Spectrophotometer absorbance for incubations from iodine radiotracer incubation experiments conducted on the R/V Atlantic Explorer cruise AE1825 with samples collected at BATS and Hydrostation S in September of 2018

Website: https://www.bco-dmo.org/dataset/914962
Data Type: experimental
Version: 1
Version Date: 2023-11-14

Project
» Collaborative Research: Experimental constraints on the rates and mechanisms of iodine redox transformations in seawater (Iodine Redox)

Contributors	Affiliation	Role
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Abstract
This dataset includes spectrophotometer absorbance for selected incubations showing shift in trough location at 320nm from experiments conducted on the R/V Atlantic Explorer (cruise number AE1825) in September, 2018. Samples were collected from the Bermuda Atlantic Time Series (BATS) and Hydrostation S (HYDRO) (32°N, 64°W) at 21 and 10 separate depths, respectively, between 1-4500m (BATS) and 1-500m (Hydro). See "Related Datasets" section for other data from these experiments which include 129I/127I isotope ratios of selected incubations and incubation and depth profile iodine redox (I-, IO3-, DOI) concentration measurements.

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Coverage

Spatial Extent: **Lat**:32.165 **Lon**:-64.501
Temporal Extent: 2018-09-11 - 2018-09-18

Methods & Sampling

Seawater was collected from the Bermuda Atlantic Time Series (BATS) and Hydrostation S (Hydro) sites in the Sargasso Sea in September 2018. Depth profile investigations at BATS were taken at 32.343ºN 64.594ºW at 21 separate depths between 1m and 4500m. Hydrostation S samples were taken at 32.165ºN 64.501ºW at 10 depths between 1m and 500m. Incubation water was taken from two depths (1m and 240m) and collected into four carboys (two euphotic (1m) and two subphotic (240m)). One carboy from each depth was filtered using a 0.2µm filter to remove bacteria and other biology and particles while another was left unfiltered. 129I

(t1/2 ~15.7 My) (Eckert and Ziegler Isotope Products ©) (Hardisty et al., 2020, Hardisty et al., 2021), was added directly to each of the carboys at a targeted concentration of ~70nM 129I- for investigating iodine redox reactions in natural seawater over time. 129I- was added before aliquoting the carboy water for individual incubations to ensure homogenous 129I- concentrations at t0 for all incubations. 200ml from each carboy were fractionated into separated incubation containers. Samples for t0 were immediately subsampled from spiked incubation containers, with this and subsequent (t1, t2, tf) subsamples being ~50ml. All subsamples were immediately filtered at 0.2µm to end interaction with biology after sampling. Subsamples were refrigerated and stored at 4°C until they returned to Michigan State University and were frozen for storage.

Five incubation factors were used to create 20 incubation trials using a ship-deck light-filtering incubator to mimic at-depth light filtration, cooled with a continuous flow of ambient surface seawater and stored in translucent and amber Nalgene bottles for dark incubations: each done in triplicate. Factors included: 1) filtering of samples through a 0.2µm syringe filter, meant as a control to screen filtered seawater of bacteria and macro-organisms and particles, kept in either the light or the dark depending on incubation, (Campos et al., 1996, Farrenkoph et al., 1997, Hardisty et al., 2020); 2) addition of O_2^- dismutase (SOD) to incubations both filtered and unfiltered, but all left in the dark, intended as a control to remove ambient O_2^- in seawater (Sutherland et al., 2020, Li et al., 2012, Diaz et al., 2013); 3) addition of superoxide thermal source (SOTS) and hydrogen peroxide (H_2O_2) to filtered samples kept in the dark in separate experiments, both suspected of being able to aid in oxidation of I- to IO_3^- in seawater, 4) unfiltered water in the dark to determine the role, if any, of photochemical reactions that may cause the reduction of IO_3^- to I- in the presence of organic matter (Chance et al., 2014, Spokes and Liss 1996); five additions of $MnCl_2$ to iterations of the above in order to consider the potential of preferential Mn^{2+} oxidation relative to I-. Note that controls 2 and 5 were only relevant if I- oxidation was detected in the other controls.

Seawater for samples was taken from both photic (1m) and subphotic (240m) depths and collected in carboys. Superoxide thermal source was kept frozen (-80°C) until it was added by pipette to two of the incubations (11 and 19) as a combination of 1ml dimethyl sulfoxide (DMSO) + 1mg SOTS (3027.55µM SOTS) (Cayman Chemicals, CAS number 223507-96-8) at a volume targeting 10 nM O_2^- (Heller and Croot, 2010). This was made fresh daily immediately before adding to samples and added daily to account for natural decay. The O_2^- concentration of the SOTS stock was not analyzed but O_2^- concentration was analyzed in one experiment a few hours post-SOTS addition – to allow to reach steady state concentrations – to confirm O_2^- accumulation near target levels. Hydrogen peroxide (30%) was added at a volume targeting 50nM H_2O_2 in each solution. SOD was added by pipette daily – thus accounting for decay and titration via potentially newly formed O_2^- within the incubations – from a stock volume of 4kU/ml to incubations to produce samples with SOD volume of 0.32kU/ml. Given potential long oxidation timescales of I-, all incubations were performed over a 140-hour time period, with subsamples collected for iodine species measurement at t0, ~t40, ~t88, and ~t140 hours.

The steady-state concentration of O_2^- was determined as previously described with some minor modifications (Sutherland et al., 2020). Water samples were collected using 12L Ocean Test Equipment bottles on a 24-position Sea-Bird CTD rosette. Samples were transferred into dark, acid washed bottles and measured between 30 mins and six hours of the collection time. Thirty minutes was chosen as a sample delay period because it is greater than 10 half-lives of O_2^- in typical marine waters, meaning that any O_2^- remaining is the result of light-independent O_2^- production by microbial communities in the bottles (Roe et al., 2016). Samples collected above the thermocline were incubated on deck with continuously flowing surface water and samples below the thermocline were incubated at 4°C. Superoxide concentrations were measured using an FeLume Mini (Waterville Analytical) and the O_2^--specific chemiluminescent probe methyl cypridina luciferin analog (MCLA, Santa Cruz Biotechnology, Rose et al. 2008). Recent work using these methods has demonstrated that filtration of natural seawater can produce additional O_2^- (Roe et al. 2016). To avoid introducing this bias into sample measurements, we used the following equation: $[O_2^-]sample=[O_2^-]USW - [O_2^-]AFSW$, where $[O_2^-]USW$ represents the measured concentration of O_2^- in unfiltered seawater (USW) and $[O_2^-]AFSW$ represents the concentration of O_2^- in aged (>24 hours) filtered (0.2µm Sterivex filter) seawater (AFSW) amended with 75µM diethylene-triaminepentaacetic acid (DTPA) to complex any metals present in the sample. Each measurement consisted of running a 25mL USW sample through the FeLume system (3mL/min) for several minutes until a steady signal was recorded. After a steady signal was recorded, 2µL superoxide dismutase (SOD; Superoxide Dismutase from bovine erythrocytes >3,000 U mg-1, Sigma, stock prepared in DI water to 4,000 U/mL) was added to the sample to quench all O_2^- in the sample. The same procedure was followed for the AFSW samples. The reported O_2^- concentrations represent the difference between the USW and the AFSW concentrations, the latter allowing us to eliminate the portion of the measured signal due to MCLA auto-oxidation in each particular sample matrix. Calibration curves were generated daily from three or more paired observations of time-zero O_2^- concentration (dependent variable) and extrapolated chemiluminescence (independent variable) using linear regression. Because chemiluminescence values were

baseline-corrected, regression lines were forced through the origin. Calibrations yielded highly linear curves (typically R2 >0.9), with a typical sensitivity of one chemiluminescence unit per pM O2−.

The concentrations of IO3- and I- from the incubations were determined at MSU after sample collection via the methods outlined by Jickells (1988) for spectrophotometry (IO3-) and by Hardisty et al., (2020) for ion exchange chromatography (I-, DOI) and ICP-MS.

See the related dataset "BATS/Hydrostation S: Iodine speciation and isotope ratio values" (https://www.bco-dmo.org/dataset/914915) for details of the iodine isotope ratio methodology.

Data Processing Description

Matlab was used for processing iodine isotope data.

BCO-DMO Processing Description

* Sheet name "Supplementary Table 3" of file "Schnur_BATS_Supplement_Table_BCO-DMO_20230817.xlsx" was imported into the BCO-DMO data system as the primary table for this dataset.
* Column names adjusted to conform to BCO-DMO naming conventions designed to support broad re-use by a variety of research tools and scripting languages. [Only numbers, letters, and underscores. Can not start with a number]
* Sheet name "Supplementary Table 4" of file "Schnur_BATS_Supplement_Table_BCO-DMO_20230817.xlsx" added as a supplemental file "ICP-MS runs blanks and yields" to this dataset.

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Related Publications

Roe, K. L., Schneider, R. J., Hansel, C. M., & Voelker, B. M. (2016). Measurement of dark, particle-generated superoxide and hydrogen peroxide production and decay in the subtropical and temperate North Pacific Ocean. Deep Sea Research Part I: Oceanographic Research Papers, 107, 59–69. doi:10.1016/j.dsr.2015.10.012
Methods

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Related Datasets

IsRelatedTo

Hardisty, D., Sutherland, K. (2023) **Iodine speciation and superoxide concentration depth profile value from iodine radiotracer incubation experiments conducted on the R/V Atlantic Explorer cruise AE1825 with samples collected at BATS and Hydrostation S in September of 2018.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2023-11-14 http://lod.bco-dmo.org/id/dataset/914955 [view at BCO-DMO]
Relationship Description: Data from the same radiotracer incubation experiments conducted on the R/V Atlantic Explorer cruise AE1825 with samples collected at BATS and Hydrostation S in September of 2018.

Hardisty, D., Sutherland, K., Schnur, A. (2023) **Iodine speciation and isotope ratio values from iodine radiotracer incubation experiments conducted on the R/V Atlantic Explorer cruise AE1825 with samples collected at BATS and Hydrostation S in September of 2018.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2023-11-14 http://lod.bco-dmo.org/id/dataset/914915 [view at BCO-DMO]
Relationship Description: Data from the same radiotracer incubation experiments conducted on the R/V Atlantic Explorer cruise AE1825 with samples collected at BATS and Hydrostation S in September of 2018.

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Parameters

Parameter	Description	Units
incubation_num	Incubation number 1-20	unitless
sample	Sample number as part of an incubation beginning with "DH-BATS2018-"	unitless
nm	nm value at which absorbance was measured	nanometers (nm)
abs	Absorbance value measured at nm wavelengths ("nm" column)	unknown
timepoint	Timepoint of incubation, between t0 and tfinal	unitless
ROS	Reactive oxygen species factor for sample	unitless
hours	Timepoint in hours	hours

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Deployments

AE1825

Website	https://www.bco-dmo.org/deployment/914952
Platform	R/V Atlantic Explorer
Start Date	2018-09-10
End Date	2018-09-14

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Project Information

Collaborative Research: Experimental constraints on the rates and mechanisms of iodine redox transformations in seawater (Iodine Redox)

Coverage: Martha's Vineyard Sound and the Eastern Tropical North Pacific oxygen deficient zone

NSF Award Abstract:
The goal of this study is to constrain the chemical and biological reactions controlling the iodine cycle in the marine environment. Seawater iodine plays a key role in the cycling of carbon, dissolved oxygen, and ozone, and has been hypothesized to also influence the elemental cycles of manganese and nitrogen. The composition of iodine in sedimentary rocks has also been proposed as an archive of ancient seawater oxygen availability. Unfortunately, few constraints currently exist on iodine reaction rates and mechanisms in seawater, limiting quantitative applications. To remedy this, scientists from Michigan State University (MSU) and Woods Hole Institute of Oceanography (WHOI) will use a rare iodine isotope, iodine-129, as a tracer of iodine chemical reactions in controlled seawater incubations designed to determine specific reaction rates and mechanisms from two end-member environments: well-oxygenated mid-Atlantic seawater as part of the United Kingdom-based Atlantic Meridional Transect (AMT) annual time series and low oxygen zones in the Pacific Ocean. The project will contribute to building the future United States STEM (Science Technology, Engineering and Mathematics)-trained workforce via the training of one graduate student and at least one undergraduate student from the campus of MSU. This includes hands-on field training and experience through two research cruises, extensive analytical training at WHOI, as well as experience in Earth system modeling simulations of iodine-oxygen interactions at the modern and ancient sea surface. The experimental constraints are designed to inform broader modeling of iodine-related chemical cycles for scientific communities including atmospheric and marine chemists, environmental regulators, and geologists.

The redox potential of iodate-iodide is uniquely poised for probable applications as both a redox tracer of Oxygen Minimum Zone (OMZ)-like conditions in modern and past oceans as well as a critical component of air-sea exchange reactions regulating tropospheric ozone levels. However, a currently limited understanding of the first-order rates and mechanisms of iodine redox transformations in seawater limits applications, which our research seeks to address. Specifically: (1) Marine iodate production, the oxidized and most abundant species, has yet to be observed experimentally despite the fact that most marine inputs from estuarine and other sources consist of the reduced species, iodide. Mass balance demands that in situ marine oxidation is widespread. The oxidant is unknown, but it is unlikely oxygen (O2) due to thermodynamic barriers. (2) Unconstrained in situ processes drive significant accumulation of reduced iodide in photic waters globally, particularly at low latitudes, which ultimately act as a major tropospheric ozone sink. (3) Constraints on rates and reaction mechanisms in OMZs are limited despite iodine being amongst the first redox-sensitive species to reduce under declining O2. We will employ an isotope tracer—iodine-129 as both iodide and iodate—in shipboard seawater incubation experiments to determine the rates and mechanisms of iodine redox transformations governing these widespread trends. This method will be deployed across the largest known gradients in marine iodine speciation—the Eastern Tropical North Pacific oxygen minimum zone and a latitudinal transect of photic and sub-photic waters as part of the Atlantic Meridional Transect. Incubation experiments from these cruises will be used to place first order constraints on the rates of iodine redox transformations at high- and low-[O2], the loci of most intense iodine redox cycling (both vertically and spatially), as well as the mechanisms driving redox transformations. Controls will test oxidants, biotic versus abiotic processes, as well as interactions and comparisons with similar redox cycles such as manganese and nitrogen.

This award reflects NSF's statutory mission and has been deemed worthy of support through evaluation using the Foundation's intellectual merit and broader impacts review criteria.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1829406

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