

Shipboard flow injection analysis (FIA) of dissolved Al, Fe, and Mn from R/V Knorr cruise KN204-01 (GA03) in the Subtropical northern Atlantic Ocean in 2011 (U.S. GEOTRACES NAT project)

Website: <https://www.bco-dmo.org/dataset/3822>

Data Type: Cruise Results

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Version Date: 2013-10-14

Project

» [U.S. GEOTRACES North Atlantic Transect](#) (U.S. GEOTRACES NAT)

Program

» [U.S. GEOTRACES](#) (U.S. GEOTRACES)

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Abstract

Shipboard flow injection analysis (FIA) of dissolved Al, Fe, and Mn from R/V Knorr cruise KN204-01 (GA03) in the Subtropical northern Atlantic Ocean in 2011 as part of the U.S. GEOTRACES North Atlantic project.

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Coverage

Spatial Extent: N:17.4 E:39.701 S:-24.5 W:-69.8029

Temporal Extent: 2011-11-06 - 2011-12-11

Dataset Description

Shipboard flow injection analysis (FIA) data of dissolved metals from the GT11 cruise (KN204-01). Samples were collected using GO-FLO bottles and filtered through 0.2 µm Acropak filters. Concentrations

and quality flags are reported for each metal.

Acquisition Description

Sampling Methods

The samples (with the exception of surface samples) were collected for trace metal determinations at 21 stations from the RV Knorr using a custom-built US GEOTRACES trace metal clean rosette consisting of an epoxy painted Al rosette frame containing 24x12 L GO-FLO bottles (Cutter and Bruland, 2012). Immediately after the package was recovered, the tops of the GO-FLO bottles were covered with plastic bags and the bottles were removed from the frame and carried into the US GEOTRACES clean van for sub-sampling. The GO-FLO bottles were pressurized to 10 psi using 0.2 µm-filtered compressed air and samples were filtered through 0.2 µm Acropak filters. All sub-sampling was undertaken in the clean van using rigorous trace metal protocols. Surface samples are from the towed fish surface sampling system.

Analytical Methods

FIA Sample Preparation: 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. Prior to determination samples were acidified by the addition of 125 µl sub-boiling distilled 6N HCl (hereinafter 6N HCl) and were microwaved in groups of 4 for 3 minutes in a 900 W microwave oven to achieve a temperature of 60+10 °C. Samples were allowed to cool for at least 1 hour prior to determination. Samples were determined in groups of 8.

FIA Standards: 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 + 10°C. After 1 hour, 200 + 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, +100µL, +200µL spikes of the shipboard mixed standard to these bottles, to yield a standard curve of +20.77nM and +31.53nM for Al, +0.97nM and +1.94nM for Fe, +3.84nM and +7.68nM 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 µl 6N HCl and 5 ml of sample buffer to the replicate bottle and comparing the resulting signal to the original sample.

Dissolved Al Concentrations: 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 0.24 and a precision of 4.8% at 1.67 nM.

Dissolved Fe: 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 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 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 oxidised 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 0.064 nM and a precision of 2.8%.

Dissolved Mn: 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 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 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 0.03 nM and a precision of 2.9% at 0.05 nM.

Calculation of FIA data: 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.

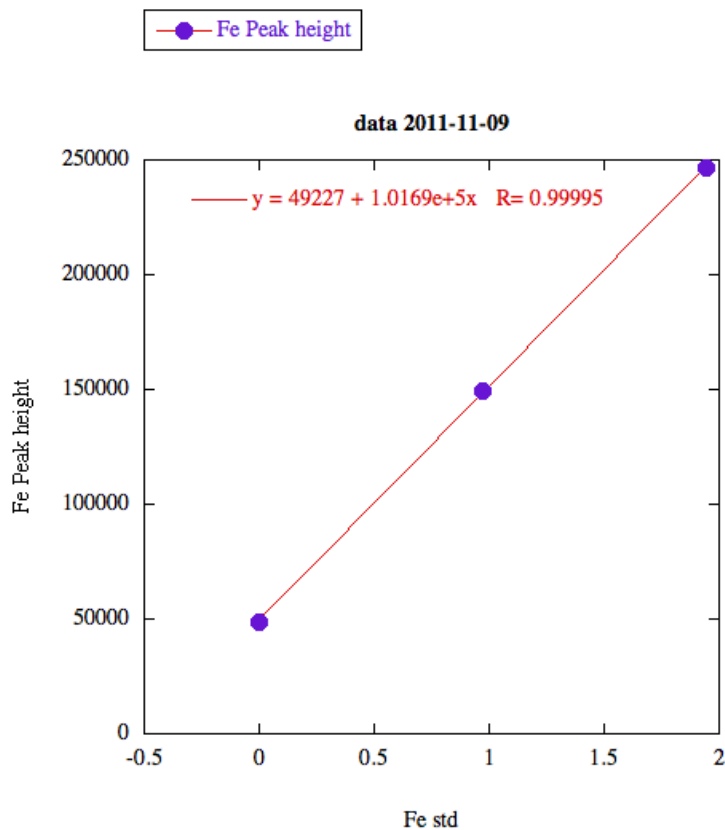
Data correction with shore-based ICPMS data

Shipboard determined dissolved Fe and Mn have been corrected using the shore-based ICPMS data that was measured by co-PI Dr. Jingfeng Wu. That data will be submitted separately. The corrected FIA data was calculated using the slope and the intercept of the correlation plot between the ICPMS data and FIA data on each of the days the FIA was run.

Shipboard dissolved Fe: Shipboard calculation:

The Fe concentration of samples was determined by dividing the sample peak height by the slope of the Fe standard solution. The standard curve was produced by adding +0 μ L (+0 nM), +100 μ L (+0.972 nM), +200 μ L (+1.944 nM) of the shipboard standard solution into 200 mL aliquots of seawater. This seawater was obtained from a 1L sample of seawater (usually from near the chlorophyll max) that had been filtered through a 0.2 μ m pore-size Acropack cartridge, acidified with 1 ml of 6N HCl (sub boiling distilled) and microwaved to achieve a temperature of 60 + 10°C. A typical standard curve is shown in Figure 1.

Figure 1. Fe standard curve from the standard addition method. (click on the image to view a larger version)



The shipboard standard solution was 1.944 μM and had been prepared by gravimetric dilution from a high purity standard solution (1000 $\mu\text{g}/\text{mL}$) at the shore-based laboratory of University of Hawaii. Overall precision is 2.8%, and the average detection limit is 0.064 nM.

Shipboard dissolved Fe: Blank calculation:

At sea the blank calculation of the data was made using the value derived from a sample that had been spiked with EDTA. This process yields a sample that should have no uncomplexed Fe thus allowing subtraction of the system blank.

Shore based adjustment of the shipboard data was made by comparison with the shore-based ICP MS data measured by J. Wu at U Miami. A plot of each station's data (FIA vs ICP MS) yielded a slope and intercept that was then used to recalculate the shipboard data. This indicated that the shipboard blank correction was underestimating the system blank.

Table 1. Slope and intercept between shipboard FIA (substituted EDTA blank) and ICPMS data

| Station | Slope | Intercept | R2 |
|-----------|-------|-----------|-------|
| USGT11-01 | 1.470 | -0.022 | 0.944 |
| USGT11-02 | 1.272 | 0.057 | 0.869 |
| USGT11-03 | 1.144 | 0.205 | 0.948 |
| USGT11-06 | 1.079 | 0.277 | 0.930 |
| USGT11-08 | 1.036 | 0.208 | 0.948 |
| USGT11-10 | 1.399 | 0.103 | 0.974 |
| USGT11-12 | 1.114 | 0.441 | 0.797 |
| USGT11-14 | 1.152 | 0.199 | 0.947 |
| USGT11-16 | 1.216 | 0.105 | 0.988 |
| USGT11-18 | 0.943 | 0.180 | 0.932 |
| USGT11-20 | 0.980 | 0.256 | 0.903 |
| USGT11-22 | 0.967 | 0.394 | 0.964 |
| USGT11-24 | 1.605 | 0.318 | 0.964 |

The ICPMS data reported by Miami (Dr. Wu) were only for full depth stations. Two of the demi stations

were determined at sea on the same day that full depth stations were run specifically GT11-17 and GT 16; GT11-23 and GT11-22. Thus, these samples were adjusted using the same slope and intercept used for the full depth station. However, the other demi station samples were determined on separate days. Thus, the samples cannot currently be adjusted with existing ICPMS data.

The following demi stations have not been adjusted and are not reported: USGT11-05, USGT11-11, USGT11-13, USGT11-18, and USGT11-21.

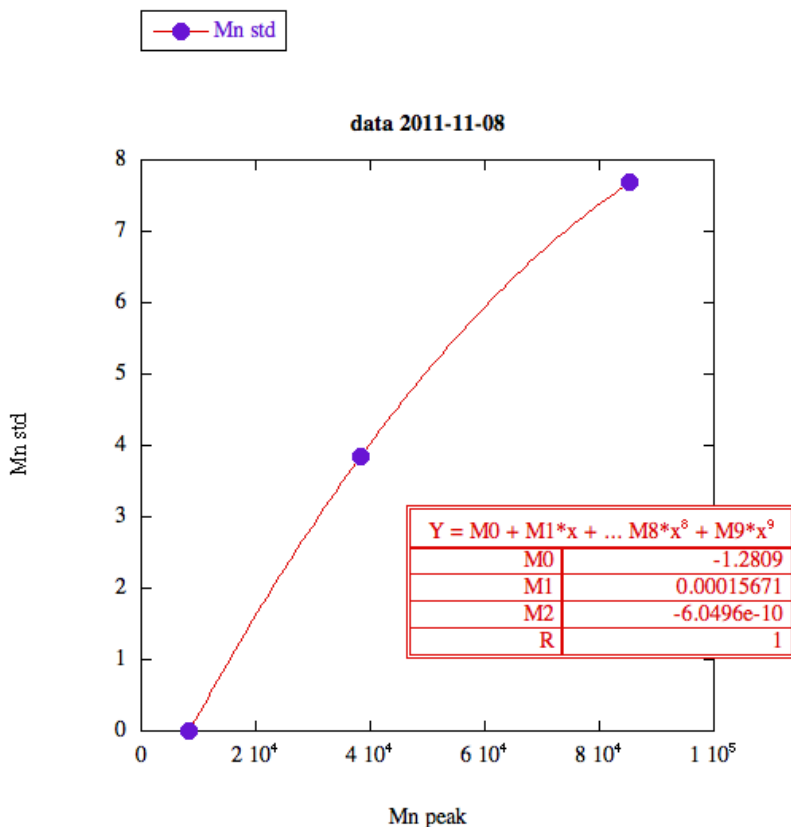
Shipboard dissolved Fe: Accuracy results:

There are no shipboard results for the recoveries of Certified Reference Materials (CRMs) or consensus reference materials (e.g., SAFe water) as these samples are too acid to be run using this protocol. Instead these data are corrected using the shore-based ICP MS values which are calibrated against SaFe samples.

Shipboard dissolved Mn: Details about calibration:

The Mn concentration of sample was calculated using the quadratic polynomial (x = the peak height, y = the Mn standard concentrations, $y= M0+M1x+M2x^2$). The coefficients ($M0$, $M1$, $M2$) of the polynomial were obtained based on the standard curve. This was produced by the standard addition method adding (+0 μ L (+0 nM), +100 μ L (+3.842 nM), +200 μ L (+7.683 nM) of the spike standard solution added into the 200mL of seawater which had been filtered through a 0.2 μ m pore-size Acropack cartridge.). A typical standard curve is shown in Figure 2.

Figure 2. Mn standard curve from the standard addition method, the polynomial fit, and the coefficients of the polynomial approximation. (click on the image to view a larger version)



The shipboard standard solution was 7.683 μ M and had been prepared by gravimetric dilution from a high purity standard solution (1000 μ g/mL) at the shore-based laboratory of University of Hawaii. The precision of the method, the relative standard deviation (RSD, %), and detection limit (3sigma; D.L.) were calculated on each analysis day from the triplicate analysis of a spiked standard seawater solution. Results are shown in Mn Table 1, below.

Overall average precision (from Mn Table 1 below) is 2.9%, and the average detection limit is 0.05 nM.

Shipboard dissolved Mn: Blank calculation:

There is no blank calculation of the data made at sea. Shore based adjustment of the shipboard data was made by comparison between the shore-based ICP MS data measured by J Wu at RSMAS, and the shipboard calculated data, the intercept being the blank offset between the methodologies. The ICPMS data has been submitted separately. In general, the difference was very small (average difference was + 0.029nM) which is similar to the analytical uncertainty of the shipboard method. The detailed value of the blank for each station is shown in Mn Table 2.

Shipboard dissolved Mn: Accuracy results:

There are no shipboard result for the recoveries of Certified Reference Materials (CRMs) or consensus reference materials (e.g., SAFe water) as these samples are too acid to be run using this protocol. Instead these data are corrected to the shore-based ICP MS values which are calibrated against SaFe samples.

Mn Table 1. Precision, Relative Standard Deviation, and Detection Limit of the shipboard FIA method for dissolved Mn

| | Concentration of std. solution for the precision (nM) | RSD % | D.L (nM) |
|--------------|--|--------------|-----------------|
| USGT11-01 | 1.243 | 2.1 | 0.079 |
| USGT11-02 | 1.027 | 3.4 | 0.103 |
| USGT11-03 | 0.653 | 2.2 | 0.043 |
| USGT11-05 | 0.533 | 3.9 | 0.062 |
| USGT11-06 | 0.620 | 1.6 | 0.030 |
| USGT11-08 | 0.443 | 1.6 | 0.021 |
| USGT11-10 | 1.109 | 2.1 | 0.070 |
| USGT11-11 | 0.708 | 3.6 | 0.076 |
| USGT11-12 | 0.396 | 3.2 | 0.038 |
| USGT11-13 | 0.271 | 2.7 | 0.022 |
| USGT11-14&15 | 0.334 | 1.5 | 0.015 |
| USGT11-16&17 | 0.183 | 1.1 | 0.006 |
| USGT11-18 | 0.160 | 4.2 | 0.020 |
| USGT11-19 | 0.128 | 1.2 | 0.005 |
| USGT11-20 | 1.371 | 1.2 | 0.050 |
| USGT11-21 | 0.713 | 8.5 | 0.181 |
| USGT11-22&23 | 0.123 | 4.9 | 0.018 |
| USGT11-24 | 0.563 | 3.6 | 0.061 |

Mn Table 2.

| Station | Blank (Intercept) | Memo |
|--------------------------------|--------------------------|--|
| USGT11-01 | 0.0298 | |
| USGT11-02 | 0.0626 | |
| USGT11-03 | -0.0151 | |
| USGT11-05 | 0.000 | |
| USGT11-06 | 0.0812 | |
| USGT11-08 | 0.0099 | |
| USGT11-10 | 0.0546 | |
| USGT11-11 | 0.000 | |
| USGT11-12 | 0.0610 | |
| USGT11-13 | 0.000 | |
| USGT11-14 | 0.0383 | |
| USGT11-15* | 0.0383 | |
| USGT11-16 (hydrothermal plume) | -0.00910 | |
| USGT11-17 | -0.0091 | |
| USGT11-18 | 0.0154 | |
| USGT11-19 | 0.000 | |
| USGT11-20 | 0.256 | Blank problem |
| USGT11-21 | 0.029 | No ICP MS use average blank correction |
| USGT11-22 | -0.0047 | |
| USGT11-23 | -0.0047 | |

Shipboard dissolved Al data: UH Shipboard methodology

UH Dissolved Al samples are run at sea using standards prepared from a bulk standard which has been diluted using gravimetry. We make two bottles of each working standard and take both bottles to sea but only use one of the bottles at sea (unless we think a bottle has been compromised). We bring both the unused and the partially used bottles of standard back to our laboratory for long term intercalibration. Aliquots of the shipboard standard are added to 200ml seawater samples that are obtained from a single bottle of 1L of seawater that has been acidified and microwaved and then cooled, to produce a standard curve that has +0, +20.77, +31.53 nM added Al. The concentration of Al in any sample is obtained by dividing the peak height of the sample by the slope of the peak height/nM of the standard curve. The intercept of the standard curve is not used since the "0" standard is not a true 0, but is the amount of Al already in the water used to produce the standards. We have not found that there is any procedural blank in this method (from double spiking samples with buffer and acid) and thus do not subtract any blank from the calculated values.

Comparison between UH and NIOZ Al data sets at BATS

In our opinion, the offset between the University of Hawaii and the NIOZ Al data sets in the Atlantic crossover station at Bermuda (Station S), appears to be a result of standard disagreement. This conclusion is based on the following analysis.

A plot of the two profiles shows the vertical distribution of the two data sets (24 NIOZ samples collected 12 June 2010 and 36 UH samples collected 19 November 2011). There are significant differences between the two profiles in the upper waters, particularly the surface waters, but this is hardly surprising given the 1.5 years between the two occupations and the times of year that they were conducted (June and November). Given that the upper water concentrations of dissolved Al are predominantly a function of atmospheric deposition and its incorporation into subsurface waters (Sub-Tropical Mode Waters) through subduction processes we have not attempted to derive conclusions from this part of the water column since they are likely to be highly temporally variable.

We are also excluding the data deeper than 4002 m since the shape of the two profiles which both appear to be oceanographically consistent appear to be quite different from each other, which we take to also be a difference due to variations in the strength of, or presence of, a bottom nepheloid layer between the two occupations.

Instead we focus on the region from 974m to 4002m where there is a clear and consistent offset between the two data sets.

A complicating factor in making the comparison though is that the samples from the two data sets are not at the same depths. In order to make a cross plot we have binned the two data sets to correspond to similar sampling depths (see attached table for the binning). Most of the samples are within ~50m depth, but two samples, (3600 and 3900 are ~ 100m apart).

The plot of the 9 corresponding data points from the two, shows a very clear correlation between the data sets ($R=0.993$) with a slope of 1.251. Virtually all of the data fall exactly on this line. If the somewhat anomalous point at 2500m in the UH data set is eliminated R increases slightly to $R=0.9965$ and the slope drops slightly to 1.24.

The implication of this is that the difference between these data sets is the result of a simple standard offset. A blank offset would lead to a constant difference between the data sets, which is not what this plot implies.

We do not have access to the NIOZ standards and have been informed by R. Middag that there are no aliquots left of the standard they actually used at sea. He is trying to track down the original stock standard that their shipboard standard was prepared from and we plan to obtain an aliquot of this to check against our standard.

Meanwhile, in an attempt to identify any possible source of the offset in our own standards we have rerun both our original concentrated standard used to produce our shipboard standards as well as the actual

standards that we used on board ship during both GT10 and GT11 cruises. The results are as follows:

- UH Concentrated standard (used to produce the shipboard standards) was diluted to produce a standard curve. (Standard A)
- GT10 and GT11 shipboard standards were then run and calculated against this concentrated standard curve.
- Another concentrated AI standard (Standard B) was procured from a different laboratory at UH and a dilution was made of this standard and it was run against Standard A.

Results of the standard intercomparison as a % of the expected value--all relative to Standard A:

GT10 93.0%

GT11 95.3%

Standard B 95.5%

Conclusions: Relative to Standard B, Standard A is 4.5% high, which could be the result of evaporation in that bottle. However these results which imply our standard maybe 4.5% high are preliminary and we intend to rerun all the standards again when we can get an aliquot of the NIOZ standard. We are also purchasing a new stock standard to evaluate the agreement between Standards A and B.

An evaporated stock standard will lead to an underestimate in the true value of the sample, so if anything our current understanding of our AI values is that they maybe 4.5% lower than the true value. We note an ~2.5% offset between the GT10 and GT11 standards which maybe a result of evaporation of the GT10 shipboard standard. We will compare the unused GT10 standard with the newly purchased concentrated standard when it arrives. We also hope to have an aliquot of the NIOZ standard at that point.

We also note that the NIOZ data are reported as per kg, whereas ours are volume based (we measure by volume at sea and so report in those units). Depending on the value they used to convert their data (we are assuming here that their values were originally on a per volume basis), the NIOZ data would be ~2.8% lower than the UH data.

Processing Description

Quality Flags:

Data have been flagged using the WOCE system of flags. Good is 2. Questionable is 3. Bad is 4. Samples that appear to be contaminated have been flagged 3.

Determination of contamination was by agreement with ICP MS data after adjustment (see above).

For dissolved Fe, samples in which both the ICP MS and the FIA data appear to be bad (not oceanographically consistent) have been flagged 4.

Flagged data from GT11 (2011 cruise):

Total reported sample count: 420

Flag 2 (Good): 368

Flag 3 (Questionable): 49

Flag 4 (Bad): 3

BCO-DMO Processing Notes

- Parameter names were modified to conform with BCO-DMO conventions.
- '-999' values were replaced with 'nd' to indicate 'no data'.
- The 'lon' parameter was calculated using the 'lon_360' values provided in the original data submission. ($lon = lon_{360} - 360$).
- Original data submission received on 12/18/12 was replaced with updated data received on 12/21/12, in which a small error and quality flags have been corrected.
- 04 March 2013: joined to master GEOTRACES file for consistency with other GEOTRACES datasets. Note: removed BTL_ISO_DateTime_UTC because values were all 'nd'.
- Dataset updated to new version on 22 May 2013.
- The dataset was again updated to a newer version (including updates and error fixes) on 14 October

2013 (most recent version).

Additional GEOTRACES Processing:

After the data were submitted to the International Data Management Office, BODC, the office noticed that important identifying information was missing in many datasets. With the agreement of BODC and the US GEOTRACES lead PIs, BCO-DMO added standard US GEOTRACES information, such as the US GEOTRACES event number, to each submitted dataset lacking this information. To accomplish this, BCO-DMO compiled a 'master' dataset composed of the following parameters: station_GEOTRC, cast_GEOTRC (bottle and pump data only), event_GEOTRC, sample_GEOTRC, sample_bottle_GEOTRC (bottle data only), bottle_GEOTRC (bottle data only), depth_GEOTRC_CTD (bottle data only), depth_GEOTRC_CTD_rounded (bottle data only), BTL_ISO_DateTime_UTC (bottle data only), and GeoFish_id (GeoFish data only). This added information will facilitate subsequent analysis and inter comparison of the datasets.

Bottle parameters in the master file were taken from the GT-C_Bottle_GT10, GT-C_Bottle_GT11, ODF_Bottle_GT10, and ODF_Bottle_GT11 datasets. Non-bottle parameters, including those from GeoFish tows, Aerosol sampling, and McLane Pumps, were taken from the Event_Log_GT10 and Event_Log_GT11 datasets. McLane pump cast numbers missing in event logs were taken from the Particulate Th-234 dataset submitted by Ken Buesseler.

A standardized BCO-DMO method (called "join") was then used to merge the missing parameters to each US GEOTRACES dataset, most often by matching on sample_GEOTRC or on some unique combination of other parameters.

If the master parameters were included in the original data file and the values did not differ from the master file, the original data columns were retained and the names of the parameters were changed from the PI-submitted names to the standardized master names. If there were differences between the PI-supplied parameter values and those in the master file, both columns were retained. If the original data submission included all of the master parameters, no additional columns were added, but parameter names were modified to match the naming conventions of the master file.

See the dataset parameters documentation for a description of which parameters were supplied by the PI and which were added via the join method.

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Related Publications

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

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 |
|----------------------|---|-----------------|
| cruise_id | Official cruise identifier e.g. KN199-04 = R/V Knorr cruise number 199-04. | text |
| station | Station identifier; provided in original data submission. | unitless |
| lon_360 | Longitude ranging from 0 to 360 degrees. | decimal degrees |
| lon | Longitude ranging from 0 to +/- 180. Negative values = West. Added by BCO-DMO based on lon_360. | decimal degrees |
| lat | Latitude ranging from 0 to +/- 180. Positive values = North. | decimal degrees |
| cast_GEOTRC | Cast identifier, numbered consecutively within a station. PI-supplied values were identical to those in the intermediate US GEOTRACES master file. Originally submitted as 'CAST No.', this parameter name has been changed to conform to BCO-DMO's GEOTRACES naming conventions. | unitless |
| depth_w | Bottom depth from the log sheet during each cast. | meters |
| sample_bottle_GEOTRC | Unique identification numbers given to samples taken from bottles; ranges from 1 to 24; often used synonymously with bottle number. PI-supplied values were identical to those in the intermediate US GEOTRACES master file. Originally submitted as 'GO-Flo No.', this parameter name has been changed to conform to BCO-DMO's GEOTRACES naming conventions. | unitless |
| sample_GEOTRC | Unique identifying number for US GEOTRACES samples; ranges from 5033 to 6078 for KN199-04 and from 6112 to 8148 for KN204-01. PI-supplied values were identical to those in the intermediate US GEOTRACES master file. Originally submitted as 'GEO Sample No.', this parameter name has been changed to conform to BCO-DMO's GEOTRACES naming conventions. | unitless |
| press | Pressure in decibars. | db |
| Al | Dissolved aluminum concentration. | nM |
| Al_flag | Quality flag for Al. 2 = good; 3 = questionable; 4 = bad; 9 = missing data. | unitless |
| Fe | Dissolved iron concentration. (lt = 'less than') | nM |
| Fe_flag | Quality flag for Fe. 2 = good; 3 = questionable; 4 = bad; 9 = missing data. | unitless |
| Mn | Dissolved manganese concentration. | nM |
| Mn_flag | Quality flag for Mn. 2 = good; 3 = questionable; 4 = bad; 9 = missing data. | unitless |
| cruise_name | GEOTRACES cruise identifier. | text |
| station_GEOTRC | GEOTRACES station number; ranges from 1 through 12 for KN199-04 and 1 through 24 for KN204-01. Stations 7 and 9 were skipped on KN204-01. Some GeoFish stations are denoted as X_to_Y indicating the tow occurred between stations X and Y. Values were added from the intermediate US GEOTRACES master file (see Processing Description). | dimensionless |

| | | |
|----------------------|--|---------------|
| depth_GEOTRC_CTD | Observation/sample depth in meters; calculated from CTD pressure. PI-supplied values were identical to those in the intermediate US GEOTRACES master file. Originally submitted as 'Depth [m]', this parameter name has been changed to conform to BCO-DMO's GEOTRACES naming conventions. | meters |
| event_GEOTRC | Unique identifying number for US GEOTRACES sampling events; ranges from 2001 to 2225 for KN199-04 events and from 3001 to 3282 for KN204-01 events. Values were added from the intermediate US GEOTRACES master file (see Processing Description). | dimensionless |
| bottle_GEOTRC | Alphanumeric characters identifying bottle type (e.g. NIS representing Niskin and GF representing GOFLO) and position on a CTD rosette. Values were added from the intermediate US GEOTRACES master file (see Processing Description). | dimensionless |
| BTL_ISO_DateTime_UTC | Date and time (UTC) of bottle firing | unitless |

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Instruments

| | |
|---|--|
| Dataset-specific Instrument Name | GO-FLO Bottle |
| Generic Instrument Name | GO-FLO Bottle |
| Dataset-specific Description | Samples were collected using a custom-built US GEOTRACES trace metal clean rosette consisting of an epoxy painted Al rosette frame containing 24x12 L GO-FLO bottles |
| Generic Instrument Description | 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. |

| | |
|---|--|
| Dataset-specific Instrument Name | GeoFish |
| Generic Instrument Name | GeoFish Towed near-Surface Sampler |
| Dataset-specific Description | Surface samples are from the towed fish surface sampling system. |
| Generic Instrument Description | The GeoFish towed sampler is a custom designed near surface (|

| | |
|---|--|
| Dataset-specific Instrument Name | Flow Injection Analyzer |
| Generic Instrument Name | Flow Injection Analyzer |
| Dataset-specific Description | Dissolved Fe and Mn were 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. |
| Generic Instrument Description | 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. |

| | |
|---|---|
| Dataset-specific Instrument Name | Flow injection lumogallion system with fluorometer |
| Generic Instrument Name | Flow injection lumogallion system with fluorometer |
| Dataset-specific Description | 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. |
| Generic Instrument Description | 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) |

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Deployments

KN204-01

| | |
|--------------------|--|
| Website | https://www.bco-dmo.org/deployment/58786 |
| Platform | R/V Knorr |
| Report | http://bcodata.whoi.edu/US_GEOTRACES/AtlanticSection/STS_Prelim_GT11_Doc.pdf |
| Start Date | 2011-11-06 |
| End Date | 2011-12-11 |
| Description | <p>The US GEOTRACES North Atlantic cruise aboard the R/V Knorr completed the section between Lisbon and Woods Hole that began in October 2010 but was rescheduled for November-December 2011. The R/V Knorr made a brief stop in Bermuda to exchange samples and personnel before continuing across the basin. Scientists disembarked in Praia, Cape Verde, on 11 December. The cruise was identified as KN204-01A (first part before Bermuda) and KN204-01B (after the Bermuda stop). However, the official deployment name for this cruise is KN204-01 and includes both part A and B. Science activities included: ODF 30 liter rosette CTD casts, ODU Trace metal rosette CTD casts, McLane particulate pump casts, underway sampling with towed fish and sampling from the shipboard "uncontaminated" flow-through system. Full depth stations are shown in the accompanying figure (see below). Additional stations to sample for selected trace metals to a depth of 1000 m are not shown. Standard stations are shown in red (as are the ports) and "super" stations, with extra casts to provide large-volume samples for selected parameters, are shown in green. Station spacing is concentrated along the western margin to evaluate the transport of trace elements and isotopes by western boundary currents. Stations across the gyre will allow scientists to examine trace element supply by Saharan dust, while also contrasting trace element and isotope distributions in the oligotrophic gyre with conditions near biologically productive ocean margins, both in the west, to be sampled now, and within the eastern boundary upwelling system off Mauritania, sampled last year. The cruise was funded by NSF OCE awards 0926204, 0926433 and 0926659. Additional information may be available from the vessel operator site, URL: http://www.whoi.edu/cruiseplanning/synopsis.do?id=1662. Cruise information and original data are available from the NSF R2R data catalog. ADCP data are available from the Currents ADCP group at the University of Hawaii at the links below: KN204-01A (part 1 of 2011 cruise; Woods Hole, MA to Bermuda) KN204-01B (part 2 of 2011 cruise; Bermuda to Cape Verde)</p> |

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Project Information

U.S. GEOTRACES North Atlantic Transect (U.S. GEOTRACES NAT)

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

Coverage: Subtropical western and eastern North Atlantic Ocean

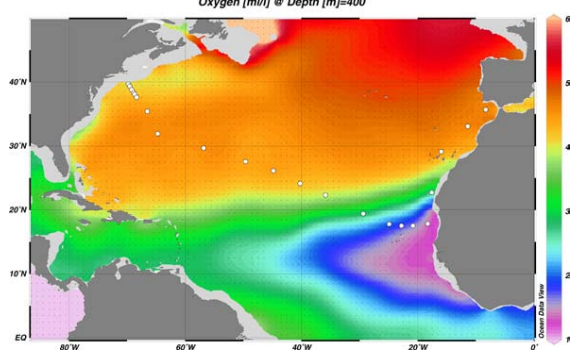
Much of this text appeared in an article published in OCB News, October 2008, by the OCB Project Office.

The first U.S. GEOTRACES Atlantic Section will be specifically centered around a sampling cruise to be carried out in the North Atlantic in 2010. Ed Boyle (MIT) and Bill Jenkins (WHOI) organized a three-day planning workshop that was held September 22-24, 2008 at the Woods Hole Oceanographic Institution. The main goal of the workshop, sponsored by the National Science Foundation and the U.S. GEOTRACES Scientific Steering Committee, was to design the implementation plan for the first U.S. GEOTRACES Atlantic Section. The primary cruise design motivation was to improve knowledge of the sources, sinks and

internal cycling of Trace Elements and their Isotopes (TEIs) by studying their distributions along a section in the North Atlantic (Figure 1). The North Atlantic has the full suite of processes that affect TEIs, including strong meridional advection, boundary scavenging and source effects, aeolian deposition, and the salty Mediterranean Outflow. The North Atlantic is particularly important as it lies at the "origin" of the global Meridional Overturning Circulation.

It is well understood that many trace metals play important roles in biogeochemical processes and the carbon cycle, yet very little is known about their large-scale distributions and the regional scale processes that affect them. Recent advances in sampling and analytical techniques, along with advances in our understanding of their roles in enzymatic and catalytic processes in the open ocean provide a natural opportunity to make substantial advances in our understanding of these important elements. Moreover, we are motivated by the prospect of global change and the need to understand the present and future workings of the ocean's biogeochemistry. The GEOTRACES strategy is to measure a broad suite of TEIs to constrain the critical biogeochemical processes that influence their distributions. In addition to these "exotic" substances, more traditional properties, including macronutrients (at micromolar and nanomolar levels), CTD, bio-optical parameters, and carbon system characteristics will be measured. The cruise starts at Line W, a repeat hydrographic section southeast of Cape Cod, extends to Bermuda and subsequently through the North Atlantic oligotrophic subtropical gyre, then transects into the African coast in the northern limb of the coastal upwelling region. From there, the cruise goes northward into the Mediterranean outflow. The station locations shown on the map are for the "fulldepth TEI" stations, and constitute approximately half of the stations to be ultimately occupied.

Figure 1. The proposed 2010 Atlantic GEOTRACES cruise track plotted on dissolved oxygen at 400 m depth. Data from the World Ocean Atlas (Levitus et al., 2005) were plotted using Ocean Data View (courtesy Reiner Schlitzer). [click on the image to view a larger version]

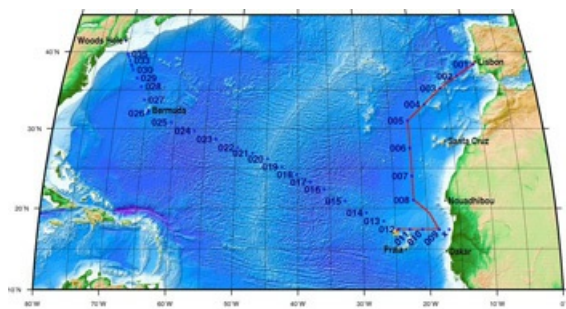


Hydrography, CTD and nutrient measurements will be supported by the Ocean Data Facility (J. Swift) at Scripps Institution of Oceanography and funded through NSF Facilities. They will be providing an additional CTD rosette system along with nephelometer and LADCP. A trace metal clean Go-Flo Rosette and winch will be provided by the group at Old Dominion University (G. Cutter) along with a towed underway pumping system.

The North Atlantic Transect cruise began in 2010 with KN199 leg 4 (station sampling) and leg 5 (underway sampling only) (Figure 2).

[KN199-04 Cruise Report \(PDF\)](#)

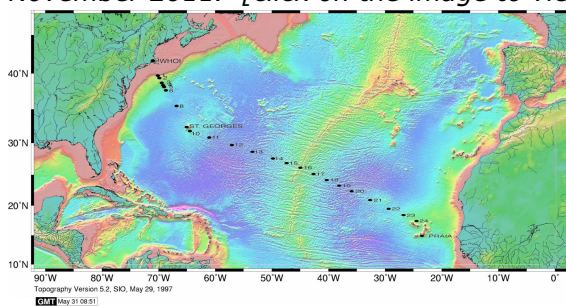
Figure 2. The red line shows the cruise track for the first leg of the US Geotraces North Atlantic Transect on the R/V Knorr in October 2010. The rest of the stations (beginning with 13) will be completed in October-December 2011 on the R/V Knorr (courtesy of Bill Jenkins, Chief Scientist, GNAT first leg). [click on the image to view a larger version]



The section completion effort resumed again in November 2011 with KN204-01A,B (Figure 3).

[KN204-01A,B Cruise Report \(PDF\)](#)

Figure 3. Station locations occupied on the US Geotraces North Atlantic Transect on the R/V Knorr in November 2011. [click on the image to view a larger version]



Data from the North Atlantic Transect cruises are available under the Datasets heading below, and consensus values for the SAFe and North Atlantic GEOTRACES Reference Seawater Samples are available from the GEOTRACES Program Office: [Standards and Reference Materials](#)

ADCP data are available from the Currents ADCP group at the University of Hawaii at the links below:

- [KN199-04](#) (leg 1 of 2010 cruise; Lisbon to Cape Verde)
- [KN199-05](#) (leg 2 of 2010 cruise; Cape Verde to Charleston, NC)
- [KN204-01A](#) (part 1 of 2011 cruise; Woods Hole, MA to Bermuda)
- [KN204-01B](#) (part 2 of 2011 cruise; Bermuda to Cape Verde)

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Program Information

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

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

Coverage: Global

GEOTRACES is a [SCOR](#) sponsored program; and funding for program infrastructure development is provided by the [U.S. National Science Foundation](#).

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.

Expand "Projects" below for information about and data resulting from individual US GEOTRACES research projects.

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Funding

| Funding Source | Award |
|--|-----------------------------|
| NSF Division of Ocean Sciences (NSF OCE) | OCE-0928741 |
| NSF Division of Ocean Sciences (NSF OCE) | OCE-1137812 |

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