Total dissolved, dissolved labile, and soluble nickel concentrations determined in water column samples collected on the 2019 Bermuda Atlantic Iron Time-series (BAIT) cruises in the Western Subtropical North Atlantic Gyre

Website: <https://www.bco-dmo.org/dataset/940164> **Data Type**: Cruise Results **Version**: 1 **Version Date**: 2024-10-11

Project

» [NSFGEO-NERC:](https://www.bco-dmo.org/project/822807) Collaborative Research: Using Time-series Field Observations to Constrain an Ocean Iron Model (BAIT)

Program

» U.S. [GEOTRACES](https://www.bco-dmo.org/program/2022) (U.S. GEOTRACES)

Abstract

This dataset includes the total dissolved, dissolved labile, and soluble nickel concentration results determined in water column samples collected using a trace-metal clean CTD rosette, or an inflatable dinghy, during four cruises in the Bermuda Atlantic Time-series Study (BATS) region in March, May, August, and November 2019. The samples and associated data were collected for the Bermuda Atlantic Iron Time-series (BAIT) project (GEOTRACES Process Study GApr13). Post-cruise sample analyses were performed at the University of South Florida (labile dissolved nickel) and Old Dominion University (dissolved nickel, soluble nickel).

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Coverage

Spatial Extent: **N**:32.151 **E**:-63.58 **S**:31.177 **W**:-64.815 **Temporal Extent**: 2019-03-11 - 2019-11-21

Methods & Sampling

Sample Collection:

Trace metal clean techniques were employed to collect seawater samples from the BATS site (Fig. 1; 31°40′N, 64°10′W) in 2019 on 12 March, 14 May, 19 August, and 19 November aboard the R/V Endeavor (March) and R/V Atlantic Explorer (May-November). A trace metal clean carousel (SeaBird Electronics) with a conductivitytemperature-depth sensor (SBE 19 plus, SeaBird Electronics) was fitted with custom-modified 5-liter (L) Teflonlined external-closure Niskin-X samplers (General Oceanics) and deployed on an Amsteel non-metallic line for the collection of hydrographic data and water column samples from twelve depths (Sedwick et al. 2023). In August, an additional surface (0.3 meter (m)) sample was collected \sim 500 m upwind of the ship by deploying a Niskin-X sampler from an inflatable dinghy. All seawater samples collected for dissolved nickel analyses were filtered (0.2 micrometer (µm)) (AcroPak, Pall) into acid-cleaned low-density polyethylene (LDPE; Nalgene) bottles, acidified to pH 1.7 (0.024 molar (M) Q-HCl, Fisher Optima) by addition of 6 M ultrapure hydrochloric acid (Fisher Optima), and stored double bagged in buckets at room temperature. For soluble (<0.02 µm) nickel analyses, 0.2 µmfiltered seawater was passed through a Milli-Q (≥18.2 MΩ cm) and sample-rinsed 0.02 µm Anotop syringe filter (Sigma-Aldrich) using a peristaltic pump and collected in acid-cleaned LDPE bottles (Ussher et al. 2010); soluble nickel samples were also acidified to pH 1.7 and stored at room temperature. Seawater samples collected for dissolved nickel speciation analyses were 0.2 µm-filtered into acid-cleaned and Milli-Q conditioned fluorinated high-density polyethylene (FPE; Nalgene) bottles and stored at -20 degrees Celsius (°C) until analysis.

Total Dissolved and Soluble Ni Concentrations:

Concentrations of total dissolved and soluble nickel (Ni) were determined in the acidified seawater filtrates using inductively-coupled plasma mass spectrometry (ICP-MS, Thermo Fisher Scientific ElementXR), with in-line separation-preconcentration (Elemental Scientific SeaFAST SP3) modified after Lagerström et al. (2013). Calibration standards were prepared in low-analyte concentration filtered seawater for which initial concentrations were determined using the method of standard additions. Calibration standards were introduced using the same in-line separation-preconcentration procedure as the seawater filtrate samples, with yttrium was used as an internal standard for all samples except where indicated. Analytical blank concentrations were assessed by applying the in-line separation-preconcentration procedure including all reagents and loading air in place of the seawater filtrate sample ("air blank").

Labile Dissolved Ni:

A stock solution of dimethylglyoxime (DMG; Acros Organics, 99+%) was made in methanol (Optima, Fisher) to a concentration of 0.1 M (Saito and Moffett 2001). A working solution of DMG was prepared by diluting the 0.1 M stock with methanol to a concentration of 0.01 M. A 1.5 M borate-ammonium buffer (Ellwood and Van den Berg 2000) was prepared by dissolving 18.55 grams (g) boric acid (Aldrich, 99.999% trace metals basis) in 200 milliliters (mL) 0.4 N ammonium hydroxide (Optima, Fisher). The borate-ammonium buffer was purified of trace metal contaminants by passing through two consecutive chromatography columns containing cleaned and preconditioned Chelex® 100 resin (100-200 mesh, Bio-Rad Laboratories) at a speed of 2 milliliters per minute (mL min-1) (Mellett and Buck 2020). Ni and copper (Cu) standards at various concentrations were prepared from 1000-fold dilutions of atomic absorption standards in 0.024 M HCl (Optima, Fisher).

Labile dissolved Ni (DNi) concentrations were measured in seawater samples using competitive ligand exchangeadsorptive cathodic stripping voltammetry (CLE-AdCSV) with DMG as the added competitive ligand (van den Berg and Nimmo 1987, Saito et al. 2004, Boiteau et al. 2016). Seawater samples were thawed in the refrigerator overnight and then allowed to reach room temperature before 10 mL aliquots were dispensed into acid-cleaned Teflon vials (Savillex) and amended with 7.5 millimolar (mM) borate-ammonium buffer (pH=8.2, NBS scale, Ellwood and Van den Berg 2000) and 200 micromolar (µM) DMG (Boiteau et al. 2016). Samples were then allowed to equilibrate for at least 12 hours prior to analysis (Boiteau et al. 2016) and analyzed within 24 hours of the DMG addition (van den Berg and Nimmo 1987). Previous work indicated that some natural ligands preferentially bind Cu over Ni (Boiteau et al. 2016). To investigate the specificity of Ni-binding ligands in this study, a duplicate of each seawater sample was equilibrated with Cu prior to the DMG addition. For these Cu replicates, 10 mL seawater sample aliquots were amended with 7.5 mM borate-ammonium buffer and 10 nanomolar (nM) Cu and allowed to equilibrate for 12 hours. After the Cu equilibration period, DMG was added to a concentration of 200 µM, and samples were allowed to equilibrate for an additional 12 hours before analysis.

A BioAnalytical Systems (BASi) controlled growth hanging mercury drop electrode (CGME) was interfaced with an Epsilon 2 (BASi) analyzer for measurement of labile DNi concentrations. At the time of analysis, samples were purged for 5 minutes with high-purity nitrogen gas (N2) to minimize oxygen interference. For each run, a 30 second deposition time at -0.7 volts (V) was followed by a 10-second quiet time, and a linear sweep from -0.7 V to -1.4 V with a scan rate of 10 volts per second (V s-1) was performed (Dupont et al. 2010). A drop size of ten was used with a stirrer speed of 600 rpm. Samples were measured for ambient labile DNi at least three times before Ni standard additions. For each standard addition, 0.5 nM or 1 nM Ni was dispensed into the electrochemical cell, which was subsequently purged for another 30 seconds before the sample was measured

again in at least triplicate. Ni additions continued until the resulting peak heights were double those produced by the natural sample.

Data Processing Description

Voltammograms were imported to ElectroChemistry Data SOFTware (ECDSOFT) for baseline subtraction and measurement of peak heights (Omanovic and Branica 1998). The concentration of labile dissolved Ni in each sample was determined by dividing triplicate initial peak heights by the slope found from linear regression of the dissolved nickel additions and averaging the results of all measurements.

Quality Flags:

Data were flagged using the SeaDataNet quality flag scheme recommended by GEOTRACES [\(https://www.geotraces.org/geotraces-quality-flag-policy/\)](https://www.geotraces.org/geotraces-quality-flag-policy/) and described below. Notes specific to the application of these flags to this dataset are noted in brackets […].

1: Good Value: Good quality data value that is not part of any identified malfunction and has been verified as consistent with real phenomena during the quality control process. [Used for samples with replicate measurements].

2: Probably Good Value: Data value that is probably consistent with real phenomena, but this is unconfirmed or data value forming part of a malfunction that is considered too small to affect the overall quality of the data object of which it is a part. [Used when no replicate measurements were available to check the quality of the data].

3: Probably Bad Value: Data value recognized as unusual during quality control that forms part of a feature that is probably inconsistent with real phenomena. [Not used].

4: Bad Value: An obviously erroneous data value. [Used when a soluble nickel concentration was much greater than the dissolved nickel concentration measured].

5: Changed Value: Data value adjusted during quality control. Best practice strongly recommends that the value before the change be preserved in the data or its accompanying metadata. [Not used].

6: Value Below Detection Limit: The level of the measured phenomenon was less than the limit of detection (LOD) for the method employed to measure it. The accompanying value is the detection limit for the technique or zero if that value is unknown. [Not used].

7: Value in Excess: The level of the measured phenomenon was too large to be quantified by the technique employed to measure it. The accompanying value is the measurement limit for the technique. [Not used].

8: Interpolated Value: This value has been derived by interpolation from other values in the data object. [Not used].

9: Missing Value: The data value is missing. Any accompanying value will be a magic number representing absent data [When sample was not collected the notation 'na' for 'not applicable' was used; when sample collected but there is no result for this parameter, the notation 'nda' for 'no data available' was used].

A: Value Phenomenon Uncertain: There is uncertainty in the description of the measured phenomenon associated with the value such as chemical species or biological entity. [Not used.]

NOTE: For at least one sample, the soluble nickel concentration measured was significantly higher than the total dissolved nickel concentration measured; flagged with "4: bad value" in the dataset.

GEOTRACES IDP:

The dissolved Nickel parameters have been registered in the GEOTRACES DOoR portal with the following names: EN631: Ni_D_CONC_BOTTLE::fpar5o (nmol/kg) AE1909: Ni_D_CONC_BOTTLE::8py4r6 (nmol/kg) AE1921: Ni_D_CONC_BOTTLE::p5qm4p (nmol/kg) AE1930: Ni D CONC BOTTLE::y4bxhp (nmol/kg).

- Imported original file "Dataset_BAIT_ParenteBuck_NiSpeciation.csv" into the BCO-DMO system.
- Marked "nda", "na", "ND", and "NAN" as missing data values (missing data are empty/blank in the final CSV file).
- Created ISO Date-Time column from original DATE_GMT and GMT fields.
- Split original Cruise_ID column into: CRUISE, PROJECT_CRUISE, and CRUISE_NAME.
- Saved the final file as "940164 v1 2019 bait dissolved nickel speciation.csv".

Problem Description

For at least one sample, the soluble nickel concentration measured was significantly higher than the total dissolved nickel concentration measured; flagged with "4: bad value" in the dataset.

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Related Publications

Boiteau, R. M., Till, C. P., Ruacho, A., Bundy, R. M., Hawco, N. J., McKenna, A. M., … Repeta, D. J. (2016). Structural Characterization of Natural Nickel and Copper Binding Ligands along the US GEOTRACES Eastern Pacific Zonal Transect. Frontiers in Marine Science, 3. doi[:10.3389/fmars.2016.00243](https://doi.org/10.3389/fmars.2016.00243) **Methods**

Dupont, C. L., Buck, K. N., Palenik, B., & Barbeau, K. (2010). Nickel utilization in phytoplankton assemblages from contrasting oceanic regimes. Deep Sea Research Part I: Oceanographic Research Papers, 57(4), 553–566. https://doi.org/[10.1016/j.dsr.2009.12.014](https://doi.org/10.1016/j.dsr.2009.12.014) **Methods**

Ellwood, M. J., & Van den Berg, C. M. G. (2000). Zinc speciation in the Northeastern Atlantic Ocean. Marine Chemistry, 68(4), 295–306. [https://doi.org/10.1016/s0304-4203\(99\)00085-7](https://doi.org/10.1016/S0304-4203(99)00085-7) https://doi.org/10.1016/S0304- 4203(99)00085-7

Methods

Lagerström, M. E., Field, M. P., Séguret, M., Fischer, L., Hann, S., & Sherrell, R. M. (2013). Automated on-line flow-injection ICP-MS determination of trace metals (Mn, Fe, Co, Ni, Cu and Zn) in open ocean seawater: Application to the GEOTRACES program. Marine Chemistry, 155, 71–80. doi[:10.1016/j.marchem.2013.06.001](https://doi.org/10.1016/j.marchem.2013.06.001) **Methods**

Mellett, T., & Buck, K. N. (2020). Spatial and temporal variability of trace metals (Fe, Cu, Mn, Zn, Co, Ni, Cd, Pb), iron and copper speciation, and electroactive Fe-binding humic substances in surface waters of the eastern Gulf of Mexico. Marine Chemistry, 227: 103891. doi[:10.1016/j.marchem.2020.103891](https://doi.org/10.1016/j.marchem.2020.103891) **Methods**

Parente, C. (2024). Dissolved nickel speciation at the Bermuda Atlantic Time-series Study (BATS) site, University of South Florida, Tampa, FL. Results

Saito, M. A., & Moffett, J. W. (2001). Complexation of cobalt by natural organic ligands in the Sargasso Sea as determined by a new high-sensitivity electrochemical cobalt speciation method suitable for open ocean work. Marine Chemistry, 75(1-2), 49–68. doi[:10.1016/s0304-4203\(01\)00025-1](https://doi.org/10.1016/s0304-4203(01)00025-1) **Methods**

Saito, M. A., Moffett, J. W., & DiTullio, G. R. (2004). Cobalt and nickel in the Peru upwelling region: A major flux of labile cobalt utilized as a micronutrient. Global Biogeochemical Cycles, 18(4), n/a-n/a. doi[:10.1029/2003gb002216](https://doi.org/10.1029/2003gb002216) Methods

Sedwick, P. N., Sohst, B. M., Buck, K. N., Caprara, S., Johnson, R. J., Ohnemus, D. C., Sofen, L. E., Tagliabue, A., Twining, B. S., & Williams, T. E. (2023). Atmospheric Input and Seasonal Inventory of Dissolved Iron in the Sargasso Sea: Implications for Iron Dynamics in Surface Waters of the Subtropical Ocean. Geophysical Research Letters, 50(6). Portico. https://doi.org[/10.1029/2022GL102594](https://doi.org/10.1029/2022GL102594) **Methods**

Ussher, S. J., Achterberg, E. P., Sarthou, G., Laan, P., de Baar, H. J. W., & Worsfold, P. J. (2010). Distribution of size fractionated dissolved iron in the Canary Basin. Marine Environmental Research, 70(1), 46–55. doi[:10.1016/j.marenvres.2010.03.001](https://doi.org/10.1016/j.marenvres.2010.03.001) **Methods**

Van Den Berg, C. M. G., & Nimmo, M. (1987). Determination of interactions of nickel with dissolved organic

material in seawater using cathodic stripping voltammetry. Science of The Total Environment, 60, 185–195. https://doi.org/[10.1016/0048-9697\(87\)90415-3](https://doi.org/10.1016/0048-9697(87)90415-3) Methods

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Deployments

EN631

AE1909

AE1930

AE1921

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Project Information

NSFGEO-NERC: Collaborative Research: Using Time-series Field Observations to Constrain an Ocean Iron Model (BAIT)

Coverage: Bermuda Atlantic Time-Series Study region, waters of the western Subtropical North Atlantic Gyre

NSF and NERC Award Abstract:

Iron is an essential nutrient for the growth of phytoplankton in the oceans. As such, iron plays key roles in regulating marine primary production and the cycling of carbon. It is thus important that models of ocean biology and chemistry consider iron, in order to explore past, present and future variations in marine productivity and the role of the ocean in the global carbon cycle. In this joint project involving researchers in the U.S. and the U.K., supported by both NSF and the Natural Environment Research Council (U.K.), field data from the Bermuda Atlantic Time-series Study (BATS) region will be combined with an established, state-of-the-art ocean biogeochemical model. By leveraging the known seasonal-scale physical, chemical and biological changes in the BATS region, the oceanographic context provided by the BATS core data, and an existing model of the regional physical circulation, the proposed study will yield process-related information that is of general applicability to the open ocean. In particular, the proposed research will focus on understanding the atmospheric input, biological uptake, regeneration and scavenging removal of dissolved iron in the oceanic water column, which have emerged as major uncertainties in the ocean iron cycle. The project will include significant educational and training contributions at the K-12, undergraduate, graduate and postdoctoral levels, as well as public outreach efforts that aim to explain the research and its importance.

The ability of ocean models to simulate iron remains crude, owing to an insufficient understanding of the mechanisms that drive variability in dissolved iron, particularly the involvement of iron-binding ligands, colloids and particles in the surface input, biological uptake, regeneration and scavenging of dissolved iron in the upper ocean. Basin-scale data produced by the GEOTRACES program provide an important resource for testing and improving models and, by extension, our mechanistic understanding of the ocean iron cycle. However such data provide only quasi-synoptic 'snapshots', which limits their utility in isolating and identifying the processes that control dissolved iron in the upper ocean. The proposed research aims to provide mechanistic insight into these governing processes by combining time-series data from the BATS region with numerical modeling experiments. Specifically, seasonally resolved data on the vertical (upper 2,000 meters) and lateral (tens of kilometers) distributions of particulate, dissolved, colloidal, soluble and ligand-bound iron species will be obtained from the chemical analysis of water column samples collected during five cruises, spanning a full annual cycle, shared with the monthly BATS program cruises. These data, along with ancillary data from the BATS program, will be used to test and inform numerical modeling experiments, and thus derive an improved understanding of the mechanisms that control the distribution and dynamics of dissolved iron in the oceanic water column.

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.

This is a project jointly funded by the National Science Foundation's Directorate for Geosciences (NSF/GEO) and the National Environment Research Council (NERC) of the United Kingdom (UK).

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Program Information

U.S. GEOTRACES (U.S. GEOTRACES)

Website: <http://www.geotraces.org/>

Coverage: Global

GEOTRACES is a [SCOR](http://www.jhu.edu/scor/GEOTRACES.htm) sponsored program; and funding for program infrastructure development is provided by the U.S. National Science [Foundation.](http://www.nsf.gov)

GEOTRACES gained momentum following a special symposium, S02: Biogeochemical cycling of trace elements and isotopes in the ocean and applications to constrain contemporary marine processes (GEOSECS II), at a 2003 Goldschmidt meeting convened in Japan. The GEOSECS II acronym referred to the Geochemical Ocean Section Studies To determine full water column distributions of selected trace elements and isotopes, including their concentration, chemical speciation, and physical form, along a sufficient number of sections in each ocean basin to establish the principal relationships between these distributions and with more traditional hydrographic

parameters;

* To evaluate the sources, sinks, and internal cycling of these species and thereby characterize more completely the physical, chemical and biological processes regulating their distributions, and the sensitivity of these processes to global change; and

* To understand the processes that control the concentrations of geochemical species used for proxies of the past environment, both in the water column and in the substrates that reflect the water column.

GEOTRACES will be global in scope, consisting of ocean sections complemented by regional process studies. Sections and process studies will combine fieldwork, laboratory experiments and modelling. Beyond realizing the scientific objectives identified above, a natural outcome of this work will be to build a community of marine scientists who understand the processes regulating trace element cycles sufficiently well to exploit this knowledge reliably in future interdisciplinary studies.

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