

# 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

**Website:** <https://www.bco-dmo.org/dataset/914915>

**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
<a href="#">Hardisty, Dalton</a>	Michigan State University (MSU)	Principal Investigator
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## Abstract

This dataset includes iodine speciation and isotope ratio values from iodine radiotracer incubation 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 incubation and depth profile iodine redox (I<sup>-</sup>, IO<sub>3</sub><sup>-</sup>, DOI) concentration measurements and measured spectrophotometer absorbance values for three incubations.

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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 32.343°N 64.594°W at 21 separate depths between 1m and 4500m. Hydrostation S samples were taken at 32.165°N 64.501°W 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. 129l

( $t_{1/2} \sim 15.7$  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  $\sim 70$  nM  $^{129}\text{I}^-$  for investigating iodine redox reactions in natural seawater over time.  $^{129}\text{I}^-$  was added before aliquoting the carboy water for individual incubations to ensure homogenous  $^{129}\text{I}^-$  concentrations at  $t_0$  for all incubations. 200 ml from each carboy were fractionated into separated incubation containers. Samples for  $t_0$  were immediately subsampled from spiked incubation containers, with this and subsequent ( $t_1$ ,  $t_2$ ,  $t_f$ ) subsamples being  $\sim 50$  ml. All subsamples were immediately filtered at  $0.2 \mu\text{m}$  to end interaction with biology after sampling. Subsamples were refrigerated and stored at  $4^\circ\text{C}$  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  $0.2 \mu\text{m}$  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  $\text{O}_2^-$  dismutase (SOD) to incubations both filtered and unfiltered, but all left in the dark, intended as a control to remove ambient  $\text{O}_2^-$  in seawater (Sutherland et al., 2020, Li et al., 2012, Diaz et al., 2013); 3) addition of superoxide thermal source (SOTS) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) to filtered samples kept in the dark in separate experiments, both suspected of being able to aid in oxidation of  $\text{I}^-$  to  $\text{IO}_3^-$  in seawater, 4) unfiltered water in the dark to determine the role, if any, of photochemical reactions that may cause the reduction of  $\text{IO}_3^-$  to  $\text{I}^-$  in the presence of organic matter (Chance et al., 2014, Spokes and Liss 1996); five additions of  $\text{MnCl}_2$  to iterations of the above in order to consider the potential of preferential  $\text{Mn}^{2+}$  oxidation relative to  $\text{I}^-$ . Note that controls 2 and 5 were only relevant if  $\text{I}^-$  oxidation was detected in the other controls.

Seawater for samples was taken from both photic (1 m) and subphotic (240 m) depths and collected in carboys. Superoxide thermal source was kept frozen ( $-80^\circ\text{C}$ ) until it was added by pipette to two of the incubations (11 and 19) as a combination of 1 ml dimethyl sulfoxide (DMSO) + 1 mg SOTS ( $3027.55 \mu\text{M}$  SOTS) (Cayman Chemicals, CAS number 223507-96-8) at a volume targeting 10 nM  $\text{O}_2^-$  (Heller and Croot, 2010). This was made fresh daily immediately before adding to samples and added daily to account for natural decay. The  $\text{O}_2^-$  concentration of the SOTS stock was not analyzed but  $\text{O}_2^-$  concentration was analyzed in one experiment a few hours post-SOTS addition – to allow to reach steady state concentrations – to confirm  $\text{O}_2^-$  accumulation near target levels. Hydrogen peroxide (30%) was added at a volume targeting 50 nM  $\text{H}_2\text{O}_2$  in each solution. SOD was added by pipette daily – thus accounting for decay and titration via potentially newly formed  $\text{O}_2^-$  within the incubations – from a stock volume of 4 kU/ml to incubations to produce samples with SOD volume of 0.32 kU/ml. Given potential long oxidation timescales of  $\text{I}^-$ , all incubations were performed over a 140-hour time period, with subsamples collected for iodine species measurement at  $t_0$ ,  $\sim t_{40}$ ,  $\sim t_{88}$ , and  $\sim t_{140}$  hours.

The concentrations of  $\text{IO}_3^-$  and  $\text{I}^-$  from the incubations were determined at MSU after sample collection via the methods outlined by Jickells (1988) for spectrophotometry ( $\text{IO}_3^-$ ) and by Hardisty et al., (2020) for ion exchange chromatography ( $\text{I}^-$ , DOI) and ICP-MS.

Iodine isotope ratios were determined via the methods outlined in Hardisty et al., (2020) and Hardisty et al., (2021) using chromatographic separation and subsequent analysis via multi-collector ICP-MS (MC-ICP-MS).

See the related dataset "BATS/Hydrostation S: iodine speciation and superoxide concentration" (<https://www.bco-dmo.org/dataset/914955>) for details of the steady-state concentration of  $\text{O}_2^-$  methodology.

## Data Processing Description

Matlab was used for processing iodine isotope data.

## BCO-DMO Processing Description

\* Sheet name "Table 1" 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]

\* ISO\_DateTime\_UTC added in ISO 8601 format using the datetime provided in time zone "AST" which was assumed to be Atlantic Standard Time (AST) which is UTC-4. Confirming with submitter it is not ADT UTC-3 since this dataset is in september.

\* 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

Campos, M. L. A. M., Farrenkopf, A. M., Jickells, T. D., & Luther, G. W. (1996). A comparison of dissolved iodine cycling at the Bermuda Atlantic Time-series Station and Hawaii Ocean Time-series Station. Deep Sea Research Part II: Topical Studies in Oceanography, 43(2-3), 455-466. [https://doi.org/10.1016/0967-0645\(95\)00100-x](https://doi.org/10.1016/0967-0645(95)00100-x)  
*Methods*

Chance, R., Baker, A. R., Carpenter, L., & Jickells, T. D. (2014). The distribution of iodide at the sea surface. Environ. Sci.: Processes Impacts, 16(8), 1841-1859. <https://doi.org/10.1039/c4em00139g>  
*Methods*

Diaz, J. M., Hansel, C. M., Voelker, B. M., Mendes, C. M., Andeer, P. F., & Zhang, T. (2013). Widespread Production of Extracellular Superoxide by Heterotrophic Bacteria. Science, 340(6137), 1223-1226. <https://doi.org/10.1126/science.1237331>  
*Methods*

Farrenkopf, A. M., Dollhopf, M. E., Chadhain, S. N., Luther, G. W., & Neilson, K. H. (1997). Reduction of iodate in seawater during Arabian Sea shipboard incubations and in laboratory cultures of the marine bacterium Shewanella putrefaciens strain MR-4. Marine Chemistry, 57(3-4), 347-354. [https://doi.org/10.1016/S0304-4203\(97\)00039-x](https://doi.org/10.1016/S0304-4203(97)00039-x)  
*Methods*

Hardisty, D. S., Horner, T. J., Evans, N., Moriyasu, R., Babbin, A. R., Wankel, S. D., ... Nielsen, S. G. (2021). Limited iodate reduction in shipboard seawater incubations from the Eastern Tropical North Pacific oxygen deficient zone. Earth and Planetary Science Letters, 554, 116676. doi:[10.1016/j.epsl.2020.116676](https://doi.org/10.1016/j.epsl.2020.116676)  
*Methods*

Hardisty, D. S., Horner, T. J., Wankel, S. D., Blusztajn, J., & Nielsen, S. G. (2020). Experimental observations of marine iodide oxidation using a novel sparge-interface MC-ICP-MS technique. Chemical Geology, 532, 119360. doi:[10.1016/j.chemgeo.2019.119360](https://doi.org/10.1016/j.chemgeo.2019.119360)  
*Methods*

Jickells, T. D., Boyd, S. S., & Knap, A. H. (1988). Iodine cycling in the Sargasso Sea and the Bermuda inshore waters. Marine Chemistry, 24(1), 61-82. [https://doi.org/10.1016/0304-4203\(88\)90006-0](https://doi.org/10.1016/0304-4203(88)90006-0)  
*Methods*

Li, H.-P., Yeager, C. M., Brinkmeyer, R., Zhang, S., Ho, Y.-F., Xu, C., Jones, W. L., Schwehr, K. A., Otosaka, S., Roberts, K. A., Kaplan, D. I., & Santschi, P. H. (2012). Bacterial Production of Organic Acids Enhances H<sub>2</sub>O<sub>2</sub>-Dependent Iodide Oxidation. Environmental Science & Technology, 46(9), 4837-4844. <https://doi.org/10.1021/es203683v>  
*Methods*

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](https://doi.org/10.1016/j.dsr.2015.10.012)  
*Methods*

Rose, A. L., Webb, E. A., Waite, T. D., & Moffett, J. W. (2008). Measurement and Implications of Nonphotochemically Generated Superoxide in the Equatorial Pacific Ocean. Environmental Science & Technology, 42(7), 2387-2393. <https://doi.org/10.1021/es7024609>  
*Methods*

Spokes, L. J., & Liss, P. S. (1996). Photochemically induced redox reactions in seawater, II. Nitrogen and iodine. Marine Chemistry, 54(1-2), 1-10. [https://doi.org/10.1016/0304-4203\(96\)00033-3](https://doi.org/10.1016/0304-4203(96)00033-3)  
*Methods*

Sutherland, K. M., Wankel, S. D., & Hansel, C. M. (2020). Dark biological superoxide production as a significant flux and sink of marine dissolved oxygen. *Proceedings of the National Academy of Sciences*, 117(7), 3433–3439. <https://doi.org/10.1073/pnas.1912313117>  
*Methods*

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## Related Datasets

### IsRelatedTo

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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. (2023) **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.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2023-11-14 <http://lod.bco-dmo.org/id/dataset/914962> [[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
sample	Sample number as part of an incubation beginning with "DH-BATS2018-"	unitless
incubation_num	Incubation number 1-20	unitless
timepoint	Timepoint of incubation, between t0 and tfinal	unitless
hours	Timepoint in hours	hours
date_time_collected_AST	Date and time of seawater sample collection in Atlantic Standard Time	unitless
depth_m	Depth of sample taken	meters
iodate_spec_nM	Concentration of iodate measured on spectrophotometer	nanomolar (nM)
iodate_ICPMS_nM	Concentration of iodate measured on an Inductively-Coupled Plasma Mass Spectrometer (ICPMS)	nanomolar (nM)
DOI_ICPMS_nM	Concentration of dissolved organic iodine (DOI) measured on an Inductively-Coupled Plasma Mass Spectrometer (ICPMS)	nanomolar (nM)
iodide_ICPMS_nM	Concentration of iodide measured on an Inductively-Coupled Plasma Mass Spectrometer (ICPMS)	nanomolar (nM)
Riodate	Ratio iodate 129I/127I. Ratio of iodine radioactive isotope 129I to stable isotope 127I in iodate (IO3-).	unitless
Riodide	Ratio of iodide 129I/127I. Ratio of iodine radioactive isotope 129I to stable isotope 127I in iodide (I-).	unitless
RDOI	Ratio of DOI 129I/127I. Ratio of iodine radioactive isotope 129I to stable isotope 127I in dissolved inorganic iodine (DOI).	unitless
notes	Special notes for dataset	unitless
ISO_DateTime_Collected_UTC	Date and time of seawater sample collection in UTC time zone. ISO 8601 format.	unitless

## Instruments

<b>Dataset-specific Instrument Name</b>	Triple Quadrupole Inductively-Coupled Plasma Mass Spectrometer
<b>Generic Instrument Name</b>	Inductively Coupled Plasma Mass Spectrometer
<b>Dataset-specific Description</b>	All iodide and DOI concentrations were measured via a Triple Quadrupole Inductively-Coupled Plasma Mass Spectrometry (ICP-MS-TQ) after ion exchange chromatography with AG1-X8 resin (Hardisty 2020) was used to separate species from whole seawater samples.
<b>Generic Instrument Description</b>	An ICP Mass Spec is an instrument that passes nebulized samples into an inductively-coupled gas plasma (8-10000 K) where they are atomized and ionized. Ions of specific mass-to-charge ratios are quantified in a quadrupole mass spectrometer.

<b>Dataset-specific Instrument Name</b>	ThermoFinnigan Neptune MC-ICP-MS
<b>Generic Instrument Name</b>	Multi Collector Inductively Coupled Plasma Mass Spectrometer
<b>Dataset-specific Description</b>	All iodine isotope ratios were measured on a ThermoFinnigan Neptune MC-ICP-MS at the Woods Hole Oceanographic Institute (WHOI) Plasma Facility (Hardisty et al., 2020).
<b>Generic Instrument Description</b>	A Multi Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS) is a type of mass spectrometry where the sample is ionized in a plasma (a partially ionized gas, such as Argon, containing free electrons) that has been generated by electromagnetic induction. A series of collectors is used to detect several ion beams simultaneously. A MC-ICPMS is a hybrid mass spectrometer that combines the advantages of an inductively coupled plasma source and the precise measurements of a magnetic sector multicollector mass spectrometer. The primary advantage of the MC-ICPMS is its ability to analyze a broader range of elements, including those with high ionization potential that are difficult to analyze by Thermal Ionization Mass Spectrometry (TIMS). The ICP source also allows flexibility in how samples are introduced to the mass spectrometer and allows the analysis of samples introduced either as an aspirated solution or as an aerosol produced by laser ablation.

<b>Dataset-specific Instrument Name</b>	VWR UV-Vis Scanning 3100 PC spectrophotometer
<b>Generic Instrument Name</b>	Spectrophotometer
<b>Dataset-specific Description</b>	All iodate concentrations were measured via spectrophotometry on a VWR UV-Vis Scanning 3100 PC spectrophotometer and accompanying UV-Vis Analyst software via a method outlined by Jickells (1988).
<b>Generic Instrument Description</b>	An instrument used to measure the relative absorption of electromagnetic radiation of different wavelengths in the near infra-red, visible and ultraviolet wavebands by samples.

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## Deployments

## AE1825

Website	<a href="https://www.bco-dmo.org/deployment/914952">https://www.bco-dmo.org/deployment/914952</a>
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 (O<sub>2</sub>) 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 O<sub>2</sub>. 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-photoc 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-[O<sub>2</sub>], 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
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1829406</a>

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