

# Shipboard FIA dissolved Al, Fe, and Mn from samples collected by GO-FLO bottles during USCGC Healy cruise HLY1502 (GN01) in the Canada and Makarov Basins of the Arctic Ocean from August to October 2015

**Website:** <https://www.bco-dmo.org/dataset/764096>

**Data Type:** Cruise Results

**Version:** 2

**Version Date:** 2020-09-28

## Project

» [GEOTRACES Arctic Section: Shipboard determination of key trace elements](#) (GEOTRACES Arctic Al Fe Mn)

Contributors	Affiliation	Role
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## Abstract

Shipboard FIA dissolved Al, Fe, and Mn from samples collected by GO-FLO bottles during USCGC Healy cruise HLY1502 (GN01) in the Canada and Makarov Basins of the Arctic Ocean from August to October 2015.

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## Coverage

**Spatial Extent:** N:90 E:179.7 S:60.2 W:-179

**Temporal Extent:** 2015-08-12 - 2015-10-08

## Methods & Sampling

Water samples (water column, surface water, water under sea-ice, sea-ice, snow, and melt pond) were collected at 28 stations from the USCG Healy during the GEOTRACES Western Arctic research expedition, which took place during the US GEOTRACES Arctic cruise aboard USCGC Healy (HLY1502) from August 9 to October 11, 2015 in the Arctic Ocean. This dataset contains data resulting from BOTTLE samples.

Water column samples were obtained using the custom-built U.S. GEOTRACES trace-metal clean CTD rosette, consisting of a plastic-coated aluminum frame, titanium pressure housings for electronics and sensors, no sacrificial zinc anodes, and 24 12 L General Oceanic GO-FLO bottles modified for trace metal sampling (Cutter and Bruland, 2012). Before deployment and immediately upon recovery, the tops of the GO-FLO bottles were

covered with polyethylene shower-caps, and the bottles were removed from the frame and carried into the U.S. GEOTRACES clean container laboratory for sub-sampling. The GO-FLO bottles were pressurized to 10 psi using HEPA-filtered compressed air, and samples were filtered through 0.2  $\mu\text{m}$  Pall Acropak Supor filter capsules that had been pre-cleaned by soaking overnight and flushed with 5 L of un-acidified seawater. The 0.2  $\mu\text{m}$ -filtered seawater samples were acidified to pH 2 using trace metal-grade HCl. All sub-sampling was undertaken in the clean container using rigorous trace-metal clean protocols (Cutter and Bruland, 2012).

Samples were drawn into pre-numbered 125 ml PMP bottles after three rinses and were stored in plastic bags in the dark at room temperature before determination which was usually within 12-36 hours of collection.

Samples were analyzed shipboard for dissolved Al, Fe & Mn using flow injection analysis methods (Resing and Measures, 1994; Measures et al., 1995, Resing and Mottl, 1992 respectively). Prior to determination samples were acidified by the addition of 125  $\mu\text{l}$  sub-boiling distilled 6N HCl and were microwaved in groups of 4 for 3 minutes in a 900 W microwave oven to achieve a temperature of  $60 \pm 10$  °C. Samples were allowed to cool for at least 1 hour prior to determination. Samples were determined in groups of 8.

**For preparation for standard solutions:** Shipboard mixed standards (Al and Fe, Mn) were prepared in the shore-based laboratory by serial dilution of commercial Al, Fe, and Mn standards (BDH Aristar) into distilled water which was acidified with the equivalent of 4 ml sub-boiled 6N HCl. Standards for instrument calibration were prepared daily from filtered seawater by acidifying 1 L of low Fe seawater from a previous cast with 1 ml of 6N HCl and microwaving for 5 minutes to reach a temperature of  $60 \pm 10$  °C. After 1 hour, 200  $\pm$  2 ml of the cooled seawater was added to each of three 250 ml PMP bottles each of which had been rinsed three times with the microwaved seawater and shaken dry. Working standards were prepared by adding 0, +100 $\mu\text{L}$ , +200 $\mu\text{L}$  spikes of the shipboard mixed standard to these bottles, to yield a standard curve of +10.58nM and +21.16nM for Al, +0.528nM and +1.057nM for Fe, +1.45nM and +2.90nM for Mn. The system blank from the addition of the acid and buffer to samples was determined by double spiking a replicate sample i.e. by adding 2 x 125  $\mu\text{l}$  6N HCl and 5 ml of sample buffer to the replicate bottle and comparing the resulting signal to the original sample.

**For dissolved Al analysis:** Dissolved Al was determined using a Flow Injection Analysis scheme with fluorometric detection. Major components were a Rabbit peristaltic pump, a Dynamax FL-1 fluorometer, a Rainin A/D board and a Macintosh G3 computer running Rainin MacIntegrator v 1.4.3 to log and reduce data. The analytical scheme produces a complex between lumogallion and dissolved Al which when excited at 484 nm produces fluorescence at 552 nm. Detailed description of the methodology is published in Resing and Measures (1994). A 3-minute pre-concentration of sample (~9 ml) onto an 8-hydroxyquinoline (8-HQ) resin column yielded a detection limit of 0.27 and a precision of 2.1% at 12.8 nM.

**For dissolved Fe analysis:** Dissolved Fe was determined using a Flow Injection Analysis scheme with spectrophotometric detection (Rainin Dynamax UV-C). Major components were a Rabbit peristaltic pump, a Rainin Dynamax UV-C, a Rainin A/D board and a Macintosh G3 computer running Rainin MacIntegrator v 1.4.3 to log and reduce data. The spectrophotometric detection of the iron eluted from the column is achieved through its catalytic effect on the oxidation of N,N-dimethylp-phenylenediamine dihydrochloride (DPD) the oxidized product is measured at 514 nm. Detailed description of the methodology is published in Measures et al (1995). A 3-minute pre-concentration of sample (~9 ml) onto an 8-hydroxyquinoline (8-HQ) resin column yielded a detection limit of 0.090 nM and a precision of 0.67% at 2.96nM.

**For dissolved Mn analysis:** Dissolved Mn was determined using a Flow Injection Analysis scheme with spectrophotometric detection (Rainin Dynamax UV-C). Major components were a Rabbit peristaltic pump, a Rainin Dynamax UV-C, a Rainin A/D board and a Macintosh G3 computer running Rainin MacIntegrator v 1.4.3 to log and reduce data. The spectrophotometric detection of the manganese eluted from the column is achieved through its catalytic effect on the formation of malachite green which is measured at 620 nm. Detailed description of the methodology is published in Resing and Mottl (1992). A 3-minute pre-concentration of sample (~9 ml) onto an 8-hydroxyquinoline (8-HQ) resin column yielded a detection limit of 0.55 nM and a precision of 1.16% at 2.7 nM.

**Calculation of each dissolved trace element concentrations:** Calculation of sample concentrations was by dividing the peak height derived from sample using the A/D software by the calculated slope of the standard curve. Variations in the slope of the standard curve during a day's run were corrected by the following procedure.

The change in the value of the slope of the standard curve between each run of standards was divided by the number of samples run between those standards to provide a calculated value for the slope of the standard curve at the point each sample was run. The value of the peak height for each sample was then recalculated by the estimated ratio of the standard curve slope at the point that sample was run. The estimate of the slope at

each sample run is calculated by: (Initial slope + (incremental change per sample X # of samples run since initial standard was run)). The sample concentration is then calculated from the initial standard curve slope.

The analytical blanks of dissolved Fe and Mn were determined by the shore-based ICPMS data that was measured by co-PI Dr. J. Fitzsimmons (Texas A&M University). The ICPMS data and its metadata will be submitted separately. The blank corrected FIA data was obtained from the intercept of the correlation plot between the ICPMS data and FIA data on each of the days the FIA was run.

**Intercalibration for dissolved Al:** GEOTRACES standard seawater and internal standard seawater were analyzed periodically. A large batch of seawater was acidified prior to the cruise and used as a primary standard during measurements. This standard seawater was run along with each sample analysis. Our laboratory has participated the GEOTRACES intercalibration effort using this flow injection method.

We report our laboratory values for the GEOTRACES GS standard analyses using this flow injection method to be: GEOTRACES GS =  $29.63 \pm 1.15$  nM (n=2). Using  $1L=1.027$  kg, our Al value is calculated as  $28.85 \pm 1.12$  nmol/kg and it is within the error of the consensus value ( $27.5 \pm 0.2$  nmol/kg).

These results are in good agreement with this from the GEOTRACES intercalibration effort for Al and demonstrate that the methodologies employed to produce this dataset detect concentrations within the standard deviation of current consensus values.

The Al data from the GEOTRACES Arctic Ocean cruise were compared with several published data set in the various basins in the Arctic Ocean (Makarov Basin, Middag et al., 2009), the Amundsen Basin (Middag et al., 2009), and the Canada Basin (Giesbrecht et al 2013) which all show very similar results throughout the water column.

## Data Processing Description

### Quality flags for dissolved Al, Fe, and Mn:

- 1 = Below detection limit (Measurement was determined but was found to be below the detection limit);
- 2 = Good;
- 3 = Questionable/suspect;
- 4 = Bad;
- 9 = Missing data (no sample).

### BCO-DMO Processing:

- modified parameter names;
- replaced "<0.55" with "lt\_0.55";
- added longitude values in -180 to 180.

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## Data Files

File
<b>AlFeMn_Bottle.csv</b> (Comma Separated Values (.csv), 17.64 KB) MD5:c7d19eb1f22980ac7172235c13125912
Primary data file for dataset ID 764096

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## Related Publications

Cutter, G. A., & Bruland, K. W. (2012). Rapid and noncontaminating sampling system for trace elements in global ocean surveys. *Limnology and Oceanography: Methods*, 10(6), 425–436. doi:[10.4319/lom.2012.10.425](https://doi.org/10.4319/lom.2012.10.425)

Giesbrecht, T., Sim, N., Orians, K. J., & Cullen, J. T. (2013). The distribution of dissolved and total dissolvable

aluminum in the Beaufort Sea and Canada Basin region of the Arctic Ocean. *Journal of Geophysical Research: Oceans*, 118(12), 6824–6837. doi:10.1002/2013jc009202 <https://doi.org/10.1002/2013JC009202>

*Related Research*

Measures, C. I., Yuan, J., & Resing, J. A. (1995). Determination of iron in seawater by flow injection analysis using in-line preconcentration and spectrophotometric detection. *Marine Chemistry*, 50(1-4), 3–12.

doi:[10.1016/0304-4203\(95\)00022-j](https://doi.org/10.1016/0304-4203(95)00022-j)

*Methods*

Middag, R., de Baar, H. J. W., Laan, P., & Bakker, K. (2009). Dissolved aluminium and the silicon cycle in the Arctic Ocean. *Marine Chemistry*, 115(3-4), 176–195. doi:[10.1016/j.marchem.2009.08.002](https://doi.org/10.1016/j.marchem.2009.08.002)

*Related Research*

Resing, J. A., & Measures, C. I. (1994). Fluorometric Determination of Al in Seawater by Flow Injection Analysis with In-Line Preconcentration. *Analytical Chemistry*, 66(22), 4105–4111. doi:[10.1021/ac00094a039](https://doi.org/10.1021/ac00094a039)

*Methods*

Resing, J. A., & Mottl, M. J. (1992). Determination of manganese in seawater using flow injection analysis with on-line preconcentration and spectrophotometric detection. *Analytical Chemistry*, 64(22), 2682–2687.

doi:[10.1021/ac00046a006](https://doi.org/10.1021/ac00046a006)

*Methods*

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## Parameters

Parameter	Description	Units
Station	Station number	unitless
LONGITUDE	Longitude; -180-180. Positive values = East.	degrees East
LATITUDE	Latitude North; 0-90. Positive values = North.	degrees North
LONGITUDE_360	Longitude from 0 to 360 degrees East.	degrees East
Depth	Sample depth	meters (m)
GT_Sample_ID	GEOTRACES sample number	unitless
Al_D_CONC_BOTTLE_nipyko	Dissolved Aluminum concentration	nanomoles per liter (nmol/L)
Flag_Al_D_CONC_BOTTLE_nipyko	Quality flag for Al_D_CONC_BOTTLE_nipyko. Definitions: 1 = Below detection limit (Measurement was determined but was found to be below the detection limit); 2 = Good; 3 = Questionable/suspect; 4 = Bad; 9 = Missing data (no sample).	unitless
Fe_D_CONC_BOTTLE	Dissolved Iron concentration	nanomoles per liter (nmol/L)
Fe_D_CONC_BOTTLE_QF	Quality flag for Fe_D_CONC_BOTTLE. Definitions: 1 = Below detection limit (Measurement was determined but was found to be below the detection limit); 2 = Good; 3 = Questionable/suspect; 4 = Bad; 9 = Missing data (no sample).	unitless
Mn_D_CONC_BOTTLE	Dissolved Manganese concentration	nanomoles per liter (nmol/L)
Mn_D_CONC_BOTTLE_QF	Quality flag for Mn_D_CONC_BOTTLE. Definitions: 1 = Below detection limit (Measurement was determined but was found to be below the detection limit); 2 = Good; 3 = Questionable/suspect; 4 = Bad; 9 = Missing data (no sample).	unitless

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## Instruments

<b>Dataset-specific Instrument Name</b>	Flow injection for dMn system with Rainin Dynamax Absorbance detector UV-C
<b>Generic Instrument Name</b>	Flow Injection Analyzer
<b>Dataset-specific Description</b>	Dissolved Mn was determined using a Flow Injection Analysis scheme with spectrophotometric detection (Rainin Dynamax UV-C). Major components were a Rabbit peristaltic pump, a Rainin Dynamax UV-C, a Rainin A/D board and a Macintosh G3 computer running Rainin MacIntegrator v 1.4.3 to log and reduce data.
<b>Generic Instrument Description</b>	An instrument that performs flow injection analysis. Flow injection analysis (FIA) is an approach to chemical analysis that is accomplished by injecting a plug of sample into a flowing carrier stream. FIA is an automated method in which a sample is injected into a continuous flow of a carrier solution that mixes with other continuously flowing solutions before reaching a detector. Precision is dramatically increased when FIA is used instead of manual injections and as a result very specific FIA systems have been developed for a wide array of analytical techniques.

<b>Dataset-specific Instrument Name</b>	FIA
<b>Generic Instrument Name</b>	Flow Injection Analyzer
<b>Dataset-specific Description</b>	Dissolved Fe was determined using a Flow Injection Analysis scheme with spectrophotometric detection (Rainin Dynamax UV-C). Major components of the scheme include a Rabbit peristaltic pump, a Dynamax FL-1 fluorometer, a Rainin A/D board, and a Macintosh G3 computer running Rainin MacIntegrator v 1.4.3 to log and reduce data.
<b>Generic Instrument Description</b>	An instrument that performs flow injection analysis. Flow injection analysis (FIA) is an approach to chemical analysis that is accomplished by injecting a plug of sample into a flowing carrier stream. FIA is an automated method in which a sample is injected into a continuous flow of a carrier solution that mixes with other continuously flowing solutions before reaching a detector. Precision is dramatically increased when FIA is used instead of manual injections and as a result very specific FIA systems have been developed for a wide array of analytical techniques.

<b>Dataset-specific Instrument Name</b>	Flow injection for dFe DPD system with Rainin Dynamax Absorbance detector UV-C
<b>Generic Instrument Name</b>	Flow Injection Analyzer
<b>Dataset-specific Description</b>	Dissolved Fe was determined using a Flow Injection Analysis scheme with spectrophotometric detection (Rainin Dynamax UV-C). Major components were a Rabbit peristaltic pump, a Rainin Dynamax UV-C, a Rainin A/D board and a Macintosh G3 computer running Rainin MacIntegrator v 1.4.3 to log and reduce data. The spectrophotometric detection of the iron eluted from the column is achieved through its catalytic effect on the oxidation of N,N-dimethylp-phenylenediamine dihydrochloride (DPD) the oxidized product is measured at 514 nm.
<b>Generic Instrument Description</b>	An instrument that performs flow injection analysis. Flow injection analysis (FIA) is an approach to chemical analysis that is accomplished by injecting a plug of sample into a flowing carrier stream. FIA is an automated method in which a sample is injected into a continuous flow of a carrier solution that mixes with other continuously flowing solutions before reaching a detector. Precision is dramatically increased when FIA is used instead of manual injections and as a result very specific FIA systems have been developed for a wide array of analytical techniques.

<b>Dataset-specific Instrument Name</b>	Flow injection for dAl lumogallion system with Rainin Dynamax FL-1 fluorometer
<b>Generic Instrument Name</b>	Flow injection lumogallion system with fluorometer
<b>Dataset-specific Description</b>	Dissolved Al was determined using a Flow Injection Analysis scheme with fluorometric detection. The scheme produces a complex between lumogallion and dissolved Al. Major components of the scheme include a Rabbit peristaltic pump, a Dynamax FL-1 fluorometer, a Rainin A/D board, and a Macintosh G3 computer running Rainin MacIntegrator v 1.4.3 to log and reduce data.
<b>Generic Instrument Description</b>	An analytical system used to determine concentrations of chemical species in a sample based on the fluorescence from the reaction between lumogallion and the species of interest. The system typically comprises individual components typically including pumps, injection and autosampler valves, preconcentration columns and a fluorometer. The system is normally uniquely assembled for each analysis. (From SeaDataNet)

<b>Dataset-specific Instrument Name</b>	GO-FLO
<b>Generic Instrument Name</b>	GO-FLO Bottle
<b>Dataset-specific Description</b>	Pre-conditioned, teflon-coated 12L Go-Flo sampling bottles (General Oceanics, Miami, FL) were deployed on a polyurethane powder-coated aluminum rosette with titanium pilings and pressure housings (Sea-Bird Electronics, Inc., Bellevue, WA) attached to a Kevlar, non-metallic conducting cable.
<b>Generic Instrument Description</b>	GO-FLO bottle cast used to collect water samples for pigment, nutrient, plankton, etc. The GO-FLO sampling bottle is specially designed to avoid sample contamination at the surface, internal spring contamination, loss of sample on deck (internal seals), and exchange of water from different depths.

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## Deployments

### HLY1502

<b>Website</b>	<a href="https://www.bco-dmo.org/deployment/638807">https://www.bco-dmo.org/deployment/638807</a>
<b>Platform</b>	USCGC Healy
<b>Report</b>	<a href="https://datadocs.bco-dmo.org/docs/302/geotraces/GEOTRACES_ARCTIC/data_docs/cruise_reports/healy1502.pdf">https://datadocs.bco-dmo.org/docs/302/geotraces/GEOTRACES_ARCTIC/data_docs/cruise_reports/healy1502.pdf</a>
<b>Start Date</b>	2015-08-09
<b>End Date</b>	2015-10-12
<b>Description</b>	Arctic transect encompassing Bering and Chukchi Shelves and the Canadian, Makarov and Amundsen sub-basins of the Arctic Ocean. The transect started in the Bering Sea (60°N) and traveled northward across the Bering Shelf, through the Bering Strait and across the Chukchi shelf, then traversing along 170-180°W across the Alpha-Mendeleev and Lomonosov Ridges to the North Pole (Amundsen basin, 90°N), and then back southward along ~150°W to terminate on the Chukchi Shelf (72°N). Additional cruise information is available in the GO-SHIP Cruise Report (PDF) and from the Rolling Deck to Repository (R2R): <a href="https://www.rvdata.us/search/cruise/HLY1502">https://www.rvdata.us/search/cruise/HLY1502</a>

## Project Information

### GEOTRACES Arctic Section: Shipboard determination of key trace elements (GEOTRACES Arctic AI Fe Mn)

#### *NSF Award Abstract:*

In this project, investigators participating in the 2015 U.S. GEOTRACES Arctic expedition will make shipboard measurements of dissolved aluminum, iron, and manganese in seawater, ice, snow, and melt pond samples collected during the cruise. In common with other national initiatives in the International GEOTRACES Program, the goals of the U.S. Arctic expedition are to identify processes and quantify fluxes that control the distributions of key trace elements and isotopes in the ocean, and to establish the sensitivity of these distributions to changing environmental conditions. Some trace elements are essential to life, others are known biological toxins, and still others are important because they can be used as tracers of a variety of physical, chemical, and biological processes in the sea. This project will be of particular importance to the success of the overall Arctic expedition because measurements of trace metals in seawater require highly-specialized clean sampling techniques to prevent contamination. Accordingly, the shipboard measurements made by this scientific team will allow for the early detection and rectification of any sample contamination problems while still at sea. In terms of broader impacts, education and training of the next generation of marine trace element scientists, including undergraduate and graduate students, as well as public outreach will be key aspects of this project.

The shipboard determinations of dissolved aluminum, iron, and manganese in this study will provide near real-time insights into the distribution of these parameters, which can be used to potentially modify sampling strategies and can also be used to identify any systemic sampling contamination issues during the GEOTRACES Arctic expedition. Definitive data for dissolved iron and manganese will be produced by shore-based ICP MS, a type of mass spectrometry capable of detecting metals at very low concentrations. However, since dissolved aluminum data cannot be determined by shore-based ICP MS, the shipboard data set collected as part of this project will provide the definitive data set for this key GEOTRACES parameter. In addition, the researchers will undertake high resolution water sampling in the upper 10 m of the water column to characterize the trace metal distribution in this highly stratified region, which cannot be sampled by a conventional rosette. This sampling will be conducted from the edge of ice-floes or a small boat, away from the disturbing effects of the research vessel.

## Funding

Funding Source	Award
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1439253</a>