

# Iodine speciation and isotope data from iodine tracer experiments at the WHOI Environmental Systems Laboratory on Martha's Vineyard Sound

**Website:** <https://www.bco-dmo.org/dataset/865249>

**Data Type:** Other Field Results

**Version:** 1

**Version Date:** 2022-01-04

## 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 iodine speciation and isotope measurements from iodine tracer experiments. Water samples were collected from a depth of 5 meters at the Woods Hole Oceanographic Institution's Environmental Systems Laboratory on Martha's Vineyard Sound, Massachusetts, USA.

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## Acquisition Description

See Hardisty et al., 2020 for a detailed description. A brief description is provided below.

Seawater was collected from Martha's Vineyard Sound at the Woods Hole Oceanographic Institution's (WHOI) Environmental Systems Laboratory (ESL). ESL intakes seawater from polypropylene pipes located approximately 200 meters (m) offshore from WHOI's Quissett Campus where water depths reach ~5 m. The pipes are located at approximately 0.5 m from the bottom and contain approximately 2.5 cm mesh.

We performed four separate incubation treatments. A large t0 batch was made for each experimental treatment, but each individual time point was allocated into a separate incubation vial, such that incubations were performed individually for each time point. Each treatment included independently

incubated duplicates for each time point (10 mL). A t0 sub-sample was collected immediately following the addition of the Iodine-129 spike and sub-samples were harvested periodically over the course of 67 days. In order to prevent de-oxygenation and subsequent IO<sub>3</sub><sup>-</sup> reduction, the seawater was kept aerated through the use of loose caps, which minimized any contamination through airborne particles but maintained equilibrium between the headspace and ambient atmosphere. The incubations were maintained on a shaker table at 180 rpm throughout the duration of the experiment.

The treatments from seawater collected from the ESL coastal station included: A.) unamended seawater; B.) seawater passed through passive sand-bed filtration (~0.5 mm) C.) a "kill treatment" which consisted of seawater passed through a 0.22-micrometer (um) filter and subsequently irradiated with UV light at 254 nm.

Incubations were conducted under both ambient laboratory light near an uncovered window and dark conditions, all at room temperature. For each experiment, the 129I spike was gravimetrically added, allowing for quantification of initial seawater I<sup>-</sup> concentrations.

Upon harvesting each time point, samples were immediately filtered (0.22 um syringe-filter) and stored at 4°C to maintain speciation.

The oxidized iodine, or IOX (IO<sub>3</sub><sup>-</sup> + dissolved organic iodine), and I<sup>-</sup> were separated according to the chromatographic method described in detail in Hardisty et al., 2020. For the unamended seawater and "kill treatment", the time points were put through the chromatographic separation <7 days after collection.

## Processing Description

### Data Processing:

Matlab was used for processing iodine isotope data.

### BCO-DMO Processing:

- Adjusted field/parameter names to comply with BCO-DMO naming conventions;
- Missing data identifier 'NA' replaced with 'nd' (BCO-DMO's default missing data identifier);
- Added a conventional header with dataset name, PI names, version date.

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## Related Publications

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)  
*General*

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)  
*Results*

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## Parameters

Parameter	Description	Units
Sample_ID	identification of sample	unitless
Sample_Treatment	treatment of sample	unitless
Light_Dark	samples incubated under both ambient laboratory light near an uncovered window and dark conditions	unitless
Time_Point	time of sample treatment in hours	unitless
Ratio129_127_ox_Iodine	Oxidized iodine 129/127	unitless
Ratio129_127_ox_Iodine_SD	One standard deviation of Ratio129_127_ox_Iodine	unitless
Ratio129_127_Iodide	Iodide isotope ratios 129/127	unitless
Ratio129_127_Iodide_SD	One standard deviation of Ratio_129_127_Iodide	unitless
Iodide_127	Iodine 127	nM
Iodine_127_ox	Oxidized iodine 127	nM
Total_Iodide	Total iodide in sample	nM
Total_Iodine_ox	Total oxidized iodine in sample	nM

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## Instruments

<b>Dataset-specific Instrument Name</b>	ThermoFinnigan Neptune MC-ICP-MS
<b>Generic Instrument Name</b>	Isotope-ratio Mass Spectrometer
<b>Dataset-specific Description</b>	ThermoFinnigan Neptune MC-ICP-MS at the WHOI Plasma Facility.
<b>Generic Instrument Description</b>	The Isotope-ratio Mass Spectrometer is a particular type of mass spectrometer used to measure the relative abundance of isotopes in a given sample (e.g. VG Prism II Isotope Ratio Mass-Spectrometer).

<b>Dataset-specific Instrument Name</b>	Thermo iCAP ICP-MS
<b>Generic Instrument Name</b>	Inductively Coupled Plasma Mass Spectrometer
<b>Dataset-specific 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>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.

## 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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