Padilla Bay (PDB) NERR Nutrient Metadata January – December 2003 Latest Update: July 14, 2025

I. Data Set and Research Descriptors

1) Principal investigator(s) and contact persons

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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 of Padilla Bay to the west. Data from a preliminary study have indicated an offshore to onshore 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

a) Monthly Grab Sampling Program

Bi-monthly grab samples were taken at the three principal PBNERR datasonde stations within Padilla Bay (Bayview Channel, Ploeg Channel, and Joe Leary slough). Bi-monthly grabs samples at the 4th principal PBNERR datasonde station (Gong Surface) began April 4, 2003. No distinction was made between neap and spring tide conditions. Replicate (N=2) samples were taken at the datasonde sensor depth (0.5 meters from the bottom for Bayview and Ploeg and 0.5 meters from the surface for Gong Surface). Bayview and Ploeg channels and Gong Surface 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 were obtained with nalgene bottles harnessed together with nylon webbing and capped with rubber corks that were attached by a line to the surface. Once at the sampling depth, the corks were pulled to obtain water from the sensor depth. At the time of sample collection, water temperature, salinity and dissolved oxygen were measured with a YSI Model 85 meter. All samples were collected in amber, wide-mouth, nalgene sample bottles that were previously acid washed (10% HCI), rinsed (3x) with distilled-deionized water, dried and followed by rinsing (1x) of ambient water prior to collection of the sample. Samples were immediately placed on ice, in the dark, and returned to the laboratory. Once in the laboratory, samples were shaken, filtered and processed for nutrient and Chlorophyll a analysis the same day. (See section 11 for details of sample processing.)

b) Diel Sampling Program

Diel sampling occurred once a month at the Bayview Channel site using a Sigma sampler. The sampler was programmed, when possible, to begin and end at low tide. The Sigma was deployed using a floating platform that was towed by boat to the location and 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 0.5 meters from the surface. All samples went into bottles previously acidwashed (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. (See section 11 for details of sample processing.)

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.

Joe Leary Slough Site: $(48^{\circ} 31' 05.3" \ N; 122^{\circ} 28' 22.8" \ W)$ 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 $0.5\text{-}1.5 \ m$. 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 2000. 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 $\pm 5 \ m$.

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 - 5 meters from MLLW to MHHW. 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 ± 5 m.

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 - 5 meters from MLLW to MHHW. 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 \pm 5 m.

Gong Surface site: $(48^{\circ} 33' 30" \ N; 122^{\circ} 34' 21" \ W)$ 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. 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 $\pm 5 \ m$.

5) Code variable definitions

Station Code Names

Bayview Channel (pdbbynut), Ploeg Channel (pdbbpnut), Joe Leary Slough (pdbjlnut), Gong Surface (pdbgsnut). Monitoring Program Code Names: Padilla Bay National Research Reserve nutrients monthly grab sample program (1), and diel grab sample program (2).

6) Data collection period

Monthly Grab Samples

| Site | Start Date | Start Time | End Time |
|------|------------|---------------|----------|
| | | | |
| BP | 1/21/2003 | 11:45 | 11:45 |
| BP | 2/6/2003 | 10:45 | 10:45 |
| BP | 2/25/2003 | 11:10 | 11:10 |
| BP | 3/25/2003 | 10:15 | 10:15 |
| BP | 4/11/2003 | 9:15 | 9:15 |
| BP | 4/28/2003 | 10:15 | 10:15 |
| BP | 5/8/2003 | 10:00 | 10:00 |
| BP | 6/10/2003 | 12:55 | 12:55 |
| BP | 6/24/2003 | 14:12 | 14:12 |
| BP | 7/8/2003 | 13:20 | 13:20 |
| BP | 7/22/2003 | 13:30 | 13:30 |

| BP | 8/13/2003 | 8:06 | 8:06 |
|----|------------|-------|-------|
| BP | 8/22/2003 | 13:36 | 13:36 |
| BP | 9/5/2003 | 12:45 | 12:45 |
| BP | 9/17/2003 | 9:55 | 9:55 |
| BP | 10/1/2003 | 12:55 | 12:55 |
| BP | 10/15/2003 | 9:10 | 9:10 |
| BP | 10/29/2003 | 10:11 | 10:11 |
| BP | 11/12/2003 | 14:14 | 14:14 |
| BP | 12/3/2003 | 10:21 | 10:21 |
| BP | 12/17/2003 | 14:45 | 14:45 |
| BY | 1/21/2003 | 11:25 | 11:25 |
| BY | 2/6/2003 | 10:10 | 10:10 |
| BY | 2/25/2003 | 10:40 | 10:40 |
| BY | 3/25/2003 | 9:50 | 9:50 |
| BY | 4/11/2003 | 8:50 | 8:50 |
| BY | 4/28/2003 | 11:24 | 11:24 |
| BY | 5/8/2003 | 11:00 | 11:00 |
| BY | 6/10/2003 | 12:10 | 12:10 |
| BY | 6/24/2003 | 13:40 | 13:40 |
| BY | 7/8/2003 | 12:58 | 12:58 |
| BY | 7/22/2003 | 13:50 | 13:50 |
| BY | 8/13/2003 | 9:10 | 9:10 |
| BY | 8/22/2003 | 13:55 | 13:55 |
| BY | 9/5/2003 | 12:20 | 12:20 |
| BY | 9/17/2003 | 10:10 | 10:10 |
| BY | 10/1/2003 | 12:25 | 12:25 |
| BY | 10/15/2003 | 8:47 | 8:47 |
| BY | 10/29/2003 | 10:40 | 10:40 |
| BY | 11/12/2003 | 13:54 | 13:54 |
| BY | 12/3/2003 | 10:40 | 10:40 |
| BY | 12/17/2003 | 15:05 | 15:05 |
| GS | 4/11/2003 | 12:30 | 12:30 |
| GS | 4/28/2003 | 10:45 | 10:45 |
| GS | 5/8/2003 | 10:15 | 10:15 |
| GS | 6/10/2003 | 12:35 | 12:35 |
| GS | 6/24/2003 | 14:36 | 14:36 |
| GS | 7/8/2003 | 13:50 | 13:50 |
| GS | 7/22/2003 | 13:11 | 13:11 |

| GS | 8/13/2003 | 8:25 | 8:25 |
|----|------------|-------|-------|
| GS | 8/22/2003 | 13:00 | 13:00 |
| GS | 9/5/2003 | 13:00 | 13:00 |
| GS | 9/17/2003 | 9:28 | 9:28 |
| GS | 10/1/2003 | 13:10 | 13:10 |
| GS | 10/15/2003 | 9:25 | 9:25 |
| GS | 10/29/2003 | 10:00 | 10:00 |
| GS | 11/12/2003 | 14:45 | 14:45 |
| GS | 12/3/2003 | 10:00 | 10:00 |
| GS | 12/17/2003 | 14:35 | 14:35 |
| JL | 1/21/2003 | 9:50 | 9:50 |
| ЛL | 2/6/2003 | 11:48 | 11:48 |
| 几 | 2/25/2003 | 12:10 | 12:10 |
| 几 | 3/25/2003 | 11:20 | 11:20 |
| 几 | 4/11/2003 | 14:00 | 14:00 |
| JL | 5/8/2003 | 12:50 | 12:50 |
| JL | 6/10/2003 | 10:05 | 10:05 |
| JL | 6/24/2003 | 9:47 | 9:47 |
| JL | 7/8/2003 | 9:55 | 9:55 |
| JL | 7/22/2003 | 10:45 | 10:45 |
| JL | 8/13/2003 | 10:31 | 10:31 |
| JL | 8/22/2003 | 8:40 | 8:40 |
| JL | 9/5/2003 | 10:15 | 10:15 |
| JL | 9/17/2003 | 11:10 | 11:10 |
| JL | 10/1/2003 | 10:18 | 10:18 |
| JL | 10/15/2003 | 10:40 | 10:40 |
| JL | 10/29/2003 | 11:35 | 11:35 |
| JL | 11/12/2003 | 15:35 | 15:35 |
| JL | 12/17/2003 | 16:05 | 16:05 |

Diel Sampling

| Site | Start Date | Start Time | End Date | End Time |
|------|------------|------------|----------|----------|
| | | | | |
| BY | 1/14/03 | 15:00 | 1/15/03 | 23:17 |
| BY | 2/25/03 | 18:05 | 2/26/03 | 20:09 |
| BY | 3/25/03 | 16:35 | 3/26/03 | 10:00 |
| BY | 4/15/03 | 22:05 | 4/17/03 | 00:09 |
| BY | 5/19/03 | 13:35 | 5/20/03 | 14:31 |
| BY | 6/25/03 | 08:05 | 6/26/03 | 10:09 |
| BY | 8/26/03 | 10:05 | 8/27/03 | 12:09 |
| BY | 9/17/03 | 03:05 | 9/18/03 | 05:09 |

| BY | 10/30/03 | 01:05 | 10/30/03 | 14:41 |
|----|----------|-------|----------|-------|
| BY | 11/24/03 | 23:05 | 11/26/03 | 01:09 |
| BY | 12/09/03 | 23:05 | 12/11/03 | 01:09 |

7) Associated researchers and projects

None

8) Distribution

NOAA/ERD retains the right to analyze, synthesize and publish summaries of the NERRS System-wide Monitoring Program data. The PI, Dr. Douglas Bulthuis, retains the right to be fully credited for having collected and processed the data. Following academic courtesy standards, the PI and NERR site, Padilla Bay National Estuarine Research Reserve, 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 water quality data and metadata can be obtained from the Research Coordinator at the individual NERR site (please see Section 1. 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, Microsoft Excel spreadsheet format and comma-delimited format.

II. Physical Structure Descriptors

9) Entry verification –

Data were received from the analytical laboratory and were entered into a Microsoft Excel spreadsheet. Data were examined for suspect, anomalous or outlying data. Missing data were inserted into the spreadsheet and were denoted by a blank (). Data were flagged when values were above or below the Minimum Detection Limits (MDL). Data entry verification was completed by Paula Margerum and Douglas Bulthuis. Final verification and this metadata documentation were checked by Douglas Bulthuis and Paula Margerum before being sent to the CDMO permanent database.

10) Parameter Titles and Variable Names by Data Category

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

| Data Category | Parameter | Variable Name | Units of Measure |
|----------------|------------------------------|---------------|------------------|
| i) Phosphorus | and Nitrogen: | | |
| | *Orthophosphate | PO4F | mg/L as |
| | *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 Carbon | DOC | mg/L as N |
| | Total Nitrogen | TN | mg/L as N |
| | Total Phosphorus | TP | mg/L as P |
| ii) Plant Piam | ants: | | |

ii) Plant Pigments;

| Chlorophyll a | CHLA_N | $\mu g/L$ |
|---------------|--------|-----------|
| Phaeophytin | PHEA | ug/L |

iii) Other Lab Parameters:

| Silicate, Filtered | SiO4F | mg/L as SI |
|------------------------|-------|------------|
| Total Suspended Solids | TSS | mg/L |

Notes:

- 1. Time is coded based on a 2400 hour clock and is referenced to Pacific Standard Time (PST).
- 2. Reserves have the option of measuring either NO23 or NO2 and NO3.

11) Measured and Calculated Laboratory Parameters

University of Washington, Seattle conducted the analyses for all parameters. All samples were kept cool from time of collection until return to Padilla Bay laboratory, usually within 4 hours of collection for grab samples and within 2 hours of collection of the last sample in the 26-hour tidal sampling. 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 through 0.45 µm filter and placed in sample bottles provided by the Chemical Oceanography Laboratory of the University of Washington. Within 1 hour of filtering, sample bottles were placed in a freezer and kept frozen at –25°C. Within 1-4 days, samples were sent via overnight express in a cooler to the Chemical Oceanography Laboratory at the University of Washington where they were stored in a freezer until analysis.

a. Variables Measured Directly

Nitrogen species: NO2, NO23, NH4

Phosphorus species: PO4F

Other: SiO4F, CHLA N, TN, TP, DOC, TSS, PHEA

b. Computed Variables

NO3: NO23-NO2 DIN: NO23+NH4 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-1 based on atomic weights of 14, 31, 28, and 12 for N, P, Si, and C respectively. Therefore the concentrations reported by the University of Washington Marine Chemistry Laboratory are multiplied by 0.014, 0.031, 0.028, and 0.012 for N, P, Si, and C respectively by Padilla Bay NERR staff and entered into the data spreadsheet.

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. Table 1 lists the current MDL values, which are reviewed and revised periodically.

Table 1. Method Detection Limits (MDL) for measured water quality parameters.

| Parameter | Variable | Range: µM | [Avg] μM | MDL μM | MDL mg/L | Dates in use |
|-------------------|----------|-----------|-------------|-----------|-------------|--------------|
| Ammonium | NH4F | 0-3.0 | 1.04 | 0.05 | 0.0007 | 2003 |
| Nitrite | NO2F | 0-3.0 | 0.99 | 0.01 | 0.0001 | 2003 |
| Nitrite + Nitrate | NO23F | 0-20 | 11.59 | 0.15 | 0.0021 | 2003 |
| Orthophosphate | PO4F | 0-3.0 | 1.00 | 0.02 | 0.0001 | 2003 |
| Silicate | SIF | 0-50 | 15.96 | 0.21 | 0.0059 | 2003 |

Chl a (and Phaeopigments):

Fluorometric analysis done on a Turner Model TD700 fluorometer. Published detection limit is $0.02 \mu g/L$. This is the lowest EXTRACT concentration measurable on the instrument. Turner Designs (1999) TD-700 Laboratory Fluorometer Operating Manual. p. 49.

DOC

Analysis performed on a Shimadzu TOC-5000 Total Organic Carbon Analyzer. Published detection limit of 100 μ g C/L. Shimadzu Corporation (1991) Total Organic Carbon Analyzer TOC-5000/5050 Instruction Manual. p. 18.

TSS

University of Washington

If necessary, we can see differences down to 1 μg . Basically limited by the limits of the balance we use to weigh our filters.

POC/PON

Analysis performed on a CEC 440-SHA Elemental Analyzer (Leeman Labs, Inc. currently supported by Exeter Analytical, Inc.). Detection limit is $\sim \! 10~\mu g$ C/filter and $\sim \! 1~\mu g$ Nitrogen/filter (as determined by this lab).

13) Laboratory Methods

a) Parameter NH4F:

- 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 $0.45~\mu m$ disposable disk filter and stored at -20 °C until analyzed.

b) Parameter: NO3F

- 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 μm disposable disk filter and stored at $-20^{\circ}C$ until analyzed.

c) Parameter: SiO4F, Si(OH)4

- i) <u>Method Reference:</u> 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 $0.45~\mu m$ disposable disk filter and stored at $-20^{\circ} C$ until analyzed.

d) Parameter: PO4F

i) <u>Method Reference:</u> 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 μm 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). Several drops (5-7) of 10% HCI are added to convert the CHLA to phaeopigments (PHAE). The fluorescence is again measured and recorded (Fa). The concentration (μg/L) of CHLA and PHAE are calculated using the Fo/Fa ratio.
- iii) <u>Preservation Method:</u> A known volume of sample is filtered onto a 25 mm GF/F filter, folded in half and wrapped in aluminum foil. Foil is stored at -20°C until analysis.

f) Parameter: TN, TP

- 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) Preservation Method: Sample is filtered through a 0.45 μm disposable disk filter and stored at $-20^{\circ}C$ until analysis.

g) Parameter: TSS (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, cooled in a desiccator to balance temperature, and weighed. This 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.
- iii) <u>Preservation Method:</u> A known volume of sample is filtered through the pre-weighed filter, which is then folded in half, returned to numbered analyslide, and stored at -20°C until analysis.

h) Parameter: TN

- i) <u>Method References:</u> 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 filtered through a carbon-cleaned glass fiber filter and stored at -20°C until analysis.

i) Parameter: DOC

- i) <u>Method References:</u> Sharp, J.H. (1973) total organic carbon in seawater comparison of measurements using persulfate oxidation and high temperature combustion. *Marine Chemistry*, 1:211-229.
 - Sharp, J.H, and Pelzer, E.T. (1993) Procedures subgroup report. *Marine Chemistry*, 1:211-229.
 - *UNESCO* (1994) Determination of dissolved organic carbon by a high temperature combustion/direct injection technique. pp. 104-118.
- ii) Method descriptor: This method is based on the complete oxidation of organic compounds to CO2 followed by quantitative measurement of the CO2 produced by non-dispersive infrared (NDIR) analysis. Interferences from the particulate carbon and inorganic carbon in seawater are first removed by filtration through glass fiber filters and sparging with CO2-free gas after acidification of the sample.
- iii) <u>Preservation Method:</u> A known volume of sample is filtered through a carbon-cleaned glass fiber filter into a carbon-cleaned scintillation vial and stored at -20°C until analysis.

Reporting of Missing Data, Data with Concentrations Lower than Method Detection Limits

Nutrient/Chla comment codes and definitions are provided in the following table. Missing data are denoted by a blank cell " " and commented coded with an "M". Laboratories in the NERRS System submit data that are censored at a lower detection rate limit, called the Method Detection Limit or MDL. MDL's for specific parameters are listed in the Laboratory Methods and Detection Limits Section (Section II, Part 14) of this document. Measured concentrations that are less than this limit are replaced with the minimum detection limit value and comment coded with a "B" in the variable code comment column. For example, the measured concentration of NO23F was 0.0005 mg/L as N (MDL=0.0008), the reported value would be 0.0008 with a "B" placed in the NO23F comment code column. Calculated parameters are comment coded with a "C" and if any of the components used in the calculation are below the MDL, the calculated value is removed and also comment coded with a "B". If a calculated value is negative, the value is removed and comment coded with an "N".

Note: The way below MDL values are handled in the NERRS SWMP dataset was changed in November of 2011. Previously, below MDL data from 2002-2006 were also coded with a B, but replaced with -9999 place holders. Any 2002-2006 nutrient/pigment data downloaded

from the CDMO prior to December November of 2011 will contain -9999s representing below MDL concentrations.

| Comment | Definition |
|---------|--|
| Code | |
| A | Value above upper limit of method detection |
| В | Value below method detection limit |
| С | Calculated value |
| D | Data deleted or calculated value could not be determined due to |
| | deleted data, see metadata for details |
| Н | Sample held beyond specified holding time |
| K | Check metadata for further details |
| M | Data missing, sample never collected or calculated value could not |
| | be determined due to missing data |
| P | Significant precipitation (reserve defined, see metadata for further |
| | details) |
| U | Lab analysis from unpreserved sample |
| S | Data suspect, see metadata for further details |

14) QA/QC Programs

a) Precision

- i) **Field Variability** 80 field grab samples, 80 replicates (100%). Field replicates are taken for all monthly grab samples. The replicates are true field replicates with the two sample bottles placed side by side in a harness, lowered to the sample depth and filled simultaneously.
- ii) Laboratory Variability 20 laboratory replicates.
- iii) Inter-organizational splits None.

b) Accuracy

- i) **Sample Spikes** Cannot be done on samples analyzed directly from filters.
- ii) Standard Reference Material Analysis None for 2003
- iii) Cross Calibration Exercises None for 2003

15) Other Remarks

On 7/14/2025 this dataset was updated to include embedded QAQC flags and codes for anomalous/suspect, rejected, missing, and below detection limit data. System-wide monitoring data beginning in 2007 were processed to allow for QAQC flags and codes to be embedded in the data files rather than using the original single letter codes used for the nutrient and pigment dataset along with the detailed sections in the metadata document for suspect, missing, and rejected data. Please note that prior to 2007, rejected data were deleted from the dataset so they are unavailable to be used at all. Suspect, missing, rejected and below minimum detection flags and appropriate three letter codes were embedded retroactively for dataset consistency. The QAQC flag/codes corresponding to the original letter codes are detailed below.

| | | Historic | |
|---|------------|-------------|--|
| Flag/code | If also C | Letter Code | Historic Code Definition |
| <1> [SUL] | | Α | Value above upper limit of method detection |
| <-4> [SBL] | <-4> [SCB] | В | Value below method detection limit |
| no need to flag/code unless combined | | С | Calculated value |
| <-3> [GQD] | <3> [GCR] | D | Data deleted or calculated value could not be determined due to deleted data, see metadata for details |
| <1> (CHB) | | Н | Sample held beyond specified holding time |
| <0> (CSM) unless other flag | | K | Check metadata for further details |
| <-2> [GDM] | <-2> [GCM] | М | Data missing, sample never collected or calculated value could not be determined due to missing data |
| <-3> [SNV] and <1> [SCC] for components | | N | Negative calculated value |
| (CRE) or F_Record (CRE) | | Р | Significant precipitation (reserve defined, see metadata for further details) |
| <0> (CUS) | | U | Lab analysis from unpreserved sample |
| <1> (CSM) | | S | Data suspect, see metadata for further details |

Only 6 sporadic samples were collected during the diel sampling month of March 25-26 due to battery failure. Small craft advisory was also in affect.

DOC sample for BY rep. 2 Mar.25 was broken upon arrival at U of WA Laboratory.

Only 23 samples were collected for the diel month of May 19-20 due to daylight savings time.

Laboratory lights were accidentally left on while filtering for Chlorophyll "a" for the grab period of June 10.

Only 13 samples collected for the diel sampling for the month of October 30 because a "Small Craft Advisory" was upgraded to 'Gale Force" which would have prevented the sampler from being picked up.

There were strong winds during the diel sampling for the month of November 24 –26.

No grab samples were taken for Joe Leary on Dec. 3 because it was inaccessible.