# Padilla Bay Reserve (PDB) NERR Nutrient Metadata

January to December 2008 Latest Update: 08/29/2013

### I. Data Set and Research Descriptors

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# 2) Research objectives

### a) Monthly Grab

Two of the objectives of the semi-monthly sampling series are to determine if there are onshore to offshore gradients in nutrient concentrations, and to determine whether these change seasonally. The Joe Leary Slough site is located at the mouth of the largest freshwater drainage to Padilla Bay. 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. A fourth site, Gong, is in the offshore channels to

the west of Padilla Bay. 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.

### b) Diel Sampling Program

Two of the objectives of the 26 hour 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. The Bayview Channel site is in a small channel that drains inter-tidal flats that are mainly covered with dense eelgrass, *Zostera marina* and *Z. japonica*. The small channel is flooded by water coming up Bayview Channel, the largest tidal channel in Padilla Bay.

# 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

Semi-monthly grab samples were taken at the four principal PBNERR datasonde stations within Padilla Bay (Bayview Channel, Ploeg Channel, Gong and Joe Leary Slough). 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.

Bayview and Ploeg Channels and Gong 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% HCI) and rinsed (3x) with distilled-deionized water. Bottles were rinsed (3x) with ambient 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), total suspended solids (TSS), and total volatile solids (TVS). Tier II parameters (TN, TDN, TP, TDP, TSS and TVS) were only filtered for grab samples. Filtering for the dissolved inorganic nutrient parameters (P04, NH4, NO2 and NO3) was done by taking 45ml of sample water and filtering it into previously acid-washed bottles through a 0.45 um 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 um 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 % HCI), 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.

- a) Joe Leary Slough Site: (48° 31' 05.3" N; 122° 28' 22.8" W) 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 4 ft. 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, most recently October 2006. The deployment site is on the freshwater side of the tide gates. The latitude/longitude were measured with a Trimble GeoExplorer II and differentially corrected with post processing providing a manufacturer's stated accuracy of  $\pm$  5m.
- b) Bayview Channel Site: (48° 29' 46.6" N; 122° 30' 01.8" 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 meters 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 GeoExplorer II and differentially corrected with post processing providing a manufacturer's stated accuracy of  $\pm$  5 m.

- c) Ploeg Channel Site: (48° 33' 23.5" N; 122° 31' 46.7" 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 meters 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 GeoExplorer II and differentially corrected with post processing providing a manufacturer's stated accuracy of ± 5 m.
- d) Gong Surface and Gong Deep sites: (48° 33' 30" N; 122° 34' 21" 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 are mud. Depth at this site is 18-20 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 were measured with a Trimble GeoExplorer II and differentially corrected with post processing providing a manufacturer's stated accuracy of ± 5 m.

### 5) Coded variable definitions

Sampling Site Codes:

pdbbpnut = 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 pdbjlnut = Padilla Bay Research Reserve nutrient and chlorophyll data for Joe Leary Slough site

Monitoring program codes:

1 = grab sample

2 = diel sample

Replicate codes for grab samples:

1 = first sample

2 = second sample

S = laboratory split/replicate

Replicate codes for diel samples:

1 =first sample

S = laboratory split/replicate

# 6) Data collection period

Diel Data Collection Period – January 2008 thru December 2008

Site	Start Date and Time	End Date and Time
pdbbynut	1/16/08 18:02	1/17/08 21:14
pdbbynut	2/20/08 22:50	2/21/08 0:54
pdbbynut	3/12/08 14:45	3/13/08 16:49
pdbbynut	4/9/08 13:24	4/10/08 15:28
pdbbynut	5/7/08 13:20	5/8/08 14:16
pdbbynut	6/18/08 10:45	6/19/08 12:49
pdbbynut	7/16/08 9:51	7/17/08 11:55
pdbbynut	9/24/08 6:33	9/25/08 8:37
pdbbynut	10/28/08 22:46	10/30/08 5:30
pdbbynut	11/18/08 2:19	11/19/08 4:23
pdbbynut	12/10/08 21:15	12/11/08 23:19

Grab Sample Collection Period – January 2008 thru December 2008

Site	Start Date and Time	End Date and Time
pdbbynut	1/16/08 9:00	1/16/08 9:01
pdbbynut	1/31/08 14:05	1/31/08 14:06
pdbbynut	2/14/08 11:20	2/14/08 11:21
pdbbynut	2/26/08 11:31	2/26/08 11:32
pdbbynut	3/13/08 9:55	3/13/08 9:56
pdbbynut	4/8/08 10:22	4/8/08 10:23
pdbbynut	4/22/08 8:58	4/22/08 8:59
pdbbynut	5/8/08 8:18	5/8/08 8:19
pdbbynut	5/22/08 9:03	5/22/08 9:04
pdbbynut	6/11/08 10:15	6/11/08 10:16
pdbbynut	6/24/08 8:41	6/24/08 8:42
pdbbynut	7/10/08 9:46	7/10/08 9:47
pdbbynut	7/24/08 10:51	7/24/08 10:52
pdbbynut	8/7/08 8:30	8/7/08 8:31
pdbbynut	8/21/08 8:50	8/21/08 8:51
pdbbynut	9/5/08 9:22	9/5/08 9:23
pdbbynut	9/16/08 11:20	9/16/08 11:21
pdbbynut	10/1/08 7:23	10/1/08 7:24
pdbbynut	10/15/08 8:50	10/15/08 8:51
pdbbynut	10/28/08 10:15	10/28/08 10:16
pdbbynut	11/13/08 9:45	11/13/08 9:46
pdbbynut	11/25/08 11:09	11/25/08 11:10
pdbbynut	12/10/08 10:08	12/10/08 10:09
pdbbynut	12/30/08 10:00	12/30/08 10:01

Site	Start Date and Time	End Date and Time
pdbbpnut	1/16/08 10:25	1/16/08 10:26
pdbbpnut	1/31/08 14:35	1/31/08 14:36
pdbbpnut	2/14/08 11:05	2/14/08 11:06
pdbbpnut	2/26/08 11:02	2/26/08 11:03
pdbbpnut	3/13/08 9:16	3/13/08 9:17
pdbbpnut	4/8/08 9:34	4/8/08 9:35
pdbbpnut	4/22/08 7:55	4/22/08 7:56
pdbbpnut	5/8/08 8:36	5/8/08 8:37
pdbbpnut	5/22/08 7:40	5/22/08 7:41
pdbbpnut	6/11/08 10:40	6/11/08 10:41
pdbbpnut	6/24/08 9:02	6/24/08 9:03
pdbbpnut	7/10/08 9:15	7/10/08 9:16
pdbbpnut	7/24/08 9:35	7/24/08 9:36
pdbbpnut	8/7/08 9:00	8/7/08 9:01
pdbbpnut	8/21/08 9:30	8/21/08 9:31
pdbbpnut	9/5/08 9:52	9/5/08 9:53
pdbbpnut	9/16/08 10:05	9/16/08 10:06
pdbbpnut	10/1/08 8:17	10/1/08 8:18
pdbbpnut	10/15/08 9:17	10/15/08 9:18
pdbbpnut	10/28/08 10:55	10/28/08 10:56
pdbbpnut	11/13/08 10:05	11/13/08 10:06
pdbbpnut	11/25/08 10:40	11/25/08 10:41
pdbbpnut	12/10/08 10:58	12/10/08 10:59
pdbbpnut	12/30/08 10:36	12/30/08 10:37
Cita	Start Date and Time	End Date and Time
Site pdbgsnut	1/16/08 10:55	1/16/08 10:56
	1/31/08 14:58	1/31/08 14:59
pdbgsnut	2/14/08 10:35	2/14/08 10:36
pdbgsnut	* *	
pdbgsnut	2/26/08 10:35	2/26/08 10:36
pdbgsnut	3/13/08 9:00	3/13/08 9:01
pdbgsnut	4/8/08 9:10	4/8/08 9:11
pdbgsnut	4/22/08 8:35	4/22/08 8:36
pdbgsnut	5/8/08 8:52	5/8/08 8:53
pdbgsnut	5/22/08 8:30	5/22/08 8:31
pdbgsnut	6/11/08 11:03	6/11/08 11:04
pdbgsnut	6/24/08 9:20	6/24/08 9:21
11	7 /10 /00 0.22	7 /10 /00 0.22

7/10/08 8:32

7/24/08 8:51

8/7/08 9:25

8/21/08 9:50

9/5/08 10:30

9/16/08 10:34

10/15/08 9:50

10/28/08 11:31

11/13/08 10:24

10/1/08 7:54

7/10/08 8:33

7/24/08 8:52

8/7/08 9:26 8/21/08 9:51

9/5/08 10:31

9/16/08 10:35

10/15/08 9:51

10/28/08 11:32

11/13/08 10:25

10/1/08 7:55

pdbgsnut

pdbgsnut	11/25/08 10:11	11/25/08 10:12
pdbgsnut	12/10/08 11:33	12/10/08 11:34
pdbgsnut	12/30/08 10:50	12/30/08 10:51

Site	Start Date and Time	End Date and Time
pdbgdnut	1/16/08 10:57	1/16/08 10:58
pdbgdnut	1/31/08 15:05	1/31/08 15:06
pdbgdnut	2/14/08 10:40	2/14/08 10:41
pdbgdnut	2/26/08 10:37	2/26/08 10:38
pdbgdnut	3/13/08 9:02	3/13/08 9:03
pdbgdnut	4/8/08 9:05	4/8/08 9:06
pdbgdnut	4/22/08 8:37	4/22/08 8:38
pdbgdnut	5/8/08 8:54	5/8/08 8:55
pdbgdnut	5/22/08 8:32	5/22/08 8:33
pdbgdnut	6/11/08 11:05	6/11/08 11:06
pdbgdnut	6/24/08 9:22	6/24/08 9:23
pdbgdnut	7/10/08 8:34	7/10/08 8:35
pdbgdnut	7/24/08 8:53	7/24/08 8:54
pdbgdnut	8/7/08 9:27	8/7/08 9:28
pdbgdnut	8/21/08 9:52	8/21/08 9:53
pdbgdnut	9/5/08 10:32	9/5/08 10:33
pdbgdnut	9/16/08 10:36	9/16/08 10:37
pdbgdnut	10/1/08 7:56	10/1/08 7:57
pdbgdnut	10/15/08 9:55	10/15/08 9:56
pdbgdnut	10/28/08 11:33	10/28/08 11:34
pdbgdnut	11/13/08 10:26	11/13/08 10:27
pdbgdnut	11/25/08 10:13	11/25/08 10:14
pdbgdnut	12/10/08 11:35	12/10/08 11:36
Pdbgdnut	12/30/08*	12/30/08*
1		•

<sup>\*</sup>samples not collected due to high winds

Site	Start Date and Time	End Date and Time
pdbjlnut	1/16/08 14:15	1/16/08 14:16
pdbjlnut	1/31/08 16:10	1/31/08 16:11
pdbjlnut	2/14/08 14:15	2/14/08 14:16
pdbjlnut	2/26/08 15:00	2/26/08 15:01
pdbjlnut	3/13/08 10:55	3/13/08 10:56
pdbjlnut	4/8/08 13:15	4/8/08 13:16
pdbjlnut	4/22/08 10:45	4/22/08 10:46
pdbjlnut	5/8/08 10:20	5/8/08 10:21
pdbjlnut	5/22/08 10:32	5/22/08 10:33
pdbjlnut	6/11/08 12:46	6/11/08 12:47
pdbjlnut	6/24/08 10:49	6/24/08 10:50
pdbjlnut	7/10/08 12:47	7/10/08 12:48
pdbjlnut	7/24/08 12:55	7/24/08 12:56
pdbjlnut	8/7/08 10:55	8/7/08 10:56
pdbjlnut	8/21/08 11:15	8/21/08 11:16
pdbjlnut	9/5/08 11:45	9/5/08 11:46

pdbjlnut	9/16/08 13:24	9/16/08 13:25
pdbjlnut	10/1/08 10:32	10/1/08 10:33
pdbjlnut	10/15/08 11:30	10/15/08 11:31
pdbjlnut	10/28/08 13:00	10/28/08 13:01
pdbjlnut	11/13/08 12:15	11/13/08 12:16
pdbjlnut	11/25/08 12:54	11/25/08 12:55
pdbjlnut	12/10/08 13:15	12/10/08 13:16
pdbjlnut	12/30/08 12:47	12/30/08 12:48

# 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 within the reserve boundaries. The sondes collect such parameters as water temperature, salinity, dissolved oxygen, depth, pH, and turbidity. The weather part of SWMP consists of weather parameters (air temperature, barometric pressure, relative humidity, precipitation, wind speed, wind direction, and photosynthetically active radiation) being collecting and averaged or totaled for fifteen minute intervals.

Other projects at Padilla Bay include a zooplankton monitoring project (monthly sampling) and a barnacle settlement project. The sampling for each of these projects occurs at the three water quality/nutrient sampling sites within the 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 <a href="http://cdmo.baruch.sc.edu/">http://cdmo.baruch.sc.edu/</a>. 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, 28.09, and 12.01 for N, P, Si, and C respectively. Therefore, Padilla Bay NERR staff multiply the concentrations reported by the University of Washington Marine Chemistry Laboratory by 0.01401, 0.03097, 0.02809, and 0.01201 to yield concentrations in mg/L as N, P, Si, and C 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 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 verification was completed by Heath Bohlmann and Nicole Burnett. Final verification and this metadata documentation were checked by Douglas Bulthuis and Heath Bohlmann before being sent to the CDMO permanent database.

### 10) Parameter titles and variable names by category

Data Category	Parameter	Variable Name J	Units of Measure
Phosphorus and	l 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:	C		Ü
C	*Chlorophyll a	CHLA_N	N μg/L
	Phaeophytin	PHEA	μg/L

### Other Lab Parameters:

Silicate, Filtered	SiO4F	mg/L as Si
Total Suspended Solids	TSS	mg/L
Total Volatile Solids	TVS	mg/L

#### Field Parameters

Water Temperature	$WTEM_N$	$^{\circ}\mathrm{C}$
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: NH4, NO2, NO23, TDN, TN

Phosphorus species: PO4F, TDP, TP

Other: CHLA, PHEA, SiO4, TSS, TVS

# b) Calculated parameters

NO3	NO23-NO2
DIN	NO23+NH4
DON	TDN-NH4-NO23
TON	TN-NH4-NO23
PN	TN-TDN
DOP	TDP-PO4
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.

Parameter	Start Date	End Date	MDL
NH4F	01/01/08	12/31/08	0.0005
NO23F	01/01/08	12/31/08	0.0010
NO2F	01/01/08	12/31/08	0.0001
NO3F	01/01/08	12/31/08	0.0010
PO4F	01/01/08	12/31/08	0.0004

```
SiO4F
         01/01/08 12/31/08 0.0188
TDN
         01/01/08 12/31/08 0.0048
TDP
         01/01/08 12/31/08 0.0009
TN
         01/01/08 12/31/08 0.0055
TP
         01/01/08 12/31/08 0.0009
TSS
         01/01/08 12/31/08 0.01
TVS
         01/01/08 12/31/08 0.01
         01/01/08 12/31/08 0.09
CHLA N
PHEA
         01/01/08 12/31/08 0.16
```

# 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) <u>Preservation Method:</u> Sample is filtered through a 0.45 um disposable disk filter and stored at 20°C until analyzed.

# b) Parameter: NO3F, NO2F, NO23F

- 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) <u>Preservation Method:</u> Sample is filtered through a 0.45 um disposable disk filter and stored at 20°C until analyzed.

### c) Parameter: SiO4F, 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) <u>Preservation Method:</u> 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) <u>Preservation Method:</u> Sample is filtered through a 0.45 um disposable disk filter and stored at 20°C until analysis.

### e) Parameter: CHLA, PHEA

- i) <u>Method References:</u> 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 and fluorescence is measured and recorded (Fo). 150 μL of 0.1N HCI are added to convert the CHLA to phaeopigments (PHEA). The fluorescence is again measured and recorded (Fa). The concentration (μg/L) of CHLA and PHEA are calculated using the Fo/Fa ratio (see note below).
- iii) <u>Preservation Method:</u> 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.

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 site. 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 molyddate reagent reduces the free chorine formed in seawater samples.
- iii) <u>Preservation Method:</u> A known volume of sample is poured directly into a wide-mouth plastic bottle and stored at -20° C until analysis.

# g) Parameter: TN and TDN

- i) Method References: Gordon, D.C. (1969) Examination of methods of particulate organic carbon analysis. *Deep Sea Res.* 16:661-665.
  - i) Kerambrun, P. and Szekielda, K.H. (1969) Note technique. Tethys, 1: 581-584.
  - ii) 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 CO2 and the nitrogen oxides are subsequently reduced to N2 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) <u>Preservation Method:</u> A known volume of sample is poured directly into a wide-mouth plastic bottle and stored at -20 °C until analysis.

### h) Parameter: TSS and TVS (University of Washington)

- i) Method Reference: Greenberg, A.E., Clesceri, L.S. and Eaton, A.D. (1992) Total suspended solids dried at 103-105°C in Standard Methods for the Examination of Water and Wastewater 18th ed. 2-56.
- ii) Method Descriptor: A glass-fiber filter disc is vacuum washed with 20 mL portions of reagent-grade water, dried at 60°C, placed in a muffle furnace, cooled in a desiccator to balance temperature, and weighed, then dried at 60°C. The drying procedure is repeated until the weight change is <4% or <0.5 mg, whichever is less. The final filter weight is recorded and the filter is stored in a numbered analyslide. 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. Then the filter is placed in the muffle furnace to obtain the volatile component.
- iii) <u>Preservation Method:</u> A known volume of sample is filtered through the 25mm GF/F Whatman pre-weighed filters (pore size 0.7uM), which is then folded in half, returned to numbered analyslide, and stored at –20°C until analysis.

**14) Field and Laboratory QAQC programs** – This section describes field variability, laboratory variability, the use of inter-organizational splits, sample spikes, standards, and cross calibration exercises.

# a) Precision

- (1) **Field variability** 117 field grab samples, 117 replicates (100%). Field replicates are usually 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).
- ii) **Laboratory variability** 24grab laboratory replicates and 24 diel laboratory replicates. **Inter-organizational splits** Samples for chlorophyll analysis were split with the University of Washington, Marine Chemistry Lab several times during 2008. See section13) e) above for further details.

# b) Accuracy

- i) Sample spikes None for 2008
- ii) Standard reference material analysis Data not yet available for 2008.
- iii) Cross calibration exercises None for 2008

# 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 error	rs
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
000	Data suspect due to Q11/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
D	
Parameter Co	
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 comm	
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	7 1 1
CCL	clear (0-10%)
CSP	scattered to partly cloudy (10-50%)
CPB	partly to broken (50-90%)
COC	overcast (>90%)
CFY	foggy
CHY	
CCC	hazy cloud (no percentage)
	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
Tido atago	

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 \text{ to} > 1.0 \text{ meters}
  WH4
            1.0 to 1.3 meters
  WH5
            1.3 or greater meters
Wind direction
  Ν
            from the north
  NNE
            from the north northeast
  NE
            from the northeast.
  ENE
            from the east northeast
  Е
            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 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.

<b>Station Code</b>	<b>DateTimeStamp</b> 1/16/08 9:00 -	Monitoring Program
all stations	1/16/08 14:16	1
	1/16/08 18:02	
pdbbynut	- 1/17/08 21:14	2

Chlorophyll and phaeopigment from sample dates of Jan 16th and Jan 17th 2008 were processed at the University of Washington. See CHL, PHEA (Section 13, Part (e)), for detailed description and correction factors when using this data.

Station Code	<b>DateTimeStamp</b>	Monitoring Program
pdbjlnut	10/28/08 13:00	
pdbjlnut	10/28/08 13:01	1

Chlorophyll and Phea samples were freshwater but run as saltwater samples and are not directly comparable to to other CHLA data collected throughout the rest of 2008. Interpret data with caution.

<b>Station Code</b>	DateTimeStamp	Monitoring Program
pdbjlnut	12/10/08 13:15	
pdbjlnut	12/10/08 13:16	1

Chlorophyll processed as salt water due to salinity of 2.6%.

Station Code	DateTimeStamp	Monitoring Program
pdbbynut	1/16/08 9:00 -	
pdbbpnut	8/21/08 11:16	1,2
pdbgsnut		
pdbgdnut		
pdbjlnut		

TSS and TVS from the 16th of January through the 21st of August were flagged as <1> Suspect data due to a quality control review which indicated high variance and other issues with the data for this period of time. Lab procedures were changed after August 21 and TSS and TVS data for the rest of the year had normal variance and are not considered suspect.

Station Code	DateTimeStamp	Monitoring Program
pdbbynut pdbbynut	4/08/08 10:22 4/08/08 10:23	1
pdbbpnut pdbbpnut	4/08/08 09:34 4/08/08 09:35	1

pdbbynut	4/09/08 19:04-	
pdbbynut	4/09/08 22:28	2

High chlorophyll values may be due to algal bloom. Higher than normal chlorophyll values were also observed in diel samples taken 4/09/08 and visual observations of increased phytoplankton densities were recorded on 4/22/08.

<b>Station Code</b>	DateTimeStamp	Monitoring Program
pdbbynut	10/28/08 10:15 -	
pdbbpnut	10/28/08 12:48	1
pdbgsnut		
pdbgdnut		
pdbjlnut		

For TSS and TVS, temp dropped to 350 degrees C while in muffle furnace during pre-filter preparations (door may not have been shut properly). Filters were kept in the muffle furnace for an extra 20 min. at 550 degrees C.