dissolved nitrogen (TDN), total phosphorus (TP), total dissolved phosphorus (TDP) and total suspended solids (TSS). Tier II parameters (TN, TDN, TP, TDP and TSS) were only filtered for grab samples. Filtering for the dissolved inorganic nutrient parameters (PO₄, NH₄, NO₂ and NO₃) was done by taking 45ml of sample water and filtering it into previously acid-washed bottles through a 0.45 µm membrane filter using a syringe. The samples were then immediately frozen at –20° C. Chlorophyll *a* processing included filtering 50 ml (or 25 ml depending on turbidity) of sample water through a vacuum manifold with Whatman GF/F 25 mm filters. The filters were then folded in half and put into plastic vials and immediately frozen at –20° C. Filtering for TDN and TDP was done by taking 20 ml of sample water and filtering it into previously acid-washed bottles through a 0.45 µm membrane filter using a syringe. The samples are then immediately frozen at –20° C. TN and TP were obtained by pouring 20 ml of sample water directly into wide-mouth plastic bottles and immediately frozen at –20° C. TSS and TVS were filtered by pouring 100 ml to 500 ml of sample water into the flasks of a vacuum manifold using pre-numbered filters. The filters were then processed immediately according to standard methods.

Within 1-4 days, the frozen samples were sent via overnight express in a cooler with ice to the Chemical Oceanography Laboratory at the University of Washington where they were stored in a freezer until analysis.

b) Diel Sampling Program

Diel sampling occurred once a month at the Bayview Channel site using a Sigma automated sampler. The sampler was programmed, when possible, to begin and end at low tide. The Sigma was deployed using a floating platform that is anchored in a channel beside the Bayview Channel datasonde site. One sample was taken every 68 minutes for a total of 24 samples over a 26 hour period. Because the sampler was deployed on a floating platform, samples were taken at .5 meter from the surface. All samples went into plastic bottles previously acid-washed (10 % HCl), rinsed (3X) with distilled-deionized water and dried. Ice was placed in the sampler to keep samples cool during summer months. At the end of the 26 hour sampling cycle, samples were returned to the laboratory for filtering and processing on the same day. These samples are filtered for dissolved inorganic nutrients (PO₄, NH₄, NO₂, NO₃, NO₂3, SiO₄), chlorophyll *a* and phaeophytin. The methods for filtering these parameters are described above in the Monthly Grab Sampling Program. Within 1-4 days, the frozen samples were sent via overnight express in a cooler with ice to the Chemical Oceanography Laboratory at the University of Washington where they were stored in a freezer until analysis.

4) Site location and character –

General: Padilla Bay (48° 30' N; 122° 30' W) is a shallow embayment in northern Puget Sound. The tide flats are dominated by the eelgrass *Zostera marina*, which covers approximately 3,000 ha. *Zostera japonica*, a recent invader to the region, now covers about 350 ha of the bay. Tides are mixed semi-diurnal with a mean range of 1.55 m. Salinity varies from about 20 to 32 PSU. Padilla Bay is an "orphaned" estuary in that the Skagit River no longer empties directly into it. Most of the land in the 9300 ha Padilla Bay watershed is agricultural, and is drained by four sloughs which empty into the bay. The salinity in Padilla Bay reflects both the sloughs that flow into the bay and the greater Puget Sound-Georgia Basin estuary in which Padilla Bay is located. Major freshwater flows into this area of the Puget Sound-Georgia Basin estuary come from the Fraser and Nooksack Rivers to the north and from the Skagit River to the south.

b) Joe Leary Estuary Site: (48° 31' 08.1" N; 122° 28' 29.74" W) The Joe Leary Estuary site is located on the marine (downstream) side of the tide gates connecting Joe Leary Slough to Padilla Bay. This site is characterized by fully marine water ranging in salinity 23 to 32 PSU when the tide gates are closed and by water that is fully fresh (< 1 PSU) when the tide gates are open. The switch from marine to fresh water and vice versa occurs rapidly (< 30 min) each time there is a tide change. Sample collection is attempted at tides less than 1m which ensures the tide gates are open and samples represent the freshwater flowing out of Joe Leary Slough. On occasion, it is not possible to collect freshwater samples due to the tidal cycle. These samples are still collected but represent estuarine water from the bay, not Joe Leary slough. The latitude/longitude were measured with a Trimble 5800 GPS RTK system in 2010.

Joe Leary Slough drains land that is predominantly annual crop agriculture and pasture land with some low-density housing. The slough is characterized by high fecal and nutrient inputs, high turbidity, and low dissolved oxygen concentrations. During the summer, there is low flow and the depth ranges from 0.5-1.5 m. During winter flooding, the slough can reach a depth of 4 m. There is a dam at the mouth of the slough with twelve 1.22 m diameter outfall pipes that have one-way hinged tide gates. Upstream water flows out of Joe Leary Slough when water height in Padilla Bay is lower than water height in Joe Leary Slough (i.e. ebbing tide and low water). Some saline water from Padilla Bay seeps through the tide gates during high water. The bottom of the slough is composed of very soft sediment, which is periodically dredged upstream of the tide gates, most recently early Sept. through mid Nov. 2009. The latitude/longitude were measured with a handheld GPS unit with an accuracy of ± 6.7 m.

c) Bayview Channel Site: (48° 29' 46.1" N; 122° 30' 07.6" W) Bayview Channel, a major Padilla Bay tributary/distributary, floods and drains intertidal flats including eelgrass beds, mats of macroalgae, and flats without macro-vegetation. The YSI datasonde is located in a tributary channel to Bayview Channel. The tributary drains predominately eelgrass (*Zostera marina* and *Z. japonica*) covered intertidal flats. Depth range at this site is about 2 - 4 m from LLW to HHW. Bottom sediments beneath the deployment site are fine silt and clay overlying sand. Pollutants entering the bay include general non-point source, agricultural non-point source, and fecal coliform bacteria from agriculture, failing septic tanks and wildlife. The latitude/longitude were measured with a Trimble 5800 GPS RTK system in 2011.

d) Ploeg Channel Site: (48° 33' 22.76" N; 122° 31' 51.22" W) Ploeg Channel floods and drains intertidal flats at the north end of Padilla Bay that are comprised of mud flats and eelgrass beds (*Zostera marina* and *Z. japonica*) in approximately equal amounts. Depth range at this site is about 2 - 4 m from LLW to HHW. Bottom sediments beneath the deployment site are fine to medium sands. The Ploeg Channel site was added to the sites being monitored as part of the Padilla Bay NERR System-Wide Monitoring Program in July 2001 as part of the SWMP expansion. The Ploeg Channel site was selected to extend the geographic coverage and to indicate if there is a north to south gradient in water quality in Padilla Bay. A fourth site was added in 2003 in the deep channel west of Ploeg Channel. The Ploeg Channel site is now one site along a gradient from fresh water sources to marine sources of water to Padilla Bay. Pollutants entering the bay include general non-point source, agricultural non-point source, and fecal coliform bacteria from agriculture, failing septic tanks and wildlife. The latitude/longitude were measured with a Trimble 5800 GPS RTK system in 2011.

e) Gong Surface site: (48° 33' 26.6" N; 122° 34' 20.8" W)

The Gong site is located at -18 m on a gradually sloping bottom (from -1 m to -75 m over 2 km) in the strait between Samish and Guemes Islands. Water in the strait flows north and south with tidal currents, the net water movement is apparently south toward the inlet to Guemes Channel. Water from the strait flows onto the intertidal flats in the northern part of Padilla Bay with each tidal cycle. Bottom sediments at this site are soft mud and the depth ranges between 19-23 m. The Gong site is at the "marine" end of a gradient of sites extending from freshwater in Joe Leary Slough (JL), Bayview Channel (BY) and Ploeg Channel (BP) in mid Padilla Bay to Gong located in the straits west of Padilla Bay that are a source of

marine water to the bay. The only apparent pollution sources are the general sources of pollution to the Strait of Georgia and Northwest Straits. The latitude/longitude was measured in March 2013 with a Garmin GPSmap 276C. Samples are collected 1m below the surface.

f) Gong Deep site: (48° 33' 26.6" N; 122° 34' 20.8" W)

The Gong site is located at –18 m on a gradually sloping bottom (from –1 m to –75 m over 2 km) in the strait between Samish and Guemes Islands. Water in the strait flows north and south with tidal currents, the net water movement is apparently south toward the inlet to Guemes Channel. Water from the strait flows onto the intertidal flats in the northern part of Padilla Bay with each tidal cycle. Bottom sediments at this site are soft mud and the depth ranges between 19-23 m. The Gong site is at the “marine” end of a gradient of sites extending from freshwater in Joe Leary Slough (JL), Bayview Channel (BY) and Ploeg Channel (BP) in mid Padilla Bay to Gong located in the straits west of Padilla Bay that are a source of marine water to the bay. The only apparent pollution sources are the general sources of pollution to the Strait of Georgia and Northwest Straits. The latitude/longitude was measured in March 2013 with a Garmin GPSmap 276C. Samples are collected at either 20m or 21.5m from the surface (depending on the tide).

5) Coded variable definitions –

Sampling Site Codes:

pdbbnpnut = Padilla Bay Research Reserve nutrient and chlorophyll data for Ploeg Channel site
 pdbbynut = Padilla Bay Research Reserve nutrient and chlorophyll data for Bayview Channel site
 pdbgsnut = Padilla Bay Research Reserve nutrient and chlorophyll data for Gong Surface site
 pdbgdnut = Padilla Bay Research Reserve nutrient and chlorophyll data for Gong Deep site
 pdbjenut = Padilla Bay Research Reserve nutrient and chlorophyll data for Joe Leary Estuary site

Monitoring program codes:

1 = grab sample
 2 = diel sample

Replicate codes for grab samples:

1 = first sample
 2 = second sample
 S = laboratory replicate

Replicate codes for diel samples:

1 = first sample
 S = laboratory replicate

6) Data collection period –

Diel Sample Collection Period – January 2013 thru December 2013

Sample Site	Start Date	Time	End Date	Time
pdbbynut	1/9/2013	9:13	1/10/2013	11:17
pdbbynut	2/5/2013	19:09	2/6/2013	21:13
pdbbynut	3/17/2013	15:04	3/18/2013	17:08
pdbbynut	4/14/2013	13:33	4/15/2013	15:37
pdbbynut	5/8/2013	10:10	5/9/2013	12:14
pdbbynut	6/9/2013	11:22	6/10/2013	13:26

pdbbbynut	7/17/2013	6:13	7/18/2013	8:17
pdbbbynut	8/20/2013	10:06	8/21/2013	12:10
pdbbbynut	9/12/2013	3:52	9/13/2013	5:56
pdbbbynut	10/10/2013	2:23	10/11/2013	4:27
pdbbbynut	11/20/2013	0:04	11/21/2013	2:08
pdbbbynut	12/17/2013	23:08	12/19/2013	1:12

Grab Sample Collection Period – January 2013 thru December 2013

Grab sample collection at the Bayview site began in Feb 2002.

Sample Site	Start Date	Time	End Date	Time
pdbbbynut	1/16/2013	10:49	1/16/2013	10:51
pdbbbynut	2/20/2013	11:04	2/20/2013	11:05
pdbbbynut	3/22/2013	9:33	3/22/2013	9:34
pdbbbynut	4/17/2013	9:30	4/17/2013	9:35
pdbbbynut	5/23/2013	10:40	5/23/2013	10:45
pdbbbynut	6/12/2013	9:21	6/12/2013	9:23
pdbbbynut	7/18/2013	11:05	7/18/2013	11:07
pdbbbynut	8/14/2013	8:40	8/14/2013	8:41
pdbbbynut	9/18/2013	10:40	9/18/2013	10:42
pdbbbynut	10/17/2013	10:38	10/17/2013	10:40
pdbbbynut	11/14/2013	10:12	11/14/2013	10:15
pdbbbynut	12/11/2013	10:44	12/11/2013	10:46

Grab sample collection at the Ploeg site began in Feb 2002.

Sample Site	Start Date	Time	End Date	Time
pdbbpnut	1/16/2013	9:58	1/16/2013	9:59
pdbbpnut	2/20/2013	10:10	2/20/2013	10:11
pdbbpnut	3/22/2013	8:45	3/22/2013	8:46
pdbbpnut	4/17/2013	8:58	4/17/2013	9:00
pdbbpnut	5/23/2013	8:42	5/23/2013	8:44
pdbbpnut	6/12/2013	8:45	6/12/2013	8:47
pdbbpnut	7/18/2013	9:57	7/18/2013	10:00
pdbbpnut	8/14/2013	10:18	8/14/2013	10:20
pdbbpnut	9/18/2013	9:00	9/18/2013	9:02
pdbbpnut	10/17/2013	9:12	10/17/2013	9:15
pdbbpnut	11/14/2013	9:40	11/14/2013	9:43
pdbbpnut	12/11/2013	10:05	12/11/2013	10:08

Grab sample collection at the Gong Shallow site began in April 2003.

Sample Site	Start Date	Time	End Date	Time
pdbgsnut	1/16/2013	9:31	1/16/2013	9:32
pdbgsnut	2/20/2013	9:40	2/20/2013	9:41
pdbgsnut	3/22/2013	8:12	3/22/2013	8:13
pdbgsnut	4/17/2013	8:30	4/17/2013	8:31

pdbgsnut	5/23/2013	9:50	5/23/2013	9:56
pdbgsnut	6/12/2013	7:55	6/12/2013	7:56
pdbgsnut	7/18/2013	9:27	7/18/2013	9:30
pdbgsnut	8/14/2013	9:50	8/14/2013	9:52
pdbgsnut	9/18/2013	10:04	9/18/2013	10:06
pdbgsnut	10/17/2013	10:00	10/17/2013	10:03
pdbgsnut	11/14/2013	9:08	11/14/2013	9:10
pdbgsnut	12/11/2013	9:43	12/11/2013	9:45

Grab sample collection at the Gong Deep site began in Jan 2007.

Sample Site	Start Date	Time	End Date	Time
pdbgdnut	1/16/2013	9:26	1/16/2013	9:27
pdbgdnut	2/20/2013	9:44	2/20/2013	9:45
pdbgdnut	3/22/2013	8:08	3/22/2013	8:10
pdbgdnut	4/17/2013	8:25	4/17/2013	8:26
pdbgdnut	5/23/2013	9:38	5/23/2013	9:39
pdbgdnut	6/12/2013	7:58	6/12/2013	7:59
pdbgdnut	7/18/2013	9:17	7/18/2013	9:20
pdbgdnut	8/14/2013	9:40	8/14/2013	9:43
pdbgdnut	9/18/2013	9:58	9/18/2013	10:00
pdbgdnut	10/17/2013	9:52	10/17/2013	9:55
pdbgdnut	11/14/2013	9:00	11/14/2013	9:03
pdbgdnut	12/11/2013	9:35	12/11/2013	9:38

Grab sample collection at the Joe Leary Estuary site began in July 2009.

Sample Site	Start Date	Time	End Date	Time
pdbjenut	1/16/2013	14:33	1/16/2013	14:34
pdbjenut	2/20/2013	16:34	2/20/2013	16:35
pdbjenut	3/22/2013	16:21	3/22/2013	16:22
pdbjenut	4/17/2013	12:45	4/17/2013	12:50
pdbjenut	5/23/2013	12:44	5/23/2013	12:46
pdbjenut	6/12/2013	12:05	6/12/2013	12:06
pdbjenut	7/18/2013	7:20	7/18/2013	7:22
pdbjenut	8/14/2013	7:05	8/14/2013	7:06
pdbjenut	9/18/2013	11:54	9/18/2013	11:56
pdbjenut	10/16/2013	8:04	10/16/2013	8:06
pdbjenut	11/14/2013	18:12	11/14/2013	18:15
pdbjenut	12/11/2013	17:03	12/11/2013	17:05

7) Associated researchers and projects

In coordination with the SWMP nutrient data collected at Padilla Bay, water quality and weather data are also collected. The water quality part of SWMP consists of placing YSI 6600 datasondes at four sites in Padilla Bay. The sondes collect such parameters as water temperature, salinity, dissolved oxygen, depth, pH, and turbidity. The weather component of SWMP consists of monitoring and

recording air temperature, relative humidity, barometric pressure, wind speed and direction, photosynthetically active radiation, and precipitation. These parameters are measured with a Campbell Scientific weather station at the Padilla Demonstration Farm near the southeast shore of Padilla Bay.

Other projects currently conducted at Padilla Bay include a zooplankton monitoring project with monthly sampling occurring at the three water quality/ nutrient sampling sites within the bay. In August 2009 Padilla Bay started long term monitoring of the rocky intertidal habitat in partnership with the Multi-Agency Rocky Intertidal Network (MARINE). See the MARINE website for further information on this monitoring project: <http://www.marine.gov/index.htm>. In 2011, Padilla Bay started a long term monitoring project focused on vegetative characteristics of two species of eelgrass: *Zostera marina* and *Z. japonica* on transects extending from the shoreline to the lower limit of distribution of eelgrasses. Dr. John Rybczyk, Western Washington University, established and maintains eighteen Surface Elevation Tables (SETs) throughout Padilla Bay. Padilla Bay sponsors graduate research in the bay through the Padilla Bay Research Assistantships in Estuarine Science and Coastal Zone Management. NOAA/OCRM/ERD sponsors graduate research in the NERRS, including Padilla Bay, through the Graduate Research Fellowship program. See the Padilla Bay NERR web site, <http://padillabay.gov/researchoverview.asp>, or contact the Research Coordinator (see I. above) for further information about these projects and other monitoring or research in Padilla Bay.

8) Distribution –

NOAA/ERD retains the right to analyze, synthesize and publish summaries of the NERRS System-wide Monitoring Program data. The PI retains the right to be fully credited for having collected and processed the data. Following academic courtesy standards, the PI and NERR site where the data were collected will be contacted and fully acknowledged in any subsequent publications in which any part of the data are used. Manuscripts resulting from this NOAA/OCRM supported research that are produced for publication in open literature, including refereed scientific journals, will acknowledge that the research was conducted under an award from the Estuarine Reserves Division, Office of Ocean and Coastal Resource Management, National Ocean Service, National Oceanic and Atmospheric Administration. 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.

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 <http://cdmo.baruch.sc.edu/>. Data are available in text tab-delimited format.

II. Physical Structure Descriptors

9) Entry verification –

Data were received from the University of Washington Marine Chemistry Laboratory and were entered into a Microsoft Excel spreadsheet. The University of Washington Marine Chemistry Laboratory calculates and reports results in μM . For purposes of consistency in the NERR System, Padilla Bay 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, Padilla Bay NERR staff multiplies the concentrations reported by the University of Washington Marine Chemistry Laboratory by 0.01401, 0.03097, and 0.02809, to yield concentrations in mg/L as N, P, and Si respectively. Data were examined for suspect, anomalous or outlying data by graphing the data. Missing data were inserted into the spreadsheet and were denoted by a blank cell.

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 automatically flags/codes values below 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 verification was completed by Heath Bohlmann and Nicole Burnett. Final verification and this metadata documentation were checked by Heath Bohlmann and Nicole Burnett before being sent to the CDMO permanent database.

10) Parameter titles and variable names by category

Data Category	Parameter	Variable Name	Units of Measure
Phosphorus and Nitrogen:			
	*Orthophosphate	PO4F	mg/L as P
	Dissolved Organic Phosphorus	DOP	mg/L as P
	Total Dissolved Phosphorus	TDP	mg/L as P
	Total Phosphorus	TP	mg/L as P
	Particulate Phosphorus	PHOSP	mg/L as P
	*Ammonium, Filtered	NH4F	mg/L as N
	*Nitrite, Filtered	NO2F	mg/L as N
	*Nitrate, Filtered	NO3F	mg/L as N
	*Nitrite + Nitrate, Filtered	NO23F	mg/L as N
	Dissolved Inorganic Nitrogen	DIN	mg/L as N
	Dissolved Organic Nitrogen	DON	mg/L as N
	Total Dissolved Nitrogen	TDN	mg/L as N
	Total Nitrogen	TN	mg/L as N
	Total Organic Nitrogen	TON	mg/L as N
	Particulate Nitrogen	PN	mg/L as N
Plant Pigments:			
	*Chlorophyll a	CHLA_N	µg/L
	Phaeophytin	PHEA	µg/L
Other Lab Parameters:			
	Silicate, Filtered	SiO4F	mg/L as Si
	Total Suspended Solids	TSS	mg/L
Field Parameters			
	Water Temperature	WTEM_N	°C
	Dissolved Oxygen % Saturation	DO_S_N	%
	Salinity	SALT_N	PPT

Notes:

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

11) Measured or calculated laboratory parameters –

a) **Parameters measured directly**

Nitrogen species:	NH ₄ , NO ₂ , NO ₂₃ , TDN, TN
Phosphorus species:	PO ₄ F, TDP, TP
Other:	CHLA, PHEA, SiO ₄ , TSS, TVS

b) **Calculated parameters**

NO ₃	NO ₂₃ -NO ₂
DIN	NO ₂₃ +NH ₄
DON	TDN-NH ₄ -NO ₂₃
TON	TN-NH ₄ -NO ₂₃
PN	TN-TDN
DOP	TDP-PO ₄
PHOSP	TP-TDP

The University of Washington Marine Chemistry Laboratory measures NO₂₃ and NO₂ in the analytical process. However, the laboratory calculates NO₃ as the difference between the values as part of their internal calculations. The laboratory reports only NO₃ and NO₂ concentrations to Padilla Bay NERR. For purposes of consistency in the NERR System, Padilla Bay NERR determines the previously measured concentration of NO₂₃ by adding the reported values for NO₂ and NO₃. Therefore, NO₃ is considered a calculated parameter in the dataset, and the NO₂ and NO₂₃ parameters are considered measured parameters, since they were originally measured in the laboratory.

12) Limits of detection –

Method Detection Limits (MDL), the lowest concentration of a parameter that an analytical procedure can reliably detect, have been established by the University of Washington Marine Chemistry Laboratory. These values are reviewed and revised periodically. The UW lab provides MDL's for NO₂ and NO₃ and states it is perfectly acceptable to use the NO₃ MDL value for NO₂₃. MDL's for TSS, CHLA and PHEA are calculated by staff at the Padilla Bay Reserve as these parameters are processed in house.

Parameter	Start Date	End Date	MDL
NH ₄ F	01/01/13	12/31/13	0.0017
NO ₂ F	01/01/13	12/31/13	0.0003
NO ₃ F	01/01/13	12/31/13	0.0021
NO ₂₃ F	01/01/13	12/31/13	0.0021
TN	01/01/13	12/31/13	0.0062
TDN	01/01/13	12/31/13	0.0062
PO ₄ F	01/01/13	12/31/13	0.0009
TP	01/01/13	12/31/13	0.0011

TDP	01/01/13	12/31/13	0.0011
CHLA_N	01/01/13	12/31/13	0.13
PHEA	01/01/13	12/31/13	0.05
SiO4F	01/01/13	12/31/13	0.0166
TSS	01/01/13	12/31/13	0.01

13) Laboratory methods –

a) Parameter: Ammonium

- i) Method Reference: Slawyk, G. and MacIsaac, J.J. (1972) Comparison of two automated ammonium methods in a region of coastal upwelling. *Deep Sea Research* 19:521-524.
- ii) Method Descriptor: A water sample is treated with phenol and alkaline hypochlorite in the presence of NH₃ to form indophenol blue (Berthelot reaction). Sodium nitroferricyanide is used as a catalyst in the reaction. Precipitation of Ca and Mg hydroxides is eliminated by the addition of sodium citrate-complexing reagent. The sample stream is passed through a 55 °C heating bath, then through a 50 mm flowcell and absorbance is measured at 640 nm.
- iii) Preservation Method: Sample is filtered through a 0.45 um disposable disk filter and stored at –20°C up to 30 days.

b) Parameter: NO3F, NO2, NO23

- i) Method Reference: Armstrong, F.A., Stearns, C.R. 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* 14:381-389.
- ii) Method Descriptor: 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 an azo dye. The sample is then passed through a 15 mm flowcell and absorbance is measured at 540 nm. A 50 mm flowcell is required for nitrite (NO₂). The procedure is the same for the nitrite analysis less the cadmium column. Nitrate concentration equals the (nitrate+nitrite) concentration minus the nitrite concentration. NO₂₃ is calculated by adding NO₂ + NO₃.
- iii) Preservation Method: Sample is filtered through a 0.45 um disposable disk filter and stored at –20°C up to 30 days.

c) Parameter: SI, SiO2

- i) Method Reference: Armstrong, F.A., Stearns, C.R. 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* 14:381-389.
- ii) Method Descriptor: 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 15 mm flowcell and absorbance is measured at 820 nm.
- iii) Preservation Method: Sample is filtered through a 0.45 um disposable disk filter and stored at –20°C until analyzed.

d) Parameter: PO4F

- i) Method Reference: Bernhardt, H. and Wilhelms, A. (1967) The continuous determination of low level iron, soluble phosphate, and total phosphate with the AutoAnalyzer. *Technicon Symp.* 1:386.

- ii) Method Descriptor: 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 (or hydrazine) sulfate. The sample is passed through a 50 mm flowcell and absorbance is measured at 820 nm.
- iii) Preservation Method: Sample is filtered through a 0.45 um disposable disk filter and stored at -20°C up to 30 days.

e) Parameter: CHLA, PHEA

- i) Method References: EPA method 445.0 *UNESCO* (1994) Protocols for the joint global ocean flux study (JGOFS) core measurements. pp. 97-100.
- ii) Method Descriptor: CHLA is extracted in 10 ml 90% acetone. Fluorescence is measured on a Turner Designs Trilogy fluorometer (model 7200-000) and recorded (F_o). 150 μL of 0.1N HCl are added to convert the CHLA to phaeopigments (PHEA). The fluorescence is again measured and recorded (F_a). The concentration ($\mu\text{g/L}$) of CHLA and PHEA are calculated using the F_o/F_a ratio. Reagent blanks are subtracted out of reported values during the calculation of CHLA concentrations (see note below).
- iii) Preservation Method: A known volume of sample is filtered onto a 25 mm GF/F filter, folded in half and placed in a plastic vial. Vial is stored at -20°C until analysis.

Note: The marine sites (BY, BP, GS, GD) are analyzed as described above in e) ii so that values for both chlorophyll *a* and phaeopigments are recorded. However, samples from the Joe Leary Estuary site are only analyzed for chlorophyll *a*. Samples from Joe Leary Estuary (JE) are collected when the site is comprised of freshwater (< 5 psu, when the tide gates are open). Because freshwater samples often contain high amounts of chlorophyll *b*, which can interfere with the analysis as performed for the marine sites, Joe Leary Estuary samples are analyzed using the Welschmeyer non-acidification method using a separate fluorometer (Turner Designs TD-700 model 7000-000).

In 2013 the Padilla Bay Laboratory started subtracting out reagent blanks when calculating CHLA and PHEA values after consultation with the University of Washington Laboratory and Turner Designs.

In 2008 the Padilla Bay Laboratory began performing the chlorophyll analysis in-house instead of sending the samples to be processed at the University of Washington. During sampling times over several seasons in 2007, duplicate chlorophyll samples were analyzed at each lab for comparison of methods and results. Due to small differences in methodology between the labs, there were consistent differences in the amounts of chlorophyll and phaeopigment reported by each lab. This makes trend analysis over multiple years (including this transition time) difficult to interpret. In order to get a more accurate comparison, a correction factor has been developed for the chlorophyll and phaeopigment values. When the correction factors are applied to chlorophyll or phaeopigment data in this database prior to January 31st 2008, it yields a value that is comparable to what the value would have been reported, if it had been analyzed by the Padilla Bay Laboratory.

The 3 correction factors are:

- 1) $Y = 1.0928x - 0.0001$
- 2) $Y = 0.9069x + 0.3878$
- 3) $Y = 1.436x + 0.0328$

Where x is the value reported by the University of Washington (the data provided) and Y is the theoretical Padilla Bay equivalent value. Equation 1 is for the chlorophyll data from any of the sites in the bay at Padilla Bay (Gong Surface, Gong Deep, Bayview, Ploeg). Equation 2 is for the chlorophyll data from Joe Leary

Slough and Joe Leary Estuary sites. Equation 3 is for the phaeopigment data for any of the three sites in the bay.

A report has been drafted with detailed information on the comparison of results from the two labs along with the derivation and performance of the correction factors. It is recommended that the user read the full report when applying these correction factors. The report can be accessed by contacting the Research Coordinator or one of the Environmental Specialists.

f) Parameter: TP and TDP

- i) Method Reference: Valderrama, J.C. (1981) The simultaneous analysis of total nitrogen and total phosphorus in natural waters. *Marine Chemistry*, 10:109-122.
- ii) Method Descriptor: The simultaneous persulfate oxidation of nitrogen and phosphorus compounds starts at pH 9.7 and ends at pH 5-6, because it is necessary to oxidize nitrogen compounds in an alkaline medium to produce quantifiable amounts. Conversely, oxidation of phosphorus compounds is obtained using a boric acid-sodium hydroxide system. Adding ascorbic acid before the molybdate reagent reduces the free chorine formed in seawater samples.
- iii) Preservation Method: A known volume of sample is poured directly into a wide-mouth plastic bottle and stored at -20°C up to 30 days.

g) Parameter: TN and TDN

- i) Method References:
 - i) Gordon, D.C. (1969) Examination of methods of particulate organic carbon analysis. *Deep Sea Res.* 16:661-665.
 - ii) Kerambrun, P. and Szekiolda, K.H. (1969) Note technique. *Tethys*, 1: 581-584.
 - iii) Sharp, J.H. (1974) Improved analysis for the “particulate” organic carbon and nitrogen from seawater. *Limnology and Oceanography*, 19:984-989.
- ii) Method descriptor: A dried, acidified sample of particulate matter is combusted at 980°C . The organic carbon is converted to CO_2 and the nitrogen oxides are subsequently reduced to N_2 gas. Both gases are measured by thermal conductivity. Concentrations of particulate organic C and particulate N are given in mg C/L or mg N/L. The analytical software stores all pertinent analytical information for each sample and produces a printout of the signal level at the C, H, and N detector filaments. Regression equation are calculated for each element from the acetanilide standards and Ni sleeve blanks, using the formulaic C, H, and N weights of the individual blanks and standards as the dependent variable and the C, H, N signals as the independent variable in the calculations. The regression equations are then applied to the sample signals to calculate the C, H, N content of each sample in μg . If volume filtered is indicated, each element is calculated as mg/L.
- iii) Preservation Method: A known volume of sample is poured directly into a wide-mouth plastic bottle and stored at -20°C up to 30 days.

h) Parameter: TSS

- i) Method Reference:
 - i) Greenberg, A.E., Clesceri, L.S. and Eaton, A.D. (1995) Total suspended solids dried at $103-105^{\circ}\text{C}$ in *Standard Methods for the Examination of Water and Wastewater 19th ed.* 2-56.
- ii) Method Descriptor: A Whatman 934-AH 47 mm filter disc is vacuum washed with 100 ml of distilled/deionized water, dried at 105°C , cooled in a desiccator to balance temperature, and weighed. This procedure is repeated until the weight change is $<4\%$ or $<0.5\text{ mg}$, whichever is less. The final filter weight is recorded and the filter is stored in a dessicator. After the sample is filtered, the cycle of drying, cooling, desiccating, and weighing is repeated until the weight change is $<4\%$ or 0.5 mg as before.

- iii) Preservation Method: Samples are refrigerated at 1°C and filtered within 7 days of collection. Sample filters are processed immediately after filtering process.

14) Field and Laboratory QAQC programs –

a) Precision

- i) **Field variability** – 55 field grab samples, 55 replicates (100%). Field replicates are collected for all grab samples. The replicates are true field replicates. Field replicates were taken as sequential grab samples obtained with a 2.2 liter Kemmerer water sampler. (See Research Methods I, 3) a) above for further detail).

Laboratory variability – 110 grab samples/field replicates taken, 11 grab sample laboratory replicates (10%). 287 diel grab samples taken, 24 diel laboratory replicates (8.33%).

- ii) **Inter-organizational splits** – None for 2013

b) Accuracy

- i) **Sample spikes** – None for 2013
- ii) **Standard reference material analysis** – None for 2013
- iii) **Cross calibration exercises** – None for 2013

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

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/notes –

Data may be missing due to problems with sample collection or processing. Laboratories in the NERRS System submit data that are censored at a lower detection rate limit, called the Method Detection Limit or MDL. MDLs for specific parameters are listed in the

Laboratory Methods and Detection Limits Section (Section II, Part 12) of this document. Concentrations that are less than this limit are censored with the use of a QAQC flag and code, and the reported value is the method detection limit itself rather than a measured value. For example, if the measured concentration of 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.

General Data Comments:

The following table represents the sample collection dates and when each sample was processed at the Chemical Oceanography Laboratory at the University of Washington. All samples processed more than 30 days after the collection date (highlighted red) were flagged as suspect in accordance with sample preservation time limits.

Sample Date	(G=grabs, D=Diel)	Date Processed		
		[PO ₄] [Si(OH) ₄] [NO ₃] [NO ₂] [NH ₄]	[TP] [TN]	[TDP] [TDN]
1/9/2013	D	18-Jan-13		
1/16/2013	G	18-Jan-14	28-Jan	28-Jan
2/5/2013	D	14-Feb-13		
2/20/2013	G	21-Mar-13	21-Mar	21-Mar
3/17/2013	D	2-Apr-13		
3/22/2013	G	5-Apr-13	10-Apr	10-Apr
4/14/2013	D	9-May-13		
4/17/2013	G	8-May-14	5-Jun	5-Jun
5/8/2013	D	17-May-13		
5/23/2013	G	31-May-13	5-Jun	5-Jun
6/9/2013	D	23-Jul-13		
6/12/2013	G	23-Jul-13	30-Jul	30-Jul
7/17/2013	D	9-Aug-13		
7/18/2013	G	9-Aug-13	22-Aug	22-Aug
8/14/2013	G	28-Aug-13	24-Sep	24-Sep
8/20/2013	D	7-Oct-13		
9/12/2013	D	4-Dec-14		
9/18/2013	G	26-Sep-13	17-Oct	17-Oct
10/10/2013	D	18-Oct-14		
10/16/2013	G	30-Oct-14	26-Nov	26-Nov
11/14/2013	G	3-Dec-14	15-Jan	15-Jan
11/20/2013	D	3-Dec-14		
12/11/2013	G	11-Apr-14	28-Apr	28-Apr
12/17/2013	D	16-Jan-14		

Diel Samples

The following samples had an unusually large amount of sediment in them. This may be due to higher winds stirring up sediment at low tide. This data should be interpreted with caution.

1/10/2013 7:53

1/10/2013 9:01

1/10/2013 10:09

The autosampler did not collect full samples for much of this sample period. Flagged samples from the following time series were very small and marked as suspect. Some of these samples were too small to collect chlorophyll and these data are missing.

2/5/2013 7:09 through 2/6/2013 21:13

Chlorophyll a/Phaeophytin Samples

Samples from the following date/time were very dark, suggesting that there may have been a increased level of sediment in the sample due to the low tide and higher winds. Interpret these data with caution.

1/9/2013 9:13

1/9/2013 10:21

1/9/2013 11:29

Samples from the following period were in acetone for longer than 24 hrs. Data should be interpreted with caution.

9/12/2013 3:52 through 9/13/2013 5:56

9/18/2013 9:00 through 9/18/2013 11:56

Lab blanks from this sample period make up 2% of most of the samples. This is pretty high for us, but our QA manual says no action necessary until 10%. Interpret data with caution.

1/16/2013 9:26 through 1/16/2013 2:34

The following samples from Joe Leary Estuary were run as saltwater samples on the wrong machine so data is not directly comparable to the rest of the JE dataset. These data were rejected.

10/16/2013 8:04

10/16/2013 8:06