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 ManganeseIII)

Contributors	Affiliation	Role
Luther, George W.	University of Delaware	Principal Investigator
Tebo, Bradley M.	Oregon Health & Science University (IEH/OHSU)	Co-Principal Investigator
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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

Dataset Description

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

See Related Publicatons (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_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 3.0 nanomolar.

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* pump profiler cast** 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. 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_X solids:
Altmann (1972)

Krumbein & Altmann (1973)

Dissolved Fe speciation parameters:
Stookey (1970)

Lewis et al. (2007)

O_2 and H_2S, polysulfides:
Luther et al. (2008)

Luther et al. (2013)

S_8:
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";
- coverted 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
Pump_HRS1415.csv (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 gel⁄stem Sauerstoff mit Leukoberbelinblau I. Fresenius' Zeitschrift F⁄r 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
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
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
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
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
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
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
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
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
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
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
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
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
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
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
Methods

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

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

Black Sea sediments. Chemical Geology, 269(3-4), 364–375. doi:10.1016/j.chemgeo.2009.10.010
Methods

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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

Dataset-specific Instrument Name	AS-ALK2 Apollo Scitech titrator
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	AS-C3, Apollo Scitech infrared CO2 analyzer
Generic Instrument Name	CO2 Analyzer
Generic Instrument Description	Measures atmospheric carbon dioxide (CO2) concentration.

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

Dataset-specific Instrument Name	
Generic Instrument Name	Voltammetry Analyzers
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 model 350
Generic Instrument Name	Water Temperature Sensor
Dataset-specific Description	The YSI model 350 probe measures salinity and temperature.
Generic Instrument Description	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

Website	https://www.bco-dmo.org/deployment/717689
Platform	R/V Hugh R. Sharp
Start Date	2014-08-18
End Date	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

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1155385

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