# Iodine speciation depth profile measurements from the Gotland Deep and Fårö Deep, Baltic Sea, collected aboard R/V Elisabeth Mann Borgese cruise EMB276 in Sep 2021

**Website**: https://www.bco-dmo.org/dataset/1000767
**Data Type**: Cruise Results
**Version**: 1
**Version Date**: 2026-06-10

**Project**
» Collaborative Research: Manganese Cycling and Coupling Across Redox Boundaries within Stratified Basins of the Baltic Sea (MnIONS)

| Contributors | Affiliation | Role |
|---|---|---|
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**Abstract**
The Baltic Sea samples were collected from depth profiles including the surface layer and chemocline at 6 stations in the Gotland Deep and 1 station from the adjacent Fårö Deep, during the R/V Elisabeth Mann Borgese EMB276 cruise September 17 to 29, 2021. The samples focused on these intervals to understanding the cycling of iodine and other redox-sensitive elements at low but present oxygen conditions. Measurements for iodine speciation were made at Michigan State University within 1 year of sampling. Methods specifically applied iodine exchange chromatography to separate and individually measure each total dissolved iodine, dissolved iodate, dissolved iodide, and dissolved organic iodine with inductively coupled plasma mass spectrometry.

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## Table of Contents

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## Coverage

**Location**: The Baltic Sea samples were collected from the surface layer and chemocline at 6 stations in the Gotland Deep and 1 station from the adjacent Fårö Deep, during the R/V “Elisabeth Mann Borgese” EMB276 cruise September 17 to 29, 2021.
**Spatial Extent**: **N**:58.0004 **E**:20.6501 **S**:56.6334 **W**:19.1831
**Temporal Extent**: 2021-09-20 - 2021-09-27

### Methods & Sampling

Seawater depth profiles for iodine analyses was collected onboard through HYDRO-BIOS free flow water samplers on a SBE32 water sampler which were mounted on a CTD rosette (conductivity-temperature-depth profiler). The samples were filtered through 0.2µm Sterivex$^{TM}$ filters and collected in 125ml or 60ml amber Nalgene bottles once on deck and were frozen immediately afterwards for iodine preservation (Campos, 1997; Farrenkopf and Luther, 2002; Hou et al., 2001). Iodine speciation analyses occurred at Michigan State

University within 1 year of sampling, mostly much sooner.

Glass columns for separating iodine species were washed by ultra-pure water produced from the Milli-Q® water purification system, followed by packing with PYREX glass wool and 1ml of Bio-rad AG ® 1-X8 anion exchange resin. During the chromatography procedure, the $I^-$ fraction is specifically adsorbed onto the surface of the resin and eluted following the addition of a 2M $HNO_3$ (Fisher Scientific, TraceMetal™ Grade)-18% (v/v) Tetramethylammonium hydroxide (TMAH, Fisher Scientific) solution. The eluent containing $IO_3^-$ and DOI fractions were collected separately during the elution steps prior to the $I^-$ collection, followed by an acidification (pH <2) and reduction step which converts iodine to $I^-$ by the addition of concentrated hydrochloric acid (HCl, Fisher Scientific) and sodium metabisulfite ($Na_2S_2O_5$, VWR Analytical) (Hardisty et al., 2020). The treated eluent was left overnight for reaction and was processed through the same chromatographic procedure to collect the $I^-$ derived from the $IO_3^-$ and DOI fractions. For independent measurement of total dissolved iodine (TI) and as a quality control, a separate split of seawater samples was treated with HCl/ $Na_2S_2O_5$ to reduce iodine completely to $I^-$ and subsequently processed through the chromatographic method. The eluents from chromatography were collected in Savillex® PFA Teflon vials and then diluted 20 times in 0.2M $HNO_3$-0.9% TMAH before instrumental analysis. The iodine concentrations were measured using a Thermo Scientific iCAP Q triple-quadrupole inductively coupled plasma mass spectrometer (ICP-MS-TQ) using Qtegra software version 2.10.3324.131 in both single-quad (SQ) and triple-quad (TQ) modes with $O_2$ reaction cell gas.

For quality control, a 200ppb $I^-$ solution, which was gravimetrically diluted from the Inorganic Ventures© 1000±4ug/ml $I^-$ ICP-MS standard solution in 1% tetraethyl ammonium (TEA), was processed through chromatography alongside the seawater samples to estimate the yield of $I^-$, DOI and TI fractions. Similarly, for estimating the yield of $IO_3^-$ reduction and column separation, a 200ppb $KIO_3$ solution dissolved from gravimetrically weighed solid $KIO_3$ powder (Fisher Scientific Education) was reduced and chromatographically processed. Yields from standards were applied to corrections for unknown samples. For monitoring contamination, ultra-pure water was processed through the columns. Among each set of seawater samples (11 samples) which were processed at the same time, one of them was randomly selected as a replicate.

The eluents from the chromatography were collected in Savillex PFA Teflon vials and then diluted 20 times (0.2M $HNO_3$-0.9% TMAH) before instrumental analysis. The iodine concentrations were measured using a Thermo Scientific iCAP Q triple-quadrupole inductively coupled plasma mass spectrometer (ICP-MS-TQ) using Qtegra software version 2.10.3324.131 in both single-quad (SQ) and triple-quad (TQ) mode with $O_2$ reaction cell gas. The samples were introduced into the ICP-MS via a Teledyne Cetac ASX-520 autosampler. We used 5ppb internal standard solution diluted from 1001±3ug/ml indium (In) in 2% $HNO_3$, 999±5ug/ml Rhodium (Rh) in 15% HCl, and 1000±4ug/ml Cesium 0.1% $HNO_3$ (Cs) elemental standards from Inorganic Ventures© to calibrate the intensity of iodine and to correct for instrumental drift during the analytical run. The internal standard was either spiked into each sample or was introduced into the ICP-MS after being mixed with sample within an inline mixing chamber. Detection limits for samples were determined as 10 nmol/kg iodine.

## Data Processing Description

Data were processed using Excel.

## BCO-DMO Processing Description

- Loaded CSV file "EMB276_iodine_depth_profiles-utf-8.csv" with header row 1; treated "", "nd", and "N/A" as missing values
- Applied find/replace on station_number column to correct a unicode-corrupted value, replacing "Far" with "Faro"
- Extracted non-numeric values (e.g., "<10") from iodate_concentration and DOI_concentration into new flag columns iodate_concentration_flag and DOI_concentration_flag, setting original columns to None where values were non-numeric
- Combined ISO_DateTime_collected_UTC (parsed as %m/%d/%y) and UTC_Time (parsed as %H:%M) into a

single ISO 8601 datetime column ISO_DateTime_collected_UTC formatted as %Y-%m-%dT%H:%MZ
- Deleted now-redundant UTC_Time column
- Renamed Total I_concentration to Total_I_concentration to remove space from parameter and depth_m to depth to remove units from parameter to align with BCO-DMO guidance
- Output written to 1000767_v1_emb276_iodine_depth_profiles.csv

[ table of contents | back to top ]

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## Related Datasets

### IsRelatedTo

Taenzer, L., Hansel, C. (2024) **Pump CTD profiles from the EMB276 cruise on R/V Elisabeth Mann Borgese in the Baltic Sea from September 20-27, 2021.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2024-08-16 doi:10.26008/1912/bco-dmo.934904.1 [view at BCO-DMO]

Taenzer, L., Hansel, C. (2024) **SOLARIS superoxide and standard CTD profiles from the EMB276 cruise on R/V Elisabeth Mann Borgese in the Baltic Sea from September 20-27, 2021.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2024-10-09 doi:10.26008/1912/bco-dmo.935118.1 [view at BCO-DMO]

### References

(2023). Cruise EMB276 - Fine scale nutrient, oxygen and elemental associations across the redox boundary in the central Baltic Sea. Leibniz Institute for Baltic Sea Research Warnemünde (IOW). https://iowmeta.iow.de/geonetwork/srv/eng/catalog.search#/metadata/IOW-IOWMETA-EMB276-2021

[ table of contents | back to top ]

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## Parameters

| Parameter | Description | Units |
|---|---|---|
| sample_ID | Sample ID | unitless |
| station_number | Station number | unitless |
| depth | Depth of sample collection | meters |
| iodide_concentration | Iodide concentration; 10 nanomole/kg detection limit | nanomole/kg |
| iodate_concentration | Iodate concentration; 10 nanomole/kg detection limit | nanomole/kg |
| iodate_concentration_flag | Flag indicating the iodate concentration is <10 | unitless |
| DOI_concentration | Dissolved organic iodine concentration; 10 nanomole/kg detection limit | nanomole/kg |
| DOI_concentration_flag | Flag indicating the DOI concentration is <10 | unitless |
| Total_I_concentration | Total iodine concentration; 10 nanomole/kg detection limit | nanomole/kg |
| ISO_DateTime_collected_UTC | Datetime of sampling event, UTC | unitless |
| Latitude | Latitude of sampling, positive is North | decimal degrees |
| Longitude | Longitude of sampling, positive is East | decimal degrees |

[ table of contents | back to top ]

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## Instruments

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|---|---|
| **Dataset-specific Instrument Name** | CTD rosette |
| **Generic Instrument Name** | CTD - profiler |
| **Dataset-specific Description** | Seawater depth profiles for iodine analyses was collected onboard through HYDRO-BIOS free flow water samplers on a SBE32 water sampler which were mounted on a CTD rosette (conductivity-temperature-depth profiler). |
| **Generic Instrument Description** | The Conductivity, Temperature, Depth (CTD) unit is an integrated instrument package designed to measure the conductivity, temperature, and pressure (depth) of the water column. The instrument is lowered via cable through the water column. It permits scientists to observe the physical properties in real-time via a conducting cable, which is typically connected to a CTD to a deck unit and computer on a ship. The CTD is often configured with additional optional sensors including fluorometers, transmissometers and/or radiometers. It is often combined with a Rosette of water sampling bottles (e.g. Niskin, GO-FLO) for collecting discrete water samples during the cast. This term applies to profiling CTDs. For fixed CTDs, see https://www.bco-dmo.org/instrument/869934. |

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| **Dataset-specific Instrument Name** | Teledyne Cetac ASX-520 autosampler |
| **Generic Instrument Name** | Laboratory Autosampler |
| **Dataset-specific Description** | The samples were introduced into the ICP-MS via a Teledyne Cetac ASX-520 autosampler. |
| **Generic Instrument Description** | Laboratory apparatus that automatically introduces one or more samples with a predetermined volume or mass into an analytical instrument. |

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|---|---|
| **Dataset-specific Instrument Name** | SBE32 water sampler |
| **Generic Instrument Name** | Seabird SBE 32 Carousel Water Sampler |
| **Dataset-specific Description** | Seawater depth profiles for iodine analyses was collected onboard through HYDRO-BIOS free flow water samplers on a SBE32 water sampler which were mounted on a CTD rosette (conductivity-temperature-depth profiler). |
| **Generic Instrument Description** | The SBE 32 is a Carousel Water Sampler. With an accessory Deck Unit, the Carousel provides water sampling and real-time CTD data acquisition with any Sea-Bird profiling CTD (requires electro-mechanical cable and slip-ring equipped winch). With an accessory underwater unit, the Carousel can operate autonomously with a Sea-Bird Scientific profiling CTD and can be programmed to close bottles at selected depths, allowing deployment using non-electrical wire or line. The Carousel is available in two models: • Full-size SBE 32 for a 12 or 24-position system (36-position custom). • Compact SBE 32C for a 12-position sampler with bottles up to 8 liters, for use with limited vertical clearance. |

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| **Dataset-specific Instrument Name** | Thermo Scientific iCAP Q triple-quadrupole inductively coupled plasma mass spectrometer (ICP-MS-TQ) |
| **Generic Instrument Name** | Thermo Fisher Scientific iCAP TQ inductively coupled plasma mass spectrometer |
| **Dataset-specific Description** | The iodine concentrations were measured using a Thermo Scientific iCAP Q triple-quadrupole inductively coupled plasma mass spectrometer (ICP-MS-TQ) using Qtegra software version 2.10.3324.131 in both single-quad (SQ) and triple-quad (TQ) modes with O2 reaction cell gas. |
| **Generic Instrument Description** | A benchtop triple quadrupole (TQ) inductively coupled plasma mass spectrometer (ICP-MS) with a four channel peristaltic pump, three plasma gas flow controllers, and four QCell mass flow controllers. The iCAP TQ utilises triple quadrupole technology which allows the analyte signal to be isolated from interferences, enabling the analysis of complex or high-matrix samples. The high frequency (4 MHz) quadrupole mass analyser has pre and post filters for isolation of wanted ions. The instrument features Peltier cooled high purity quartz or perfluoroalkoxy alkane (PFA), and low volume, baffled cyclonic or double pass spray chambers to efficiently filter out larger aerosol droplets for improved plasma stability. A reaction finder method development assistant aids easy method development. The plasma system is designed to rapidly adapt to changing matrices and provide robustness for challenging samples such as highly volatile organic solvents. The argon ICP ion source has a digital, solid state radiofrequency generator, and dynamic frequency impedance matching the plasma at 27 MHz. The iCAP TQ has applications in trace element analysis of solid or liquid (particularly sediment or sea water) samples. It has a nebuliser default flow rate of 400 uL/min. |

[ table of contents | back to top ]

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## Deployments

**EMB276**

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|---|---|
| **Website** | https://www.bco-dmo.org/deployment/934931 |
| **Platform** | R/V Elisabeth Mann Borgese |
| **Start Date** | 2021-09-17 |
| **End Date** | 2021-09-29 |

[ table of contents | back to top ]

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## Project Information

### Collaborative Research: Manganese Cycling and Coupling Across Redox Boundaries within Stratified Basins of the Baltic Sea (MnIONS)

**Coverage**: Baltic Sea

*NSF Award Abstract:*
The trace element manganese (Mn) is distributed widely throughout the global ocean where it cycles among three dominant oxidation states. Manganese in the higher oxidation states is highly reactive and thereby influences the cycling of nearly all other elemental cycles, including those of oxygen and nitrogen. The intermediate Mn species has only recently become recognized as an abundant component of the Mn pool, presenting now a previously unrecognized factor that may control the chemistry of the ocean. The Baltic Sea contains high Mn concentrations and preliminary investigations have pointed to the presence of an operationally defined "reactive" form of Mn but the composition and consequence of this Mn pool are unknown. This research will explore the cycling of Mn within the Baltic Sea enabled by an established collaboration with

the Leibniz Institute for Baltic Sea Research in Warnemunde, Germany. By coupling field measurements and targeted shipboard incubations, this study will shed light on the processes controlling the Mn cycle and its link to the oxygen, iodine, and nitrogen cycles. This project will educate several undergraduate and graduate students and promote scientific exchange between research groups within the United States and Germany. Further, outreach efforts associated with this research will continue an existing collaboration between the PIs and the Boston Green Academy in South Boston to introduce high school students to chemical oceanography, and in particular biogeochemistry.

Manganese (Mn) is intricately linked to nearly all elemental cycles, and yet we know little about the processes governing its redox cycling within natural systems. Over the past decade a number of key scientific discoveries have provided greater insight into the diversity of processes and mechanisms involved in Mn redox cycling and introduced Mn(III) ligand complexes as important components of the dissolved Mn pool. The Baltic Sea is one of the most well studied stratified marine systems and reactive Mn has been implicated as a key factor in the formation and maintenance of suboxic zones. Thus, the goal of this research is to explore the cycling and elemental coupling of Mn within stratified basins of the Baltic Sea. The PIs predict that reactive Mn, as Mn(III) ligand complexes and Mn oxide particles, is a primary control on the redox landscape of stratified marine waters, particularly at redox boundaries and within the suboxic zone. The PIs propose fieldwork in a local permanently stratified brackish pond to refine experimental procedures followed by two cruises to suboxic basins in the Baltic Sea enabled by an established collaboration with the Leibniz Institute for Baltic Sea Research in Warnemunde. Field measurements will be obtained using a combination of in situ sensors and ship/lab-based instrumentation at several Baltic Sea sites to define the distribution of Mn species and the rates of Mn redox transformations spanning the redoxcline along with a suite of chemical information. Further, a matrix of shipboard incubations will be conducted to constrain the underlying (a)biotic processes responsible for the observed Mn profiles. Specifically, across oxygen and Mn gradients spanning the redoxcline, the PIs will interrogate the link between the Mn cycle and iodine and nitrogen species, which will ultimately help constrain current gaps in the mass balance of these elements in Baltic Sea models.

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.

[ table of contents | back to top ]

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## Funding

| Funding Source | Award |
|---|---|
| NSF Division of Ocean Sciences (NSF OCE) | OCE-1924236 |

[ table of contents | back to top ]