HPLC pigment concentrations from the Bermuda Atlantic Timeseries Study (BATS) site from 1988-2022

Website: https://www.bco-dmo.org/dataset/893521 Data Type: Cruise Results Version: 1 Version Date: 2023-04-22

Project

» Bermuda Atlantic Time-series Study (BATS)

Programs

- » <u>Ocean Carbon and Biogeochemistry</u> (OCB)
- » <u>U.S. Joint Global Ocean Flux Study</u> (U.S. JGOFS)
- » <u>Ocean Time-series Sites</u> (Ocean Time-series)

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Abstract

Data presented here contain HPLC derived phytoplankton pigments and fluorometric chlorophyll-a from the BATS site for years 1988 to 2022. Water samples are typically collected from 12 depths in the upper 250 meters of the water column, and then filtered under low vacuum through a 25mm GF/F filter. The filter is then flash frozen in liquid nitrogen and stored at -80 degrees C. Shoreside, analysis is performed on an HPLC using a method modified by Dr. R. Bidigare from the Wright et al. (1991) procedure. This method identifies the pigments chlorophyll-c3, chlorophyll-c2, peridinin, 19'-butanoyloxyfucoxanthin, fucoxanthin, 19'-hexanoyloxyfucoxanthin, prasinoxanthin, diadinoxanthin, alloxanthin, diatoxanthin, lutein, zeaxanthin, chlorophyll-b, chlorophyll-a, divinyl chlorophyllide-a, alpha and beta carotene. Additionally, chlorophyll-a and phaeopigments are analyzed using a fluorometric assay.

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Coverage

Spatial Extent: N:33.142 **E**:-62.718 **S**:27.823 **W**:-65.343 **Temporal Extent**: 1988-10-21 - 2022-12-16

Methods & Sampling

Phytoplankton use pigments to absorb energy from the sun to drive photosynthesis. Chlorophyll-a is used as the primary light harvesting molecule while other accessory pigments, such as chlorophyll-b, -c, and carotenoids assist by expanding the light absorption capability of the organism, therefore increasing efficiency and adaptability (Bidigare et al., 2002).

Many individual algal pigments or combinations and ratios are taxon-specific. Therefore, pigment composition from seawater samples can be used to separate major algal groups and result in chemotaxonomic characterization. These analyses can be used to determine phytoplankton community structure and physiological state of the autotrophic assemblage (Wallerstein et al., 1999; Bidigare et al., 2002)

The methodology described here is based on the Protocols for the Joint Global Ocean Flux Study (JGOFS) Core Measurements (BATS, 1997), and describes the use of high performance liquid chromatography (HPLC) for the rapid separation of phytoplankton pigments with detection limits for chlorophylls and carotenoids on the order of one nanogram (Bidigare, 1991). This HPLC method was adopted as BATS protocol in July 1994 (BATS 70 cruise). This method uses less solvent and gives improved peak separation and better resolution at lower concentrations.

Field sampling

Discrete samples are collected monthly using Niskin bottles at the Bermuda Atlantic Time-series Study site from depths ranging from the surface to 250 meters. Expeditious sampling and contamination prevention protocols were used to obtain the best possible samples, since the physico-chemical and biological parameters of the Niskin water become increasingly altered with time spent on deck, especially if in full sunlight. Sea water is filtered using glass fiber filters (GF/F) with standard pore size of 0.7 microns and the filtered samples then flash frozen and stored at -80°C until analysis.

HPLC pigment measurements

Water samples were analyzed for the concentration of various phytoplankton pigments following the method of Wright et al. (1991) as modified by Dr. Robert Bidigare. Pigments present in a seawater sample can be separated by high-performance liquid chromatography (HPLC) based on differences in polarity. Pigment polarities determine how the pigments interact with the solid phase (column) and the mobile phase (solvent) within the HPLC. Pigments that are less polar will be more attracted to the non-polar stationary phase and take longer to pass through than more polar pigments, thus a temporal separation is achieved. The length of time it takes for the pigment to elute is known as the retention time. Under comparable conditions, pigment retention times are determined using a diode array detector (DAD), which detects absorption across a range of wavelengths in the UV-Vis portion of the spectrum. The separated pigments are transported by the flowing mobile phase to the detector, where the solution passes through a flow cell and is dispersed by a diffraction grating. Photodiode arrays detect the light intensity for each wavelength, which is converted to an electrical signal, resulting in a visible peak on a chromatogram. Concentration is proportional to the area of the peak, and can be calculated using calibration factors determined from known standards (aka response factor), in addition to other parameters such as volume of water sampled and dilution factors.

The HPLC currently in use is an Agilent 1100 series. The results from two different wavelengths are reported in this method, 436nm and 450nm. All pigments except divinyl chlorophyll-a produce a signal at 436nm. However, divinyl and monovinyl chl-a cannot be separated at 436nm due to a similar detector response, so 450nm is also used to try and separate mono and divnyl chl-a since divnyl absorbs at this wavelength and monovinyl does not.

Fluorometric measurements

In addition to the HPLC measurements, pigment samples from BATS are also analyzed using fluorometric techniques. Fluorescence is the physical property of compounds to absorb light energy and instantaneously re-emit light at a different wavelength to the absorbed light. Fluorescent compounds, such as chlorophyll-a, have characteristic absorption and emission wavelengths. In fluorometry, a sample is excited at the appropriate absorption wavelength and the intensity of the emitted light is measured using a photodiode detector to give a raw fluorescence recorded value that is proportional to concentration. When compared to reference standards, the raw fluorescence measurements are used to calculate the concentration of the fluorescent material in the sample.

Prior to January 2020, fluorometry was performed on the Turner 10-AU fluorometer, whereas samples are currently analyzed using the Trilogy Fluorometer at BIOS. Data from the fluorometer is compared to the chlorophyll-a data from the HPLC which allows an extra quality control method to ensure data from both methods are similar. This data is being released as part of the BATS dataset since fluorometry is often used

instead of HPLC in the oceanographic community for chlorophyll analysis.

Additional information

Additional details on methods, standardization, and calibration can be found in the BATS methods document (Protocols for the Bermuda Atlantic Time-series Study Core Measurements)

Data Processing Description

BCO-DMO Processing Notes:

- added conventional header with dataset name, PI name, version date
- modified parameter names to conform with BCO-DMO naming conventions
- converted longitude values to decimal degrees (degrees West are negative)
- converted date to yyyy-mm-dd format
- added vessel name based on cruise number

- added filename, cruise_type, cruise_type_text, cruise_number, cast_number, and niskin number columns (extracted from ID column)

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Data Files

File	
bats_pigments.csv	(Comma Separated Values (.csv), 1,002.78 KB) MD5:1c95a23d23cbd911092c45be26c63104
Pigment data measured with HPLC and fluorometer at BATS site from 1988-2022	

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Related Publications

Bermuda Atlantic Time-series Study Methods (online at <u>https://bats.bios.edu/about/cruise-information/</u>) *Methods*

Bidigare R. R., L. Van Heukelem, C. C. Trees, Analysis of algal pigments by high performance liquid chromatography, in Algal Culturing Techniques (R. A. Andersen, ed.), Academic Press, New York, 327-345 (2005). *Methods*

Bidigare, R. R., Van Heukelem, L., & Trees, C. C. (2002). HPLC phytoplankton pigments: sampling, laboratory methods, and quality assurance procedures. Ocean optics protocols for satellite ocean color sensor validation, revision, 3(2), 258-268. *Methods*

Bidigare, R.R., 1991. Analysis of algal chlorophylls and carotenoids. In: D.C. Hurd and D.W. Spencer (Editors), Marine Particles: Analysis and Characterization. Am. Geophys. Union, Washington, DC, pp. 119-123. *Methods*

Grasshoff, K., Kremling, K., & Ehrhardt, M. (Eds.). (1999). Methods of Seawater Analysis. doi:<u>10.1002/9783527613984</u> *Methods*

Holm-Hansen, O., Lorenzen, C. J., Holmes, R. W., & Strickland, J. D. H. (1965). Fluorometric Determination of Chlorophyll. ICES Journal of Marine Science, 30(1), 3–15. doi:<u>10.1093/icesjms/30.1.3</u> *Methods*

JGOFS (1996) Protocols for the joint global ocean flux study (JGOFS) core measurements (Report 19), Bergen, Norway: IOC SCOR. *Methods* Strickland, J. D. H. and Parsons, T. R. (1972). A Practical Hand Book of Seawater Analysis. Fisheries Research Board of Canada Bulletin 157, 2nd Edition, 310 p. *Methods*

Wallerstein, P., & Liebezeit, G. (n.d.). Determination of photosynthetic pigments. Methods of Seawater Analysis, 557–566. https://doi.org/<u>10.1002/9783527613984.ch27</u> *Methods*

Wright, S., Jeffrey, S., Mantoura, R., Llewellyn, C., Bjornland, T., Repeta, D., & Welschmeyer, N. (1991). Improved HPLC method for the analysis of chlorophylls and carotenoids from marine phytoplankton. Marine Ecology Progress Series, 77, 183–196. https://doi.org/<u>10.3354/meps077183</u> *Methods*

Yentsch, C. S., & Menzel, D. W. (1963). A method for the determination of phytoplankton chlorophyll and phaeophytin by fluorescence. Deep Sea Research and Oceanographic Abstracts, 10(3), 221–231. doi:<u>10.1016/0011-7471(63)90358-9</u> *Methods*

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Parameters

Parameter	Description	Units
Vessel	Name of vessel used for cruise	unitless
Cruise_type	Cruise type (BATS Core, Bloom A, or Bloom B)	unitless
Cruise_num	Cruise number	unitless
Cast_type	Cast type (CTD or Hydrocast)	unitless
Cast	Cast Number (1-80 = CTD, 81-99 = Hydrocast)	unitless
Bottle_number	Niskin bottle number	unitless
Date	Date of collection	unitless
ID	Sample identification; a unique number which identifies cruise, cast, and bottle number	unitless
decy	Decimal year	unitless
Latitude	Latitude of sample collection	decimal degrees
Longitude	Longitude of sample collection (West is negative)	decimal degrees
Depth	Collection depth	meters (m)
pl	pigment 1 = Chlorophyll c3	nanograms per kilogram (ng/kg)
p2	pigment 2 = Chlorophyllide_a	nanograms per kilogram (ng/kg)
р3	pigment $3 = Chlorophyll c1 + c2$	nanograms per kilogram (ng/kg)
p4	pigment 4 = Peridinin	nanograms per kilogram (ng/kg)
р5	pigment 5 = 19-prime-Butanoyloxyfucoxanthin	nanograms per kilogram (ng/kg)
р6	pigment 6 = Fucoxanthin	nanograms per kilogram (ng/kg)
p7	pigment 7 = 19-prime-Hexanoyloxyfucoxanthin	nanograms per kilogram (ng/kg)
p8	pigment 8 = Prasinoxanthin	nanograms per kilogram (ng/kg)

p9	pigment 9 = Diadinoxanthin	nanograms per kilogram (ng/kg)
p10	pigment 10 = Alloxanthin	nanograms per kilogram (ng/kg)
p11	pigment 11 = Diatoxanthin	nanograms per kilogram (ng/kg)
p12	pigment 12 = Zeaxanthin + Lutein	nanograms per kilogram (ng/kg)
p13	pigment 13 = Chlorophyll b	nanograms per kilogram (ng/kg)
p14	pigment 14 = Chlorophyll a	nanograms per kilogram (ng/kg)
p15	pigment 15 = a + b Carotene	nanograms per kilogram (ng/kg)
p16_Chl	pigment 16 = fluorometric Chlorophyll a	micrograms per kilogram (ug/kg)
p17_Phae	pigment 17 = fluorometric Phaeopigments	micrograms per kilogram (ug/kg)
p18	pigment 18 = Lutein	nanograms per kilogram (ng/kg)
p19	pigment 19 = Zeaxanthin	nanograms per kilogram (ng/kg)
p20	pigment 20 = alpha-Carotene	nanograms per kilogram (ng/kg)
p21	pigment 21 = beta-Carotene	nanograms per kilogram (ng/kg)
yyyymmdd	Year Month Day of collection	unitless
time	Time of collection	unitless

Instruments

Dataset- specific Instrument Name	Agilent 1100 series with diode array detector
Generic Instrument Name	High-Performance Liquid Chromatograph
Dataset- specific Description	The HPLC currently in use is an Agilent 1100 series
	A High-performance liquid chromatograph (HPLC) is a type of liquid chromatography used to separate compounds that are dissolved in solution. HPLC instruments consist of a reservoir of the mobile phase, a pump, an injector, a separation column, and a detector. Compounds are separated by high pressure pumping of the sample mixture onto a column packed with microspheres coated with the stationary phase. The different components in the mixture pass through the column at different rates due to differences in their partitioning behavior between the mobile liquid phase and the stationary phase.

Dataset- specific Instrument Name	Niskin bottle
Generic Instrument Name	Niskin bottle
	A Niskin bottle (a next generation water sampler based on the Nansen bottle) is a cylindrical, non-metallic water collection device with stoppers at both ends. The bottles can be attached individually on a hydrowire or deployed in 12, 24, or 36 bottle Rosette systems mounted on a frame and combined with a CTD. Niskin bottles are used to collect discrete water samples for a range of measurements including pigments, nutrients, plankton, etc.

Dataset- specific Instrument Name	Turner 10-AU fluorometer
Generic Instrument Name	Turner Designs Fluorometer 10-AU
Dataset- specific Description	Prior to January 2020, fluorometry was performed on the Turner 10-AU fluorometer.
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	Trilogy fluorometer
Generic Instrument Name	Turner Designs Trilogy fluorometer
Dataset- specific Description	Samples are currently analyzed using the Trilogy Fluorometer.
Generic Instrument Description	

Deployments

BATS_cruises

Website	https://www.bco-dmo.org/deployment/58883	
Platform	Unknown Platform	
Report	http://bats.bios.edu/bats-data/	
Start Date	1988-10-20	
Description	Bermuda Institute of Ocean Science established the Bermuda Atlantic Time-series Study with the objective of acquiring diverse and detailed time-series data. BATS makes monthly measurements of important hydrographic, biological and chemical parameters throughout the water column at the BATS Study Site, located at 31 40N, 64 10W.	

Project Information

Bermuda Atlantic Time-series Study (BATS)

Website: http://bats.bios.edu

Coverage: Northwest Sargasso Sea at 31 deg 40' N, 64 deg 10' W

A full description of the BATS research program (including links to the processed BATS data) is available from the BATS Web site (see above for Project URL/ Project Website links). Any data contributed from selected ancillary projects are listed (linked) in the 'Datasets Collection' section below.

Collaborative Research: The Bermuda Atlantic Time-series Study: Sustained Biogeochemical, Ecosystem and Ocean Change Observations and Linkages in the North Atlantic (Years 31-35) *Awards OCE-1756105, OCE-1756054, and OCE-1756312)*

NSF award abstract

Long-term observations over several decades are a powerful tool for investigating ocean physics, biology, and chemistry, and the response of the oceans to environmental change. The Bermuda Atlantic Time-Series Study, known as BATS, has been running continuously since 1988. The research goals of the BATS program are: (1) to improve our understanding of the time-varying components of the ocean carbon cycle and the cycles of related nutrient elements such as nitrogen, phosphorus, and silicon; and, (2) to identify the relevant physical, chemical and ecosystem properties responsible for this variability. In addition, the BATS program has strong and diverse broader impacts, contributing to the field of ocean sciences by providing high quality ocean observations and data for seagoing scientists and modelers, and a framework through which researchers can conceive and test hypotheses. This award will support the operations of the BATS program for five more years.

The primary BATS research themes are as follows: (1) Quantify the role of ocean-atmosphere coupling and climate variability on air-sea exchange of CO2, and carbon export to the ocean interior; (2) Document trends and the controls on the interannual to decadal scale variability in carbon and nutrient cycles to their coupling in the surface and deep ocean via the Redfield Ratio paradigm; (3) Quantify the response of planktonic community structure and function, and impact on biogeochemical cycles to variability in surface fluxes and dynamical processes; (4) Facilitate development, calibration and validation of next generation oceanographic sensors, tools and technologies; and, (5) Generate a dataset that can be utilized by empiricists, modelers and students. This research integrates ocean physics, chemistry and biology into a framework for understanding oceanic processes and ocean change in the North Atlantic subtropical gyre. The existing 29 years of BATS data provide robust constraints on seasonal and interannual variability, the response of the Sargasso Sea ecosystem to natural climate variability, and signal detection of potential ocean changes. This project would extend the BATS program through years 31-35 to address a series of ten interlinked questions through integrated research approaches and a multitude of collaborative efforts. In addition to the themes above, and embedded into the ten questions and approaches, the BATS team will focus on, for example, coupling of particle production and biogeochemistry; revisiting the complexities of the biological carbon pump; oxygen decline; and changes in the hydrography, physics, ocean carbon cycle and biogeochemistry of the Sargasso Sea. The highest quality data observation and collection will be maintained and used to address these questions. Importantly, a wide range of collaborations at the BATS site, spanning the physical and

biogeochemical disciplines, will aid these broad goals. Strong links to community stakeholders, and close collaboration (including methods intercomparisons and personnel exchanges) with the Hawaii Ocean Timeseries are proposed. This work will extend the research findings of the project into educational and training opportunities within and beyond the oceanographic community, including training and mentorship of both undergraduate and graduate students.

Please see the BATS Web site (<u>http://bats.bios.edu</u>) for additional information.

List of References (PDF)

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Program Information

Ocean Carbon and Biogeochemistry (OCB)

Website: <u>http://us-ocb.org/</u>

Coverage: Global

The Ocean Carbon and Biogeochemistry (OCB) program focuses on the ocean's role as a component of the global Earth system, bringing together research in geochemistry, ocean physics, and ecology that inform on and advance our understanding of ocean biogeochemistry. The overall program goals are to promote, plan, and coordinate collaborative, multidisciplinary research opportunities within the U.S. research community and with international partners. Important OCB-related activities currently include: the Ocean Carbon and Climate Change (OCCC) and the North American Carbon Program (NACP); U.S. contributions to IMBER, SOLAS, CARBOOCEAN; and numerous U.S. single-investigator and medium-size research projects funded by U.S. federal agencies including NASA, NOAA, and NSF.

The scientific mission of OCB is to study the evolving role of the ocean in the global carbon cycle, in the face of environmental variability and change through studies of marine biogeochemical cycles and associated ecosystems.

The overarching OCB science themes include improved understanding and prediction of: 1) oceanic uptake and release of atmospheric CO2 and other greenhouse gases and 2) environmental sensitivities of biogeochemical cycles, marine ecosystems, and interactions between the two.

The OCB Research Priorities (updated January 2012) include: ocean acidification; terrestrial/coastal carbon fluxes and exchanges; climate sensitivities of and change in ecosystem structure and associated impacts on biogeochemical cycles; mesopelagic ecological and biogeochemical interactions; benthic-pelagic feedbacks on biogeochemical cycles; ocean carbon uptake and storage; and expanding low-oxygen conditions in the coastal and open oceans.

U.S. Joint Global Ocean Flux Study (U.S. JGOFS)

Website: http://usjgofs.whoi.edu/

Coverage: Global

The United States Joint Global Ocean Flux Study was a national component of international JGOFS and an integral part of global climate change research.

The U.S. launched the Joint Global Ocean Flux Study (JGOFS) in the late 1980s to study the ocean carbon cycle. An ambitious goal was set to understand the controls on the concentrations and fluxes of carbon and associated nutrients in the ocean. A new field of ocean biogeochemistry emerged with an emphasis on quality measurements of carbon system parameters and interdisciplinary field studies of the biological, chemical and physical process which control the ocean carbon cycle. As we studied ocean biogeochemistry, we learned that our simple views of carbon uptake and transport were severely limited, and a new "wave" of ocean science was born. U.S. JGOFS has been supported primarily by the U.S. National Science Foundation in collaboration with the National Oceanic and Atmospheric Administration, the National Aeronautics and Space Administration, the Department of Energy and the Office of Naval Research. U.S. JGOFS, ended in 2005 with the conclusion of the Synthesis and Modeling Project (SMP).

Ocean Time-series Sites (Ocean Time-series)

Coverage: Bermuda, Cariaco Basin, Hawaii

Program description text taken from Chapter 1: Introduction from the **Global Intercomparability in a Changing Ocean: An International Time-Series Methods Workshop** report published following the workshop held November 28-30, 2012 at the Bermuda Institute of Ocean Sciences. The full report is available from the workshop Web site hosted by US OCB: <u>http://www.whoi.edu/website/TS-workshop/home</u>

Decades of research have demonstrated that the ocean varies across a range of time scales, with anthropogenic forcing contributing an added layer of complexity. In a growing effort to distinguish between natural and human-induced earth system variability, sustained ocean time-series measurements have taken on a renewed importance. Shipboard biogeochemical time-series represent one of the most valuable tools scientists have to characterize and quantify ocean carbon fluxes and biogeochemical processes and their links to changing climate (Karl, 2010; Chavez et al., 2011; Church et al., 2013). They provide the oceanographic community with the long, temporally resolved datasets needed to characterize ocean climate, biogeochemistry, and ecosystem change.

The temporal scale of shifts in marine ecosystem variations in response to climate change are on the order of several decades. The long-term, consistent and comprehensive monitoring programs conducted by time-series sites are essential to understand large-scale atmosphere-ocean interactions that occur on interannual to decadal time scales. Ocean time-series represent one of the most valuable tools scientists have to characterize and quantify ocean carbon fluxes and biogeochemical processes and their links to changing climate.

Launched in the late 1980s, the US JGOFS (Joint Global Ocean Flux Study; <u>http://usjgofs.whoi.edu</u>) research program initiated two time-series measurement programs at Hawaii and Bermuda (HOT and BATS, respectively) to measure key oceanographic measurements in oligotrophic waters. Begun in 1995 as part of the US JGOFS Synthesis and Modeling Project, the CARIACO Ocean Time-Series (formerly known as the CArbon Retention In A Colored Ocean) Program has studied the relationship between surface primary production, physical forcing variables like the wind, and the settling flux of particulate carbon in the Cariaco Basin.

The objective of these time-series effort is to provide well-sampled seasonal resolution of biogeochemical variability at a limited number of ocean observatories, provide support and background measurements for process-oriented research, as well as test and validate observations for biogeochemical models. Since their creation, the BATS, CARIACO and HOT time-series site data have been available for use by a large community of researchers.

Data from those three US funded, ship-based, time-series sites can be accessed at each site directly or by selecting the site name from the Projects section below.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	<u>OCE-0752366</u>
NSF Division of Ocean Sciences (NSF OCE)	<u>OCE-1756105</u>