Water column data from samples collected on R/V Hugh Sharp cruise HRS1803GL in the Chesapeake Bay during July-August 2018

Website: https://www.bco-dmo.org/dataset/853038
Data Type: Cruise Results
Version: 1
Version Date: 2021-06-04

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

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

Water column data from samples collected on R/V Hugh Sharp cruise HRS1803GL in the Chesapeake Bay during July-August 2018. Samples were collected by CTD and from an in situ pump profiler system attached to the CTD rosette.

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Coverage

Spatial Extent: **N**:39.5015 **E**:-75.924 **S**:38.9767 **W**:-76.3688
Temporal Extent: 2018-07-28 - 2018-08-03

Methods & Sampling

***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). Water was pumped aboard to make measurements on discrete samples for Mn and Fe speciation as well. See Hudson et al (2019).

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 CO_2 analyzer (AS-C3, Apollo Scitech).

Uses Dickson CRM for calibration. DIC/TA samples were filtered (0.45um) and fixed with 100 ul 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 leucoberbelein blue method is that of Jones et al (2019, this work) in 1 cm cells, but can be modified for longer path length cells.

H_2S
O_2 and H_2S by the voltammetry method of Luther et al (2008) and Hudson et al (2019) using a flow cell. O_2 also from CTD sensor.

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). 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 [$Mn^{3+} = MnT – Mn^{2+}$]. 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)

Data Processing Description

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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Data Files

File
water_column2018.csv(Comma Separated Values (.csv), 29.00 KB) MD5:6ebf661f52700359c90bb3c41ddf72b0 Primary data file for dataset ID 853038

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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
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
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
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., 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
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
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., 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

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

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Related Datasets

Continues

Luther, G. W., Tebo, B. M. (2021) **Water column data from samples collected on R/V Hugh Sharp cruise HRS1709 in the Chesapeake Bay in August 2017.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2021-02-17 doi:10.26008/1912/bco-dmo.840678.1 [view at BCO-DMO]

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Parameters

Parameter	Description	Units
Region	Sampling location	unitless
cruise	Cruise identifier	unitless
cast	Cast number	unitless
sample	Bottle numer or pump-profiler number	unitless

date_local_EST	Date of sample collection (local; EST); 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)
voltage_fluorescence	Fluorescence voltage	volts
H2S	H2S; detection limit = 0.2 (uM)	micromolar (uM)
TA	TA	micromoles per kilogram (umol/kg)
DIC	DIC	micromoles per kilogram (umol/kg)
pH	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)
pMnOx_stdev	Standard deviation of pMnOx	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 = 10 nM	nanomolar (nM)
pFe2plus	Particulate Fe2+; no filtering of water; detection limit = 10 nM	micromolar (uM)
dFeTotal	Dissolved Fe total = FeT = [Fe2+] + [Fe3+]; filtered through 0.20 micrometer filters; detection limit = 10 nM	nanomolar (nM)
pFeTotal	Particulate Fe total = FeT = [Fe2+] + [Fe3+]; no filtering of water; detection limit = 10 nM	nanomolar (nM)
dFe3plus	Dissolved Fe3+ by difference; Fe3+ = [FeT - Fe2+]	nanomolar (nM)
pFe3plus	Particulate Fe3+ by difference; Fe3+ = [FeT - Fe2+]	nanomolar (nM)
Nitrite	Nitrite; single measurement; dissolved, filtered through 0.20 micrometer filters	nanomolar (nM)
Comments	Notes/comments about the sampling events	unitless

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Instruments

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.

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

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Deployments

HRS1806

Website	https://www.bco-dmo.org/deployment/853365
Platform	R/V Hugh R. Sharp
Start Date	2018-07-28
End Date	2018-08-04
Description	Additional cruise information is available from the Rolling Deck to Repository (R2R): https://www.rvdata.us/search/cruise/HRS1806

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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.

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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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