

Water column data from samples collected on R/V Hugh Sharp cruise HRS1709 in the Chesapeake Bay in August 2017

Website: <https://www.bco-dmo.org/dataset/840678>

Data Type: Cruise Results

Version: 1

Version Date: 2021-02-17

Project

» [Collaborative Research: Transformations of soluble Mn\(III\) along horizontal and vertical oxygen gradients](#) (Manganese3)

| Contributors | Affiliation | Role |
|-----------------------------------|---|---------------------------|
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Abstract

Water column data from samples collected on R/V Hugh Sharp cruise HRS1709 in the Chesapeake Bay in August 2017.

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Coverage

Spatial Extent: N:38.9815 E:-76.3618 S:38.9764 W:-76.3687

Temporal Extent: 2017-08-04 - 2017-08-09

Acquisition Description

In situ pump profiler cast refers to profiling with a pump profiler for O₂ and H₂S using solid state gold-amalgam electrodes for voltammetry (Luther et al, 2008; Analytical Instrument Systems DLK-60). Water was pumped aboard to make measurements on discrete samples for Mn and Fe speciation as well. See Hudson et al (2019) for more information.

Samples for Mn and Fe parameters were filtered through 0.20 um filters. Whatman track etched polycarbonate filters were soaked in 1M HCl for 1 week before rinsing and storage in DI.

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 CO₂ analyzer (AS-C3, Apollo Scitech).

Uses Dickson CRM for calibration. DIC/TA samples were filtered (0.45µm) and fixed with 100 µl of saturated mercury bichloride. Uses the methods of Gran (1952) and Huang, et al. (2012).

Dissolved Mn parameters:

The porphyrin spectrophotometric method of Madison et al (2011, 2013) 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 et al for Mn(III) bound to strong ligands by adding a reducing agent to a separate subsample with the porphyrin to obtain total Mn (Oldham 2015, 2017; Thibault de Chanvalon and Luther, 2019). Mn(III) bound to strong ligand complexes is determined by difference. Typically, triplicate measurements performed. Detection limit can be extended to 3.0 nanomolar with a 1m path length cell.

Modification of Madison et al. for water column samples by adding higher Cd(II) so that cadmium-chloride complex formation would not inhibit cadmium-porphyrin formation and thus incorporation of Mn into the porphyrin by Cd replacement (Thibault de Chanvalon and Luther, 2019, this work). This modification enhanced the kinetics of the reaction progress for both Mn(II) and weak Mn(III)-L complexes.

MnO_x on unfiltered samples

The leucoberberlein blue method is that of Jones et al (2019, this work) in 1 cm cells, but can be modified for longer path length cells.

H₂S

O₂ and H₂S by the voltammetry method of Luther et al (2008) and Hudson et al (2019) using a flow cell. O₂ also from CTD sensor.

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). Typically, triplicate measurements performed.

Nitrite

Nitrite as determined by the method of Grasshoff (1983).

Dissolved Mn speciation references:

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 [Mn³⁺ = MnT - Mn²⁺]. 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.

Thibault de Chanvalon & Luther (2019) - Here, we modified the method of Madison et al. (2011) for water column samples by adding higher Cd(II) so that cadmium-chloride complex formation would not inhibit cadmium-porphyrin formation and thus incorporation of Mn into the porphyrin by Cd replacement. This modification enhanced the kinetics of the reaction progress for both Mn(II) and weak Mn(III)-L complexes.

Dissolved Fe speciation references:

Stookey (1970)

Lewis et al. (2007)

H₂S (in situ voltammetry)– water column:

Luther et al. (2008)

H₂S (UV-Vis spectrophotometry) – sedimentary porewater samples:

Luther et al. (2011)

MnO_x solids:

Jones et al. (2019)

pH and inorganic carbon parameters:

Gran (1952)

Huang et al. (2012)

Nitrite:

Determination of nitrite, nitrate, oxygen, thiosulphate in Grasshoff et al. (1983)

Processing Description**Data Processing:**

NM is used to indicate sensor not available or no measurement. BDL indicates measurements below the detection limit. Refer to parameter definitions for detection limits.

BCO-DMO Processing:

- converted date field to YYYY-MM-DD format;
- added date/time column in ISO8601 format (UTC/GMT);
- converted latitude and longitude to decimal degrees from degrees and decimal minutes.

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Related Publications

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

Grasshoff, K., Kremling, K., and Ehrhardt, M. (1983). *Methods of Seawater Analysis*. Verlag Chemia, Florida
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

Hudson, J. M., MacDonald, D. J., Estes, E. R., & Luther, G. W. (2019). A durable and inexpensive pump profiler to monitor stratified water columns with high vertical resolution. *Talanta*, 199, 415–424. doi:[10.1016/j.talanta.2019.02.076](https://doi.org/10.1016/j.talanta.2019.02.076)
Methods

Jones, M. R., Luther, G. W., Mucci, A., & Tebo, B. M. (2019). Concentrations of reactive Mn(III)-L and MnO₂ in estuarine and marine waters determined using spectrophotometry and the leuco base, leucoberbelin blue. *Talanta*, 200, 91–99. doi:[10.1016/j.talanta.2019.03.026](https://doi.org/10.1016/j.talanta.2019.03.026)
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., Findlay, A. J., MacDonald, D. J., Owings, S. M., Hanson, T. E., Beinart, R. A., & Girguis, P. R. (2011). Thermodynamics and Kinetics of Sulfide Oxidation by Oxygen: A Look at Inorganically Controlled Reactions and Biologically Mediated Processes in the Environment. *Frontiers in Microbiology*, 2. doi:[10.3389/fmicb.2011.00062](https://doi.org/10.3389/fmicb.2011.00062)

Methods

Luther, G. W., Glazer, B. T., Ma, S., Trouwborst, R. E., Moore, T. S., Metzger, E., ... Brendel, P. J. (2008). Use of voltammetric solid-state (micro)electrodes for studying biogeochemical processes: Laboratory measurements to real time measurements with an in situ electrochemical analyzer (ISEA). *Marine Chemistry*, 108(3-4), 221–235. doi:[10.1016/j.marchem.2007.03.002](https://doi.org/10.1016/j.marchem.2007.03.002)

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., 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

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

Thibault de Chanvalon, A., & Luther, G. W. (2019). Mn speciation at nanomolar concentrations with a porphyrin competitive ligand and UV–vis measurements. *Talanta*, 200, 15–21. doi:[10.1016/j.talanta.2019.02.069](https://doi.org/10.1016/j.talanta.2019.02.069)

Methods

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Parameters

| Parameter | Description | Units |
|------------------|---|---------------|
| Region | Sampling location | unitless |
| cruise | Cruise identifier | unitless |
| cast | Cast number | unitless |
| sample | Bottle number or pump-profiler number | unitless |
| date | Date of sample collection; format: YYYY-MM-DD | unitless |
| local_time_EST | Time of sample collection in the local time zone (US Eastern Daylight); format: hh:mm | unitless |
| ISO_DateTime_UTC | Date and time of sample collection (UTC/GMT) formatted to ISO8601 standard: YYYY-mm-ddTHH:MMZ | unitless |
| Latitude | Latitude in decimal degrees; positive values = North | degrees North |
| Longitude | Longitude in decimal degrees; negative value = West | degrees East |
| depth | Sample depth | meters (m) |

| | | |
|----------------------|---|-----------------------------------|
| temperature | Water temperature from CTD | degrees Celsius |
| salinity | Salinity from CTD | PSU |
| CTD_O2 | O2 from CTD | micromolar (uM) |
| O2_100_pcnt_sat_at_T | 100% O2 sat at T | micromolar (uM) |
| pcnt_O2_sat | Percent O2 saturation | unitless (percent) |
| fluor_voltage | Fluorescence (chl) voltage | volts |
| transmiss_voltage | Transmissometry voltage | volts |
| H2S | H2S | micromolar (uM) |
| TA | TA | micromoles per kilogram (umol/kg) |
| DIC | DIC | micromoles per kilogram (umol/kg) |
| pH_NBS | pH, NBS scale at 25 degrees C | unitless |
| pMnOx | Particulate MnOx; particulate on the 0.20 micrometer filter; single measurement; detection limit = 0.01 uM | micromolar (uM) |
| dMn2plus | Dissolved Mn2+; filtered through 0.20 micrometer filters; detection limit = 0.05 uM | micromolar (uM) |
| dMn2plus_stdev | Standard deviation of dMn2plus | micromolar (uM) |
| dMn3plus | Dissolved Mn3+ by difference; Mn3+ = [MnT - Mn2+]; detection limit = 0.05 uM | micromolar (uM) |
| dMn3plus_stdev | Standard deviation of dMn3plus | micromolar (uM) |
| dMnTotal | Mn total; filtered through 0.20 micrometer filters; detection limit = 0.05 uM | micromolar (uM) |
| dMnTotal_stdev | Standard deviation of dMnTotal | micromolar (uM) |
| dFe2plus | Dissolved Fe2+; filtered through 0.20 micrometer filters; detection limit = 0.02 uM | micromolar (uM) |
| dFe2plus_stdev | Standard deviation of dFe2plus | micromolar (uM) |
| pFe2plus | Particulate Fe2+; no filtering of water; detection limit = 0.02 uM | micromolar (uM) |
| pFe2plus_stdev | Standard deviation of pFe2plus | micromolar (uM) |
| dFeTotal | Dissolved Fe total = FeT = [Fe2+] + [Fe3+]; filtered through 0.20 micrometer filters; detection limit = 0.02 uM | micromolar (uM) |
| dFeTotal_stdev | Standard deviation of dFeTotal | micromolar (uM) |
| pFeTotal | Particulate Fe total = FeT = [Fe2+] + [Fe3+]; no filtering of water; detection limit = 0.02 uM | micromolar (uM) |
| pFeTotal_stdev | Standard deviation of pFeTotal | micromolar (uM) |
| dFe3plus | Dissolved Fe3+ by difference; Fe3+ = [FeT - Fe2+] | micromolar (uM) |
| dFe3plus_stdev | Standard deviation of dFe3plus | micromolar (uM) |
| pFe3plus | Particulate Fe3+ by difference; Fe3+ = [FeT - Fe2+] | micromolar (uM) |
| pFe3plus_stdev | Standard deviation of pFe3plus | micromolar (uM) |

| | | |
|----------|--|-----------------|
| Nitrite | Nitrite; single measurement; dissolved, filtered through 0.20 micrometer filters | micromolar (uM) |
| Comments | Notes/comments about the sampling events | unitless |

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Instruments

| | | |
|---|--|--|
| Dataset-specific Instrument Name | AS-ALK2 Apollo Scitech | |
| Generic Instrument Name | Automatic titrator | |
| Generic Instrument Description | Instruments that incrementally add quantified aliquots of a reagent to a sample until the end-point of a chemical reaction is reached. | |

| | | |
|---|--|--|
| Dataset-specific Instrument Name | In situ pump profiler | |
| Generic Instrument Name | Pump | |
| Dataset-specific Description | Profiling was conducted with a pump profiler for using solid state gold-amalgam electrodes for voltammetry (Luther et al, 2008; Analytical Instrument Systems DLK-60). See Hudson et al (2019), doi: 10.1016/j.talanta.2019.02.076. | |
| Generic Instrument Description | 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 | |

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

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Deployments

HRS1709

| | |
|--------------------|--|
| Website | https://www.bco-dmo.org/deployment/840681 |
| Platform | R/V Hugh R. Sharp |
| Start Date | 2017-08-03 |
| End Date | 2017-08-10 |
| Description | See more information from the Rolling Deck to Repository (R2R): https://www.rvdata.us/search/cruise/HRS1709GL Cruise DOI: 10.7284/907690 |

Project Information

Collaborative Research: Transformations of soluble Mn(III) along horizontal and vertical oxygen gradients (Manganese3)

Coverage: Broadkill River wetland, the Chesapeake Bay, the Lower St. Lawrence Estuary, and of 9deg 50' N East Pacific Rise

NSF Award Abstract:

Manganese (Mn) is an important trace nutrient for biological growth in marine organisms. In the past, all Mn dissolved in seawater was thought to exist in only one chemical form: Mn(II). Recent work in waters and sediments with little or no oxygen has shown that Mn(III) can be the dominant form of dissolved Mn and can even be present in oxygenated water if attached to specific organic molecules called ligands. This research will further investigate these discoveries, aiming to quantify the chemical and microbiological processes responsible for Mn(III) cycling under varying oxygen concentrations. The research will compare field sites in the Broadkill River wetland, the Chesapeake Bay, and the Lower St. Lawrence Estuary; measuring the water column and sediments known to have strong oxygen gradients and different organic carbon sources that could change the availability and binding strength of ligands that would stabilize dissolved Mn(III). In some chemical forms, Mn tends to act like iron, so this research may have broader implications by helping marine chemists to understand more about iron cycling in similar oxygen gradients. With growing concerns over diminished oxygen concentrations (hypoxia) in the ocean, and particularly in coastal regions, understanding the reactions of Mn(III) with organic ligands across oxygen gradients could become important for understanding Mn availability to organisms. The project includes support for the participation and mentoring of one graduate student and two postdoctoral researchers, and there will be a U.S.-Canada collaboration. A variety of public outreach activities are planned with a K-12 teacher to be selected as a participant on a research cruise.

Mn(III) has only recently been recognized as an important redox state for Mn in seawater. Previously, it was widely accepted that all Mn that passes through a 0.2 or 0.4 μm filter is dissolved Mn(II) while the retained portion is solid Mn(III, IV) oxide. Research in the Black Sea, the Baltic Sea, and the Chesapeake Bay has shown that soluble Mn(III) can be up to 100% of the dissolved Mn in the water column. Also, Mn(III) can exist as complexes with organic ligands in oxygenated seawater. This project will quantify and constrain the mechanisms surrounding weak and strong Mn(III) ligand transformations across vertical and horizontal oxygen gradients. Field sites to be studied include systems with a variety of organic carbon sources and oxygen dynamics: the Lower St. Lawrence Estuary, Chesapeake Bay, and Broadkill River wetland estuary. This research will continue to inform the fundamental shift that is taking place in our current understanding of Mn biogeochemistry in coastal systems. The results should also be applicable to redox processes involving Fe(III) ligand transformations, since Mn and Fe tend to exhibit similar redox chemistry under similar environmental conditions.

Funding

| Funding Source | Award |
|--|-----------------------------|
| NSF Division of Ocean Sciences (NSF OCE) | OCE-1558738 |
| NSF Division of Ocean Sciences (NSF OCE) | OCE-1558692 |

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