

# Data from in situ pump profiler system collected on R/V Hugh R. Sharp cruise HRS1415 in August 2014

**Website:** <https://www.bco-dmo.org/dataset/718887>

**Data Type:** Cruise Results

**Version:** 1

**Version Date:** 2017-11-08

## Project

» [The role of soluble Mn\(III\) in the biogeochemical coupling of the Mn, Fe and sulfur cycles](#) (Soluble ManganeseII)

Contributors	Affiliation	Role
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## Abstract

Data from in situ pump profiler system collected on R/V Hugh R. Sharp cruise HRS1415 in August 2014

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## Coverage

**Spatial Extent:** N:38.9768 E:-76.3663 S:38.9758 W:-76.368

**Temporal Extent:** 2014-08-19 - 2014-08-22

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## Dataset Description

Data from in situ pump profiler system collected on cruise HRS1415.

See Related Publications (below) for field papers published as a result of this project (methods included).

## Methods & Sampling

### Description/methods for parameters measured:

**C parameters** performed by Dr. Wei-Jun Cai's group for:

TA - Open cell Gran titration with semi-automatic AS-ALK2 Apollo Scitech titrator;

pH - glass electrode, NBS buffers;

DIC - infrared CO<sub>2</sub> analyzer (AS-C3, Apollo Scitech).

Use Dickson CRM for calibration. DIC/TA samples were filtered (0.45um) and fixed with 100 ul of saturated mercury bichloride.

Use the methods of Gran (1952) and Huang, et al. (2012).

**Fe parameters:**

The method of Stookey (1972) is used to determine dissolved Fe(II) and on addition of hydroxylamine Fe total. Fe(III) is determined by difference. Modified and calibrated by many including Lewis et al (2007) and MacDonald et al (2014). Typically, triplicate measurements performed.

**Dissolved Mn parameters:**

The porphyrin spectrophotometric method of Madison et al (2011) measures dissolved Mn(II), Mn(III) bound to weaker ligands and total Mn. Method includes calibration and intercomparison of totals with other instrumentation (ICP, AA). Detection limit is 0.050 micromolar. Detection limit (DL) is 50 micromolar with a 1 cm path length cell.

Modification of Madison for Mn(III) bound to strong ligands by adding a reducing agent to a separate subsample with the porphyrin to obtain total Mn. Mn(III) bound to strong ligand complexes is determined by difference. Typically, triplicate measurements performed. Detection limit is 3.0 nanomolar.

**MnO<sub>x</sub> on unfiltered samples:**

The leucoberberin blue method is that of Altmann (1972) and Krumbein and Altmann (1973) in 1 cm cells, but can be modified for longer path length cells.

**S parameters:**

O<sub>2</sub>, H<sub>2</sub>S and polysulfides by the voltammetry method of Luther et al (2008).

A flow cell was also used to collect in situ O<sub>2</sub> and H<sub>2</sub>S data as well as some additional samples. Analysis by voltammetry (Luther et al, 2008).

Solid and nanoparticulate S<sub>8</sub> (Yücel et al 2010 and Findlay et al 2014).

Typically, triplicate measurements performed.

***In situ* pump profiler cast** refers to profiling with a pump profiler for O<sub>2</sub> and H<sub>2</sub>S using solid state gold-amalgam electrodes for voltammetry (Luther et al, 2008; Analytical Instrument Systems DLK-60) along with a temperature and salinity sensor from YSI. Water was pumped aboard to make measurements on discrete samples for Mn and Fe speciation as well.

**Methods papers used in this project (full citations in Related Publications section)****Dissolved Mn speciation parameters:**

Madison et al. (2011)

Madison et al. (2013)

Oldham et al. (2015)

Oldham et al. (2017)

[[ Here, we modified the method of Madison et al. (2011) for water column samples to achieve a detection limit of 3.0 nM (3 times the standard deviation of a blank) by using a 100-cm liquid waveguide capillary cell and the addition of a heating step as well as a strong reducing agent for Mn Speciation [ $Mn^{3+} = Mn_T - Mn^{2+}$ ]. See Table 1 in this paper for recovery tests. As weak Mn(III)-L complexes could not be measured in our previous work (Oldham et al, 2015; paper above), this method was used throughout this cruise. ]]

**MnO<sub>x</sub> solids:**

Altmann (1972)

Krumbein & Altmann (1973)

**Dissolved Fe speciation parameters:**

Stookey (1970)

Lewis et al. (2007)

**O<sub>2</sub> and H<sub>2</sub>S, polysulfides:**

Luther et al. (2008)

Luther et al. (2013)

**S<sub>8</sub>:**

Yücel et al. (2010)

## pH and inorganic carbon parameters:

Gran (1952)

Huang & Cai (2012)

## Data Processing Description

BCO-DMO Processing:

- added column for cast (was contained in header rows);
- modified parameter names to conform with BCO-DMO naming conventions;
- formatted date to mm/dd/yyyy to match CTD dataset;
- replaced blanks/missing data with "nd" ("no data");
- replaced "ND" (in all caps) with "not\_detected\_or\_BDL";
- replaced "NA" (in all caps) with "not\_analyzed";
- converted lat and lon from degrees and decimal minutes to decimal degrees;
- added date-time in ISO8601 format using original date and time\_GMT fields.

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## Data Files

File
<b>Pump_HRS1415.csv</b> (Comma Separated Values (.csv), 25.68 KB) MD5:1278c0ac323db3b323be1bf698c07560 Primary data file for dataset ID 718887

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## Related Publications

Altmann, H. J. (1972). Bestimmung von in Wasser gelöstem Sauerstoff mit Leukoberbelinblau I. Fresenius' Zeitschrift Für Analytische Chemie, 262(2), 97–99. doi:10.1007/bf00425919

<https://doi.org/10.1007/BF00425919>

*Methods*

Cai, W.-J., Huang, W.-J., Luther, G. W., Pierrot, D., Li, M., Testa, J., ... Kemp, W. M. (2017). Redox reactions and weak buffering capacity lead to acidification in the Chesapeake Bay. Nature Communications, 8(1).

doi:[10.1038/s41467-017-00417-7](https://doi.org/10.1038/s41467-017-00417-7)

*Methods*

Findlay, A. J., Bennett, A. J., Hanson, T. E., & Luther, G. W. (2015). Light-Dependent Sulfide Oxidation in the Anoxic Zone of the Chesapeake Bay Can Be Explained by Small Populations of Phototrophic Bacteria. Applied and Environmental Microbiology, 81(21), 7560–7569. doi:10.1128/aem.02062-15

<https://doi.org/10.1128/AEM.02062-15>

*Methods*

Findlay, A. J., Di Toro, D. M., & Luther, G. W. (2017). A model of phototrophic sulfide oxidation in a stratified estuary. Limnology and Oceanography, 62(5), 1853–1867. doi:[10.1002/lno.10539](https://doi.org/10.1002/lno.10539)

*Methods*

Findlay, A. J., Gartman, A., MacDonald, D. J., Hanson, T. E., Shaw, T. J., & Luther, G. W. (2014). Distribution and size fractionation of elemental sulfur in aqueous environments: The Chesapeake Bay and Mid-Atlantic Ridge. Geochimica et Cosmochimica Acta, 142, 334–348. doi:[10.1016/j.gca.2014.07.032](https://doi.org/10.1016/j.gca.2014.07.032)

*Methods*

Gran, G. (1952). Determination of the equivalence point in potentiometric titrations. Part II. The Analyst, 77(920), 661. doi:10.1039/an9527700661 <https://doi.org/10.1039/AN9527700661>

*Methods*

Huang, W.-J., Wang, Y., & Cai, W.-J. (2012). Assessment of sample storage techniques for total alkalinity and

dissolved inorganic carbon in seawater. *Limnology and Oceanography: Methods*, 10(9), 711–717.

doi:[10.4319/lom.2012.10.711](https://doi.org/10.4319/lom.2012.10.711)

*Methods*

Krumbein, W. E., & Altmann, H. J. (1973). A new method for the detection and enumeration of manganese oxidizing and reducing microorganisms. *Helgoländer Wissenschaftliche Meeresuntersuchungen*, 25(2-3), 347–356. doi:10.1007/bf01611203 <https://doi.org/10.1007/BF01611203>

*Methods*

Lewis, B. L., Glazer, B. T., Montbriand, P. J., Luther, G. W., Nuzzio, D. B., Deering, T., ... Theberge, S. (2007). Short-term and interannual variability of redox-sensitive chemical parameters in hypoxic/anoxic bottom waters of the Chesapeake Bay. *Marine Chemistry*, 105(3-4), 296–308. doi:[10.1016/j.marchem.2007.03.001](https://doi.org/10.1016/j.marchem.2007.03.001)

*Methods*

Luther, G. W., Madison, A. S., DeLaune, R. D., Reddy, K. R., Richardson, C. J., & Megonigal, J. P. (2013). Determination of Dissolved Oxygen, Hydrogen Sulfide, Iron(II), and Manganese(II) in Wetland Pore Waters. *SSSA Book Series*. doi:[10.2136/sssabookser10.c6](https://doi.org/10.2136/sssabookser10.c6)

*Methods*

Luther, G. W., Madison, A. S., Mucci, A., Sundby, B., & Oldham, V. E. (2015). A kinetic approach to assess the strengths of ligands bound to soluble Mn(III). *Marine Chemistry*, 173, 93–99.

doi:[10.1016/j.marchem.2014.09.006](https://doi.org/10.1016/j.marchem.2014.09.006)

*Methods*

MacDonald, D. J., Findlay, A. J., McAllister, S. M., Barnett, J. M., Hredzak-Showalter, P., Krepski, S. T., ... Luther III, G. W. (2014). Using in situ voltammetry as a tool to identify and characterize habitats of iron-oxidizing bacteria: from fresh water wetlands to hydrothermal vent sites. *Environ. Sci.: Processes Impacts*, 16(9), 2117–2126. doi:[10.1039/c4em00073k](https://doi.org/10.1039/c4em00073k)

*Methods*

Madison, A. S., Tebo, B. M., & Luther, G. W. (2011). Simultaneous determination of soluble manganese(III), manganese(II) and total manganese in natural (pore)waters. *Talanta*, 84(2), 374–381.

doi:[10.1016/j.talanta.2011.01.025](https://doi.org/10.1016/j.talanta.2011.01.025)

*Methods*

Madison, A. S., Tebo, B. M., Mucci, A., Sundby, B., & Luther, G. W. (2013). Abundant Porewater Mn(III) Is a Major Component of the Sedimentary Redox System. *Science*, 341(6148), 875–878.

doi:[10.1126/science.1241396](https://doi.org/10.1126/science.1241396)

*Methods*

Oldham, V. E., Jones, M. R., Tebo, B. M., & Luther, G. W. (2017). Oxidative and reductive processes contributing to manganese cycling at oxic-anoxic interfaces. *Marine Chemistry*, 195, 122–128.

doi:[10.1016/j.marchem.2017.06.002](https://doi.org/10.1016/j.marchem.2017.06.002)

*Methods*

Oldham, V. E., Miller, M. T., Jensen, L. T., & Luther, G. W. (2017). Revisiting Mn and Fe removal in humic rich estuaries. *Geochimica et Cosmochimica Acta*, 209, 267–283. doi:[10.1016/j.gca.2017.04.001](https://doi.org/10.1016/j.gca.2017.04.001)

*Methods*

Oldham, V. E., Mucci, A., Tebo, B. M., & Luther, G. W. (2017). Soluble Mn(III)-L complexes are abundant in oxygenated waters and stabilized by humic ligands. *Geochimica et Cosmochimica Acta*, 199, 238–246.

doi:[10.1016/j.gca.2016.11.043](https://doi.org/10.1016/j.gca.2016.11.043)

*Methods*

Oldham, V. E., Owings, S. M., Jones, M. R., Tebo, B. M., & Luther, G. W. (2015). Evidence for the presence of strong Mn(III)-binding ligands in the water column of the Chesapeake Bay. *Marine Chemistry*, 171, 58–66.

doi:[10.1016/j.marchem.2015.02.008](https://doi.org/10.1016/j.marchem.2015.02.008)

*Methods*

Olson, L., Quinn, K. A., Siebecker, M. G., Luther, G. W., Hastings, D., & Morford, J. L. (2017). Trace metal diagenesis in sulfidic sediments: Insights from Chesapeake Bay. *Chemical Geology*, 452, 47–59.

doi:[10.1016/j.chemgeo.2017.01.018](https://doi.org/10.1016/j.chemgeo.2017.01.018)

*Methods*

Stookey, L. L. (1970). Ferrozine---a new spectrophotometric reagent for iron. *Analytical Chemistry*, 42(7), 779–781. doi:[10.1021/ac60289a016](https://doi.org/10.1021/ac60289a016)

*Methods*

Yücel, M., Konovalov, S. K., Moore, T. S., Janzen, C. P., & Luther, G. W. (2010). Sulfur speciation in the upper

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## Parameters

Parameter	Description	Units
Cast	Cast identifier	unitless
lat	Latitude; positive values = North	decimal degrees
lon	Longitude; positive values = East	decimal degrees
date	Date of sampling formatted as m/dd/yyyy	unitless
time_local	Time of sampling (local time zone) formatted as HH:MM	unitless
time_GMT	Time of sampling (GMT) formatted as HH:MM	unitless
ISO_DateTime_UTC	Date and time of sampling formatted to ISO8601 standard (yyyy-mm-ddTHH:MM); constructed using original date and time_GMT fields.	unitless
depth	Sample depth	meters (m)
temp	Water temperature	degrees Celsius
salinity	Salinity	unitless
O2	Oxygen	micromolar (uM)
O2_stdev	Standard deviation of oxygen	micromolar (uM)
H2Splus_HSminus	H2S+ HS-	micromolar (uM)
H2Splus_HSminus_stdev	Standard deviation of H2S+ HS-	micromolar (uM)
Particulate_MnOx_eqvln	Particulate Manganese oxide (MnOx)	nanomolar (nM)
Particulate_MnOx_eqvln_stdev	Standard deviation of Particulate Manganese oxide	nanomolar (nM)

Dissolved_MnT	Dissolved MnT	nanomolar (nM)
Dissolved_MnT_stdev	Standard deviation of dissolved MnT	nanomolar (nM)
Dissolved_Mn2plus	Dissolved Mn2+	nanomolar (nM)
Dissolved_Mn2plus_stdev	Standard deviation of dissolved Mn2+	nanomolar (nM)
Dissolved_Mn3plus	Dissolved Mn3+ where $Mn3+ = [MnT - Mn2+]$	nanomolar (nM)
pcnt_Mn3	%Mn(III)	uM or %?
Filtered_Fe2plus	Filtered Fe2+	micromolar (uM)
Filtered_Fe2plus_stdev	Standard deviation of filtered Fe2+	micromolar (uM)
Unfiltered_Fe2plus	Unfiltered Fe2+	micromolar (uM)
Unfiltered_Fe2plus_stdev	Standard deviation of unfiltered Fe2+	micromolar (uM)
Filtered_Fe3plus	Filtered Fe3+	micromolar (uM)
Filtered_Fe3plus_stdev	Standard deviation of filtered Fe3+	micromolar (uM)
Unfiltered_Fe3plus	Unfiltered Fe3+	micromolar (uM)
Unfiltered_Fe3plus_stdev	Standard deviation of unfiltered Fe3+	micromolar (uM)
nanoparticulate_S0	Nanoparticulate S(0)	nanomolar (nM)
particulate_S0	Particulate S(0)	nanomolar (nM)

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## Instruments

<b>Dataset-specific Instrument Name</b>	AS-C3, Apollo Scitech infrared CO2 analyzer
<b>Generic Instrument Name</b>	CO2 Analyzer
<b>Generic Instrument Description</b>	Measures atmospheric carbon dioxide (CO2) concentration.

<b>Dataset-specific Instrument Name</b>	
<b>Generic Instrument Name</b>	Pump
<b>Dataset-specific Description</b>	The pump is home made and consists of a West marine pump (12 V DC; flow rate of 160 L/hr) attached to 30 m of 1 inch ID and 1-3/8 inch OD high pressure clear PVC tubing. Valves and outlets are attached to the tubing outlet for sample collection and to go to the sensors onboard.
<b>Generic Instrument Description</b>	A pump is a device that moves fluids (liquids or gases), or sometimes slurries, by mechanical action. Pumps can be classified into three major groups according to the method they use to move the fluid: direct lift, displacement, and gravity pumps

<b>Dataset-specific Instrument Name</b>	YSI 350
<b>Generic Instrument Name</b>	Salinity Sensor
<b>Dataset-specific Description</b>	The YSI model 350 probe measures salinity and temperature.
<b>Generic Instrument Description</b>	Category of instrument that simultaneously measures electrical conductivity and temperature in the water column to provide temperature and salinity data.

<b>Dataset-specific Instrument Name</b>	AS-ALK2 Apollo Scitech titrator
<b>Generic Instrument Name</b>	Titrator
<b>Generic Instrument Description</b>	Titration are instruments that incrementally add quantified aliquots of a reagent to a sample until the end-point of a chemical reaction is reached.

<b>Dataset-specific Instrument Name</b>	
<b>Generic Instrument Name</b>	Voltammetry Analyzers
<b>Generic Instrument Description</b>	Instruments that obtain information about an analyte by applying a potential and measuring the current produced in the analyte.

<b>Dataset-specific Instrument Name</b>	YSI model 350
<b>Generic Instrument Name</b>	Water Temperature Sensor
<b>Dataset-specific Description</b>	The YSI model 350 probe measures salinity and temperature.
<b>Generic Instrument Description</b>	General term for an instrument that measures the temperature of the water with which it is in contact (thermometer).

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## Deployments

HRS1415

<b>Website</b>	<a href="https://www.bco-dmo.org/deployment/717689">https://www.bco-dmo.org/deployment/717689</a>
<b>Platform</b>	R/V Hugh R. Sharp
<b>Start Date</b>	2014-08-18
<b>End Date</b>	2014-08-25

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## Project Information

### **The role of soluble Mn(III) in the biogeochemical coupling of the Mn, Fe and sulfur cycles (Soluble ManganeseIII)**

**Coverage:** Chesapeake Bay and coastal Atlantic Ocean

#### *Description from NSF award abstract:*

The research conducted by investigators in the School of Marine Science and Policy at the University of Delaware and within the Department of Environmental and Biomolecular Systems of Oregon Health and Science University will examine the importance of soluble Mn(III) in the biogeochemical cycling of Mn. To date, most studies of Mn in marine environments have not considered Mn(III), the intermediate oxidation state between the soluble reduced state (Mn(II)) and the more insoluble oxidized state (Mn(IV)). The presence and stability of Mn(III) in marine systems, especially those where oxygen levels are reduced, changes the dynamics and stability, solubility and fate and transport of Mn in these locations, and at interfaces between oxic and low oxygen environments. This is not understood at present and the proposed research is poised to provide new information concerning the Mn cycle and is potentially transformative research. The PIs have developed new methods to examine Mn(III) levels in the environment and this capability will bolster the successful accomplishment of the project's goals. The studies will not only focus on understanding the cycling of Mn between its various oxidation states but will determine the concentration and distribution of Mn(III) in stratified coastal ocean waters and in sediment porewaters. The study will also examine the potentially important role of Mn(III) in mediating and influencing the biogeochemical cycling of Mn with that of Fe and S, which are both important components of the major ocean chemical cycles. A better understanding of the biogeochemistry of Mn will inform not only scientists interested in metal cycling in the ocean but also those focused on studies across redox transition zones. The proposed research has an international component and the investigators have developed plans to broadly disseminate their results to students at all levels and to the community. The Principal Investigators have a strong history in education and graduate student and post-doctoral support and mentoring and this will continue under the current grant.

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## Funding

<b>Funding Source</b>	<b>Award</b>
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1155385</a>

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