CTD rosette and Bottle data from R/V Hugh R. Sharp cruise HRS1314 in the Chesapeake Bay and coastal Atlantic Ocean in August 2013

Website: https://www.bco-dmo.org/dataset/646279
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Project
» The role of soluble Mn(III) in the biogeochemical coupling of the Mn, Fe and sulfur cycles (Soluble ManganeseIII)

Contributors	Affiliation	Role
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Dataset Description

Chesapeake Bay 2013 cruise LOG
(R/V Sharp cruise HRS1314 - 130809GL)
Chesapeake Bay / Offshore August 9 – August 16, 2013

Methods papers used in this project
Dissolved Mn speciation parameters

Madison, A., B. M. Tebo, G. W. Luther, III. 2011. Simultaneous determination of soluble manganese(III), manganese(II) and total manganese in natural (pore)waters. *Talanta* 84, 374-381. http://dx.doi.org/10.1016/j.talanta.2011.01.025

Madison, A. S, B. M. Tebo, A. Mucci, B. Sundby and G. W. Luther, III. 2013. Abundant Mn(III) in porewaters is a major component of the sedimentary redox system. *Science* 341, 875-878. http://dx.doi.org/10.1126/science.1241396

Oldham, V. O., S. M. Owings, M. Jones, B. M. Tebo and G. W. Luther, III. 2015. Evidence for the presence of strong Mn(III)-binding ligands in the water column of the Chesapeake Bay. *Marine Chemistry* 171, 58-66. http://dx.doi.org/10.1016/j.marchem.2015.02.008

MnO_X solids

Altmann, H.H., 1972. Bestimmung von inWasser gelöstem Sauerstoffmit Leukoberbelinblau I. Fresenius' Z. Anal. Chem. 6, 97–99.

Krumbein, W. E., and H. J. Altmann. 1973. ‘A New Method for the Detection and Enumeration of Manganese Oxidizing and Reducing Microorganisms’. Helgoländer Wissenschaftliche Meeresuntersuchungen 25 (2-3): 347–56. doi:10.1007/BF01611203.

Dissolved Fe speciation parameters
Stookey L.L. 1970. Ferrozine- A New Spectrophotometric Reagent for Iron. Anal. Chem. 42, 779-781.

Lewis, B. L., B. T. Glazer, P. J. Montbriand, G. W. Luther, III, D. B. Nuzzio, T. Deering, S. Ma, and S. Theberge. 2007. Short-term and interannual variability of redox-sensitive chemical parameters in hypoxic/anoxic bottom waters of the Chesapeake Bay. *Marine* Chemistry 105, 296-308.

O_2 and H_2S, polysulfides
Luther, III, G. W., B. T. Glazer, S. Ma, R. E. Trouwborst, T. S. Moore, E. Metzger, C. Kraiya, T. J. Waite, G. Druschel, B. Sundby, M. Taillefert, D. B. Nuzzio, T. M. Shank, B. L. Lewis and P. J. Brendel. 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, 221-235. http://dx.doi.org/10.1016/j.marchem.2007.03.002

Luther, G. W., III, and A. S. Madison. 2013. Determination of Dissolved Oxygen, Hydrogen Sulfide, Iron(II), and Manganese(II) in Wetland Pore Waters. In: Methods in Biogeochemistry of Wetlands, R.D. DeLaune, K.R. Reddy, C.J. Richardson, and J.P. Megonigal, editors. SSSA Book Series, no. 10. SSSA, Madison, WI. p. 87-106. http://dx.doi.org/10.2136/sssabookser10.c6

S_8
Yücel, M., S. K. Konovalov, T. S. Moore, C. P. Janzen and G. W. Luther, III. 2010. Sulfur speciation in the upper Black Sea sediments. *Chemical Geology* 269, 364-375. http://dx.doi.org/10.1016/j.chemgeo.2009.10.010

pH and inorganic carbon parameters
Gran G. 1952. Determination of the equivalence point in potentiometric titrations, Part II. *Analyst*, 77: 661-671.

Huang W.-J., Wang Y., and Cai W.-J. 2012. Assessment of sample storage techniques for total alkalinity and dissolved inorganic carbon in seawater. *Limnology and Oceanography: Methods*, 10: 711-717.

Field Papers published as a result of this project (methods included)
Madison, A. S, B. M. Tebo, A. Mucci, B. Sundby and G. W. Luther, III. 2013. Abundant Mn(III) in porewaters is a major component of the sedimentary redox system. *Science* 341, 875-878. http://dx.doi.org/10.1126/science.1241396

MacDonald, D. J., A. J. Findlay, S. M. McAllister, J. M. Barnett, P. Hredzak-Showalter, S. T. Krepski, S. G. Cone, J. Scott, S. K. Bennett, C. S. Chan, D. Emerson and G.W. Luther III. 2014. Using *in situ* voltammetry as a tool to search for iron oxidizing bacteria: from fresh water wetlands to hydrothermal vent sites. *Environmental Science: Processes & Impacts* 16, 2117-2126. http://dx.DOI.org/10.1039/c4em00073k

Findlay, A. J., A. Gartman, D. J. MacDonald, T. E. Hanson, T. J. Shaw and G. W. Luther, III. 2014. Distribution and size fractionation of elemental sulfur in aqueous environments: The Chesapeake Bay and Mid-Atlantic Ridge. *Geochimica Cosmochimica Acta* 142, 334-348. http://dx.doi.org/10.1016/j.gca.2014.07.032

Oldham, V. O., S. M. Owings, M. Jones, B. M. Tebo and G. W. Luther, III. 2015. Evidence for the presence of strong Mn(III)-binding ligands in the water column of the Chesapeake Bay. *Marine Chemistry* 171, 58-66. http://dx.doi.org/10.1016/j.marchem.2015.02.008

Luther, G.W. III, A.S. Madison, A. Mucci, B. Sundby and V. E. Oldham. 2015. A kinetic approach to assess the strengths of ligands bound to soluble Mn(III). *Marine Chemistry* 173, 93-99. http://dx.doi.org/10.1016/j.marchem.2014.09.006

Findlay, A. J., A. J. Bennet, T. E. Hanson and G. W. Luther, III. 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. http://dx.doi.org/10.1128/AEM.02062-15.

Findlay, A. J., A. Gartman, D. J. MacDonald, T. E. Hanson, T. J. Shaw and G. W. Luther, III. 2014. Distribution and size fractionation of elemental sulfur in aqueous environments: The Chesapeake Bay and Mid-Atlantic Ridge. *Geochimica Cosmochimica Acta* 142, 334-348. http://dx.doi.org/10.1016/j.gca.2014.07.032

Methods & Sampling

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_2 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 if 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 0.669 micromolar.

MnO_x on unfiltered samples
The leucoberbelein blue method is that of Altmann (1972) and Krumblein and Altmann (1973) in 1 cm cells, but can be modified for longer path length cells.

S parameters
O_2, H_2S and polysulfides by the voltammetry method of Luther et al (2008).
A flow cell was also used to collect in situ O_2 and H_2S data as well as some additional samples. Analysis by voltammetry (Luther et al, 2008).

Solid and nanoparticulate S_8 (Yücel et al 2010 and Findlay et al 2014).
Typically, triplicate measurements performed.

***In situ* refers to profiling with a pump profiler for O_2 and H_2S 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.**

Data Parameters - Glossary:
DL = detection limit in micromolar (uM); DL for soluble Mn is 0.050 micromolar
BDL = below detection limit
RSD = relative standard deviation
NA = not analyzed
ND = not detected
nd = no data; inserted into blank cells by BCO-DMO

Note: duplicate bottles at each depth

Data Processing Description

Data Parameters - Glossary:
DL = detection limit in micromolar (uM); DL for soluble Mn is 0.050 micromolar; DL for Fe is 0.100 micromolar
BDL = below detection limit
RSD = relative standard deviation; precision typically 2-5% RSD
NA = not analyzed
ND = not detected
nd = no data; inserted into blank cells by BCO-DMO

Note: duplicate bottles at each depth

BCO-DMO Processing Notes
- Generated from original file "LutherTeboCB2013RosetteSamples_CORR.xlsx" contributed by George Luther
- Parameter names edited to conform to BCO-DMO naming convention found at Choosing Parameter Name
- Date converted to YYYYMMDD
- Blank lines removed
- Lat/Lon converted from degs, decimal minutes to decimal degrees (degs, decimal minutes maintained)
- "nd" (no data) inserted into blank cells
- Stations, Casts, Dates, Times, Lat, Lons reformatted to fit on a single line (record)

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Data Files

File
RosetteSamples_CTD_Bottle.csv(Comma Separated Values (.csv), 44.98 KB) MD5:3289fb0329412820713f324693088bca Primary data file for dataset ID 646279

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Parameters

Parameter	Description	Units
Cast	Cast	text
Station	Station	text
Bottle_Num	Bottle_Num	text
Local_Date	Local_Date	YYYYMMDD
Local_time	Local_time	HHMM
Latitude	Latitude	decimal degrees
Longitude	Longitude	decimal degrees
depth	depth	meters
temp	temp	deg C
salinity	salinity	PSU
sigma_t	sigma_t	kg/m^3 (??)
CTD_O2	CTD_O2	uM
OneHundredPercentO2_sat	100%O2 sat	umol/l
percent_O2_sat	% O2 sat	percentage
fluorescence_chla	fluorescence chla; voltage = 0	volts
transmissometry	transmissometry; voltage = 4	volts
TA	TA	um/kg
DIC	DIC	um/kg
pH_primary	pH primary	pH units
Particulate_Filtered_MnOx	Particulate MnOx, (mM) caught on 0.200 um filter; MnOx DL = 0.669 micromolar; precision typically 2-5% RSD	um

Dissolved_Filtered_Mn2plus	Dissolved Mn2+ (mM) filtered through 0.2 um	um
Dissolved_Filtered_Mn2plus_stdev	Stdev Dissolved Mn2+ (mM) filtered through 0.2 um	um
Dissolved_Filtered_Mn3plus_mean	Dissolved Mn3+ (mM) filtered through 0.2 um	um
Dissolved_Filtered_Mn3plus_stdev	Stdev Dissolved Mn3+ (mM) filtered through 0.2 um	um
Dissolved_Filtered_MnT_mean	Dissolved MnT (mM) filtered through 0.2 um	um
Dissolved_Filtered_MnT_stdev	Stdev Dissolved MnT (mM) filtered through 0.2 um	um
Dissolved_Filtered_H2Splus_Hsminus	Dissolved H2S+HS- (mM) filtered through 0.2 um	um
Dissolved_Filtered_H2Splus_Hsminus_stdev	Stdev Dissolved H2S+HS- (mM) filtered through 0.2 um	um
Dissolved_Filtered_Fe2plus	Dissolved [Fe2+] (mM) filtered through 0.2 um; DL for Fe is 0.100 micromolar	um
Dissolved_Filtered_Fe2plus_stdev	Stdev Dissolved [Fe2+] (mM) filtered through 0.2 um	um
Total_UnFiltered_Fe2plus	Total UnFiltered [Fe2+] (mM)	um
Total_UnFiltered_Fe2plus_stdev	Stdev Total UnFiltered [Fe2+] (mM)	um
Dissolved_Filtered_Fe3plus	Dissolved [Fe3+] (mM) filtered through 0.2 um	um
Dissolved_Filtered_Fe3plus_stdev	Stdev Dissolved [Fe3+] (mM) filtered through 0.2 um	um
Total_UnFiltered_Fe3plus	Total UnFiltered [Fe3+] (mM)	um
Total_UnFiltered_Fe3plus_stdev	Stdev Total UnFiltered [Fe3+] (mM)	um
pH_secondary	pH secondary	pH units
Nanoparticulate_Dissolved_Filtered_S0	Nanoparticulate/Dissolved [S(0)] (uM) filtered through 0.2 um	um
Dissolved_Particulate_S0	Particulate [S(0)] (uM) filtered through 0.2 um; DL 0.1 uM	um
Total_S0_Filtered_plus_Particulate	Total S(0) filtered + particulate	um

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Instruments

Dataset-specific Instrument Name	AS-ALK2 Apollo Scitech titrator
Generic Instrument Name	Automatic titrator
Dataset-specific Description	TA - Open cell Gran titration with semi-automatic AS-ALK2 Apollo Scitech 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	AS-C3, Apollo Scitech
Generic Instrument Name	CO2 Analyzer
Dataset-specific Description	DIC - infrared CO2 analyzer (AS-C3, Apollo Scitech)
Generic Instrument Description	Measures atmospheric carbon dioxide (CO2) concentration.

Dataset-specific Instrument Name	pump profiler
Generic Instrument Name	CTD - profiler
Dataset-specific Description	In situ 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) along with a temperature and salinity sensor from YSI.
Generic Instrument Description	The Conductivity, Temperature, Depth (CTD) unit is an integrated instrument package designed to measure the conductivity, temperature, and pressure (depth) of the water column. The instrument is lowered via cable through the water column. It permits scientists to observe the physical properties in real-time via a conducting cable, which is typically connected to a CTD to a deck unit and computer on a ship. The CTD is often configured with additional optional sensors including fluorometers, transmissometers and/or radiometers. It is often combined with a Rosette of water sampling bottles (e.g. Niskin, GO-FLO) for collecting discrete water samples during the cast. This term applies to profiling CTDs. For fixed CTDs, see https://www.bco-dmo.org/instrument/869934.

Dataset-specific Instrument Name	SeaBird Electronics 911 plus CTD
Generic Instrument Name	CTD Sea-Bird SBE 911plus
Dataset-specific Description	CTD System: SeaBird Electronics 911 plus CTD, Rosette is a 12-bottle General Oceanic Model 1015, outfitted with an array of 10 liter bottles.
Generic Instrument Description	The Sea-Bird SBE 911 plus is a type of CTD instrument package for continuous measurement of conductivity, temperature and pressure. The SBE 911 plus includes the SBE 9plus Underwater Unit and the SBE 11plus Deck Unit (for real-time readout using conductive wire) for deployment from a vessel. The combination of the SBE 9 plus and SBE 11 plus is called a SBE 911 plus. The SBE 9 plus uses Sea-Bird's standard modular temperature and conductivity sensors (SBE 3 plus and SBE 4). The SBE 9 plus CTD can be configured with up to eight auxiliary sensors to measure other parameters including dissolved oxygen, pH, turbidity, fluorescence, light (PAR), light transmission, etc.). more information from Sea-Bird Electronics

Dataset-specific Instrument Name	Niskin Bottle
Generic Instrument Name	Niskin bottle
Dataset-specific Description	CTD System: SeaBird Electronics 911 plus CTD, Rosette is a 12-bottle General Oceanic Model 1015, outfitted with an array of 10 liter bottles.
Generic Instrument Description	A Niskin bottle (a next generation water sampler based on the Nansen bottle) is a cylindrical, non-metallic water collection device with stoppers at both ends. The bottles can be attached individually on a hydrowire or deployed in 12, 24, or 36 bottle Rosette systems mounted on a frame and combined with a CTD. Niskin bottles are used to collect discrete water samples for a range of measurements including pigments, nutrients, plankton, etc.

Dataset-specific Instrument Name	In situ pump - West Marine Pump
Generic Instrument Name	Pump
Dataset-specific Description	In situ pump - West Marine Pump
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	Analytical Instrument Systems DLK-60
Generic Instrument Name	Voltammetry Analyzers
Dataset-specific Description	In situ 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) along with a temperature and salinity sensor from YSI.
Generic Instrument Description	Instruments that obtain information about an analyte by applying a potential and measuring the current produced in the analyte.

Dataset-specific Instrument Name	YSI temperature and salinity sensor
Generic Instrument Name	YSI Professional Plus Multi-Parameter Probe
Dataset-specific Description	In situ 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) along with a temperature and salinity sensor from YSI.
Generic Instrument Description	The YSI Professional Plus handheld multiparameter meter provides for the measurement of a variety of combinations for dissolved oxygen, conductivity, specific conductance, salinity, resistivity, total dissolved solids (TDS), pH, ORP, pH/ORP combination, ammonium (ammonia), nitrate, chloride and temperature. More information from the manufacturer.

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Deployments

HRS1314

Website	https://www.bco-dmo.org/deployment/641156
Platform	R/V Hugh R. Sharp
Start Date	2013-08-08
End Date	2013-08-16

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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

Funding Source	Award
NSF Division of Biological Infrastructure (NSF DBI)	DBI-0424599
NSF Division of Ocean Sciences (NSF OCE)	OCE-1155385
NSF Division of Ocean Sciences (NSF OCE)	OCE-1154307
Simons Foundation (Simons)	unknown SCOPE Simons

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