# PICO biogeochemical data collected from Duke Marine Lab dock from 2011-2022

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#### Abstract

Core biogeochemical data from the Pivers Island Coastal Observatory (PICO), first described in Johnson et al. 2013. This dataset includes time-series data from ~weekly sampling near Pivers Island at the Duke University Marine Laboratory dock in Beaufort North Carolina USA. 34.7181 °N 76.6707 °W. Current dataset is from 2011-2021 and includes a variety of primary physical, chemical and biological variables.

# Table of Contents

- <u>Coverage</u>
- Dataset Description
  - <u>Methods & Sampling</u>
  - <u>Data Processing Description</u>
- <u>Related Publications</u>
- <u>Parameters</u>
- Instruments

# Coverage

**Location**: Duke University Marine LaboratoryPivers IslandBeaufort, North Carolina, USA34.7181 °N 76.6707 °WCoastal Marine / Estuary Environment

**Spatial Extent**: Lat:34.7181 Lon:-76.6707 **Temporal Extent**: 2011 - 2022

#### Methods & Sampling

Water was sampled at  $\sim$ 10:30am local from a dock using a 5 L niskin bottle centered at 1 m with a bottle length of 0.7 m. Subsamples were processed immediately following water collection.

#### DIC

DIC was measured on mercuric chloride poisoned samples by acidification and subsequent quantification of released CO<sub>2</sub> using a CO<sub>2</sub> detector (Li-Cor 7000). DIC samples were collected following recommended procedures {Dickson et al., 2007} and measurements were calibrated against Certified Reference Materials provided by Dr. A. G. Dickson at Scripps Institution of Oceanography (SIO), University of California, San Diego (UCSD).

Dickson, A.G., Sabine, C.L., and Christian, J.R. (eds) (2007) *Guide to best practices for ocean CO*<sub>2</sub> *measurements*: PICES Special Publication 3.

# Chlorophyll

Methods described in Johnson et al. 2010: Chlorophyll concentrations were measured by filtering 25 mL of seawater sample onto a 0.22 µm pore size polycarbonate filter using gentle vacuum (<100 mm Hg) and extracting in 100% MeOH at -20°C in the dark for >24 h following (Holm-Hansen and Riemann, 1978). Fluorescence was measured using a Turner Designs 10-AU fluorometer following (Welschmeyer, 1994) that was calibrated against a standard chlorophyll solution (Ritchie, 2006).

Johnson, Z.I., Shyam, R., Ritchie, A.E., Lin, Y., Mioni, C., Lance, V.P. et al. (2010) The effects of iron- and lightlimitation on phytoplankton communities of deep chlorophyll maxima of the Western Pacific Ocean. *Journal of Marine Research* **68**: 1-26.

Holm-Hansen, O., and Riemann, B. (1978) Chlorophyll a determination: Improvements in methodology. *Oikos* **30**: 438-447.

Welschmeyer, N.A. (1994) Fluorometric analysis of chlorophyll *a* in the presence of chlorophyll *b* and pheopigments. *Limnology and Oceanography* **39**: 1985-1992.

Ritchie, R. (2008) Universal chlorophyll equations for estimating chlorophylls a, b, c, and d and total chlorophylls in natural assemblages of photosynthetic organisms using acetone, methanol, or ethanol solvents. *Photosynthetica* **46**: 115-126.

## Secchi Depth

Secchi depth was measured in duplicate using a 20 cm disk with four alternating white and black quadrants by lowering the disk until no longer visible and recording the depth.

## Salinity

Salinity was measured using a calibrated handheld digital refractometer (Atago PAL-06S), using a refractometer (Vista A366ATC), YSI Pro30, YSI ProODO, YSI ProSolo or using a Guideline Portasal 8410A all according to manufacturer's instructions and calibrated against known reference materials.

## Turbidity

Turbidity reported in Nephelometric Turbidity Units [NTU] was measured in duplicate on discrete samples using a calibrated handheld turbidimeter (Orion AQ4500) according to manufacturer's instructions.

#### Temperature

Temperature was measured in duplicate using NIST traceable thermocouples (VWR#23609-232) from bottle water or from in situ probes YSI Pro30, YSI ProODO or YSI ProSolo according to manufacturer's instructions.

#### рΗ

pH was measured spectrophotometrically (Clayton and Byrne, 1993) in triplicate at standard temperature (25 degrees C) immediately following collection. pH samples were collected following recommended procedures (Dickson et al., 2007).

Clayton, T.D., and Byrne, R.H. 1993. Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. Deep Sea Research Part I: Oceanographic Research Papers 40: 2115-2129. doi: 10.1016/0967-0637(93)90048-8

Dickson, A.G., Sabine, C.L., and Christian, J.R. (eds). 2007. Guide to best practices for ocean CO2 measurements: PICES Special Publication 3.

#### Bacteria, Synechococcus, picocyanobacteria, pico-photosynthetic eukaryotes

Bacterioplankton ("bacteria", DNA containing, non-red fluorescing populations), *Synechococcus* (small, red and orange fluorescing populations), "picocyanobacteria" (small, red fluorescing populations; includes *Prochlorococcus* and 'green' *Synechococcus*), and "picoeukaryotes" (DNA containing, red and orange fluorescing populations) were measured flow cytometrically as previously described (Johnson et al., 2010) using a BD FACSCalibur, or using Hoechst 34580 or Sybr Green I DNA stains using an Attune NxT with 405 nm excitation and 440±25, 512±13, 603±24, 710±25 nm emission and 488 nm excitation and 530±15, 574±13, 695±20, 780±30 nm emission as previously described (Selph 2021)

Johnson, Z.I., Shyam, R., Ritchie, A.E., Lin, Y., Mioni, C., Lance, V.P. et al. (2010) The effects of iron- and lightlimitation on phytoplankton communities of deep chlorophyll maxima of the Western Pacific Ocean. *Journal of Marine Research* **68**: 1-26.

Selph KE Enumeration of marine microbial organisms by flow cytometry using near-UV excitation of Hoechst 34580-stained DNA. *Limnol Oceanogr Methods* **19:** 692-701.

#### Inorganic Nutrients (NH4, NO3, SiOH4)

Water was filtered through a 0.22 um Sterivex cartridge filter, Millipore #SVGPL10RC using a peristaltic pump input line at 1 m for later nutrient analysis (NO3, NH4, SiOH4). Water was sampled in duplicate into HCl-cleaned HDPE bottles (VWR#414004-110) and stored at -80 degrees C until later analysis using an Astoria-Pacific A2 autoanalyzer (NO3 and SiOH4), following the manufacturer's recommended protocols by running each replicate sample in duplicate. NH4 was measured in triplicate following Holmes et al. 1999 using a Turner 10-AU fluorometer. For some time points inorganic nutrients were processed by the Scripps Institute of Oceanography STS/ODF chemistry laboratory

Certified reference materials were used to verify protocols (Inorganic Ventures: QCP-NT, QCP-NUT-1, CGSI1-1). The detection limits were: NO2 = 0.05 uM, NO3 = 0.1 uM, PO4 = 0.05 uM, SiOH4 = 0.2 uM. Values measured below these limits are reported as zero.

## **Production and Respiration**

Production and respiration quantified using Winkler oxygen (Labasque et al., 2004) were measured using the light/dark bottle technique with 24 h incubations at ambient temperature in a sinusoidal incubator (Sanyo MLR-351H) with ~1000 µmol quanta m<sup>-2</sup> sec<sup>-1</sup> peak PAR.

#### **Data Processing Description**

Means, where replicates were available, were calculated and reported with standard deviations. All variable means represent n=2, except pH and DIC where n=3.

NaN = not a number (missing data)

[ table of contents | back to top ]

#### **Related Publications**

Dickson, A.G.; Sabine, C.L. and Christian, J.R. (eds) (2007) Guide to best practices for ocean CO2 measurement. Sidney, British Columbia, North Pacific Marine Science Organization, 191pp. (PICES Special Publication 3; IOCCP Report 8). DOI: https://doi.org/10.25607/OBP-1342 Methods

Holm-Hansen, O., & Riemann, B. (1978). Chlorophyll a Determination: Improvements in Methodology. Oikos, 30(3), 438. doi:<u>10.2307/3543338</u> *Methods* 

Johnson, Z. I., Shyam, R., Ritchie, A. E., Mioni, C., Lance, V. P., Murray, J. W., & Zinser, E. R. (2010). The effect of iron- and light-limitation on phytoplankton communities of deep chlorophyll maxima of the western Pacific Ocean. Journal of Marine Research, 68(2), 283–308. doi:<u>10.1357/002224010793721433</u> *Methods* 

Ritchie, R. J. (2008). Universal chlorophyll equations for estimating chlorophylls a, b, c, and d and total chlorophylls in natural assemblages of photosynthetic organisms using acetone, methanol, or ethanol solvents. Photosynthetica, 46(1), 115–126. doi:<u>10.1007/s11099-008-0019-7</u> *Methods* 

Welschmeyer, N. A. (1994). Fluorometric analysis of chlorophyll a in the presence of chlorophyll b and pheopigments. Limnology and Oceanography, 39(8), 1985–1992. doi:<u>10.4319/lo.1994.39.8.1985</u> *Methods* 

# Parameters

Parameters for this dataset have not yet been identified

[ table of contents | back to top ]

#### Instruments

Dataset- specific Instrument Name	
Generic Instrument Name	Apollo SciTech AS-C3 Dissolved Inorganic Carbon (DIC) analyzer
Generic Instrument Description	A Dissolved Inorganic Carbon (DIC) analyzer, for use in aquatic carbon dioxide parameter analysis of coastal waters, sediment pore-waters, and time-series incubation samples. The analyzer consists of a solid state infrared CO2 detector, a mass-flow controller, and a digital pump for transferring accurate amounts of reagent and sample. The analyzer uses an electronic cooling system to keep the reactor temperature below 3 degrees Celsius, and a Nafion dry tube to reduce the water vapour and keep the analyzer drift-free and maintenance- free for longer. The analyzer can handle sample volumes from 0.1 - 1.5 milliliters, however the best results are obtained from sample volumes between 0.5 - 1 milliliters. It takes approximately 3 minutes per analysis, and measurement precision is plus or minus 2 micromoles per kilogram or higher for surface seawater. It is designed for both land based and shipboard laboratory use.

Dataset- specific Instrument Name	
Generic Instrument Name	BD FACSCalibur Flow Cytometer
Dataset- specific Description	Flow Cytometer: BD FACSCalibur or Invitrogen Attune NxT
Generic Instrument Description	The FACSCalibur flow cytometer is an autonomous benchtop flow cytometer designed for routine cell analysis, assay development, verification and identification of cellular populations. It is equipped with a blue (488 nm) air-cooled argon laser and a red (635 nm) diode laser. For each particle (cell), five optical parameters can be recorded from the 488 nm laser beam excitation: two light scatter signals, namely forward and right angle, and three fluorescences corresponding to emissions in green (530/30 nm BP), orange (585/42 nm BP) and red (670 nm LP) wavelength ranges. A far red fluorescence (661/16 nm BP) induced by the red diode can also be recorded. Data are analysed using BD Biosciences CellQuest software. Optional features include a cell sorting option, allowing users to identify and isolate a population of interest and a HTS option (High-throughput (HT) or Standard (STD) mode), where sample volumes range from 2-10 microlitres in HT mode and 2-200 microlitres in STD mode. An optional BD FACS Loader tube-lifter can be used to verify tube position and rack identification. The instrument has a capture rate of 300 cells per second, supports 40 (12 x 75 mm) tubes per rack, and has an operating temperature ranging from 16-29 degC.

Dataset- specific Instrument Name	Invitrogen Attune NxT
Generic Instrument Name	Flow Cytometer
Generic Instrument Description	Flow cytometers (FC or FCM) are automated instruments that quantitate properties of single cells, one cell at a time. They can measure cell size, cell granularity, the amounts of cell components such as total DNA, newly synthesized DNA, gene expression as the amount messenger RNA for a particular gene, amounts of specific surface receptors, amounts of intracellular proteins, or transient signalling events in living cells. (from: http://www.bio.umass.edu/micro/immunology/facs542/facswhat.htm)

Dataset- specific Instrument Name	Astoria-Pacific A2 autoanalyzer
Generic Instrument Name	Nutrient Autoanalyzer
Dataset- specific Description	Inorganic Nutrients: Astoria-Pacific A2 autoanalyzer (NO3 and SiOH4); Turner 10-AU (NH4)
Generic Instrument Description	Nutrient Autoanalyzer is a generic term used when specific type, make and model were not specified. In general, a Nutrient Autoanalyzer is an automated flow-thru system for doing nutrient analysis (nitrate, ammonium, orthophosphate, and silicate) on seawater samples.

Dataset-specific Instrument Name	YSI ProODO
Generic Instrument Name	Oxygen Sensor
Generic Instrument Description	An electronic device that measures the proportion of oxygen (O2) in the gas or liquid being analyzed

Dataset- specific Instrument Name	Atago PAL-06S
Generic Instrument Name	Refractometer
Generic Instrument Description	A refractometer is a laboratory or field device for the measurement of an index of refraction (refractometry). The index of refraction is calculated from Snell's law and can be calculated from the composition of the material using the Gladstone-Dale relation. In optics the refractive index (or index of refraction) n of a substance (optical medium) is a dimensionless number that describes how light, or any other radiation, propagates through that medium.

Dataset- specific Instrument Name	Vista A366ATC
Generic Instrument Name	Refractometer
Generic Instrument Description	A refractometer is a laboratory or field device for the measurement of an index of refraction (refractometry). The index of refraction is calculated from Snell's law and can be calculated from the composition of the material using the Gladstone-Dale relation. In optics the refractive index (or index of refraction) n of a substance (optical medium) is a dimensionless number that describes how light, or any other radiation, propagates through that medium.

Dataset- specific Instrument Name	YSI Pro30
Generic Instrument Name	Refractometer
Generic Instrument Description	A refractometer is a laboratory or field device for the measurement of an index of refraction (refractometry). The index of refraction is calculated from Snell's law and can be calculated from the composition of the material using the Gladstone-Dale relation. In optics the refractive index (or index of refraction) n of a substance (optical medium) is a dimensionless number that describes how light, or any other radiation, propagates through that medium.

Dataset-specific Instrument Name	YSI ProSolo or Guideline Portasal 8410A
Generic Instrument Name	Salinometer
Generic Instrument Description	A salinometer is a device designed to measure the salinity, or dissolved salt content, of a solution.

Dataset-specific Instrument Name	Cary 4000
Generic Instrument Name	Spectrometer
Dataset-specific Description	pH: Spectrophotometer Cary 4000 with 10 cm cylindrical cell or Genesys 10A VIS with a 10 cm cylindrical cell
Generic Instrument Description	A spectrometer is an optical instrument used to measure properties of light over a specific portion of the electromagnetic spectrum.

Dataset-specific Instrument Name	Genesys 10A VIS
Generic Instrument Name	Spectrometer
Dataset-specific Description	Production and respiration: Incubator: Sanyo MLR-351H; Spectrophotometer: Genesys 10A VIS
Generic Instrument Description	A spectrometer is an optical instrument used to measure properties of light over a specific portion of the electromagnetic spectrum.

Dataset- specific Instrument Name	Orion AQ4500	
Generic Instrument Name	Turbidity Meter	
Generic Instrument Description	A turbidity meter measures the clarity of a water sample. A beam of light is shown through a water sample. The turbidity, or its converse clarity, is read on a numerical scale. Turbidity determined by this technique is referred to as the nephelometric method from the root meaning "cloudiness". This word is used to form the name of the unit of turbidity, the NTU (Nephelometric Turbidity Unit). The meter reading cannot be used to compare the turbidity of different water samples unless the instrument is calibrated. Description from: <a href="http://www.gvsu.edu/wri/education/instructor-s-manual-turbidity-10.htm">http://www.gvsu.edu/wri/education/instructor-s-manual-turbidity-10.htm</a> (One example is the Orion AQ4500 Turbidimeter)	

Dataset- specific Instrument Name	
Generic Instrument Name	Turner Designs Fluorometer 10-AU
Generic Instrument Description	The Turner Designs 10-AU Field Fluorometer is used to measure Chlorophyll fluorescence. The 10AU Fluorometer can be set up for continuous-flow monitoring or discrete sample analyses. A variety of compounds can be measured using application-specific optical filters available from the manufacturer. (read more from Turner Designs, turnerdesigns.com, Sunnyvale, CA, USA)

Dataset-specific Instrument Name	
Generic Instrument Name	Water Temperature Sensor
Dataset-specific Description	Temperature: Thermocouples (VWR#23609-232) in niskin bottle or from in situ probes YSI Pro30, YSI ProODO or YSI ProSo
Generic Instrument Description	General term for an instrument that measures the temperature of the water with which it is in contact (thermometer).

[ table of contents | back to top ]