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

Sampling Type	*Local time*	*GMT*	*comments*
		August 9, 2013	
CTD#1	0820	1220	**Station #1** (0.4 Sal.) 1 bottom; 2 surface C parameters 39 29.79N; 075 55.76W off Town Point
CTD#2	0909	1309	**Station #2** (0.4 Sal.) 1 bottom; 2 surface C parameters 39 26.16N; 076 00.34 W off Turkey Point
CTD#3	1021	1421	**Station #3** (2 Sal.) 1 bottom; 2 surface C parameters 39 21.49N; 076 09.03 W off Shad battery shoal
CTD#4	1112	1521	**Station #4** (4 Sal.) 1 bottom; 2 surface C parameters 39 17.41N; 076 13.60 W off stoops point
CTD#5	1207	1607	**Station #5** (6 Sal.) 1 bottom; 2 surface C parameters 39 11.09 N; 076 16.89 W
CTD#6	1300	1700	**Station #6** (8 Sal.) 1 bottom; 2 surface C parameters 39 04.8N; 076 20.51 W
CTD#7	1400	1800	**Station #7** (10 Sal.) station 858 No bottles
CTD#8	1410	1810	**Station #7** station 858 - 6 samples (2 bottles at each depth) C Mn, Fe, S parameters 38 58.54 N; 076 22.11 W
in situ #1	1445	1845	every 1 meter to 10 meters, 15 and 20 meters, recover 1515. station 858
CTD#9	1855	2255	**Station #7** station 858 - 6 samples (2 bottles at each depth) C, Mn, Fe, S parameters, 38 58.63 N; 076 21.97 W

CTD O_2 sensor reads 45 µM when in the deep and H_2S is present by voltammetry

Wynn, Sharp CTD tech) put new O_2 sensor on

FIRe failed

CTD#10	2102	0102	**Station #7** station 858 - 1 sample (2 bottles at each depth) C, Mn, Fe, S parameters, 38 58.62 N; 076 21.96 W New CTD O_2 sensor works
			Saturday August 10, 2013
CTD#11	0100	0500	**Station #7** station 858 - 4 sample (2 bottles at each depth) C parameters, 38 58.658N; 076 21.969 W
in situ #2	0645	1045	every 1 meter to10 meters, 15, 17.5 and 20 meters Recover 0715. station 858
CTD#12	0717	1117	**Station #7** station 858 - 6 samples (2 bottles at each depth) C, Mn, Fe, S parameters, 38 58.59 N; 076 21.94 W
in situ #3	0845	1245	every 1 meter to10 meters, 15, 17.5 and 20 meters **trial In situ pump CHPT cast** station 858
CTD#13	1249	1649	**Station #7** station 858 - 6 samples (2 bottles at each depth) C, Mn, Fe, S parameters, 38 58.56 N; 076 21.98 W
in situ #4 **In situ CHPT pump**	1345	1745	pump cavitated air? H_2S not observed even though One could smell it. Retrieve at 1430. station 858
CTD#14	1843	2243	**Station #7** station 858 - 1 samples (1 bottle at one depth) Mn parameters, 38 58.57 N; 076 21.96 W
FIRe#5 **In situ pump West Marine Pump**	1856	2256	FIRe to ~ 17 m; sample interface station 858 Retrieve at 2020.
CTD#15	2011	0011	**Station #7** station 858 - 6 samples (2 bottles at each depth) C, Mn, Fe, S parameters, 38 58.62 N; 076 21.96 W
CTD#16	2218	0218	**Station #8** station 858 - 4 samples (2 bottles at each depth) C parameters, 38 51.82 N; 076 24.33W

Sunday August 11, 2013

CTD#17	0039	0439	**Station #9** station 858 - 4 samples (2 bottles at each depth) C parameters, 38 32.01 N; 076 26.93W
CTD#18	0223	0623	**Station #10** station 858 - 4 samples (2 bottles at each depth) C parameters, 38 19.10 N; 076 18.34W
CTD#19	0727	1127	**Station #7** station 858 - 6 samples (2 bottles at each depth) C, Mn, Fe, S parameters, 38 58.58 N; 076 22.02 W
in situ #6	0756	1156	FIRe to ~ 20 m; sample interface station 858
In situ pump	**West Marine Pump**		Retrieve at 0934.
CTD#20	1354	1754	**Station #7** station 858 - 6 samples (2 bottles at each depth) C, Mn, Fe, S parameters, 38 58.54 N; 076 22.01 W
in situ #7	1415	1815	FIRe to ~ 20 m; sample interface station 858
In situ pump	**West Marine Pump**		Retrieve at 1500.
CTD#21	1935	2335	**Station #7** station 858 - 6 samples (1 bottle at each depth) C, Mn, Fe, S parameters, 38 58.59 N; 076 22.02 W

Monday August 12, 2013

CTD#22	1935	2335	**Station #7** station 858 - 1 sample for H_2S 38 58.54 N; 076 22.01 W
in situ #8	0400	0800	FIRe to ~ 20 m; sample interface station 858
In situ pump	**West Marine Pump**		Retrieve at 1515.
CTD#23	0716	1116	**Station #7** station 858 - 6 samples (2 bottles at each depth) C, Mn, Fe, S, P parameters, 38 58.56 N; 076 21.99 W
in situ #9	0750	1150	FIRe to ~ 20 m; sample interface station 858
In situ pump	**West Marine Pump**		Retrieve at 0845.
Multi-core#1	0919	0923	4 good multi-cores with overlying water station 858.Plastic bottoms with o-rings gone

CTD#24	1118	1518	**Station #11** - NO samples taken 39 00.36 N; 076 21.34 W
CTD#25	1139	1539	**Station #11** - 3 samples (2 bottles at each depth) C, P parameters, 39 00.37 N; 076 20.70 W
Multi-core#2	1153	1556	station 11 –only 2 cores had mud (small amount) 39 00.3939 N 076 20.7344 W
Multi-core#3	1158	1558	station 11 – only 2 cores had mud (more than core #2). Recovered 1200
Multi-core#4	1214	1614	station 11 – no cores taken as only 2 had mud (more than core #2). Recovered 1216.
CTD#26	1416	1816	**Station #7** station 858 - 6 samples (2 bottles at each depth) C, Mn, Fe, S, P parameters, 38 58.53 N; 076 22.05 W
in situ #10	1450	1850	FIRe to ~ 20 m; sample interface station 858
In situ pump	**West Marine Pump**		Retrieve at 1535.
CTD#27	2002	0002	**Station #7** station 858 - 6 samples (2 bottles at each depth) C, Mn, Fe, S parameters, 38 58.56 N; 076 22.06 W

Tuesday August 13, 2013

CTD#28	0345	0745	**Station #7** station 858 - 1 sample 21 bottle for H_2S, 38 58.56 N; 076 22.08 W
in situ #11	0400	0800	FIRe to ~ 20 m; sample interface station 858
In situ pump	**West Marine Pump**		Retrieve at 0445.
CTD#29	0731	1131	**Station #7** station 858 - 6 samples (2 bottles at each depth) C, Mn, Fe, S parameters, 38 58.60 N; 076 22.02 W
in situ #12	0805	1205	FIRe to ~ 20 m; sample interface station 858
In situ pump	**West Marine Pump**		Retrieve at 0937.

Return to Lewes

Offshore Leg
Wednesday August 14, 2013

CTD#30	1524	1925	**Station #12A** 12 samples (at surface) 25 min. soak First: bottle 12 did not fire (operator error) C, Mn parameters, 37 08.47 N; 073 24.25 W
CTD#31	1605	2005	**Station #12A** 12 samples (at surface) First: (all bottles fired) C, Mn parameters, 37 18.40 N; 073 23.75 W
CTD#32	1624	2024	**Station #12A** 12 termination failed at 530 meters No bottles! 37 18.37N 073 27.53W **Wynn redid CTD termination #1**
FIRe#13	1800	2200	FIRe to ~ 35 m ; Retrieve at 1835.
CTD#33	2043	0043	**Station #12A** 6 samples to 700 m (2 bottles at each depth) C, Mn, parameters, 37 07.84 N 073 19.72 W

Thursday August 15, 2013

CTD#34	0346	0746	**Station #12A** 1 samples to 50 m (support FIRe) 37 18.45 N 073 23.79 W
FIRe#14	0420	0820	FIRe to ~ 35 m ; Retrieve at 0455.
CTD#35	0600	1000	**Station #12A** termination failed at 1516 meters 37 18.44 N 073 23.49 W **Wynn redid CTD termination #2**
CTD#36	0901	1301	**Station #12A** 6 samples to 800 m (2 bottles at each depth) C, Mn, parameters, 37 18.32 N 073 23.90 W
CTD#37	1008	1408	**Station #12A** 1 sample to 2000 m (2 bottles) C, Mn, parameters, 37 18.32 N 073 24.03 W RS-232 time out after firing bottles at 2031 meters appears to be due to the hydrowire
CTD#38	1801	2201	**Station on shelf** 3 samples to 50 m (1 bottle each) C, 38 04.93 N 074 15.08 W : cold pool waters
CTD#39	1833	2233	**Station on shelf** 3 samples to 35 m (1 bottle each) C, 38 06.83 N 074 16.93 W : cold pool waters

Note: Latitudes for CTD's #38 and #39 corrected from 37degs in the original document to 38degs by BCO-DMO staff.

Return to Lewes

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 in 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.

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. Detection limit is 0.669 micromolar.

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.**

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